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Studies on structural and chemical characterization for boron coating films deposited by PCVD

H. Kodama [a,*], M. Oyaidzu [a], M. Sasaki [a], H. Kimura [a], Y. Morimoto [a], Y. Oya [b], M. Matsuyama [c], A. Sagara [d], N. Noda [d], K. Okuno [a]

[a] *Radiochemistry Research Laboratory, Faculty of Science, Shizuoka University, 836, Oya, Shizuoka-shi, Shizuoka 422-8529, Japan*
[b] *Radioisotope Center, The University of Tokyo, 2-11-16, Yayoi, Bunkyo-ku, Tokyo 113-0032, Japan*
[c] *Hydrogen Isotope Research Center, Toyama University, 3190 Gofuku, Toyama 930-8555, Japan*
[d] *National Institute for Fusion Science, 322-6, Oroshi-cho, Toki, Gifu 509-5292, Japan*

Abstract

Characterization of the structure and the chemical state of boron in boron coating film were performed by XRD and TDS measurements. The structure of the boron coating film was shown to be amorphous by XRD measurement. By changing the total pressure, the discharge power, and the substrate temperature, the growth rate of the boron coating film and the hydrogen retention were evaluated. It was found that the growth rate decreased as the total pressure increased, and increased with an increase in the discharge power. For the substrate temperature dependence, the hydrogen retention decreased as the substrate temperature increased. However, the growth rate remained constant, although the hydrogen retention decreased as the substrate temperature increased. This indicates that the growth rates are not controlled by the chemical form of B–H bond, but by that of B-B bond. In the TDS analysis, hydrogen atoms released from B–H–B and B–H bonds were observed.

1. Introduction

It is known that the plasma facing wall in fusion experimental devices plays an important role in impurity and fuel control. For a reduction of impurities, such as carbon, nitrogen, oxygen, and iron, plasma facing wall conditioning has been employed in many devices and investigated for many years [1–3]. In particular, in situ boron coating (boronization) deposited on plasma facing walls has been recently applied to a number of fusion devices. This achieves reduction of the carbon and oxygen impurities due to the high gettering ability compared to other low Z coating conditioning [4–6]. The boronization has produced improvement in plasma performance. In the large helical device (LHD) at National Institute for Fusion Science (NIFS), the boron coating film prepared by boronization is used to protect the stainless steel plasma facing wall from sputtering and prevent plasma dilution by iron sputtering species. This has resulted in remarkable improvement for reduction of many species of impurities reduction in LHD [7].

As hydrogen atoms are contained in borane gases, not only impurities but also hydrogen atoms are co-deposited with boron in the boron coating film on the plasma facing wall. Therefore, the dynamic behavior of the hydrogen atoms co-deposited in the boron coating film must be taken into account. The amount of hydrogen and stability of the boron coating film by plasma assisted chemical vapor deposition (PCVD) has been studied in various experimental conditions [8–10]. In this study, the characterizations of the structure and the chemical state of boron in the boron coating film were performed by X-ray diffraction (XRD) and thermal desorption spectroscopy (TDS) measurements, respectively. The effects of total pressure, discharge power, and

* Corresponding author. Tel.: +81-54 238 6436; fax: +81-54 238 3989.
E-mail address: r5344006@ipc.shizuoka.ac.jp (H. Kodama).

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substrate temperature on the growth rate of the boron coating film and the hydrogen retention have been evaluated.

2. Experimental

In order to prepare boron films, a PCVD apparatus was designed and fabricated at Shizuoka University, and is shown in Fig. 1. The PCVD chamber was evacuated by a turbomolecular pump to less than 10^{-6} Pa. Decaborane ($B_{10}H_{14}$) was used as a precursor gas for boron coating. It was vaporized at 403 K, and introduced into the PCVD chamber at the rate of 0.1–100 sccm (standard cubic centimeters per minute) with dilution by He. After achieving high vacuum conditions in the PCVD chamber, the PCVD coating was produced. During the PCVD process, the pressure was monitored by a baratoron gauge. The main chamber was equipped with an electrode (diameter: 120 mm) and a quartz oscillator, which was used to estimate the thickness of boron coating films. After the PCVD process, the sample was transferred to TDS apparatus by ways of a glove box which was connected to the PCVD chamber. There was no atmospheric exposure of samples when using this transfer vessel.

