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Dynamics of deuterium implanted in boron coating film for wall conditioning

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Abstract

Retention and desorption behavior of deuterium implanted into pure boron films has been studied by means of the secondary ion mass spectroscopy. It was found that the process controlling deuterium desorption depended on the temperature. At stage 1, below 573 K, the desorption of deuterium from B–D–B bonds dominated and its diffusion was the rate-determining process. Above 573 K, deuterium was mainly desorbed from B–D bonds, and recombination was the rate-determining process. The effective molecular recombination rate constant of deuterium bound to boron associated with B–D bond was determined by an isothermal annealing experiment.

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1. Introduction

In the first wall of fusion reactors, boronization is considered to be one of the most useful wall conditioning techniques for reduction of impurities in the plasma [1,2]. The first wall, however, will be exposed to energetic particles, especially deuterium and tritium. Therefore, from the viewpoint of tritium safety, it is important to elucidate the interaction mechanism of hydrogen isotopes implanted into boron films. In our previous studies, it was found that B–D and B–D–B bonds were formed in the boron films after D_2^+ implantation [3–6]. However, information on the dynamics of hydrogen isotopes in boron films has been limited.

In the present study, depth profile of deuterium implanted into the pure boron films was analyzed by means of the secondary ion mass spectroscopy (SIMS). To study the thermal desorption behavior of deuterium, isochronal and isothermal annealing experiments were performed and an effective molecular recombination rate constant was determined by a solution of the mass balance equations [9–11].

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2. Experimental

2.1. Sample preparation

High purity boron films were deposited on (100) silicon substrate with a size of $10 \times 10 \times 1\ \mathrm{mm}^3$ by means of the plasma assisted chemical vapor deposition (PCVD) device at Shizuoka University. The experimental conditions for preparing the boron film were the same as those in our previous studies [5,6]. After the preparation, the sample characterization was performed by means of the X-ray photoelectron spectroscopy (XPS), and it was found that boron purity was reached to be approximately 95 at%.

Thereafter, the sample was heated up to 993 K in an ultra high vacuum chamber less than 1×10^{-7} Pa and kept for 10 min to remove the residual hydrogen and water on/in the sample as a pretreatment. After heating, 1 keV D_2^+ with the ion flux of $1.0 \times 10^{18}\ D^+\ m^{-2}\ s^{-1}$ was implanted up to the ion fluence of $1.0 \times 10^{22}\ D^+\ m^{-2}$, which corresponded to the saturation by our preliminary experiments. During the implantation, the sample temperature was kept at room temperature.

Thermal desorption spectroscopy (TDS) with the heating rate of $0.5\ \mathrm{K\ s^{-1}}$ was also applied as reported in Ref. [4] to estimate the amount of desorbed deuterium from the boron film and to compare to the desorption behavior by isochronal annealing experiment.

2.2. Depth profiling of deuterium in boron film by SIMS

Depth profile of deuterium retained in the boron films was analyzed by SIMS (ULVAC-PHI ADEPT 1010 Dynamic SIMS system). In the present study, the experimental condition of SIMS was the same as the previous study [7]. The sputtering rate was determined to be nearly $0.1\ \mathrm{nm\ s^{-1}}$ by calculation and measurement of depth profiling by a profilometer (Dektak). The negative signal intensities of deuterium were normalized by those of ^{11}B for comparison [7].

Isochronal annealing experiments were carried out to understand the desorption behavior of deuterium trapped in the boron films. The sample was heated from room temperature (RT) up to 823 K, in six temperature steps, and kept for 10 min at each temperature. The SIMS measurements were carried out at a temperature of less than 340 K after heating at each temperature. Isothermal annealing experiments at 673 K were also carried out to evaluate effective molecular recombination rate constant for deuterium with B–D bond.

3. Results and discussion

3.1. Dependence of heating temperature on depth profile of deuterium

Fig. 1 shows the typical SIMS spectra after isochronal annealing for 10 min from RT to 823 K. After D_2^+ implantation, the peak position of deuterium profile in the boron film was located at the depth around 20 nm beneath the surface. This implantation depth was almost the same as that calculated by the TRIM code. It was clear from Fig. 1(a) that deuterium retained in the boron film moved slightly toward the surface by heating, and the desorption behavior of deuterium at less than 573 K was clearly different from that above 573 K.

