

Chemical Behavior of Energetic Deuterium Implanted into Silicon Carbide

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Abstract

Studies on chemical behavior of energetic deuterium (D) ions implanted into SiC were carried out by means of X-ray Photoelectron Spectroscopy (XPS) and Thermal Desorption Spectroscopy (TDS).

From XPS results, it was suggested that the implanted D was attracted strongly to Si and/or C. From TDS results, two peaks corresponding to D₂ release appeared near 470 K (1st peak) and 1080 K (2nd peak). The activation energies for the two D₂ release processes were also determined. It was found from these experimental results that the 1st peak seemed to be attributed to deuterium that existed in interstitial. The 2nd peak was considered to be caused by deuterium trapped in lattice defects produced through deuterium ion implantation.

Keywords:

XPS, TDS, deuterium, desorption, recycling, recovery

1. Introduction

Silicon carbide (SiC) is one of attractive candidate materials for plasma facing components of next fusion reactors due to its high temperature strength, good thermal conductivity, low induced radioactivity, and low plasma impurity contamination compared with other candidate materials, such as high-Z materials [1]. The plasma facing components would be expected to be exposed to energetic deuterium and tritium because those are faced directly to D-T plasma [2]. From the standpoint of tritium safety and tritium recycling on the plasma surface components, therefore, it is important to investigate chemical behavior, mobility and existing chemical states of energetic tritium implanted into SiC. Particularly, mobility of implanted tritium in SiC is useful knowledge for estimation of tritium inventory and recovery as well as tritium recycling.

In the present study, we investigated chemical

behavior of deuterium ions implanted into β -SiC crystals by mean of X-ray Photoelectron Spectroscopy (XPS) and Thermal Desorption Spectroscopy (TDS). We accumulated knowledge of chemical existing states of implanted deuterium into SiC using XPS, furthermore, its thermal desorption behavior was investigated by TDS.

2. Experimental

Beta-SiC prepared by CVD method was provided by TOYO TANSO CO., LTD., the diameter and the thickness were 1×10^{-2} m ϕ and 1×10^{-3} m, respectively.

2.1 XPS measurements

As pretreatment, the SiC surface was sputtered with 3 keV argon (Ar⁺) ions. After that, deuterium (D₂⁺) ions were implanted into the SiC, and XPS measurements

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were performed. In XPS measurements, chemical shifts of C-1s, Si-2s and Si-2p resulting from D_2^+ ions implantation were measured. As parameters, ion energies were 1 keV and 3 keV, and ion fluences were varied from 0 to $4 \times 10^{21} m^{-2}$. From calculation using the TRIM code [3], ion range of deuterium is over several ten nm, while XPS analysis depth is 0.3–3 nm [4]. So XPS spectra cannot reflect the information around the ion range region. Therefore, the depth profile of XPS spectra should be carried out through 3 keV Ar^+ sputtering.

2.2 TDS measurements

The drawing of the apparatus is shown in Fig. 1. Deuterium ions were implanted into the sample, and then, the quartz tube (QT) was evacuated for 2 hours to remove residual gases. After that, the sample was heated using an infrared heater (IRH). The temperature of the sample was increased by iso-rate manner. The deuterium gas (D_2) released from the SiC was detected by a quadrupole mass spectrometer (QMS). The mass calibration of the QMS was performed using D_2 gas

