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Behavior of deuterium in boron films covered by oxygen-containing layer

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Abstract

The behavior of deuterium in boron films covered by an oxygen-containing layer was studied by means of XPS and TDS. The pure boron films were deposited on a Si substrate by plasma chemical vapor deposition (PCVD) using a mixture of the gases, decaborane ($B_{10}H_{14}$) and helium, and two kinds of boron films covered by oxidized boron layer were prepared on pure boron films by PCVD using $B_{10}H_{14}$, He and O_2, and by oxidation using O_2 + He plasma, respectively. Boron films were irradiated by 3 keV D_2^+ at a flux of 1×10^{18} D^+ m^{-2} s^{-1} up to 1×10^{22} D^+ m^{-2}. It was found that less oxygen in the surface layer of the boron film can reduce the deuterium retention and the oxygen in the boron film is preferentially sputtered by deuterium ions due to chemical reactions between deuterium and oxygen during the D_2^+ irradiation.

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1. Introduction

Boron is a candidate plasma facing material in fusion devices. Not only can it significantly decrease impurity concentration in the core plasma and hydrogen recycling to improve the plasma confinement, but also the deuterium retained in it can be desorbed at lower temperature [1], which is very important for current tokamaks and future reactors. In-situ boronization has been applied in TEXTER [2], ASDEX [3], TFTR [4], DIII-D [5], JT-60 [6], and HL-1M [7] tokamaks, which remarkably decreased the carbon, oxygen and metal impurities in the plasma and hydrogen recycling due to its greater gettering ability compared to stainless steel wall, graphite wall and carbonized wall, resulting in an improvement of the plasma confinement performance. The hydrogen co-deposited in boron film during boronization and implanted into the film during tokamak discharges has a great influence on the hydrogen recycling during discharges. The behavior of deuterium implanted into a boron film has been studied previously [8–10]. However, oxygen and carbon are the main impurities in in-situ boronized coatings in present tokamaks and future reactors, and are difficult to remove, which affects

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the hydrogen retention and impurity release from the boronized film. This paper studies the effect of a thin oxygen-containing boron layer on the behavior of deuterium implanted into boron films by X-ray photoelectron spectroscopy (XPS) and thermal desorption spectroscopy (TDS).

2. Experiment

Three kinds of samples were used in the experiment. A pure boron film (sample $1^{\#}$) was used as a reference for others prepared by DC glow discharge in a plasma chemical vapor deposition (PCVD) apparatus at Shizuoka University, which was described in detail in Ref. [8]. The PCVD chamber was evacuated by a turbomolecular pump to less than 10^{-6} Pa. Decaborane ($B_{10}H_{14}$) was then vaporized at 403 K in the PCVD chamber at a flow rate of 2.5 sccm (standard cubic centimeters per minute) with dilution of He at 3.8 sccm. The boron films were deposited onto monocrystal silicon wafers with substrate temperature of 673 K at a power of 50 W and frequency of 13.56 MHz for 50 min. During the PCVD process, the pressure was monitored at 25 Pa by a baratron gauge. The thickness of boron film was estimated to be 150 nm using a quartz crystal oscillator. Sample $2^{\#}$ was deposited with $B_{10}H_{14}$ (2.5 sccm), He (3.8 sccm) and O_2/He (1000 vppm, 1.0 sccm) at 673 K for 7 min after being deposited by the same processes as sample $1^{\#}$. The thickness of the oxygen-containing layer was about 10 nm. Sample $3^{\#}$ was prepared by plasma oxidation of a pure boron film deposited by the same process as sample $1^{\#}$ using a gas mixture of O_2/He (1000 vppm at 5.0 sccm) at 673 K with a discharge power of 100 W for 15 min. The thickness of the oxidized layer was very thin, less than 2 nm. After the PCVD process, these samples were transferred from the PCVD apparatus to XPS and TDS apparatuses without atmospheric exposure via a special transfer lock vessel through a glove box connected to the PCVD chamber.

