



Study on retention behavior and chemical states of energetic deuterium implanted into carbon-contained boron film

Yohei Kikuchi^{a,*}, Yu Yang^b, Akira Yoshikawa^a, Taichi Suda^b, Akio Sagara^c, Nobuaki Noda^c, Yasuhisa Oya^a, Kenji Okuno^a

^a Radiochemistry Research Laboratory, Faculty of Science, Shizuoka University, 836, Ohya, Suruga-ku, Shizuoka 422-8529, Japan

^b Institute of Plasma Physics, Chinese Academy of Sciences, Hefei, Anhui 230031, PR China

^c National Institute for Fusion Science, Gifu 509-5292, Japan

A B S T R A C T

Retention behavior and chemical states of energetic deuterium (D) implanted into a carbon-contained boron film were investigated by XPS and TDS. It was found from the TDS results that D desorption processes were consisted of following four stages. Two of them were the desorptions of D bound to B as forming B–D–B and B–D bonds, and the others were thought to be that bound to C with different configurations. These results were consistent with the XPS results, showing the C–B (sp²), C–B (sp³) and C–C bonds were formed in the carbon contained boron film. These desorption peaks were attributed to B–C–D and C–C–D bonds, and most of D was mainly trapped by C and desorption temperature was higher than trapped by B, indicating that the D trapped by C would be critical issue for the hydrogen isotope retention control in fusion devices. It was concluded that D trapped by C, especially as C–C–D bond, was chemically stable even though at high temperature.

© 2009 Published by Elsevier B.V.

1. Introduction

Boronization is one of wall conditioning techniques for fusion reactors and has been applied to many devices like JT-60U at Japan Atomic Energy Agency (JAEA), Large Helical Device (LHD) at National Institute for Fusion Science (NIFS), and so on [1–3]. It is well known that boron can easily trap impurities, like oxygen, carbon, and so on, and keep stable plasma discharge [4–7]. Thus, it is predicted that large amount of impurities would be scavenged by the boron film. During fusion operation, it is expected that hydrogen isotopes including tritium, are implanted energetically into the boron film, and various chemical states of tritium are thought to be formed.

In our previous studies, the chemical behavior of deuterium (D) implanted into the pure boron films and the oxygen-contained boron films have been studied. It has been reported that B–D–B and B–D bonds were formed for the pure boron films, and B–D–B, B–D and O–D bonds for the oxygen-contained boron films with the oxygen concentration above 37% [8]. It was also found that the D retention in the oxygen-contained boron film decreased as the oxygen concentration increased. On the other hands, when carbon-based materials are applied as Plasma Facing Materials (PFMs), it is expected that carbon is also dissolved into the boron

film and stable solid carbon-contained boron films, like boron carbide will be formed and hydrogen isotope would be trapped not only by boron but also by carbon because of high affinity with hydrogen isotopes, and remained in the films. Therefore, it is required to reveal the retention behavior and chemical states of D in the carbon-contained boron films. In this study, to elucidate the D trapping and retention behaviors, implantation temperature was changed for the carbon-contained boron films with the carbon concentration of 39%.

2. Experimental

To prepare the carbon-contained boron films, Plasma Chemical Vapor Deposition (PCVD) device was designed and fabricated at Shizuoka University, which was described in our previous paper in detail [9]. The PCVD chamber was evacuated by a turbomolecular pump less than 10^{−6} Pa. Before preparation, only helium gas was purged at the flow rate of 3.8 sccm and plasma discharge was performed to clean up the chamber. After cleaning, dacaborane (B₁₀H₁₄) gas, helium gas and methane (CH₄) gas were, respectively, introduced at the rates of 2.5 sccm, 3.8 sccm and 0.5 sccm and the plasma discharge was performed to prepare the carbon-contained boron films on the silicon substrate. During the preparation, temperature of substrate was kept at 673 K. The thickness of boron film was estimated to be 150 nm by a quartz oscillator. The atomic composition ratio of boron and carbon in this film were 57% and 39%, respectively.

* Corresponding author. Tel.: +81 54 238 6436; fax: +81 54 238 3989.
E-mail address: r0732007@ipc.shizuoka.ac.jp (Y. Kikuchi).

After preparation, the sample was heated at 1200 K for 10 min. Thereafter, the deuterium ion (D_2^+) was implanted at the sample temperature between 323 K and 823 K with an ion energy of 1.0 keV, an ion flux of $1.0 \times 10^{18} D^+ m^{-2} s^{-1}$ and an ion fluence of $7.3 \times 10^{21} D^+ m^{-2}$. Before and after D_2^+ implantation, XPS (ESCA 1600 Series, ULVAC-PHI INC.) measurement was performed using Al K α X-ray source. The TDS measurement was also performed from room temperature to 1200 K with a heating rate $0.5 K s^{-1}$.

