ELSEVIER

Journal of Nuclear Materials 266–269 (1999) 247–250

journal of nuclear materials

Hydrogen absorption/desorption behavior with oxygen-contaminated boron film

K. Tsuzuki [a,*], H. Eiki [b], N. Inoue [a], A. Sagara [a], N. Noda [a], Y. Hirohata [b], T. Hino [b]

[a] *National Institute For Fusion Science, Graduate University Advanced Studies, Oroshi-cho 322-6, Toki 509-52, Japan*
[b] *Department of Nuclear Engineering, Hokkaido University, Sapporo 060, Japan*

Abstract

The effect of oxygen contamination on hydrogen absorption and desorption behavior from a boron coating film has been studied. Oxygen atoms were implanted by glow discharge in an O_2/He gas mixture until near saturation, into the boron film deposited by PCVD. The depth profile measurement by AES showed that O atoms were retained up to the depth of 20 nm. Hydrogen discharges were carried out to investigate the H absorption behavior. The capability of H absorption decreased for 30–50% compared to the pure boron film without O contamination. After the discharge, the depth profile of the oxygen atoms was not changed, which means that a stable oxide layer had formed. The reduction of the H absorption capability occurs probably because the formation of the boron oxide prevents H atoms from trapping in the form of B–H bonding. Most of the retained H atoms can be released by a heating up to 500°C with the O contamination. The required temperature for H evacuation is slightly higher than that for pure boron film. In addition, a small peak was observed at around 200°C. From these results, the applicability of boronization to future long term discharges was discussed, in which the boron film saturates with O contamination. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Boronization; Hydrogen recycling; Oxygen impurity

1. Introduction

In situ boron coating of the first wall of fusion experimental devices (boronization) has been applied to many devices [1–6]. Plasma parameters have been improved with boronization in many devices due to reduction of metal, oxygen, and carbon impurities. Hydrogen recycling from the first wall also decreased compared to carbonization with a high temperature wall. Lower H recycling is favorable for better plasma density control and energy confinement [7]. In future long term discharges, the understanding of the dynamic behavior of H atoms is also important for density control because transient release of excess H atoms occurs and it makes plasma density control difficult [8]. Thus we have studied H behavior with boron films.

So far hydrogen behavior in pure boron film has been investigated with the Surface modification teststand (SUT) [9–11]. The capability of H and O absorption was measured with high accuracy by utilizing a liner with a large surface area. The pumping effect of H and O is effective to reduce the O impurity and H recycling in the present fusion devices. For the application to future long term discharges, the dynamic behavior of H atoms in boron films was analyzed based on the experimental results. In addition, as possible application of the boronization to future long term discharge, the application as a protection layer for tritium permeation has been proposed [10] based on the following findings: (1) hydrogen atoms are retained only in the near surface region when they are implanted at a few hundreds of eV, and (2) most of them can be released by a heating up to 400°C. The temperature is relatively lower, and thus, the H removal by heating is easier compared to carbon materials.

These results show attractive features of boronization for both present and future devices. However, when we

* Corresponding author. Tel.: +81 57258222; fax: +81 572582618; e-mail: tuzuki@nifs.ac.jp

0022-3115/99/$ – see front matter © 1999 Elsevier Science B.V. All rights reserved.
PII: S0022-3115(98)00575-3

discuss the applicability of boronization to long term discharges, the effect of impurities has to be taken into account. The surface will saturate with O atoms during the discharge. The transient release of H atoms mentioned above may occur from the O saturated B coating film. Then it is important to understand H behavior with O contaminated B films for the density control. The investigation of thermal desorption behavior with the contamination is also important for the application because the required temperature for H evacuation could change due to the contamination.

In this study, the H absorption and desorption behavior of O contaminated boron films are investigated. The results are compared with that of the O free film. The mechanisms and the effect to the application are discussed.

2. Experimental

The SUT [9–11] is mainly used in this study. It is equipped with a liner made of stainless steel, which acts as a large sample with the surface area of 7000 cm^2. Boron films are coated on the whole inner surface of the liner by a dc glow discharge in 5% B_2H_6 + 95% He. The temperature of the liner is kept less than 60°C during the discharge. The hydrogen atoms retained during the coating are evacuated by raising the whole liner temperature up to 500°C. To prepare O contaminated film, the discharge in 10% O_2 + 90% He is carried out for 20 min at around room temperature, after the deposition and the heating. Hydrogen absorption behavior is investigated with the discharge in H_2. The hydrogen desorption behavior is investigated by the thermal desorption experiment up to 500°C. The temperature of the liner increased almost linearly at the ramping rate of 10°C/min. The total and partial pressure during the experiments are monitored by a diaphragm gauge and a quadrupole mass spectrometer, respectively. The net absorption rate is calculated from the pressure change by multiplying the pumping speed (typically 16 l/s). The discharge conditions are the same as the previous papers [9–11].

