

Thermal desorption behavior of deuterium implanted into polycrystalline diamond

H. Kimura ^{a,*}, M. Sasaki ^a, Y. Morimoto ^a, T. Takeda ^a,
H. Kodama ^a, A. Yoshikawa ^a, M. Oyaidzu ^a, K. Takahashi ^b,
K. Sakamoto ^b, T. Imai ^b, K. Okuno ^a

^a Radiochemistry Research Laboratory, Faculty of Science, Shizuoka University, Ohya, Shizuoka 422-8529, Japan

^b Naka Fusion Research Establishment, Japan Atomic Energy Research Institute, Japan

Abstract

In the present study, the thermal desorption behavior of deuterium implanted into diamond was investigated by means of TDS and XPS. From the results of TDS experiments, the most of all implanted deuterium was desorbed by forming D₂ mainly, and two desorption peaks were observed in the temperature range from 700 to 1100 K and from 1100 to 1300 K. The lower temperature deuterium desorption from the diamond was similar to that from HOPG. However, the D/C value of the diamond was approximately 0.2, which was almost half the value of the HOPG. The C 1s XPS spectra of diamond were shifted towards lower energy with increasing heating temperature above 773 K. In addition, the π - π^* transition peak appeared above this temperature. These meant that the disordered diamond structure were reconstructed through the desorption of deuterium, and stabilized by formation of a graphite network.

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PACS: 52.40.Hf; 81.50.Tp; 33.60.Fy; 82.30.Nr

Keywords: Carbon; Plasma facing materials; Thermal desorption; Tritium retention

1. Introduction

An Electron Cyclotron Heating and Current Drive (ECH/ECCD) system is an important tool for fusion reactors. The ECH/ECCD system with high power radio frequency (rf) power source has been developed in JAERI (Japan Atomic Energy Research Institute) for ITER (International Thermonuclear Experimental Reactor). A vacuum window is one of the most important components in the ECH/ECCD system develop-

ment [1–5]. Diamond is the leading candidate for rf windows. A window in a transmission line, so-called a torus window, belongs to the primary boundary of the tritium and the vacuum confinement [4]. The diamond using the torus window would be exposed with energetic particles, such as deuteron, triton, neutron, etc. and radiation. Understanding of these effects for the diamond is very important to realize the ECH/ECCD system with the diamond window and to evaluate the aptitude for the window from viewpoint of fusion safety.

Chemical behavior of implanted tritium into PFMs (Plasma Facing Materials) dominates plasma surface interactions, such as existing states and desorption behavior of energetic tritium implanted and erosion

* Corresponding author.

E-mail address: r0332004@ipc.shizuoka.ac.jp (H. Kimura).

processes of PFMs. In the present study, therefore, we studied the thermal desorption processes of implanted deuterium from polycrystalline diamond by means of TDS (Thermal Desorption Spectroscopy). Furthermore, to investigate surface condition of deuterium-implanted diamond during heating process, XPS (X-ray Photoelectron Spectroscopy) measurements were performed. Evolution of surface electronic states came up with sample heating was examined using XPS in detail. Thermal desorption of hydrogen isotopes implanted into diamond has not been reported so much. In the present study, thermal desorption behavior of deuterium from diamond was discussed by compare with that from HOPG (Highly Oriented Pyrolytic Graphite).

2. Experimental

The apparatus used in the present study, which was described in Ref. [6], consists of two vacuum chambers and a sample-loading chamber. These are connected to each other via a gate valve, and the vacuum chambers are kept at ultra high vacuum condition (10^{-8} Pa) using an ion pump. One vacuum chamber is used for XPS and the other for TDS, which were manufactured by UL-VAC PHI Inc. Each XPS and TDS chamber has an ion gun for ion implantation, and XPS measurements and TDS experiments are performed in the same vacuum system.

The sample used in the present study was a polycrystalline diamond made by chemical vapor deposition method purchased from Element Six Ltd. Co., developed for radio frequency applications [3]. The size of the sample was 10 mm in diameter and 0.2 mm in thickness and its density was determined to be 3.5 g/cm^3 .

The diamond sample was heated at 823 K for 10 min to remove residual gasses, such as H_2 , H_2O , O_2 , etc. After the pretreatment, XPS measurements were performed to characterize the surface. These measurements were carried out by using the Al K α characteristic X-ray source and the concentric hemispherical analyzer with pass energies 187.85 eV and 46.95 eV for the wide-energy-range (0–1400 eV) and narrow-energy-range (280–300 eV) of C 1s, respectively.

