

Effect of oxygen concentration on the chemical behavior of deuterium implanted into oxygen-containing boron thin films

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Abstract

Boronization is planned as one of the wall conditioning techniques for impurity reduction in fusion plasmas. Oxygen-containing boron films were prepared for simulating boronization, and exposed to energetic deuterium ions. From the XPS results, it was found that the B-1s peak energy was shifted to higher energy as the oxygen concentration increased. However, the deuterium retention decreased according to TDS. In addition, deuterium desorption was observed at a higher temperature, which is not found for a deuterium ion implanted pure boron film. These facts indicate that boron oxide was formed and deuterium was trapped by forming O–D bond when the oxygen concentration was above 37%. We conclude that the oxygen concentration should be kept less than 10% to prevent high tritium retention on the surface of the first wall in the future fusion devices.

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1. Introduction

Boronization has been applied to many fusion devices, JT-60U at Japan Atomic Energy Agency (JAEA), the Large Helical Device (LHD) at National Institute for Fusion Science (NIFS) and so on, as one of the first wall conditioning technique [1–3]. Boron is known to be easily bound to various impurities such as oxygen and carbon, and it keeps the impurity concentration low in plasmas [3–7]. It is thought that energetic tritium, deuterium, helium and neutron will be implanted into the boron film in

a fusion environment. Therefore, the elucidation of hydrogen isotope trapping and desorption behaviors is one of the most important issues for the evaluation of fusion safety.

In our previous studies, the effect on deuterium implantation of temperature and helium irradiation variation using high pure boron film was examined, and it was found that deuterium was trapped in the pure boron film by forming B–D–B bridge bond and B–D terminal bond [9,10]. The activation energies of B–D–B and B–D bonds were also calculated to be 1.11 ± 0.21 eV and 2.17 ± 0.36 eV, respectively [8]. The deuterium retention in the boron film was decreased by helium ion irradiation [9]. However, some impurities i.e. oxygen, will contaminate the boron film during the initial deposition of the

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coating. Therefore, it is important to elucidate the impurity effect on hydrogen retention behavior in the boron thin film. The oxygen concentration dependence on chemical behavior of energetic deuterium implanted into the oxygen-containing boron film is also discussed in the current study.

2. Experiments

The preparation of oxygen-containing boron films was performed using the plasma CVD (P-CVD) apparatus at Shizuoka University. Its detail was described in our previous paper [11]. Before the deposition, the plasma discharge for surface cleaning was performed for 30 min using only helium gas of 3.8 sccm. Thereafter, decaborane ($B_{10}H_{14}$) gas of 2.5 sccm and helium gas of 3.8 sccm were used for a material gas and a dilute gas, respectively. The substrate temperature was kept at room temperature during the deposition process and the thickness of boron was around 150 nm. By introducing oxygen gas with different concentrations into the source gas, four samples with different oxygen concentrations were prepared. The atomic composition ratios of boron in these samples were 95.9%, 82.5%, 59.0% and 58.7%, and those of oxygen were 2.0%, 11.4%, 38.8%, and 37.4%. These samples were named sample A, sample B, sample C and sample D, respectively. The concentration of oxygen for sample A was almost impurity level. The concentrations of carbon and nitrogen for the samples were less than 3%.

After heating at 993 K for 10 min as a pretreatment, deuterium ions were implanted into the samples with an ion energy of 1.0 keV and an ion flux of $1.0 \times 10^{18} D^+ m^{-2} s^{-1}$ up to the fluence of $7.3 \times 10^{21} D^+ m^{-2}$. Before the deuterium ion implantation, XPS (X-ray photoelectron spectroscopy, ALVAC-PHI Inc., ESCA 1600 Series) using Mg-K α as an X-ray source and TDS (thermal desorption spectroscopy) measurements were carried out for each sample. The heating rate for TDS was set to be $0.5 K s^{-1}$ and the sample was heated up to a temperature of 993 K. The molecules desorbed from the sample were measured using a quadrupole mass spectrometer (QMS).