The compositions and chemical state of the boron films were analyzed by X-ray photoelectron spectroscopy (XPS) using an Al Kα 1486.6 eV X-ray source and a hemispherical electron analyzer in an ESCA 1600 series, ULVAC-PHI Inc. The background pressure in the XPS and TDS chambers was 10^{-8} Pa. The boron films were heated and held at 993 K for 10 min to remove residual gas. Then, 3 keV deuterium ions were implanted into the samples at a flux of $1 \times 10^{18}\ D^{+}\ m^{-2}\ s^{-1}$ up to $1 \times 10^{22}\ D^{+}\ m^{-2}$ at normal incidence at room temperature. The projected range of deuterium ions was estimated to be 27, 29 and 34 nm for samples $1^{\#}$, $2^{\#}$ and $3^{\#}$ using the SRIM code, respectively. It was found that the projected range of deuterium ions was deeper than the thickness of the oxygen-containing layer of sample $2^{\#}$ and sample $3^{\#}$. After deuterium ion irradiation, the chemical states of the films was measured by XPS and the release behavior of deuterium from the boron films were estimated by means of thermal desorption spectroscopy (TDS) with a heating rate of 0.5 K s^{-1} up to 993 K.

3. Results and discussion

The deposited boron films used in the experiments were dense. The average atom concentration of boron in the bulk of the film of sample $1^{\#}$ was 97% and the rest was oxygen and carbon. The oxygen and carbon concentrations were 5% and 12% on the surface, respectively. For sample $2^{\#}$, the average atomic concentration of oxygen and carbon within oxygen-containing layer was 1.6% and 1.5%, respectively, but on its surface, the concentration of oxygen and carbon was 8% and 10%, respectively. On the surface of sample $3^{\#}$, the oxygen and carbon concentrations were 18% and 4.3%, respectively. At 2 nm, the oxygen and carbon concentrations were same as 1.6%. Fig. 1 shows the XPS spectra of B 1s before deuterium irradiation. The binding energy of B 1s was 187.6 eV. During the deposition of sample $2^{\#}$, the partial pressure of oxygen gas was much lower than that of decarborane vapor gas for

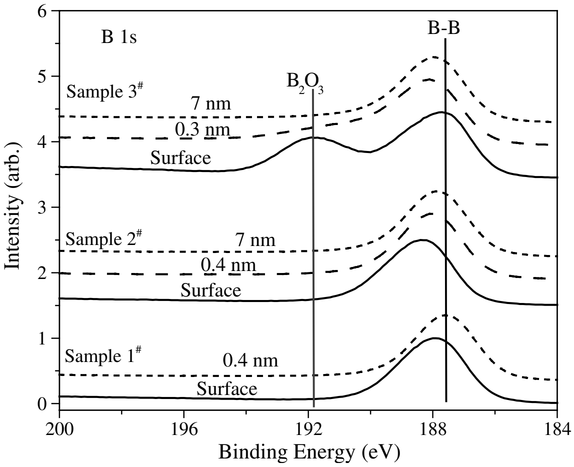

Fig. 1. The XPS spectra of B 1s obtained for the three boron films before D^{+} irradiation.

experimental safety. This resulted in a small content of oxygen in its oxygen-containing layer and B_2O_3 disappeared. The peak position of B 1s in this layer was shifted to about 0.3–0.7 eV higher energy due to formation of B–O bond compared to that of sample $1^{\#}$. For sample $3^{\#}$, two peaks of B 1s located at 192 eV and 187.6 eV were observed in the oxidized boron layer, which corresponded to the bond of B_2O_3 and pure boron, respectively [11]. It was suggested that the boron within less than 2 nm of the surface of sample $3^{\#}$ was oxidized by the plasma with a gas mixture of oxygen and helium for 15 min and B_2O_3 was formed in the oxidized boron layer.

After the deuterium irradiation, the binding energy of B 1s was increased by 0.36 eV due to trapping of deuterium in the boron film of sample $1^{\#}$, which is consistent with the results by Oya [1]. Fig. 2 shows the chemical states of boron on the surface of sample $3^{\#}$ before and after deuterium irradiation, and recovers after TDS. After deuterium irradiation, the peak in binding energy of B–B was increased by about 0.3 eV due to trapping deuterium and recovered to the original position after TDS. This result implies that the deuterium atoms trapped in the boron film were mostly desorbed. After the irradiation and TDS, the peak of B 1s at the binding energy of 192 eV, corresponding to B_2O_3, disappeared, but a small shoulder at the position can be seen and the atom concentration of oxygen on the surface decreased from 18% to 8%.