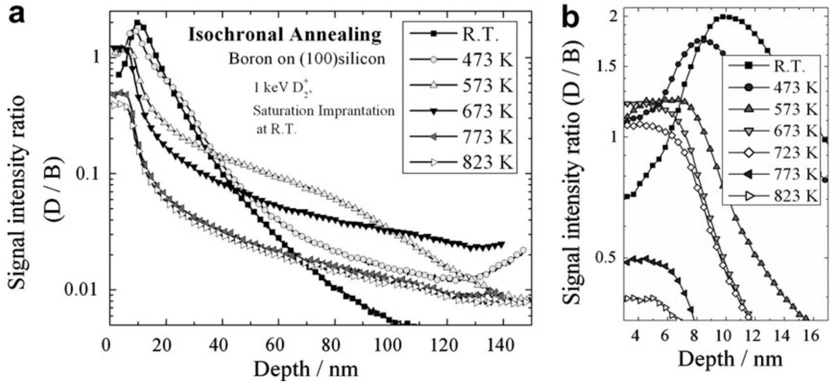

Fig. 1. Depth profiles of D/^{11}B signal intensity ratios determined by SIMS for the boron film implanted up to the saturation concentration with 1 keV D_2^+ and performed with isochronal annealing at various temperatures for 10 min (a) and enlarged view of shallow surface profiles (b).

Thus, the deuterium desorption behavior was divided into two stages: stage 1, between RT and 573 K, and stage 2, above 573 K.

By heating the sample at the temperature between RT and 573 K, the D/B ratio at the depth of 40–160 nm has increased. However, at the depth of 0–6 nm, this ratio has decreased toward the surface as shown in Fig. 1(b). On the other hand, at the temperature above 573 K, deuterium was aggregated on surface side and decreased uniformly over the whole depth.

Fig. 2 shows the decay curve of the deuterium by the isochronal annealing for 10 min. The TDS spectrum of D_2 is superposed on this figure for comparison. It was found by analysis using Redhead equation [8] that the TDS spectrum could consist of two peaks. Those corresponded to the deuterium desorption stages bound to boron by forming B–D–B and B–D bonds, respectively. Based upon previous studies, the activation energies were 1.11 ± 0.21 eV and 2.17 ± 0.36 eV, and deuterium desorption temperature ranges are 450–550 K and 600–700 K, respectively [3,4]. This result was approximately consistent with the result of isothermal annealing experiments and indicated that these temperature ranges corresponded to desorption stages 1 and 2, respectively. From the analysis of TDS spectrum, initial concentration ratio of deuterium bound to boron by forming B–D bond ($N^0_{T_{\text{B–D}}}$) was estimated to be 0.6.

In the stage 1, the deuterium forming B–D–B bond is dissociated. However, it is impossible to desorb enough because the diffusion process is limited and relatively slow because of the existence of the stable B–D bond. Therefore, it was suggested that diffusion of deuterium was the rate-determining process of the desorption at low temperatures, and the detrapped deuterium from B–D–B bonds dominated the amount of desorption in this stage. Above 573 K, namely stage 2, the D/B profile near the surface became constant and its ratio decreased as the heating temperature increased. This fact indicated that the diffusion toward the surface was relatively fast and the recombination rate at the surface would be important for the deuterium desorption. In this temperature range, deuterium forming B–D bonds would be dissociated and the diffusion process would easily proceed. Consequently, the deuterium in bulk diffused toward the surface and was retained only on the surface region. Therefore, above 573 K, the detrapped deuterium from B–D bond dominated the amount of desorption, and the recombination process at surface would govern the hydrogen retention in the boron.

