Journal of Nuclear Materials 390–391 (2009) 200–202

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Influence of carbon concentration on chemical behavior of energetic deuterium implanted into carbon-contained boron film

Sachiko Suzuki [a,*], Yu Yang [b], Akira Yoshikawa [a], Yohei Kikuchi [a], Akio Sagara [c], Yasuhisa Oya [a], Kenji Okuno [a]

[a] *Radioscience 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, Japan*

ARTICLE INFO

PACS:
52.40.Hf
33.60.Fy
82.30.Nr
81.15.Gh

ABSTRACT

Influence of carbon concentration on chemical behavior of energetic deuterium implanted into carbon-contained boron film was investigated by XPS and TDS. Total deuterium retention and the retention of deuterium trapped by boron were decreased as the carbon concentration was increased, although that by carbon was increased. 60% of the total deuterium retention was trapped by carbon for the sample at the carbon concentration of around 30%, suggesting that deuterium had more affinity with carbon than boron. Above the carbon concentration of 20%, the chemical states of carbon were clearly changed, which led to the deuterium trapping by carbon, indicating the chemical structure change would make a large influence on D trapping. It can be said that deuterium trapped by carbon should be taken into consideration for the evaluation of tritium inventory in the carbon-contained boron film with the carbon concentration above 20%.

1. Introduction

Boronization has been considered as one of the most effective techniques for first wall conditioning in many plasma testing devices because of remarkable improvement of plasma performances [1,2]. It is well known that boron can easily trap various impurities such as oxygen and carbon, and the impurities-contained boron films will be formed on the first wall surface accompanied with the implantation of energetic hydrogen isotopes including tritium [2–6]. Therefore, the role of impurities in tritium retention in impurity-contained boron films has to clarify for the tritium retention evaluation. In our previous studies, chemical behaviors of energetic deuterium implanted into the pure and oxygen-contained boron films have been studied and it has been reported that deuterium was trapped by boron with forming the B–D–B and B–D bonds for the pure boron films [7], and trapped by boron and oxygen with forming B–D–B, B–D and O–D bonds for the oxygen-contained boron films with the oxygen concentration above 37%, and the deuterium retention in the oxygen-contained boron film decreased as the oxygen concentration increased [8]. On the other hand, it is expected that carbon is also contained in the boron films and has higher affinity with hydrogen isotopes compared to boron. This motivates us to elucidate the role of carbon contamination in hydrogen retention behavior in carbon-contained boron films. In the present study, influence of carbon concentration on chemical behavior of energetic deuterium implanted into carbon-contained boron films was investigated by means of X-ray photoelectron spectroscopy (XPS) and thermal desorption spectroscopy (TDS).

2. Experimental

The carbon-contained and pure boron films were deposited on silicon substrate using the Plasma Chemical Vapor Deposition (P-CVD) apparatus at Shizuoka University as described in our previous paper [9]. Before the P-CVD processes, plasma discharge using only helium gas was performed for 30 min to clean the substrate surface. Thereafter, decaborane ($B_{10}H_{14}$) and methane gases diluted by helium gas were introduced into P-CVD to deposit the boron film with various carbon concentrations. The substrate temperature was set to be 673 K during plasma discharge and 150 nm thick boron films were derived. By changing the flow rate of methane gas, five samples with different carbon concentrations including the pure boron film were prepared. From the XPS (ESCA 1600 Series, ULVAC-PHI Inc.) measurements, it was found that the carbon concentrations in these samples were 4%, 22%, 31%, 36% and 51%, respectively. These samples were named as Sample A, Sample B, Sample C, Sample D and Sample E, respectively. The carbon concentration for Sample A was the almost same as that in pure boron film. The oxygen and nitrogen concentrations for all the samples

---

[*] Corresponding author.
E-mail address: r0832014@ipc.shizuoka.ac.jp (S. Suzuki).

0022-3115/$ - see front matter Published by Elsevier B.V.
doi:10.1016/j.jnucmat.2009.01.167

were less than 5% and influences on hydrogen isotope were negligible small among all the samples.