3. Results and discussion

Fig. 1 compares (a) D_2 TDS spectrum after D_2^+ implantation at 323 K and (b) D_2 TDS spectra after D_2^+ implantation at various implantation temperatures. In Fig. 1(a), the spectrum could be divided into four desorption stages at the peak temperature of 520 K, 720 K, 830 K and 930 K, named Peak 1, Peak 2, Peak 3 and Peak 4, respectively, by Gaussian distribution function. In the previous study [10], it was reported that Peaks 1 and 2 corresponded to the desorption of D bound to B as forming B–D–B and B–D bonds, respectively. Comparing to the TDS spectra for the carbon contained boron film as shown in Fig. 1(a) and that for the pure boron film [10], it was found that the D retention for the carbon-contained boron film was about 35% smaller than that for the pure boron film. It was also found for the carbon-contained boron film that the additional desorption stages, namely Peaks 3 and 4, were observed, indicating that both desorption stages were thought to be corresponded to those trapped by C. These results indicated that the retention of D trapped by B was remarkably decreased for the carbon-contained boron film, showing the high trapping efficiency D by C compared to that by B.

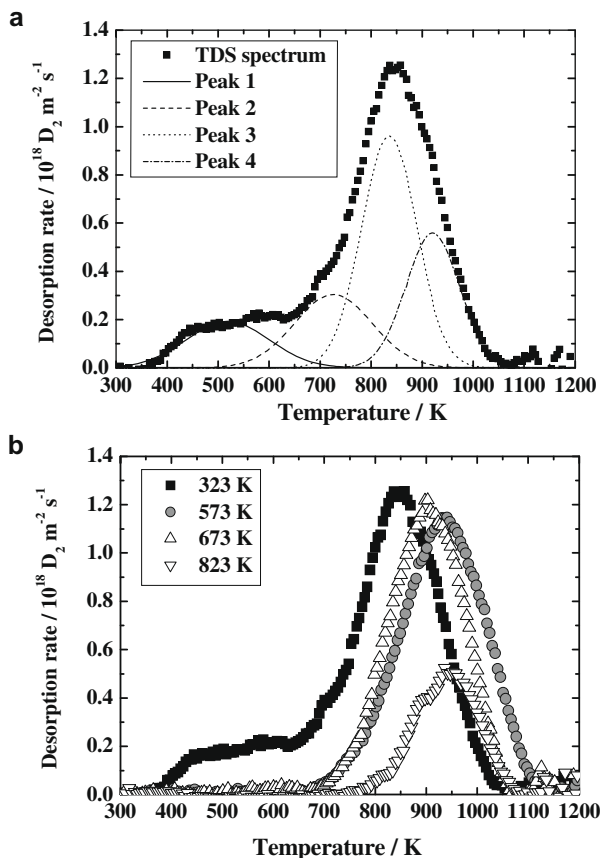


Fig. 1. (a) D_2 TDS spectrum at the implantation temperature of 323 K. (b) Comparison of D_2 TDS spectra at various implantation temperatures.

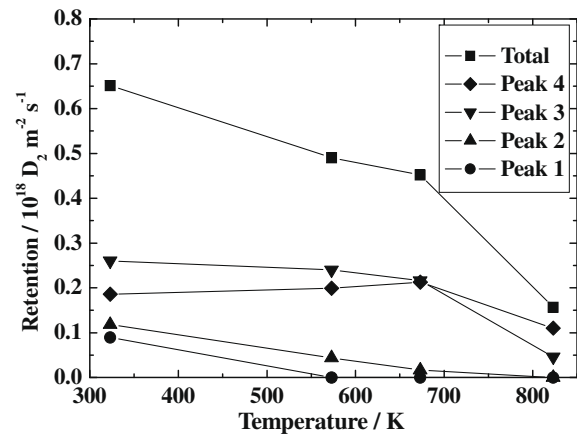


Fig. 2. The D retentions trapped as Peaks 1–4 as a function of implantation temperature.

Fig. 2 summarizes the changes of D retention trapped as Peaks 1–4 as a function of implantation temperature. It was found that D retention decreased as the implantation temperature increased. The retention of D as Peak 4 was almost constant, while those as Peaks 1–3 decreased as implantation temperature increased. It was indicated that D trapped as Peak 4 was chemically stable at high implantation temperature.