3. Results

Fig. 1 shows the B-1s XPS spectra for the samples before the deuterium ion implantation. For the samples A and B, a peak appeared at around

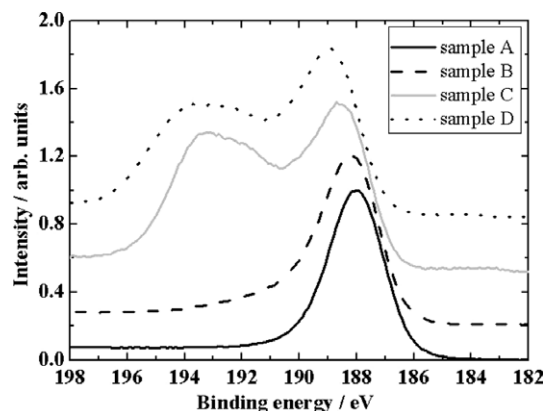


Fig. 1. The B-1s XPS spectra for each sample before deuterium ion implantation.

188 eV. For the samples C and D, two peaks were observed at around 189 eV and 193 eV, respectively. It was suggested that the peak energy of 188–189 eV corresponded to pure boron state and that of 193 eV, B_2O_3 state, respectively [12,13]. The B-1s peak energies for the samples C and D were located at pure boron state, but these peaks were slightly shifted to higher energy side by the oxygen contained in the boron film.

The TDS spectra of D_2 for the samples were shown in Fig. 2. The deuterium retentions of the samples A, B, C and D were estimated to be $4.46 \times 10^{21} D m^{-2}$, $1.25 \times 10^{21} D m^{-2}$, $7.88 \times 10^{20} D m^{-2}$ and $3.22 \times 10^{20} D m^{-2}$, respectively. The peak analysis was carried out using a Gaussian function to fit each TDS spectrum. Fig. 3 shows the typical results of peak

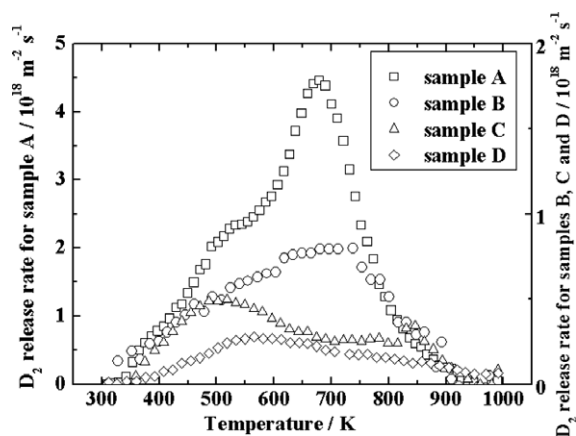


Fig. 2. TDS spectra of D_2 for each sample. The composition ratios of B and O were 95.9% and 2.0% for sample A, 82.5% and 11.4% for sample B, 59.0% and 38.8% for sample C and 58.7% and 37.4% for sample D.

analysis for the samples A and D. It was found that the TDS spectra for both samples consisted of three peaks. The peak analysis of the sample A is almost the same as the results of peak analysis performed in our previous study [9]. Peak 1 was attributed to the desorption of deuterium trapped by interstitial site, which was observed only in the sample A. This fact suggested that as the deuterium was released as D_2O during deuterium implantation and its retention was largely decreased for the oxygen-containing boron with oxygen concentration above 10%, deuterium retention trapped by interstitial site would be negligible small.

Peaks 2 and 3 corresponded to the desorption of deuterium bound to boron with forming B–D–B bridge bond and a B–D terminal bond, respectively. These bonds could be simultaneously formed. However, for the samples C and D, another desorption

peak, namely Peak 4, was observed at the higher temperature side (850 K).