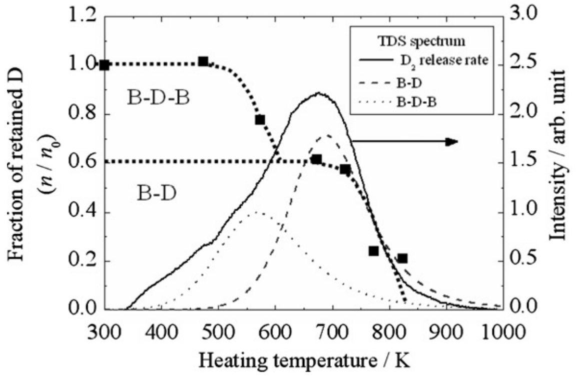

Fig. 2. Decay curve of deuterium concentration with isochronal annealing for 10 min (left axis). Each closed square indicates the retained fraction of D at each heating temperature in a boron film normalized by that of room temperature (n_0). TDS spectrum of D_2 with its analysis by Redhead equation [8] is also shown for comparison (right axis).

3.2. Thermal desorption behavior

In the above section, the deuterium desorption process was observed to consist of two stages. To understand the desorption behavior in more detailed, especially that of the deuterium bound to boron forming B–D bond which is a major chemical state in boron, an isothermal annealing experiment at 673 K was performed and the results were analyzed using mass balance equations.

Fig. 3 shows the typical SIMS spectra after isothermal annealing at 673 K from 0 to 180 min. The decay curve of the deuterium concentration by isothermal annealing at 673 K was plotted as a function of annealing time in Fig. 4. It was observed that the deuterium concentration decreased rapidly in the beginning of the annealing and then decreased gradually. The initial rapid decay in Fig. 4 indicates no retrapping of thermally detrapped deuterium due to the non-existence of available trapping sites at the saturation concentration. The consequent decay was ascribed to strong retrapping of thermally detrapped deuterium into vacant trapping sites produced during the initial decay. To analyze the desorption curve of deuterium molecules in stage 2, mass balance equations can be used [9–11]. The mass balance equations are described in the following forms:

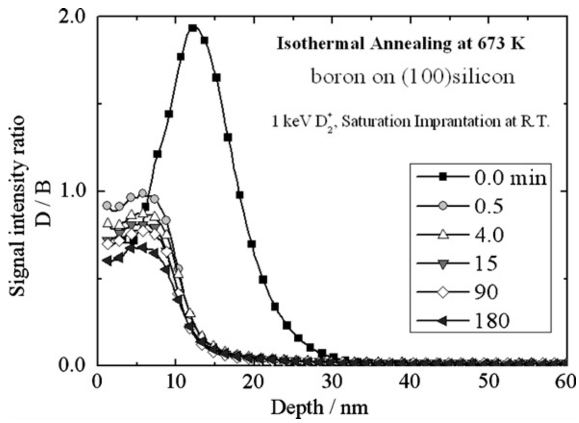

Fig. 3. Depth profiles of D/^{11}B signal intensity ratios determined by SIMS for the boron film implanted up to the saturation concentration and subject to isothermal annealing at 673 K.

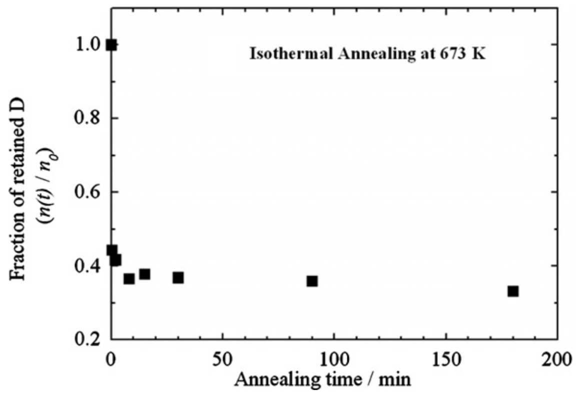

Fig. 4. The decay curve of deuterium concentration with isothermal annealing at 673 K. Closed squares indicate the retained fraction of D in a boron film. Values were normalized by that of 0 min (n_0).