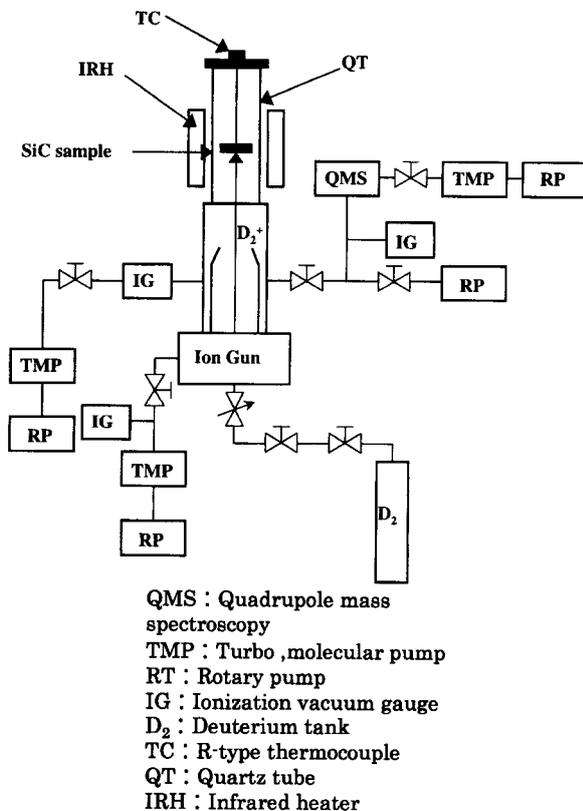


Fig. 1 Drawing of experimental apparatus for TDS.

before measurements.

The dependence of ion fluence on TDS was measured in the range from 1×10^{21} to $1.2 \times 10^{22} m^{-2}$ of deuterium atoms by 3 keV D_2^+ implantation. The thermal desorption was carried out by iso-rate heating of $30 K min^{-1}$. The dependence of ion energy on TDS was measured in the range from 1 to 5 keV of ion energy by ion fluence of $1.2 \times 10^{22} m^{-2}$. The thermal desorption was carried out by iso-rate heating of $30 K min^{-1}$.

In the experiments for determining the activation energies, heating rate of samples, where deuterium was implanted with ion energy of 3 keV and ion fluence of $8 \times 10^{21} m^{-2}$, was varied from 10 to $50 K min^{-1}$. Shifts of the peak top temperature were obtained, and activation energies were determined using Redhead's Equation [5].

3. Results and Discussion

Figure 2 shows chemical peak shifts of C-1s, Si-2s, and Si-2p of SiC with D_2^+ ion fluence increasing and D_2^+ ion energy of 1 keV. It can be seen from the figure that these peaks shift to higher energy region. Binding energy of Si-2s, 2p shifted until ion fluence reached $1 \times 10^{21} m^{-2}$, and then they become constant approximately. Besides, binding energy of C-1s also shifted until ion fluence became two times larger ($2 \times 10^{21} m^{-2}$) than for Si-2s, 2p, and then it became also changeless

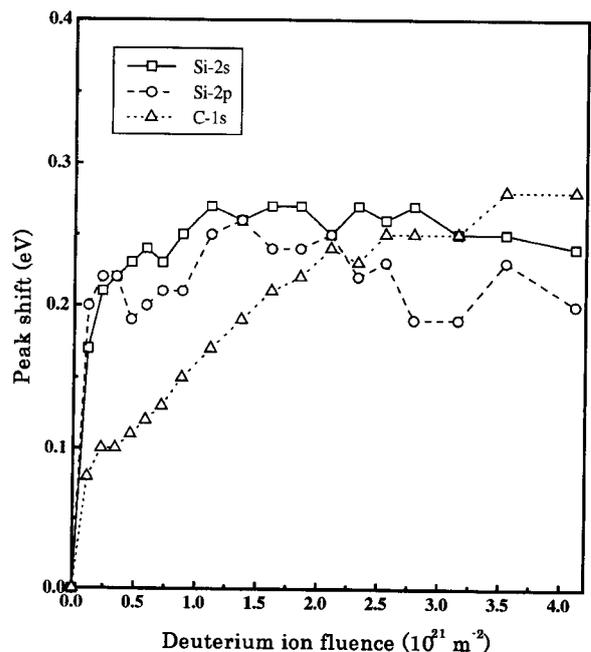


Fig. 2 Chemical peak shift of C-1s, Si-2s, and Si-2p by implantation of 1 keV D_2^+ ions.

approximately.

Figure 3 shows depth profile for chemical peak shifts of C-1s, Si-2s, and Si-2p by 3 keV Ar⁺ sputtering after D₂⁺ implantation with ion fluence of 4 × 10²¹ m⁻² and ion energy of 1 keV. On the figure, shifts of C-1s, Si-2s, and Si-2p became the maximum near the surface, while they became smaller as the depth being deeper.

By the way, it has been reported for SiC that C would be sputtered more easily than Si below ion energy of 100 eV [6]. The fact suggested for the SiC that the chemical composition of the surface could vary by deuterium implantation within the ion energy used in this study. To confirm the chemical composition of the surface, Si : C ratio with the ion implantation was obtained using each photoelectron peak area before and after implantation. It was understood from experimental results that no selective sputtering for both elements was observed in the present experimental conditions, because the Si : C ratio had no change. The fact suggested that chemical peak shift attributed to variety of the surface chemical composition could be ignorable.