Boron films were deposited on silicon substrate (99.999%: Nilaco Inc.) by PCVD through radio frequency assisted direct current glow discharge. In the present study, the total pressure p_t, the discharge power P_d, and the substrate temperature T_s were controlled within the ranges shown in Table 1, and process time and flow rates for decaborane (99.9%: Daiichi Kasei Sangyo Co. Ltd.) and helium gases (99.99995%: Nihon Sanso Co. Ltd.) were kept constant in each process.

Table 1
Deposition parameters for boron coating films

Parameter	Value
Flow rate	$B_{10}H_{14}$: 2.5 sccm He: 3.8 sccm
RF frequency	13.56 MHz
Total pressure, p_t	6.3–90 Pa
Discharge power, P_d	10–150 W
Substrate temperature, T_s	316–698 K
Process time	10 min

After sample preparation, the structure of the boron coating film was measured by XRD (RINT 1000 series: Rigaku Denki Co. Ltd.), with a CuKα (0.15405 nm) X-ray source and the hydrogen retention was evaluated by a TDS (Beamtoron Inc.) apparatus. In TDS analyses, the samples were heated at the rate of 0.5 K s^{-1}, and hydrogen gas released from the samples were measured by a quadrupole mass spectrometer (Microvision plus: MKS Instruments, Inc.).

3. Results and discussion

3.1. XRD measurement

Fig. 2 shows the X-ray diffraction pattern of silicon substrate and boron coating film prepared with the discharge conditions, T_s: 308 K, P_d: 50 W and p_t: 25 Pa. The thickness of each sample was measured by the quartz oscillator and this one was 26.8 nm thick, which is consistent with the experimental result of the depth profiling by X-ray photoelectron spectroscopy using Ar^+ ion sputtering. As shown in Fig. 2, several peaks were observed in both spectra at the same angle. The

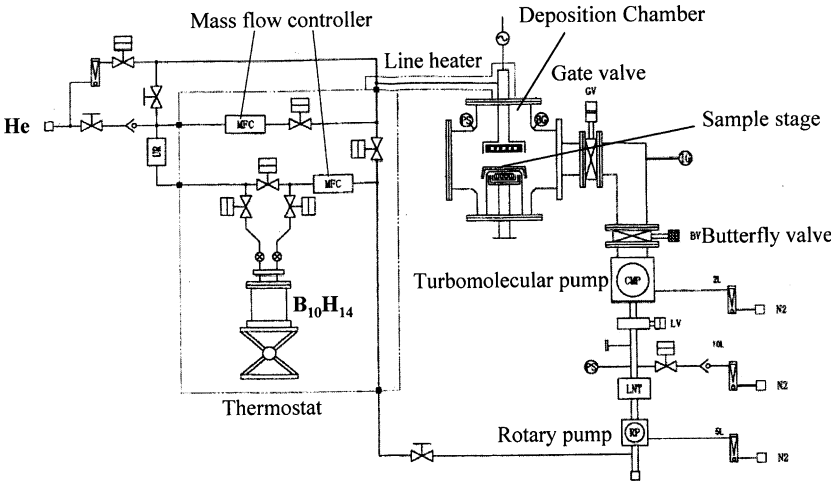

Fig. 1. Schematic diagram of PCVD apparatus.

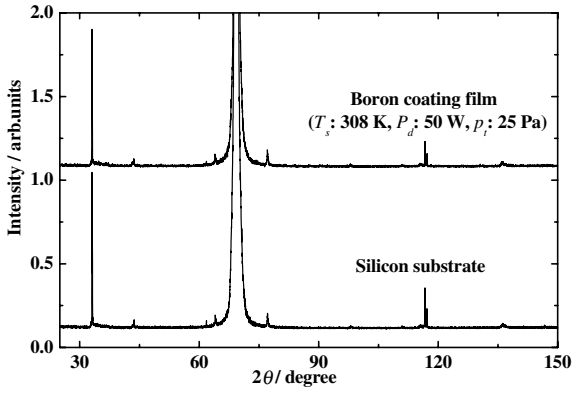

Fig. 2. XRD patterns of boron coating film and silicon substrate.

large peak at 70° was attributed to the (1 0 0) silicon surface. The results of all XRD patterns of the samples prepared in the various conditions were the same. Since other peaks were observed in both spectra at the same angle as well, two possibilities were considered: One is that the film is too thin to detect any diffraction pattern, and the other is that an amorphous structure is formed. No related peaks were observed even in the sample with the thickness of 400 nm. These results indicate that the structure of the boron coating film must be amorphous.