4. Discussion

It was found that a B–O bond occurs while forming B_2O_3 in the boron film during introduction of oxygen during the P-CVD process. By adding oxygen in the boron film, the deuterium retention was clearly decreased as shown in Fig. 4. It can be said that the implanted deuterium was trapped by oxygen with O–D bond and quickly detrapped from the sample by forming D_2O or D_2 , which was consistent with D_2O and D_2 releases observed by a mass spectrometer during the deuterium ion implantation. In Fig. 4, the deuterium retention associated with each peak of Fig. 3 is also shown. It was found that the deuterium retentions from Peaks 2 and 3 were decreased with increasing oxygen concentration, especially that from Peak 3 which was strongly decreased to less than 5% for oxygen concentrations above 37%. Therefore, it was suggested that the decrease of deuterium retention was caused by decreases of available B–D bonds. However, the deuterium retention associated with Peak 4 was slightly increased. These facts also indicate that the B–O bond formation prevents deuterium trapping through B–D bond formation in the boron film although some deuterium was likely trapped by forming O–D bonds.

Fig. 5 summarizes the ratio of B_2O_3 peak area to total boron peak area ($A_{B_2O_3}/A_{total B}$) for the deuterium implanted samples estimated by XPS as well as the deuterium retention associated with Peak 4 by

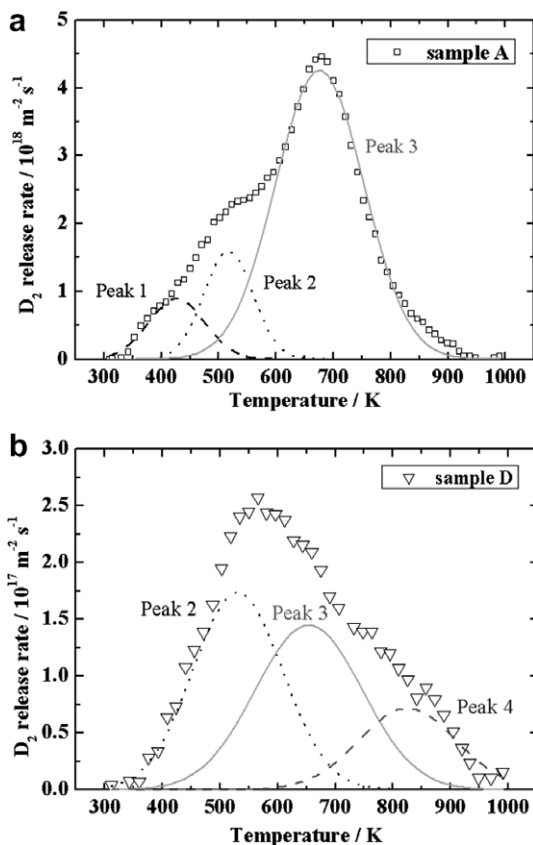


Fig. 3. The peak analysis for samples A and D. The composition ratios of B and O were 95.9% and 2.0% for sample A and 58.7% and 37.4% for sample D. Peaks 1–4 were corresponded to interstitial site, B–D–B bond, B–D bond and O–D bond, respectively.

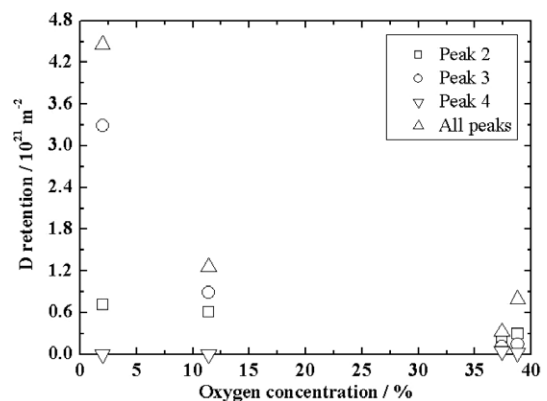


Fig. 4. The deuterium retentions of all peaks, Peak 2, Peak 3 and Peak 4 for each sample. Peaks 1–4 corresponded to interstitial site, B–D–B bond, B–D bond and O–D bond, respectively.