Fig. 3 shows XPS spectra of (a) B-1s and (b) C-1s as a function of implantation temperature. In B-1s spectra it has been known that the B–B bond and B–C bond are located at the peak energies of

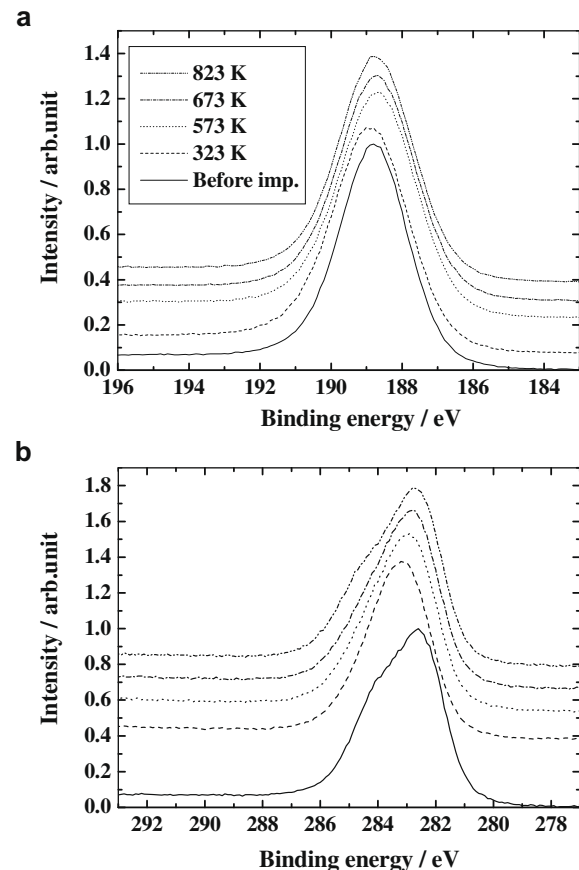


Fig. 3. The XPS spectra of (a) B-1s and (b) C-1s as a function of implantation temperature.

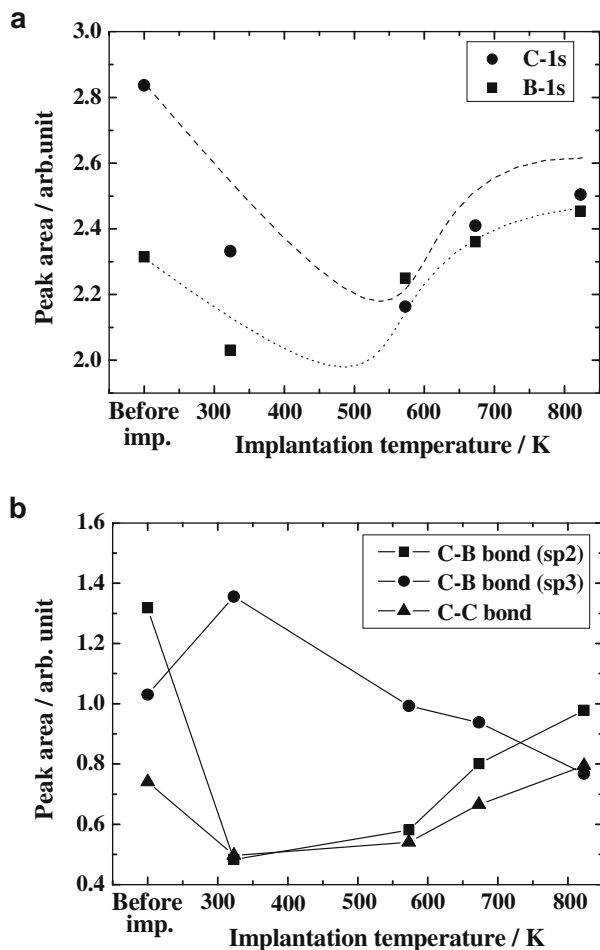


Fig. 4. The changes of peak areas for (a) B-1s and C-1s and (b) C-B (sp₂), C-B (sp₃) and C-C bonds decomposed of C-1s as a function of implantation temperature.