The experimental procedure is as follows: (1) film deposition and heating, (2) H_2 discharge and heating for the investigation of O free film, (3) O implantation, and (4) H_2 discharge and heating for the investigation of O contaminated film. The reproducibility of the experiment was checked by repeating step (2) a few times. After that, the O_2 discharge was carried out (step (3)). The effect of O contamination on H behavior was discussed by comparing the results in (2) and (4).

Small test pieces are used to measure the surface composition and the depth profile. The sample is set at the same condition of the liner surface during the experiment. It is transported to an analyzing chamber without exposure to the air. The surface concentration is measured by Auger electron spectroscopy (AES) with 2 keV e-beam. During the measurement of the depth profile, the sample is etched by 3 keV Ne^+ ion beam at the etching rate of ~1 nm/min.

3. Results

The depth profile of the boron films was measured just after the deposition. The concentration of the impurities was limited less than a few percents at the top surface. The concentration was kept less than a few percents up to the interface between stainless steel substrate. During the O_2 discharge, the change in O_2 pressure was monitored by QMS with differential pumping system. The O_2 pressure decreased when the discharge was ignited, that means O atoms are absorbed into the film. The total number of O atoms was calculated from the pressure change and estimated to be 6×10^{16} atoms/cm^2. The depth profile after the discharge is shown in Fig. 1. The concentration of O atoms at top surface was of 38%. It decreased with depth and became background level at 20 nm. The deposition was carried out several times to prepare flesh boron film without oxygen. The film property was almost reproducible.

Fig. 2 shows time evolution of total pressure during the H_2 discharge with and without oxygen impurity. The partial pressure of other gas species was not changed, and then, the total pressure was regarded as the H_2 pressure. In the case of boron film without oxygen, the pressure was almost constant at 2.6 Pa before the discharge. The pressure rapidly decreased just after the ignition of the discharge due to hydrogen absorption into the film. After the strong absorption up to 30 min, the absorption continued without saturation up to 10 h [9–11]. In the case of boron film with oxygen, the strong

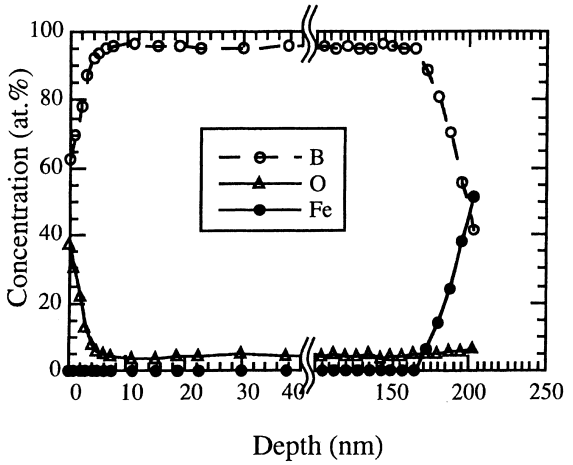

Fig. 1. Depth profile of boron film measured by Auger electron spectroscopy (AES) with 3 keV Ne^+ beam etching, after exposure to O_2/He discharge. The lines are a guide to the eye.

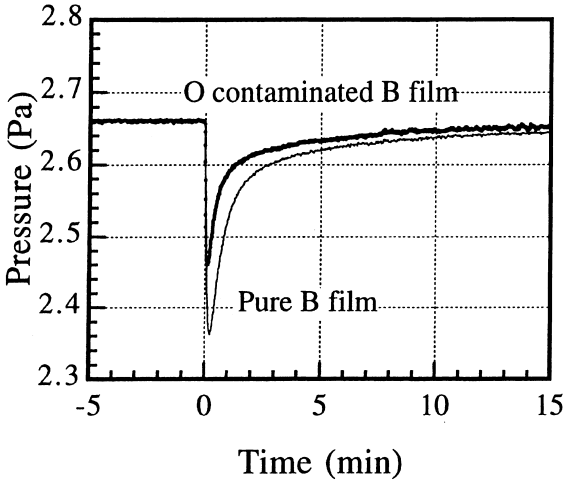

Fig. 2. Time evolution of total pressure during H_2 discharge with and without O contamination. The pressure decreased due to hydrogen absorption into the film. The absorption weakened with O contamination.