After the sample preparation, the samples were preheated at 1200 K for 10 min under ultrahigh vacuum less than 10^{-8} Pa to remove residual impurities. Thereafter, deuterium ions (D_2^+) were implanted into the films with an ion energy of 1.0 keV, an ion flux of 1.0×10^{18} D^+ m^{-2} s^{-1} and an ion fluence of 7.3×10^{21} D^+ m^{-2} at room temperature. The TDS measurements were performed from room temperature up to 1200 K with the heating rate of 0.5 K s^{-1} to evaluate the deuterium desorption behavior. The XPS measurements were also done using Al Kα as a X-ray source to clarify the chemical states of boron and carbon.

3. Results and discussion

Fig. 1 shows C-1s XPS spectra before and after D_2^+ implantation. In Fig. 1(a), it was clear that the C-1s XPS spectra consisted of three chemical states, namely C–C bond and C–B bonds with sp^3 and sp^2 hybrid orbital (C–B(sp^3) and C–B(sp^2) bonds) located at 284.5, 283.0 and 281.8 eV, respectively [10,11]. In the sample with the carbon concentration of 20%, the amount of the C–C bonds and C–B bonds were almost comparable. However, the negative peak shift was observed as the carbon concentration increased, indicating that the C–B bonds were the major chemical states in the sample with carbon concentration above 30%. After D_2^+ implantation, the peak position for all the carbon-contained boron films was located at 283.3 eV, suggesting that most of D was trapped by carbon and the C–B(sp3) bonds determine the major chemical state, which was structurally stable [12].

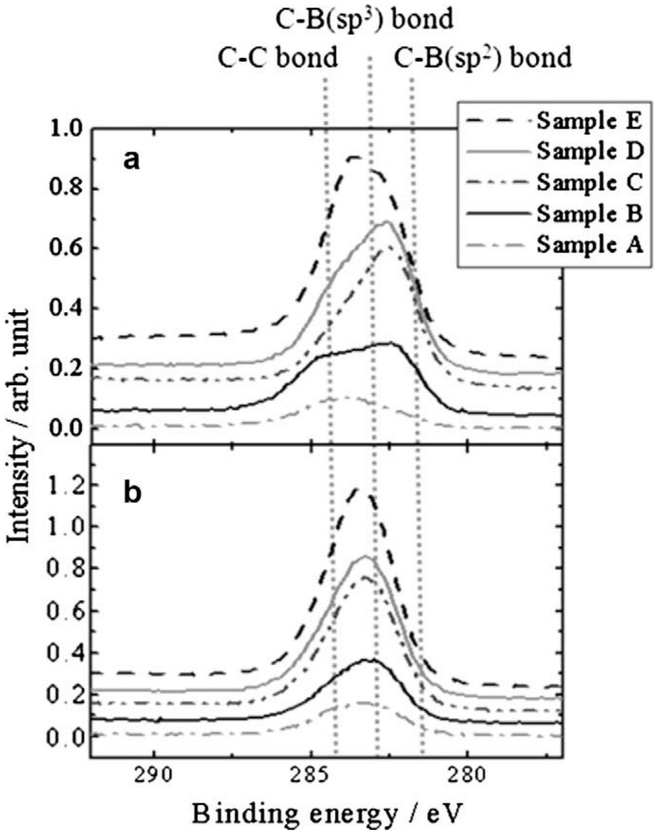

Fig. 1. The C-1s XPS spectra for each sample (a) before and (b) after D_2^+ implantation.

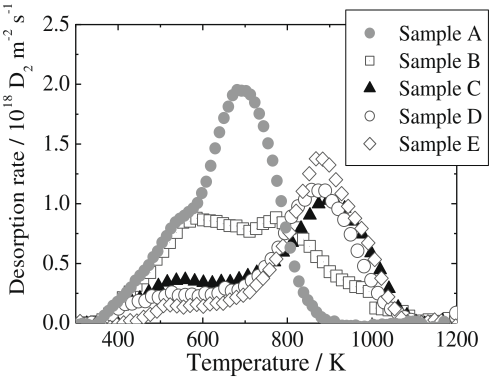

Fig. 2. The D_2 TDS spectra for each sample after D_2^+ implantation.