On the other hand, implanted deuterium ions interact chemically with the other elements in SiC, or adsorb chemically on the surface of SiC. These could cause the chemical change of constitutive elements. The change of chemical states of constitutive elements in Fig. 2 would be considered to be caused through chemical interaction among Si and/or C, D. According to the literature value [7], Si-2p photoelectron peaks of SiC and SiH₄ appear around 100–101 eV and 102–103

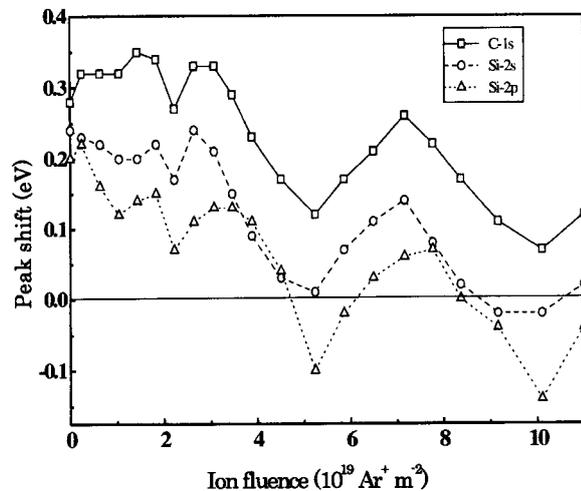


Fig. 3 Depth profile for chemical peak shifts of C-1s, Si-2s, and Si-2p by Ar⁺ sputtering after D₂⁺ ions implantations.

eV, respectively. It is suggested that the Si-2p peak shifts to higher energy region when Si of SiC bonds to H. Hence, as shown in Fig. 2, since the Si-2p peak shifted to higher energy region with implanted ions increasing, it was suggested that Si attracted D strongly in the SiC. Besides, for some carbide whose composition ratio is 1 : 1, such as ZrC, TiC, VC, and WC, binding energies of C-1s are 281.1 eV, 281.6 eV, and 282.2 eV, 282.8 eV [7], respectively. In addition, binding energy for CH₄ is around 286 eV [7]. Similar to Si, when C bonds to D, C-1s peak is considered to shift to higher energy region. As shown in Fig. 2, since the C-1s peak shifted to higher energy region with implanted ions increasing, it was suggested that C attracted D strongly in the SiC.

Here, in order to clear desorption behavior of deuterium from SiC, TDS measurements were performed. As shown in Fig. 4, there are two peaks that appeared near 470 K (1st peak) and 1080 K (2nd peak). The fact suggested that there would be two desorption process for implanted deuterium. The process for the 1st peak would be related to recycling, and could be recovered in low temperature. On the other hand, the process for the 2nd peak would not be related to the recycling, and could not be recovered in low temperature. TDS spectra were analyzed by Gaussian distribution function, and peak top temperature and peak intensity were measured from such spectra.

The dependence of ion fluence on TDS spectra is shown in Fig. 5. The peak intensity was growing with ion fluence increasing, while, there was no shift of peak top temperature for both peaks.

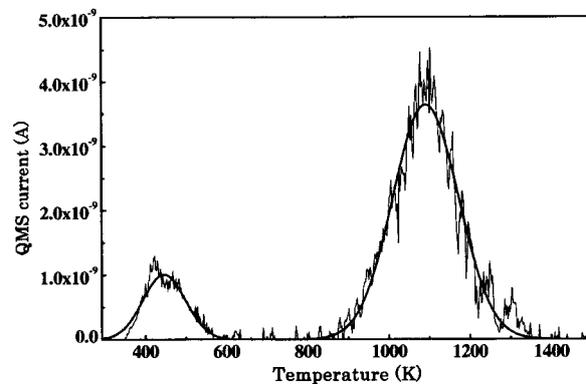


Fig. 4 TDS spectrum after deuterium implantation with ion energy of 3 keV and ion fluence of 8 × 10²¹ m⁻², and heating rate of 30 K min⁻¹.