3.2. Estimation of hydrogen retention by TDS measurement

Fig. 3 shows the total pressure dependence of growth rate and hydrogen retention in the boron coating films. The hydrogen retention differs between each sample, because thickness of samples differs from one to another. The amount of hydrogen retention of each sample was divided by the thickness of its sample, to compare the hydrogen retention between samples. Right longitude axis defined as hydrogen retention normalized at 25 Pa in unit thickness to one. As shown in Fig. 3, the growth rate decreased as the total pressure increased from 6.3 to 38.5 Pa, and stayed constant for total pressure over 38.5 Pa. In contrast, hydrogen retention increased as pressure increased from 6.3 to 38.5 Pa, and stayed constant at total pressure over 38.5 Pa. This fact indicates that the relative pressure of ions or radical species decreased on increasing the total pressure and the growth rate decreased. This behavior is approximately consistent with previous reports [8,9].

The discharge power dependence of the growth rate and the hydrogen retention normalized at 50 W in unit thickness to one is shown in Fig. 4. In this case, the growth rate was constant for all discharge power levels between 10 and 150 W. However, the hydrogen retention decreased slightly as the discharge power increased. As the resistance of plasma during PCVD process was kept constant at 50 ohms, using a matching network control system, the plasma current and the applied voltage increased as the discharge power increased. This means that the flux of radical and/or ion species in the plasma would increase. As a result, it is believed that the amount of hydrogen released from decaborane gas decomposition increased and the hydrogen retention would decrease in the high discharge power.

Fig. 5 shows the substrate temperature dependence of the growth rate and the hydrogen retention normalized at 308 K in unit thickness to one. Although the growth rates for all substrate temperatures were almost same, the hydrogen retention decreased as the substrate temperature increased. This indicates that the growth rates are not controlled by the chemical form of B–H bond, but by that of B–B bond.

The TDS spectrum of hydrogen release from boron coating film prepared for discharge conditions (T_s: 308 K, P_d: 50 W and p_t: 25 Pa) is shown in Fig. 6. Two large peaks were observed at temperature near 450 and 750 K, and divided into two peaks using Redhead's equation as

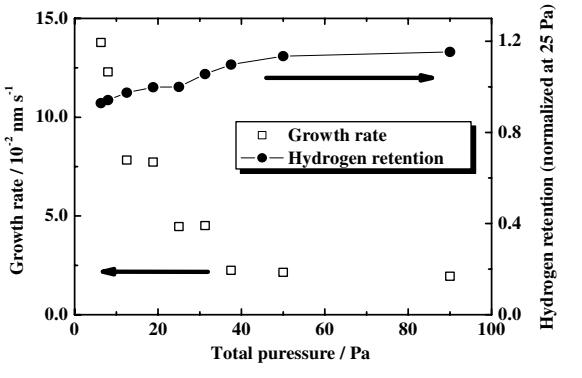

Fig. 3. Total pressure dependence of the growth rate and hydrogen retention of boron coating films.

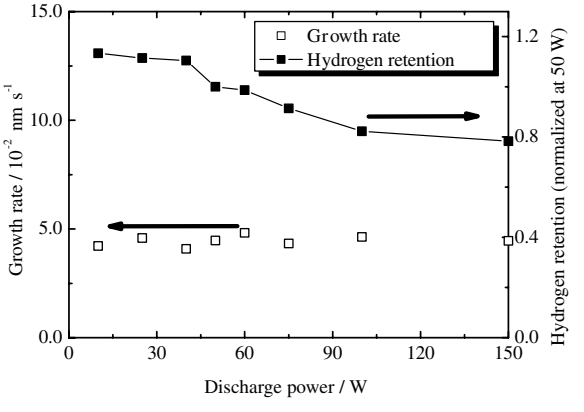

Fig. 4. Discharge power dependence of the growth rate and the hydrogen retention of boron coating films.