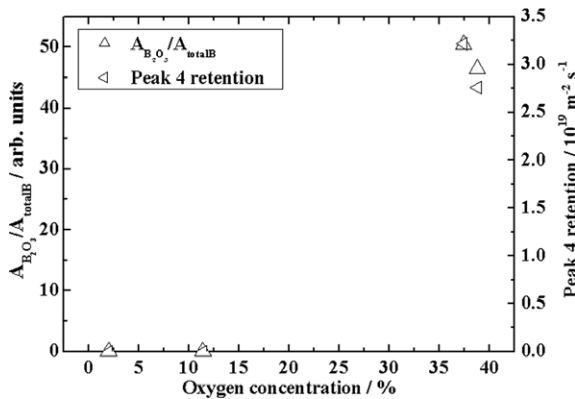


Fig. 5. The ratio of B_2O_3 peak area to total boron peak area ($A_{B_2O_3}/A_{total\ B}$) for the deuterium implanted sample estimated by XPS and the deuterium retention from Peak 4 by TDS as a function of oxygen concentration.

TDS as a function of oxygen concentration. The deuterium desorption from Peak 4 was only observed in samples C and D, and increased as the oxygen concentration increased. This result is almost consistent with the XPS results that the $A_{B_2O_3}/A_{total\ B}$ ratio for the sample C was larger than that for the sample D as shown in Fig. 5. These facts indicate that the existence of B_2O_3 induced the deuterium desorption from Peak 4, where deuterium was trapped by oxygen.

A study of the surface oxygen concentration in a boronized wall in the JT-60 reached around 20% [7]. This fact implies the B_2O_3 could be formed in the boron layer on the first wall of future fusion devices and tritium would be trapped with high binding energy, which could lead to high tritium retention on the surface of the first wall. According to the present study, B_2O_3 is not significantly formed if the oxygen concentration is less than 10%. These results conclude that the oxygen concentration should be kept less than 10% to prevent the retention of tritium trapped with high binding energy on the surface in the future fusion devices.

5. Conclusion

The four samples with different oxygen concentration were prepared using P-CVD for simulating boronization. The chemical states and desorption processes for the oxygen-containing sample with

deuterium ion implantation were studied by XPS and TDS. From XPS results, the B-1s peak energy was shifted to higher energy as the oxygen concentration increased, indicating that B_2O_3 was formed in the boron film with high oxygen concentration. However, deuterium retention was decreased according to the TDS results. The deuterium retention for the sample with the oxygen concentration above 37% was decreased to less than 5% compared to that for the pure boron film. However, deuterium desorption occurred at a higher temperature, which indicates that the deuterium was trapped by oxygen by forming an O–D bond when the oxygen concentration was above 37%. These results indicate that the oxygen concentration should be kept less than 10% to prevent tritium retention high on the surface of the first wall in the future fusion devices.

References

- [1] Institute of Gas Technology, 3424S. State Street Chicago, IL 60616, *J. Power Sources* 5 (1980) 372.
- [2] J. Winter, H.G. Esser, L. Konen, V. Philipps, H. Reimer, J.v. Seggern, J. Schluter, E. Vietzke, F. Waelbroeck, P. Wienhold, T. Banno, D. Ringer, S. Vepiek, *J. Nucl. Mater.* 162–164 (1989) 713.
- [3] J. Winter, *Plasma Phys. Control. Fus.* 38 (1996) 1503.
- [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.* 266–269 (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] Y. Oya, H. Kodama, M. Oyaizu, Y. Morimoto, M. Matsuyama, A. Sagara, N. Noda, K. Okuno, *J. Nucl. Mater.* 329–333 (2004) 870.
- [9] H. Kodama, M. Oyaizu, A. Yoshikawa, H. Kimura, Y. Oya, M. Matsuyama, A. Sagara, N. Noda, K. Okuno, *J. Nucl. Mater.* 337–339 (2005) 649.
- [10] A. Yoshikawa, M. Oyaizu, H. Kimura, T. Takeda, Y. Oya, M. Matsuyama, A. Sagara, N. Noda, K. Okuno, in: *Proceedings of the eighth Japan–China symposium, 2005*, p. 145.
- [11] M. Oyaizu, A. Yoshikawa, H. Kodama, Y. Oya, A. Sagara, N. Noda, K. Okuno, *Appl. Surf. Sci.* 244 (2005) 240.
- [12] M.M. Ennaceur, B. Terreaux, *J. Nucl. Mater.* 280 (2000) 33.
- [13] O.M. Moon, B.-C. Kang, S.-B. Lee, J.-H. Boo, *Thin solid films* 464&465 (2004) 164.