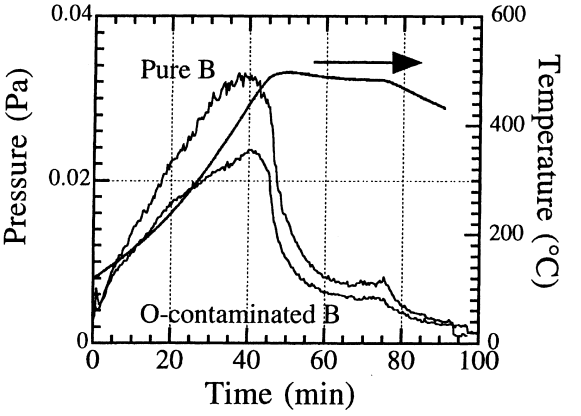

Fig. 3. Time evolution of H_2 pressure and liner temperature during heating. Solid line shows results with the pure boron film and dotted line shows that with O contaminated film. The desorbed number decreased with O contamination.

absorption just after the ignition was also observed. The pressure drop at the beginning of the discharge became smaller and the length of the strong absorption phase became shorter, compared to the case of O free film. The total amount of absorbed H atoms are calculated by integrating the pressure change from the baseline. The straight line from the initial value before the discharge and the final value after the discharge was taken as the baseline. The value is estimated to be 9×10^{16} atoms/cm^2 and 6×10^{16} atoms/cm^2, respectively. The accuracy of the integrated value is not so good because the value is strongly affected by a way to set the baseline. But it is confirmed by repetitive experiments that the hydrogen absorption decreased by 30–50% with O contamination.

Fig. 3 shows hydrogen pressure during the heating after the H_2 discharge, with and without O contamination. The pressure is measured by the QMS with differential pumping system. The QMS signal is converted to absolute partial pressure by a calibration with the diaphragm gauge. In the case of O free boron film, the desorption rate increased almost linearly with temperature up to 400°C, reached peak value, and then decreased. In the case of O contaminated film, the pressure also increased continuously, and reached peak value at 450°C. This peak position corresponds to switching off of the external heating. Thus actual peak may be exist at higher temperature. The curve had small shoulder around 200°C, that O contaminated film has the desorption peak at lower temperature.

The total amount of desorbed H atoms was calculated by integrating the curve. It is estimated to be 9×10^{16} atoms/cm^2 and 7×10^{16} atoms/cm^2, respectively. The desorbed number is almost the same with the absorbed number during the preceding H_2 discharge in each case. The most of retained H atoms can be released by the heating up to 500°C even when the surface is contaminated by oxygen.

4. Discussion

From these results, it is concluded that H retention with O contamination is 50–70% of that without O. State of H atoms in the B film is not well understood. However, it is clear from the experimental results that they are trapped in the boron film and do not move at least for a few days at room temperature [11]. Some of H atoms might be trapped in the form of B–H bond similarly to H atoms in graphite [12].

It is reported by XPS measurement that B_2O_3 are generated by O ion implantation to B_4C and pure B polycrystal [13]. In this experiment, the shape of the AES signal changed by O implantation as shown in Fig. 4. This indicates that a kind of oxide is generated by the O implantation [14].

Implanted O atoms are distributed up to 20 nm as shown in Fig. 1. The range is similar to the implantation range of H atoms of 6.5 nm, calculated by using computer simulation with TRIM code [11,15]. The number of absorbed O atoms is similar to that of H atoms. Thus the reduction of H retention by O contamination can be attributed by the formation of boron-oxide followed by the decrease in number of dangling bond for H trapping.

Lower hydrogen retention is favorable for better plasma density control because the transient release of H atoms can be suppressed. The retention will further decrease at elevated temperature. The required temperature for H evacuation of O contaminated boron film was slightly higher than that for pure boron film, but still

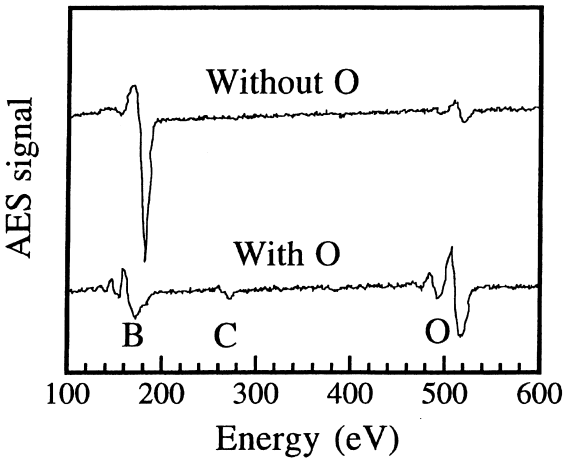

Fig. 4. AES signals with and without oxygen. The peak broadened by O implantation which corresponds to formation of oxide layer.

lower than that for carbon wall. Then the attempt to apply high temperature wall for the reduction of H recycling is easier with boron coating.