Deuterium ions (D_2^+) were implanted into the pretreated diamond sample with an energy of 1.0 keV D_2^+ , a flux of $1.0 \times 10^{18} \text{ D}^+ \text{ m}^{-2} \text{ s}^{-1}$, and a fluence of $1.0 \times 10^{22} \text{ D}^+ \text{ m}^{-2}$ at 323 K to surface normal. To investigate the thermal desorption behavior of deuterium implanted into the diamond, TDS experiments were carried out by heating the sample up to 1333 K with heating rate of 0.5 K s^{-1} . Desorption gases were analyzed with the quadrupole mass spectrometer. In addition, the implanted sample was isochronally heated from room temperature to certain temperatures such as 373, 573, 773, 973, 1173 and 1333 K with heating rate

of 0.5 K s^{-1} . After each heating, the sample surface was measured by XPS. The data obtained for diamond were compared to that for HOPG, to which the similar experiments were performed. The HOPG sample (purchased from Pechiney Co.) was used as the reference sample. As pretreatment, the sample cleaved mechanically was heated up to $\sim 1400 \text{ K}$ for 10 min to remove residual gases. The experiential conditions were the same as that for the diamond.

3. Results and discussion

From the XPS experiments after heating treatments, no impurities were observed in diamond sample except for a small amount of oxygen, which would exist in grain boundaries, and no impurities in the HOPG sample.

Most of all implanted deuterium was mainly desorbed by forming D_2 and small amount of CD_4 were observed. Fig. 1 shows the TDS spectrum of D_2 for the diamond after ion implantation. Two deuterium desorption peaks were observed, in the temperature range from 700 to 1100 K and from 1100 to 1300 K. The deuterium desorption peak at the lower temperature could be expected to consider of many overlapping peaks, but this is not our present concern. The TDS spectrum of D_2 after ion implantation for the HOPG was also shown in Fig. 1, and the implanted deuterium is desorbed in the range from 700 K to 1100 K, which was similar to those of our previous study [6,7]. These results indicate that the trapping states of deuterium in diamond desorbed at lower temperature are similar to those in the HOPG. By deuterium implantation, $\text{sp}^3\text{C-D}$ bonds and defects were produced in the HOPG, and the original graphite structure was disordered. It has been reported that deuterium desorption process in the temperature region 700 to 1100 K would be attributed to detrapping from the trapping site where deuterium could

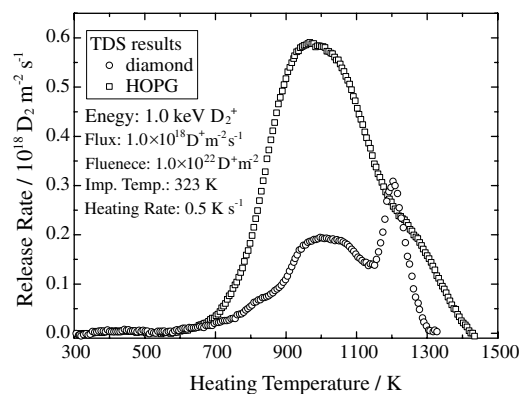


Fig. 1. Thermal desorption spectra of D_2 from diamond and HOPG with heating rate of 0.5 K s^{-1} .

interact strongly with carbon in HOPG. The deuterium desorption was resulted from the breaking bond of sp^3C-D [8,9]. Deuterium implanted into diamond could form sp^3C-D as reported in a previous paper [8]. These are the reasons why the deuterium desorption in the lower temperature region from diamond would be attributed to the detrapping caused by the breaking bond of sp^3C-D . In other words, deuterium desorption was independent on the original electronic states of carbon atoms, but dependent on bonding states between carbon and implanted deuterium formed by ion implantation. Therefore, the desorption process of deuterium implanted into diamond could be comparable with that of HOPG. The other deuterium desorption peak was observed at temperatures between 1100 and 1300 K. This peak was reproducible on any implantation conditions. It makes no sense at all that the peak was attributed to chemically trapped deuterium because of its FWHM. The deuterium desorption might come from deuterium bubbles produced in the diamond.