The D_2 TDS spectra for all the samples are shown in Fig. 2. Although large amount of D was desorbed at 700 K for Sample A, that temperature for Samples B–E was shifted to higher temperature side, suggesting that an additional desorption stage was appeared around 900 K for the carbon-contained boron film compared to the pure boron film. To estimate the D_2 desorption stages in detail, the peak analyses of the D_2 TDS spectra were carried out using a Gaussian distribution function. Fig. 3 shows the typical result of peak analysis for the 31% carbon-contained boron film, indicating that the D_2 desorption consisted of three stages. On the other hand, as reported in Ref. [9], the desorption temperatures for the pure boron film were located around 520 K and 700 K, which were attributed to the desorption stages of deuterium bound to boron with forming B–D–B bridge bond and B–D terminal bond, respectively. These two desorption stages correspond to the Peaks 1 and 2 for the carbon-contained boron film (Fig. 3). To assignment of the third desorption stage (Peak 3), which was thermally stable, the total D retention and D retentions of Peaks 1, 2 and 3 for all the samples as a function of carbon concentration were summarized in Fig. 4. It was clear that the total D retention and the D retentions of Peak 1 and 2 were decreased, whereas that of Peak 3 was increased as carbon concentration increased. In addition, it was reported that desorption temperature of D for highly oriented pyrolytic graphite (HOPG) was located around 900 K [12]. These facts suggested that Peak 3 for the carbon-contained boron films was attributed to the desorption stage of D trapped by carbon with forming C–D bond.

To elucidate the role of carbon in D retention, the ratio of D retention of Peak 3 to total D retention as a function of carbon concentration was depicted in Fig. 5. The ratio of D retention trapped by oxygen to total D retention in the oxygen-contained boron film [8] is also shown in this figure. For the carbon-contained boron film, it was found that the increasing rate of the ratio was clearly changed between the carbon concentrations of 20% and 30%, which

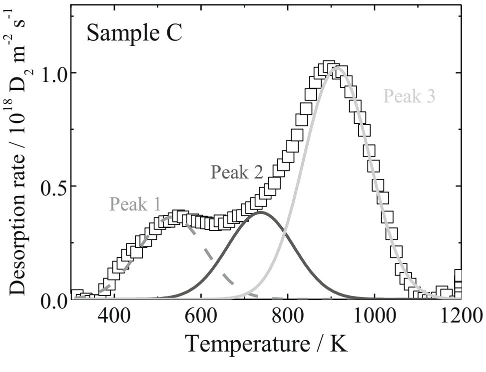

Fig. 3. The peak analysis of the D_2 TDS spectra for Sample C after D_2^+ implantation.

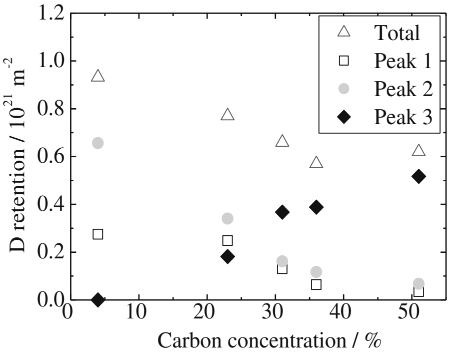

Fig. 4. The D total retention and D retentions of Peak 1, Peak 2 and Peak 3 for each sample.

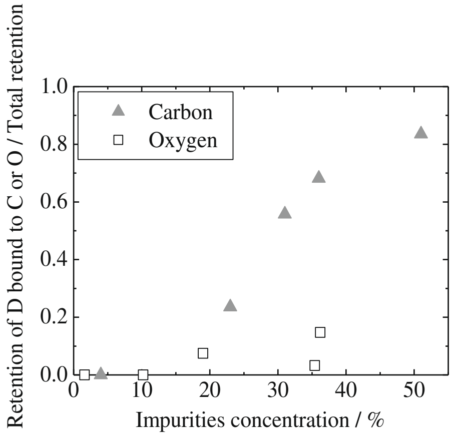

Fig. 5. The ratio of retention of D bound to C or O to total D retention P3-63.