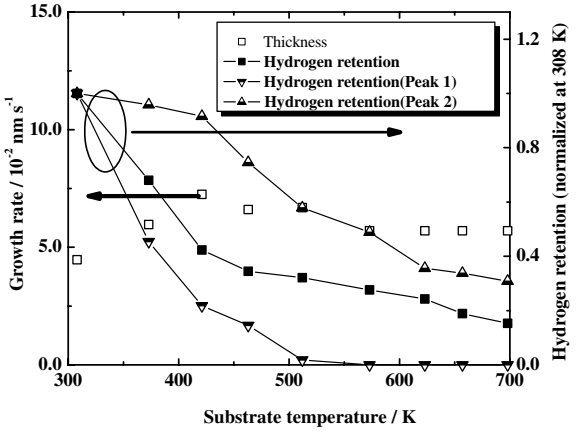

Fig. 5. Temperature dependence of the growth rate and the hydrogen retention, of which the analyzed peaks 1 and 2 were superposed, in the boron coating films.

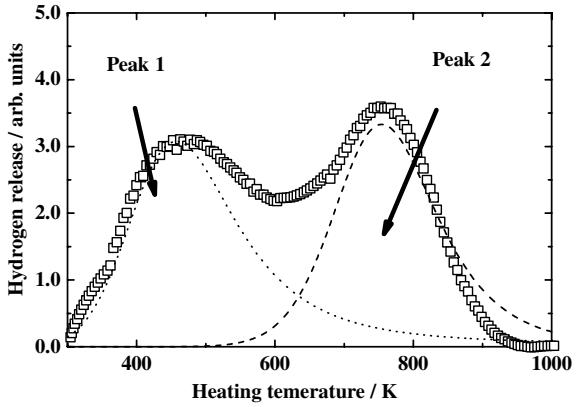

Fig. 6. TDS spectra and its analysis by Redhead's equation of hydrogen released from the boron coating film prepared in the conditions: discharge power P_d, 50 W; total pressure p_t, 25.0 Pa; and substrate temperature T_s, 308 K.

shown in this figure [11]. This means that there are two desorption processes of hydrogen from the boron coating film. These two processes are attributed to the desorption of hydrogen bound to boron as B–H–B and B–H bonds, respectively [12,13]. Fig. 5 also shows the substrate temperature dependence for the hydrogen retention of peaks 1 and 2. It is found that the hydrogen retention of peak 1 decreased rapidly on increasing the substrate temperature and became less than 0.2 at 450 K. However, that of peak 2 was almost constant by 400 K and started to decrease above 500 K. Two decreases of the rates, in the temperature regions below 400 K and above 450 K, were observed. The temperature regions of those decreases for peaks 1 and 2 almost correspond to those of hydrogen releases from B–H–B and B–H trapping sites.

These results suggest that boron coating film with low hydrogen retention can be achieved for deposition conditions of low total pressure, high discharge power, and high substrate temperature.

4. Conclusion

Characterization of the structure and the chemical state of boron in the boron coating film was performed by means of XRD and TDS measurements.

The XRD measurements indicate that the structure of the boron coating films is amorphous. By changing the total pressure, the discharge power and the substrate temperature, the growth rate of the boron coating film and the hydrogen retention were evaluated.

It was found that the growth rate decreased on increasing the total pressure. This indicates that the relative pressure of ions and/or radicals decreased on increasing the total pressure and the film grow rate would decrease. For the discharge power dependence, the flux of radical and/or ion species in the plasma would increase on increasing the discharge power. Therefore, the amount of hydrogen released from decaborane gas decomposition increased and the hydrogen retention would decrease for high discharge power. In the case of the substrate temperature dependence, the hydrogen retention in the boron coating films decreased with increasing substrate temperature. However, the growth rate stayed constant even if the substrate temperature was changed. In the TDS spectrum of hydrogen release from boron coating film, there were two hydrogen release processes, which were attributed to the desorption of hydrogen bound to boron as B–H–B and B–H bonds. This indicates that the growth rate was not controlled by the chemical form of boron or hydrogen, and that boron coating films with low hydrogen retention are achieved for formation conditions of low total pressure, high discharge power, and high substrate temperature.

Acknowledgements

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