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Dynamic hydrogen isotope behavior and its chemical states in SiC by XPS and TDS technique

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Abstract

Deuterium ions were implanted into SiC to elucidate the interaction mechanism between deuterium and SiC. The chemical states of Si and C were studied by X-ray photoelectron spectroscopy (XPS) and thermal desorption behavior of deuterium was analyzed by thermal desorption spectroscopy (TDS). It was found that the peak energies of C 1s and Si 2p by XPS were, respectively, shifted to higher and lower binding energy side by the deuterium ion irradiation. These results indicate that the deuterium was trapped by Si and C. In the TDS analysis, two desorption peaks were observed at around 800 K and 1000 K, respectively. These results show that the low temperature stage was induced by the deuterium bound to C and the high temperature stage corresponded to the desorption of deuterium bound to Si, respectively. The hydrogen isotope trapping mechanism was discussed by taking account of the reported quantum chemical analyses.

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1. Introduction

Plasma facing materials used in future fusion reactor are of high importance for the confinement of plasma. Silicon carbide (SiC) is thought to be one of candidate materials for the plasma facing material and structural components due to its minimal activation, good thermal conductivity, low radiation loss, and high chemical stability [1–7]. One of the critical issues for the usage of SiC is that the lots of hydrogen isotopes were retained in a narrow surface layer of the implantation range if SiC was implanted with a few keV deuterium ions [6]. This fact indicates that lots of tritium may be retained in SiC.

In our previous papers [8,9], the hydrogen isotope exchange behavior, and the retention and re-emission behavior in SiC were reported. The detrapping cross section of H and D implants by the D_2^+ and H_2^+ ion bombardments have been determined to be $3.2 \pm 0.3 \times 10^{-22}\,m^2/D^+$ and $2.6 \pm 0.2 \times 10^{-22}\,m^2/H^+$, respectively. The effective molecular recombination rate constant was determined to be 7.3×10^{-5}. The retention of deuterium in SiC was also evaluated by ERD

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technique and found to be 0.75 D/SiC. Hydrogen desorption behavior from SiC including helium irradiation effect was reported by other authors [5–7]. However, detailed mechanism for hydrogen trapping and detrapping was not clearly discussed with taking account of quantum chemical analyses. In this paper, the chemical states of Si and C in SiC were evaluated by X-ray photoelectron spectroscopy (XPS) and the thermal desorption behavior of hydrogen isotopes was studied by thermal desorption spectroscopy (TDS). From these experimental results, the hydrogen retention behavior was discussed with taking account of the reports of quantum chemical analyses and hydrogen trapping behavior was discussed.

2. Experimental

A silicon carbide wafer (β-SiC) supplied by Asahi Grass Co. Ltd. was used as a sample and its size was ∅10 × 1 mm. As a pre-treatment, the sample was heated up to 1300 K in a ultra high vacuum chamber below 1×10^{-7} Pa and kept constant for 10 min to remove the residual hydrogen and impurities in SiC. 1.0 keV deuterium (D_2^+) ions were implanted into SiC by TECHNICIAN'S Model 06-350 5 keV Ion Gun with the rastering area of $3 \times 3\,mm^2$ at an ion flux of 1.3×10^{18} $D^+ m^{-2} s^{-1}$ up to an ion fluence of 1.0×10^{22} $D^+ m^{-2}$ at room temperature. The projected range of 1.0 keV D_2^+ in SiC calculated by TRIM code was found to be 14 nm. The chemical states of silicon and carbon in SiC were studied by XPS (ESCA1600 system, ULVAC-PHI Inc.) at room temperature using Mg-kα X-ray source (1253.6 eV) and a hemispherical electron analyzer [10]. XPS measurements were performed before or after D_2^+ ion irradiation with various ion fluence, or after heating. After deuterium ion implantation, the sample was moved to the chamber for TDS with keeping the high vacuum condition. The TDS experiment was performed with the heating rate of $0.5\,K\,s^{-1}$ and up to 1300 K.