187.8 eV and 189.0 eV, respectively [11], and in C-1s XPS spectra, C-B (sp₂), C-B (sp₃) and C-C bonds at 281.8 eV, 283.7 eV and 284.5 eV, respectively [12,13]. The peak position of B-1s was almost remained in the original position after the D₂⁺ implantation, while positive peak shift of C-1s was found. The peak areas of B-1s and C-1s spectra are summarized in Fig. 4. It was clear that peak area of B-1s decreased by D₂⁺ implantation at 323 K, and increased as the implantation temperature increased, while that of C-1s was lowest at the implantation temperature of 573 K, indicating that chemical sputtering of C was the most effective at 573 K. This fact was consistent with the previous report that the chemical sputtering of CFC and B₄C-CF composite was most effective at the implantation temperature of 573–673 K and around 673 K, respectively [14,15]. Above the implantation temperature of 573 K, the peak area of C was recovered. This fact could be explained not only by the decrease of chemical sputtering yield but also by the segregation of C on the surface. To elucidate more detail chemical behavior, the C-1s spectra are divided into three peaks, namely C-B (sp₂), C-B (sp₃) and C-C bonds, and these peak areas as a function of implantation temperature are summarized in Fig. 4(b). By the D₂⁺ implantation, large decrease of the peak area of C-B (sp₂) was observed although the peak area of C-B (sp₃) bond was slightly increased, indicating that the D was trapped by C with forming sp₃ hybridized orbital bond from sp₂ hybridized orbital bond like B-C-D bond. It was also noted that the behavior of peak area of C-B (sp₃) bond was almost consistent with that of Peak 3 for TDS as shown in Fig. 2. Therefore, B-C-D bond with sp₃ hybridized

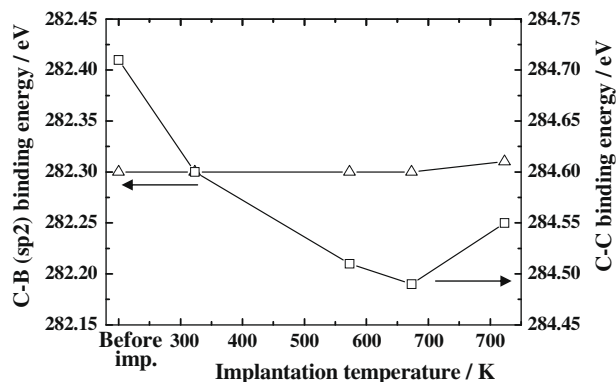


Fig. 5. The changes of peak energies for C-B (sp₂) and C-C bonds as a function of implantation temperature.

orbital bond would be the major chemical state of D trapped by C. At the implantation temperature above 573 K, the peak areas of C-B (sp₂) and C-C bonds were recovered and that of C-B (sp₃) was decreased, indicating the reconstruction of carbon-contained boron film by heating and/or subsequent D detrapping during the D₂⁺ implantation. It can be said that Peak 3 of TDS spectra was attributed to B-C-D (sp₃) bond. Fig. 5 summarizes the changes of peak energies of C-B (sp₂) and C-C bonds as a function of implantation temperature by XPS measurements. It was found that the peak energy of C-B (sp₂) bond was almost constant, indicating that B-C-D (sp₂) bond could not be formed by D₂⁺ implantation. For C-C bond, negative peak shift of peak energy was confirmed as the implantation temperature increased, indicating that carbon vacancies were formed and D could be trapped by C with forming C-C-D bond, which corresponded to the desorption stages of Peak 4.

In the previous study [16], the implantation temperature dependence for pure boron film was also studied. It was reported that the D retention decreased as implantation temperature increased and D retention for the sample with the implantation temperature of 573 K and 673 K, respectively, was refrained only 15% and 5% compared to that at 323 K. These trends were quite different from the present carbon contained boron film, showing that the D retention decreased largely at above 673 K, indicating that higher temperature will be required to remove the tritium retained in the carbon-contained boron film compared to the pure boron film [16]. It can be concluded that contamination of C in the boron film induce high D retention, leading the formation of B-C-D and C-C-D bonds with the sp₃ hybridized orbital bonds not sp₂ bond.

4. Conclusion

Retention behavior and chemical states of D implanted into the carbon-contained boron film with 39% carbon was investigated using XPS and TDS. It was found from the TDS results that D desorption processes were consisted of following four stages. Two of them were the desorption of D bound to B as forming B-D-B and B-D bonds, and the others were thought to be that bound to C with different configuration. These results were consistent with the XPS results, showing the C-B (sp₂), C-B (sp₃) and C-C bonds were formed in the carbon contained boron film. These desorption stages were attributed to those of B-C-D and C-C-D bonds, respectively. The total D retention decreased at the implantation temperature increased, that of B-D-B, B-D and B-C-D bonds decreased as implantation temperature increased, but the large decrease of C-C-D bond did not depend on the D₂⁺ implantation temperature. D was mainly trapped by carbon in carbon-contained