To confirm the stability of oxide layer, the depth profile was measured after the H_2 discharge exposure. The results are shown in Fig. 5. The concentration of top surface slightly decreased by the H_2 discharge. The profile was almost identical before and after the exposure. It means that the oxide layer is stable enough to prevent deoxidation by the hydrogen impact. This is favorable properties for the application to fusion devices. In the case of metal wall, the oxygen impurity is released from the oxide layer at the metal surface due to a reaction with hydrogen. In the case of boronized wall, the absorbed O atoms are not released even when the discharge continued for longer term.

From these consideration, we can conclude that the distinctive feature of the boron films mentioned in Section 1 was not degraded by the O contamination or slightly improved due to the reduction of H retention.

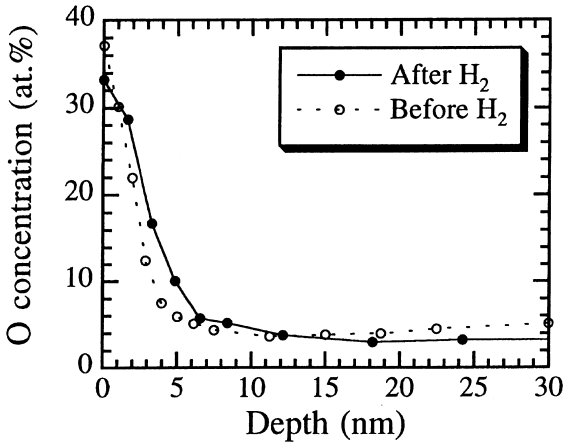

Fig. 5. Depth profile of O atoms in boron film. Open circles show the results just after the O_2 discharge, and close circles show that after H_2 discharge, following to O_2 discharge. The lines are a guide to the eye.

5. Conclusion

The hydrogen behavior with boronized wall has been investigated in the presence of oxygen impurity. The hydrogen absorption capability decreased for 30–50% compared to the pure boron film without oxygen. Most of absorbed H atoms were released by the heating up to 500°C. The required temperature for the H evacuation was slightly higher than that for pure boron film, but still lower than that for a graphite and an amorphous carbon.

The depth profile measurements by AES showed that the O atoms are implanted up to the depth of 20 nm. The profile did not change by the H_2 discharge exposure. It means that implanted O atoms are stable and not re-emitted during the discharge.

Form the results and previous report [13], the oxygen atoms seem to form boron oxide layer. The reduction of H retention can be attributed by the oxide formation followed by the decrease of dangling bond, and thus, the decrease of H trapping sites.

These are favorable results for the application to future long term discharge. The plasma density control will become easier by the reduction of H retention. The pumping effect of O impurity disappears when the film saturates with O, but they are not re-emitted to the main plasma.

References

[1] J. Winter et al., J. Nucl. Mater. 162–164 (1989) 713.
[2] H.F. Dylla et al., J. Nucl. Mater. 176&177 (1990) 337.
[3] G.L. Jackson et al., J. Nucl. Mater. 196–198 (1992) 236.
[4] U. Schneider et al., J. Nucl. Mater. 176&177 (1990) 350.
[5] M. Saidoh et al., Jpn. J. Appl. Phys. 32 (1993) 3276.
[6] H. Yamada et al., Jpn. J. Appl. Phys. 33 (1994) L1638.
[7] S. Higashijima et al., J. Nucl. Mater. 220–222 (1995) 375.
[8] N. Noda, Contribution to High-temperature Plasma Physics, Akademie Verlarg, Berlin, 1994, p. 21.
[9] K. Tsuzuki et al., Vacuum 47 (1996) 931.
[10] K. Tsuzuki et al., J. Nucl. Mater. 241–243 (1997) 1055.
[11] K. Tsuzuki et al., J. Nucl. Mater. in print.
[12] S. Yoshida, H. Sugai, H. Toyoda, Jpn. J. Appl. Phys. 28 (1988) 1101.
[13] R. Zehringer et al., J. Nucl. Mater. 176–177 (1990) 748.
[14] G. Hanke, K. Muller, J. Vac. Sci. Technol. A 2 (1984) 964.
[15] J.P. Biersack, W. Eckstein, Appl. Phys. A 34 (1984) 73.