3. Results

Fig. 1 shows the TDS spectrum of D_2 obtained from SiC after 1.0 keV D_2^+ ion implantation with the fluence of 1.0×10^{22} $D^+ m^{-2}$. It was found that the deuterium desorption consists of two stages, namely low temperature and high temperature ones. To elucidate the mechanism of each deuterium desorption stage, the SiC sample was heated up from room temperature to 1300 K and XPS analysis was performed at room temperature after heating. Fig. 2 shows the XPS spectra of C 1s and Si 2p before and after D_2^+ ion irradiation, and after heating at each temperature. It was found that the peak positions of C 1s and Si 2p were shifted to higher and lower binding energy side after D_2^+ ion implantation. These results indicate that the deuterium was trapped by C and Si in SiC. Fig. 3 summarized the peak positions of C 1s and Si 2p as a function of heating temperature. As can be seen from this figure, the C 1s peak was formerly shifted to lower energy side after heating at 800 K and the Si 2p peak was recovered to the original position after heating over 1200 K. These facts indicate that the deuterium bound to C was desorbed at low temperature stage and that bound to Si was desorbed at high temperature stage. In our previous

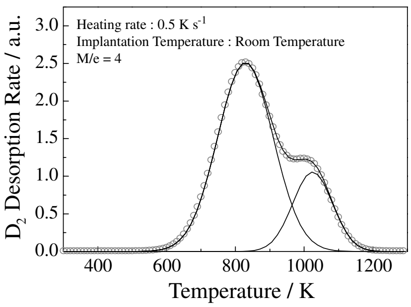

Fig. 1. Thermal desorption spectrum of D_2 obtained from SiC after 1.0 keV D_2^+ ion implantation.

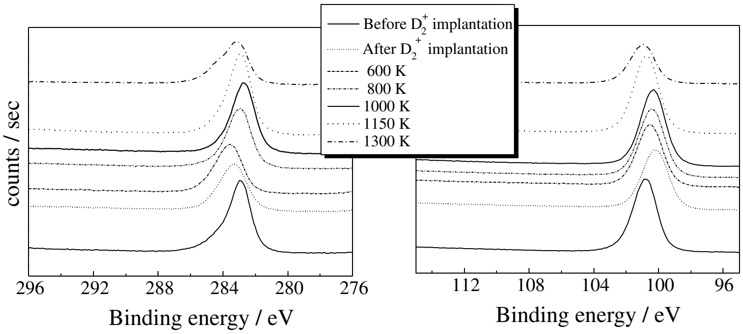

Fig. 2. XPS spectra of C 1s and Si 2p before and after D_2^+ ion irradiation and after heating.

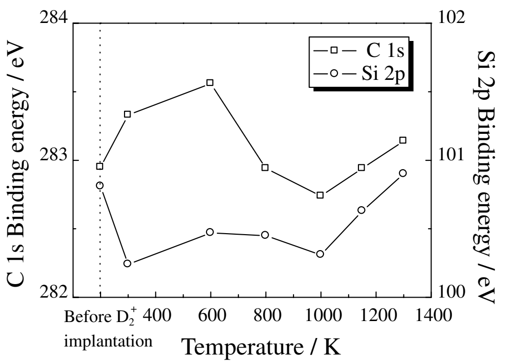

Fig. 3. Summary of XPS peaks of C 1s and Si 2p as a function of heating temperature.

study [8], the saturation concentration, namely the ratio of deuterium to SiC (D/SiC), was evaluated to be 0.75 after the deuterium ion implantation with the fluence of 1.1×10^{22} $D^+ m^{-2}$ at room temperature. Therefore, the concentration of deuterium in SiC after 1.0×10^{22} ions m^{-2} was assumed to be the same, 0.75 D/SiC, and the amount of retained deuterium in SiC was evaluated from the TDS spectrum as shown in Fig. 1. It was found that the amounts of deuterium bound to C and Si were 0.58 and 0.17, respectively. Therefore, It can be said that most of deuterium was trapped with carbon by forming C–D bond.