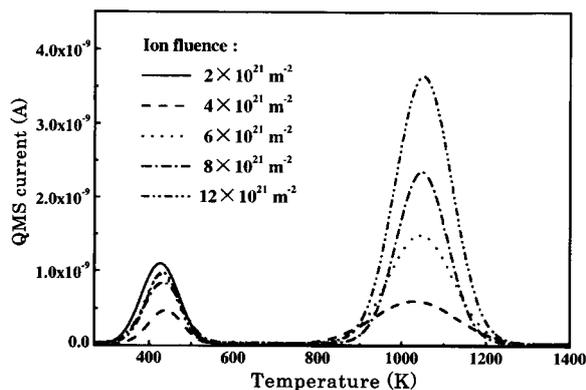


Fig. 5 The dependence of the ion fluence on TDS spectrum with ion energy of 3 keV and heating rate of 30 K min⁻¹.

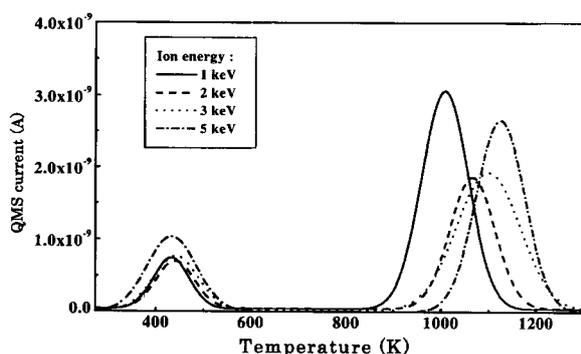


Fig. 6 The dependence of the ion energy on TDS spectra with ion fluence of $8 \times 10^{21} \text{ m}^{-2}$ and heating rate of 30 K min⁻¹.

Figure 6 shows the dependence of ion energy on TDS spectra. With increasing ion energy, the intensity and the peak top temperature for the 1st peak varied little, while the intensity for the 2nd peak tended to increase, and the peak top temperature for the 2nd peak shifted to higher temperature region as ion energy increasing.

The dependence of heating rate on the TDS spectra was investigated to determine activation energies for the two peaks. The experimental results showed shift of each peak top temperature by changing heating rate from 10 to 50 K min⁻¹. Here, in order to determine activation energies of thermal desorption process corresponded to two peaks, Eq. (1) was used,

$$E/RT_p + 2 = d(\log \beta) / d(\log T_p) \quad [5], \quad (1)$$

where, E is activation energy, β heating rate, R gas constant, and T_p peak top temperature. As shown in Fig. 7,

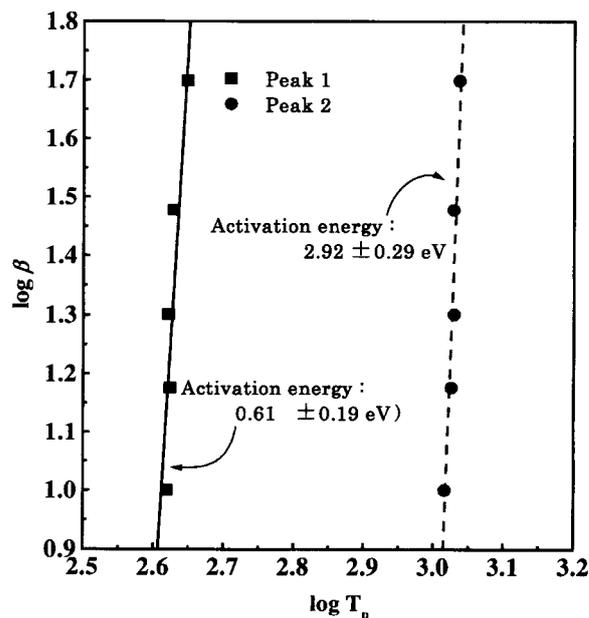


Fig. 7 Peak top temperature (T_p) for both peaks was plotted logarithmically against heating rate (β).

$\log \beta$ was plotted as a function of $\log T_p$, and activation energy was determined from the gradient. The activation energies of the 1st peak and the 2nd peak were $0.61 \pm 0.19 \text{ eV}$ and $2.92 \pm 0.29 \text{ eV}$, respectively. The activation energy of the 2nd peak is comparable to the value of 2.87 eV reported for the tritium desorption from SiC exposed to tritium by R.A. Causey, *et al* [8].