is consistent with the C-1s XPS results that the negative peak shift for the carbon concentration more than 20% was observed. According to the phase diagram, it is known that the crystal structure is changed from B_xC to B_4C structure at the carbon concentration of 23% [13], indicating that this chemical structure change would make a large influence on D trapping in the carbon-contained boron film. In addition, 60% of total deuterium retention for the carbon-contained boron film was trapped by carbon at the carbon concentration of 30%. In the case of the oxygen-contained boron film, however, only 10% of deuterium was retained at the oxygen concentration of 30%. These results suggested that D has high affinity with carbon compared to boron. As for oxygen-contained boron film, the water formation on the surface is though to contribute to low D retention in the film (Fig. 5). Therefore, the high tritium accumulation at low temperature region in the first wall would be one of key issues if the tritiated water was formed in the vacuum vessel. From the view point of tritium retention in the first wall, the contamination of carbon is thought to be a critical issue for the boronized wall. However, the correlation between chemical structure change for the carbon-contained boron film and D trapping is not clearly understood at this point and further study will be required.

4. Conclusion

Influence of carbon concentration on chemical behavior of energetic deuterium implanted into the carbon-contained boron films was investigated by means of XPS and TDS. The total D retention and the retention of D trapped by boron in the carbon-contained boron films were decreased as increasing carbon concentration, although that by carbon was increased. 60% of the total D retention was trapped by carbon for the sample with the carbon concentration of around 30%, suggesting that D had more affinity with carbon than boron in the carbon-contained boron films. The chemical states of carbon changed clearly at the carbon concentration above 20%, which led to a significant change in the retention of D trapping by carbon. This carbon concentration is almost the same as the chemical structure change from B_xC to B_4C structure, which would lead the deuterium trapping by carbon. It can be concluded that D trapped by carbon, which was stable thermally, should be taken into consideration for the evaluation of the tritium inventory in the carbon-contained boron film with the carbon concentration over 20%

Acknowledgement

This study has been performed under Japan–China Core University program, and supported by NIFS collaboration program, NIFS07KLPP306 and Center of Instrumental Analysis at Shizuoka University.

References

[1] N. Noda, K. Tsuzuki, A. Sagara, N. Inoue, T. Muroga, J. Nucl. Mater. 266–269 (1999) 234.
[2] K. Nishimura, N. Ashikawa, S. Masuzaki, J. Miyazawa, A. Sagara, M. Goto, B.J. Peterson, A. Komori, N. Noda, K. Ida, O. Kaneko, K. Kawahata, T. Kobuchi, S. Kudo, S. Moriwa, M. Osakabe, S. Sakakibara, R. Sakamoto, K. Sato, T. Shimozyma, Y. Takeiri, K. Tanaka, O. Motojima, LHD Experimental Group, J. Nucl. Mater. 337–339 (2005) 431.
[3] 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.
[4] 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.
[5] K. Tsuzuki, H. Eiki, N. Inoue, A. Sagara, N. Noda, Y. Hirohata, T. Hino, J. Nucl. Mater. 266–269 (1999) 247.
[6] T. Nakano, S. Higashijima, H. Kubo, J. Yagyu, T. Arai, N. Asakura, K. Itami, J. Nucl. Mater. 313–316 (2002) 149.
[7] Y. Oya, H. Kodama, M. Oyaidzu, Y. Morimoto, M. Matsuyama, A. Sagara, N. Noda, K. Okuno, J. Nucl. Mater. 329–333 (2004) 870.
[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] L.G. Jacobsohn, R.K. Schlze, M.E.H. Maia de Costa, M. Nastasi, Surf. Sci. 572 (2004) 418.
[11] V. Linss, S.E. Rodil, P. Reinke, M.G. Garnier, P. Oelhafen, U. Kreissig, F. Richter, Thin Solid Films 467 (2004) 76.
[12] T. Suda, H. Miyauchi, A. Yoshikawa, H. Kimura, Y. Oya, K. Okuno, Fus. Eng. Des. 82 (2007) 1762.
[13] N. Froumin, N. Frage, M. Aizenshtein, M.P. Dariel, J. Euro, Ceram. Soc. 23 (2003) 2821.