boron film. The amount of deuterium trapped by carbon (Peak 3 + Peak 4) was almost constant until 673 K and decrease largely above 673 K, indicating that deuterium trapped by carbon could not be easily desorbed and higher temperature will be required compared to pure boron film. Especially, the amount of deuterium trapped as C–C–D bond was almost constant at higher temperature. Most of D was mainly trapped by C and desorption temperature was higher than trapped by B, indicating that the D trapping by C would be critical issue for the hydrogen isotope retention control in fusion devices. It was concluded that D trapped by C, especially as C–C–D bond, was chemically stable even though at high temperature.

Acknowledgements

This study was performed using XPS and TDS devices in the Center of Instrumental Analysis at Shizuoka University and partly supported by the JSPS-CAS Core University Program in the field of 'Plasma and Nuclear Fusion' and by NIFS collaborative Research Program.

References

- [1] J. Yagyu, N. Ogiwara, M. Saidoh, J. von. Seggern, T. Okabe, Y. Miyo, H. Hiratuka, S. Yamamoto, P. Goppelt-Langer, Y. Aoki, H. Takashita, H. Naramoto, *J. Nucl. Mater.* 241–243 (1997) 579.
- [2] N. Noda, K. Tsuzuki, A. Sagara, N. Inoue, T. Muroga, *J. Nucl. Mater.* 266–269 (1999) 234.
- [3] 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. Kudo, T. Minami, S. Morita, K. Narihata, T. Ozaki, K. Sato, C. Takahashi, K. Tanaka, K. Toi, I. Yamada, *J. Nucl. Mater.* 241–243 (1997) 972.
- [4] S. Higashijima, T. Sugie, H. Kubo, S. Tsuji, M. Shimada, N. Asakura, N. Hosogane, Y. Kawano, H. Nakamura, K. Itami, A. Sakasai, K. Shimizu, T. Ando, M. Saidoh, *J. Nucl. Mater.* 220–222 (1995) 375.
- [5] T. Hino, T. Mochizuki, Y. Hirohata, K. Tsuzuki, N. Inoue, A. Sagara, N. Noda, O. Motojima, K. Mori, T. Sogabe, K. Kuroda, *J. Nucl. Mater.* 248 (1997) 38.
- [6] K. Tsuzuki, H. Eiki, N. Inoue, A. Sagara, N. Noda, Y. Hirohata, T. Hino, *J. Nucl. Mater.* 266–299 (1999) 247.
- [7] T. Nakano, S. Higashijima, H. Kubo, J. Yagyu, T. Arai, N. Asakura, K. Itami, *J. Nucl. Mater.* 313–316 (2002) 149.
- [8] A. Yoshikawa, M. Oyaidzu, H. Miyauchi, Y. Oya, A. Sagara, N. Noda, K. Okuno, *J. Nucl. Mater.* 367–370 (2007) 1527.
- [9] M. Oyaidzu, A. Yoshikawa, H. Kodama, Y. Oya, A. Sagara, N. Noda, K. Okuno, *Appl. Surf. Sci.* 244 (2005) 240.
- [10] H. Kodama, M. Oyaidzu, H. Kimura, T. Takeda, Y. Oya, M. Matsuyama, A. Sagara, N. Noda, K. Okuno, *J. Nucl. Mater.* 337–339 (2005) 649.
- [11] Y. Oya, H. Kodama, M. Oyaidzu, Y. Morimoto, M. Matsuyama, A. Sagara, N. Noda, K. Okuno, *J. Nucl. Mater.* 329–333 (2004) 870.
- [12] L.G. Jacobsohn, R.K. Schlze, M.E.H. Maia de Costa, M. Nastasi, *Surf. Sci.* 572 (2004) 418.
- [13] V. Linss, S.E. Rodil, P. Reinke, M.G. Garnier, P. Oelhafen, U. Kreissig, F. Richter, *Thin Solid Films* 467 (2004) 76.
- [14] R. Jimbou, K. Nakamura, V. Bandourko, Y. Okamura, M. Akiba, *J. Nucl. Mater.* 258–263 (1998) 724.
- [15] R. Jimbou, K. Nakamura, V. Bandpurko, M. Dairaku, Y. Okumura, M. Akiba, *J. Nucl. Mater.* 266–269 (1999) 1103.
- [16] A. Yoshikawa, K. Okuno, in: *Proceedings of the Eighth Japan–China Symposium*, 2005.