To find out the deuterium trapping behavior in SiC, TDS experiment was performed with changing the deuterium ion fluence from 0.13×10^{22} $D^+ m^{-2}$ to 1.0×10^{22} $D^+ m^{-2}$. Fig. 4 shows the TDS spectra of deuterium with various D_2^+ ion fluences. In the initial stage at ion fluence of 0.13×10^{22} $D^+ m^{-2}$, only deuterium desorption from the high temperature stage was observed. As the D_2^+ ion fluence increased, the amount of deuterium desorbed from high temperature stage, namely the desorption stage of deuterium bound to Si, was saturated. Thereafter, the amount of deuterium from low temperature stage, namely the desorption stage of deuterium bound to C, was quickly increased as the D_2^+ ion fluence increased and became the major desorption stage in the fluence of 0.5×10^{22} $D^+ m^{-2}$. The total ratio of deuterium to SiC (D/SiC) and the fraction ratios, namely D/Si and D/C, were summarized in Fig. 5. From this figure, it was found that the deuterium trapped by Si was quickly saturated in the fluence at about 0.2×10^{22} $D^+ m^{-2}$ and after the saturation of deuterium trapped by Si, the trapping of deuterium by C has begun immediately. These results indicate that the deuterium traps preferentially to the Si in SiC.

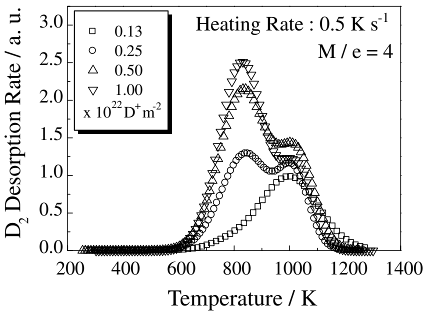

Fig. 4. Thermal desorption spectra of D_2 obtained from SiC with various D_2^+ ion implantation fluence.

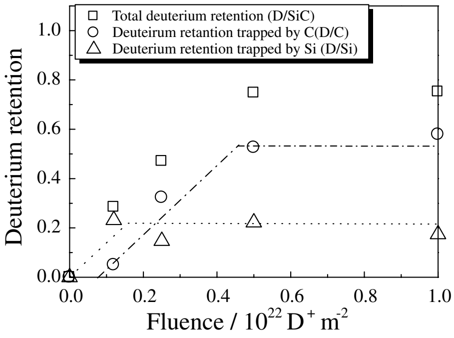

Fig. 5. Deuterium retention ratios (D/SiC, D/C and D/Si) as a function of D_2^+ ion implantation fluence.

4. Discussion

4.1. Deuterium trapping sites and their retentions in SiC

It is known that hydrogen/deuterium retention and its isotope effect have been studied [8,9,11]. However, the hydrogen trapping behavior has not been discussed except for the quantum chemical calculation by the references [12–14], in which hydrogen will be trapped by two vacancies in SiC, namely the carbon vacancy and the silicon vacancy and the stability of the trapped hydrogen in SiC have been studied using first-principles calculation with LDA to density function theory. It was reported that the hydrogen atom can be trapped in carbon vacancy by forming three-center bonded configuration, namely Si–H–Si bond. The Si–Si distance across the carbon vacancy in SiC is about 3.1 Å and the Si–H distance in carbon vacancy is 1.62 Å, while the normal Si–H bond distance is about 1.5 Å. Therefore, the hydrogen atom can interact with at least two Si atoms in SiC and maximum of two hydrogen atom can be trapped by one carbon vacancy. In case of silicon vacancy, the hydrogen atom bonds to one of the carbon neighbors by forming C–H bond and no other carbon dangling bonds interact with the hydrogen atom because C–H bond length is 1.12 Å while C–C distance across the silicon vacancy is 3.38 Å. Therefore, three carbon dangling bonds still remain and maximum of four hydrogen atoms can be trapped by one silicon vacancy. It can be said, in summary, that the amount of C–H to Si–H should be 0.25–0.5. This fact is almost consistent with our TDS experimental results of 0.30. The deuterium retentions trapped by C and Si were estimated to be 0.58 and 0.17, respectively.