$$\frac{\mathrm{d}n(t)}{\mathrm{d}(t)} = \sum_{d_{\mathrm{B\text{–}D\text{–}B}}} n_{T_{\mathrm{B\text{–}D\text{–}B}}}(t) + \sum_{d_{\mathrm{B\text{–}D}}} n_{T_{\mathrm{B\text{–}D}}}(t) - \sum_{T} n(t)\{C_0 - n_{T_{\mathrm{B\text{–}D\text{–}B}}}(t) - n_{T_{\mathrm{B\text{–}D}}}(t)\} - 2Kn^2(t), \tag{1}$$

$$\frac{\mathrm{d}n_{T_{\mathrm{B\text{–}D\text{–}B}}}(t)}{\mathrm{d}t} = -\sum_{d_{\mathrm{B\text{–}D\text{–}B}}} n_{T_{\mathrm{B\text{–}D\text{–}B}}}(t) + \sum_{T} n(t)\{C_{\mathrm{B\text{–}D\text{–}B}} - n_{T_{\mathrm{B\text{–}D\text{–}B}}}(t)\}, \tag{2}$$

$$\frac{\mathrm{d}n_{T_{\mathrm{B\text{–}D}}}(t)}{\mathrm{d}t} = -\sum_{d_{\mathrm{B\text{–}D}}} n_{T_{\mathrm{B\text{–}D}}}(t) + \sum_{T} n(t)\{C_{\mathrm{B\text{–}D}} - n_{T_{\mathrm{B\text{–}D}}}(t)\}, \tag{3}$$

where $n(t)$ is the average concentrations for deuterium migrating freely; $n_{T_{\mathrm{B\text{–}D}}}(t)$ and $n_{T_{\mathrm{B\text{–}D\text{–}B}}}(t)$ are the concentration for deuterium trapped in the sites for B–D and B–D–B bonds, respectively; $\sum_{d_{\mathrm{B\text{–}D}}}$ and $\sum_{d_{\mathrm{B\text{–}D\text{–}B}}}$ are the thermal detrapping rate constants for the trapping sites of B–D and B–D–B bonds, respectively; $\sum_T$ is the trapping rate constant, K is the local molecular recombination rate constant, and C_0 ($=C_{\mathrm{B\text{–}D}} + C_{\mathrm{B\text{–}D\text{–}B}}$) is the total trap density, where $C_{\mathrm{B\text{–}D}}$ and $C_{\mathrm{B\text{–}D\text{–}B}}$ are the densities of the respective trapping sites. The assumption of local molecular recombination is based on the fact that the decay of retained deuterium takes place uniformly over the whole depth of the boron film.

When the concentration of free deuterium atoms is assumed to reach a quasi-equilibrium, $\mathrm{d}n(t)/\mathrm{d}t = 0$, the following equation is derived from Eqs. (1)–(3):

$$\frac{\mathrm{d}\{n_{T_{\mathrm{B\text{–}D\text{–}B}}}(t) + n_{T_{\mathrm{B\text{–}D}}}(t)\}}{\mathrm{d}t} = -2K\left[\frac{\sum_{d_{\mathrm{B\text{–}D\text{–}B}}} n_{T_{\mathrm{B\text{–}D\text{–}B}}}(t) + \sum_{d_{\mathrm{B\text{–}D}}} n_{T_{\mathrm{B\text{–}D}}}(t)}{\sum T\{C_0 - n_{T_{\mathrm{B\text{–}D\text{–}B}}}(t) - n_{T_{\mathrm{B\text{–}D}}}(t)\}}\right]^2. \tag{4}$$

In stage 2, if the deuterium bound to boron by forming B–D–B bond was completely desorbed at the beginning of the heating, $n_{T_{\mathrm{B\text{–}D\text{–}B}}}(t) = 0$. Therefore, the decay curve of deuterium from B–D bonds can be expressed by the following equation as a solution of Eq. (4), and this equation is defined as Ev:

$$Ev = \frac{C_0}{n_0}\left\{\frac{1}{N^0_{T_{\mathrm{B\text{–}D}}}} - \frac{1}{N_{T_{\mathrm{B\text{–}D}}}(t)}\right\} - 2\ln\left\{\frac{N_{T_{\mathrm{B\text{–}D}}}(t)}{N^0_{T_{\mathrm{B\text{–}D}}}}\right\} + \frac{n_0}{C_0}\left\{N_{T_{\mathrm{B\text{–}D}}}(t) - N^0_{T_{\mathrm{B\text{–}D}}}\right\} = -2\frac{K}{C_0}\left(\frac{\sum_{d_{\mathrm{B\text{–}D}}}}{\sum_T}\right)^2 t, \tag{5}$$

where $N_{T_{\mathrm{B\text{–}D}}}(t)$ is the average concentration of trapped deuterium forming B–D bond normalized by the initial implantation concentration n_0: $N_{T_{\mathrm{B\text{–}D}}}(t) = n_{T_{\mathrm{B\text{–}D}}}(t)/n_0$. The value of $K/C_0\left(\sum_{d_{\mathrm{B\text{–}D}}}/\sum_T\right)^2$, which corresponds to a effective molecular recombination rate constant, can be determined by best fitting to the experimental release curve at 673 K as shown in Fig. 4 with $C_0/n_0 = 1$. Fig. 5 shows a plot of $2\ln[N_{T_{\mathrm{B\text{–}D}}}(t)/N^0_{T_{\mathrm{B\text{–}D}}}] - C_0/n_0[1/N_{T_{\mathrm{B\text{–}D}}}(t)] + n_0/C_0[n^0_{T_{\mathrm{B\text{–}D}}} - N_{T_{\mathrm{B\text{–}D}}}(t)]$ vs. annealing time best fitted by substitution of the experimental data in Fig. 4 and using $N^0_{T_{\mathrm{B\text{–}D}}} = 0.6$.

From these analyses, the value of $K/C_0\left(\sum_{d_{\mathrm{B\text{–}D}}}/\sum_T\right)^2$ was determined to be 4.20×10^{-4} min^{-1} from the slope of calculation line in Fig. 5. This is higher than that of SiC at 773 K, 7.3×10^{-5} min^{-1} [11]. It indicates that deuterium recombination on the boron surface is easier than that on SiC owing to their difference of the binding energy of deuterium

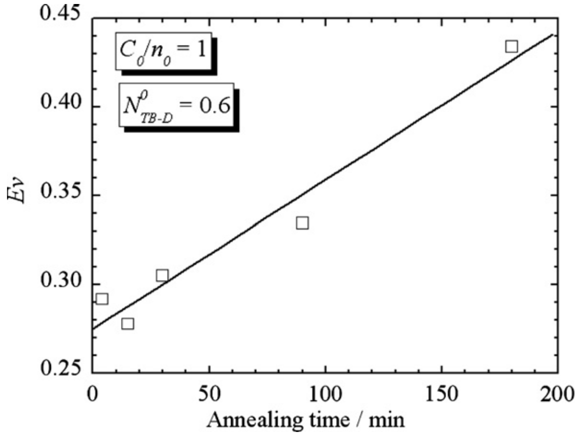

Fig. 5. A plot of *Ev* vs. annealing time best fitted by substitution of the experimental data in Fig. 4 and using $N^0_{T_{\rm B\text{-}D}} = 0.6$.

among these materials, where the binding energies of B–H, Si–H and C–H were 1.15, 1.5 and 2.35 eV, respectively [12]. Further study will reveal more detailed mechanisms.

4. Conclusion

Retention and desorption behavior of deuterium implanted into the boron films have been studied by means of SIMS. The deuterium profile in boron films was controlled by two stages depending on heating temperature. The diffusion process is the rate-determining process of the deuterium desorption between RT and 573 K. Above 573 K, control was the recombination process on the surface. By comparing to the results of TDS, it was suggested that both stages 1 and 2 had a strong correlation with trapping states of deuterium bound to boron associated with B–D–B and B–D bonds, respectively. An isothermal annealing experiment at 673 K and a solution of the mass equilibrium equations were applied to determine that the effective molecular recombination rate constant of deuterium bound to boron by B–D bonds, was $4.2 \times 10^{-4}\,\mathrm{min}^{-1}$.

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