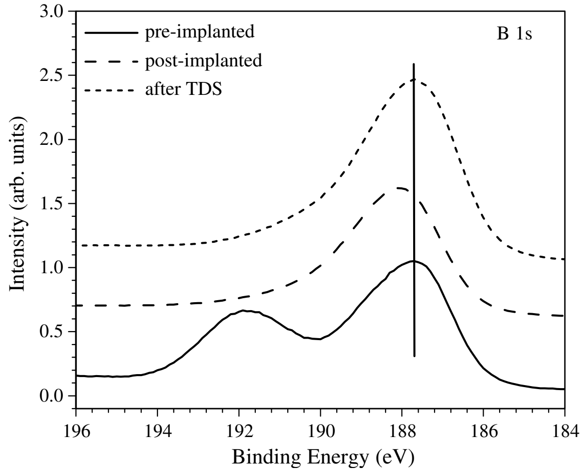

Fig. 2. Comparison of the chemical states of boron on the surface of sample 3 before and after deuterium irradiations, and after TDS.

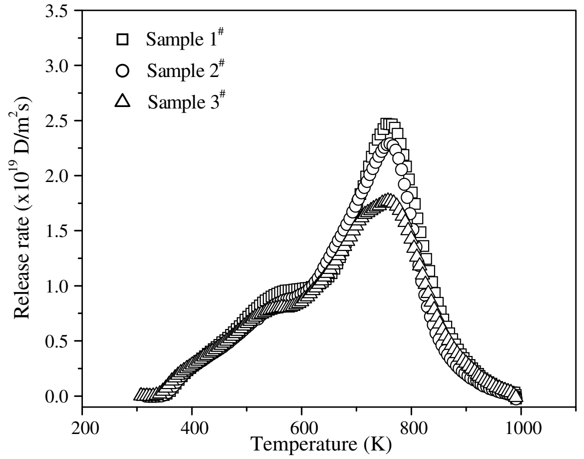

Fig. 3. The TDS spectra for three samples after 3 keV D^+ irradiation.

Fig. 3 shows the TDS spectra after deuterium irradiation for three samples. Three desorption peaks, peaks 1, 2 and 3, could be identified at about 460, 580 and 760 K, corresponding to desorption of the adsorbed D on the surface and deuterium bond to boron as B–D–B and B–D, respectively [1]. Peak 1 was at 460 K for the three samples. For samples $2^{\#}$ and $3^{\#}$, peak 2 decreased by 10% and 17% compared with the sample $1^{\#}$, respectively. Peak 3 for samples $2^{\#}$ and $3^{\#}$ decreased by 7% and 29% compared with the sample $1^{\#}$, respectively, and the peak temperature shifted slightly lower. The deuterium retention in the boron films was obtained by integration of the release rate of deuterium in time. The retention in sample $2^{\#}$ and $3^{\#}$ decreased by 8% and 16% compared with the sample $1^{\#}$, respectively. These results indicate that less oxygen in the surface layer of the boron film can decrease the deuterium retention in the boron film, especially for the release peak of B–D at high temperature, and the release peak height largely decreases with the increase of oxygen concentration in the near surface layer of the boron films as compared to the peaks of B–D–B. It may be because the oxygen is preferentially sputtered by deuterium ions due to a chemical reaction between deuterium and oxygen during the D_2^+ irradiation.

4. Conclusions

The behavior of deuterium in boron films covered by an oxygen-containing layer was studied by means of XPS and TDS. The peak position of

B 1s in the oxygen-containing layer was increased by 0.3–0.7 eV due to combination with oxygen. After D_2^+ irradiation, the peak energy of B 1s in the near surface or in the bulk of all samples was increased by about 0.3 eV due to trapped deuterium and the oxygen concentration in the oxygen-containing layers of the samples $2^\#$ and $3^\#$ obviously decreased. Compared with sample $1^\#$, peak 3 shifted to lower temperature and the peak height decreased by 7% and 29% for sample $2^\#$ and sample $3^\#$, respectively. This indicates that peak 3, corresponding to the bond of B–D, decreased more obviously with oxygen in the near surface layer of boron films than that of B–D–B at lower temperature. The deuterium retention in the boron films covered by oxidized boron, samples $2^\#$ and $3^\#$, decreased by 8% and 16% compared with the pure boron film of sample $1^\#$, respectively. This implies that less oxygen in the surface layer of the boron film can reduce the deuterium retention in the boron film. It may result from the preferentially sputtering of oxygen by deuterium ions due to chemical reactions between deuterium and oxygen during the D_2^+ irradiation.

Acknowledgements

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