4.2. Hydrogen isotope trapping processes for SiC

For the trapping processes of hydrogen isotopes, it was found that the deuterium was preferentially trapped by high temperature stage in the initial D_2^+ implantation stage as shown in Fig. 4. After the saturation of high temperature stage, the peak at low temperature stage has begun to increase. This indicates that the deuterium was mainly trapped by Si with forming Si–H in the initial stage and carbon would be selectively sputtered with the introduced deuterium, namely chemical sputtering, although deuterium would interact with both of Si and C in SiC. Fig. 6 shows the chemical composition ratio of Si and C as a function of ion fluence. As can be seen from the figure, carbon content largely decreased in the initial stage of D_2^+ implantation. Therefore, chemical sputtering of C by the D_2^+ implantation limits the hydrogen trapping by C in SiC. This fact is consistent with the previous report by Balden et al. that only hydrocarbon was desorbed from SiC after deuterium ion irradiation and no silane was formed [15,16]. After the ion fluence over 0.25×10^{22} $D^+ m^{-2}$, the carbon sputtering rate decreased and the trapping of deuterium by C would begin and C–D bonds have become the typical trapping form of hydrogen isotopes in SiC. This mechanism would corresponds to the reported facts that the hydrogen trapping by the carbon vacancy has a lower formation energy, but both types of vacancy are present implanted hydrogen is preferentially trapped by silicon vacancy. In the future work, the hydrogen interaction with vacancies, which was prepared by helium pre-irradiation to SiC, will be studied in more detail.

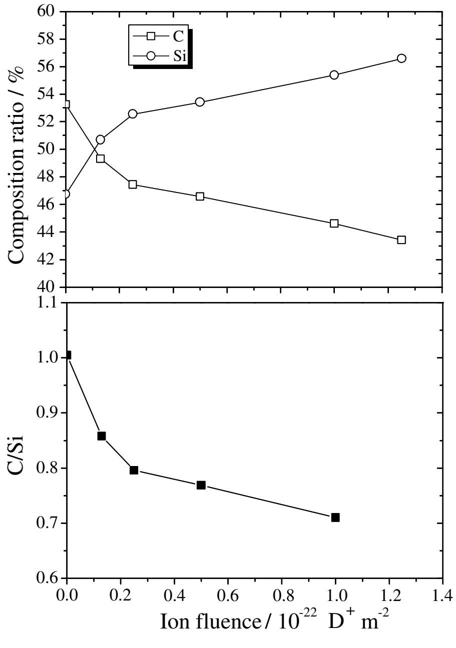

Fig. 6. Atomic composition ratios of Si and C, and C/Si ratio as a function of deuterium ion fluence.

5. Conclusion

The dynamic behavior of hydrogen isotopes in SiC has studied by TDS and the chemical states of Si and C in deuterium implanted SiC has also analyzed by XPS. It was found that the peak top energies of XPS spectra for C 1s and Si 2p were, respectively, shifted to higher and lower binding energy side by the deuterium ion irradiation. These results indicate that deuterium was trapped by Si and C, respectively. In the TDS analysis, two desorption peaks were observed at the temperature around 800 K and 1000 K, respectively. These results show that the lower desorption stage was induced by the deuterium bound to C and the higher desorption stage corresponded to the desorption of deuterium bound to Si, respectively. The hydrogen retention and trapping behavior have discussed with taking account of the reports of the quantum chemical analyses. Although the deuterium interacts with Si and C by D_2^+ implantation, only the deuterium trapped by Si remains in SiC and that by C would be detrapped by the preferential chemical sputtering of C with forming hydrocarbon in the initial stage. After the saturation of deuterium trapping by Si, the deuterium was trapped by C and C–D bond has become the typical trapping form of hydrogen isotopes in SiC.

Acknowledgments

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