From TDS results, these two peaks were interpreted as followings. For the 1st peak, both release amount and release temperature depended scarcely on ion energy, moreover, its release amount was increasing with ion fluence growth. Here, diffusion activation energy for H in Si and C are 0.48 eV [9] and 0.4–0.9 eV [10], respectively, and activation energy of $0.61 \pm 0.19 \text{ eV}$ for the 1st peak was near to these value. Consequently, it was suggested that the 1st peak was caused by interstitial deuterium.

For the 2nd peak, the peak top shifted to higher temperature region with ion energy increasing as shown in Fig. 6. Thus, it was considered that deuterium was trapped deeper place with ion energy increasing, and then it was required longer time for the deuterium to diffuse from trap site to the surface. The time lag can be related to desorption temperature shift toward higher region, therefore the trap site of D for the 2nd peak was considered to exist in bulk. In addition, the activation energy of $2.92 \pm 0.29 \text{ eV}$ was relative larger than that of the 1st peak. So the 2nd peak should not be due to

interstitial deuterium but due to that trapped in lattice defects produced by deuterium implantation. Therefore, the phenomena that desorption amount increased with ion energy increase would be attributed to the fact that ion energy increasing caused the increase of defects number, and then, trapped deuterium amounts increased.

About the dependence on ion fluence, the increase of desorption amount for the 2nd peak seemed to be due to the fact that ion fluence growth caused the increase of defects number.

From literature, binding energy of C-1s and Si-2p for a compound constituted of only C or Si, and H are 2.94 [11] and 2.50 eV [12], respectively. On the other hand, binding energy of C-1s and Si-2p for a compound constituted of C or Si, H, and other elements, are 3.50–4.80 eV [13] and 2.80–3.90 eV [14], respectively. The activation energy of 2.92 ± 0.29 eV for the 2nd peak is similar to the value of C-1s for a compound constituted of C and H. But, in view of that SiC consists Si and C, it seems that the comparison with compounds constituted of Si or C, H, and other elements is suitable, so existing states of deuterium in SiC may be Si-D.

However, it is difficult to conclude the existing states at the moment.

The investigation of Si and C as well as SiC are also need for making clear the existing states of deuterium in SiC.

4. Summary

XPS experiments were performed after energetic deuterium was implanted into SiC. From XPS results, it was suggested that the implanted D was attracted strongly to Si and/or C.

TDS experiments were also performed after energetic deuterium was implanted into SiC, and two

peaks appeared. The 1st peak seemed to be attributed to deuterium that existed in interstitial. The 2nd peak was considered to be caused by deuterium trapped in lattice defects produced through deuterium ion implantation.

References

- [1] K. Hojou, S. Furuno *et al.*, Nucl. Instr. and Meth. in Phys. Res. B **91**, 534 (1994).
- [2] S.W. Tam, J.P. Kopasz *et al.*, J. Nucl. Mater. **219**, 87 (1995).
- [3] J.F. Ziegler, J.P. Biersack *et al.*, The stopping and Range of Ions in Solids (Pergamon Press. New York 1985).
- [4] The Surface Science of Japan, X-ray Photo Electron Spectroscopy, MARUZEN.
- [5] P.A. Readhead, Vacuum **12**, 203-211 (1962).
- [6] H. Plank *et al.*, Nucl. Instr. And Meth. **B124**, 23-30 (1997).
- [7] Perkin-elmener Handbook of X-ray photoelectron Spectroscopy Corporation Physical electronics division.
- [8] R.A. Causey *et al.*, J. Nucl. Mater. **203**, 196-205 (1993).
- [9] R. Biswas, B.C. Pan *et al.*, Phys. Rev. **B57**, 2253 (1998).
- [10] G. Hansali, J.P. Biberian *et al.*, J. Nucl. Mater. **171**, 395 (1990).
- [11] A.J. Robell *et al.*, J. Phys. Chem. **68**, 2748-2753 (1964).
- [12] M. Myers *et al.*, Phys. Rev. **B45**, 3914-3917 (1992).
- [13] R. Walsh *et al.*, Acc. Chem. Res. **14**, 246 (1981).
- [14] R.C. West, CRC-handbook of Chemistry and Physics.