Fig. 2 shows the comparison of the amount of deuterium retention in diamond with that in HOPG as a function of heating temperature. The amount of retained deuterium in the diamond sample was lower than that in the HOPG. The ratio of retained deuterium against the number of carbon (the number of carbon atoms was estimated with the density and the ion range calculated by TRIM code) in HOPG at 323 K is estimated about 0.4, which is corresponding to the values reported in the previous papers [7,10–12]. However, D/C value for diamond was estimated to be about 0.2. It became clear that diamond retained less deuterium compared with HOPG at same implantation conditions. It is supposed that by ion implantation carbon atoms constituting diamond and HOPG structure are knocked out and vacancies are induced. The vacancy in diamond can trap one deuterium atom. The vacancy in HOPG can also

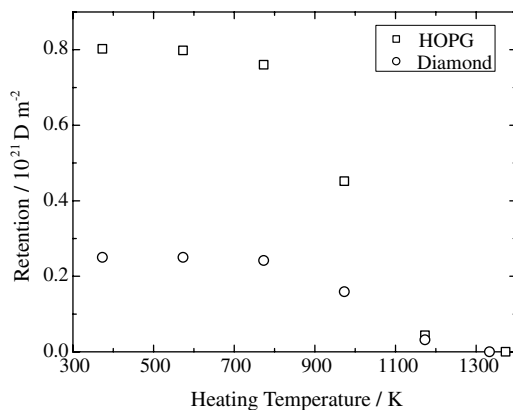


Fig. 2. Comparison of deuterium retentions in diamond and HOPG as a function of heating temperature.

trap one deuterium atom. However, remaining dangling bonds of neighbor carbon atoms in HOPG can trap one or more deuterium, because diamond structure is tighter than HOPG structure. Additionally, calculation results obtained from the TRIM code indicated the number of vacancies induced by ion implantation in diamond is lower than that in HOPG. For the above reasons, it is predicted that the deuterium retention in diamond is lower than that in HOPG.

The C 1s peaks of XPS spectra of the diamond with heating after implantation are shown in Fig. 3(a). From the results, the C 1s peak was found to shift towards lower energy with heating at more than 773 K. After heating at 1173 K and 1333 K, it was observed that a new peak appeared in the higher energy side of the C 1s peak. The diamond structure was disordered by ion implantation, with forming vacancies, sp^2C-C and sp^3C-D bonds [8]. The desorption of deuterium implanted into the diamond and the formation of local sp^2C-C bonds occurred simultaneously by heating. The localized electrons were produced by heating up to 973 K, and on 1173 and 1333 K, were also changed to sp^2C-C . Those diamond structures form graphite-like structure, which means the formation of graphite network, rather than recovery to diamond structure by heating.

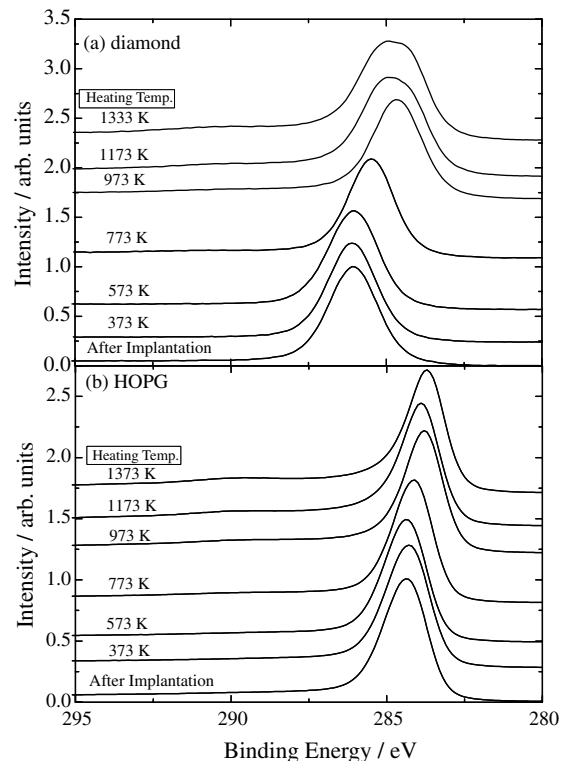


Fig. 3. Heating temperature dependence of C 1s XPS spectra after D_2^+ implantation for diamond (a) and HOPG (b).

A π - π^* transition peak was observed at approximately 290 eV, which was attributed to sp^2 - π bonding of graphite in the XPS spectra for the sample above 773 K. This also suggests that chemical structure of the deuterium-implanted diamond changed to graphite-like structure. Heating at higher temperatures, the graphite network grew up abruptly when the deuterium desorption was very high. For the non-implanted diamond sample heated in the same manner, no π - π^* transition peak was confirmed, and only the C 1s peak shifted towards lower energy. Thus, the formation of the graphite network was caused by the reconstruction of the disordered diamond structure by annealing of defects and distortion induced by ion implantation.

The C 1s spectra shown in Fig. 3(b) were obtained from HOPG sample. The C 1s peak shift began when heated the sample above 773 K, and the π - π^* transition peak appeared more than same as in the case of diamond at 773 K. This shows that HOPG structure damaged by ion implantation was recovered by heating. The disordered structure recovered to the original graphite structure with deuterium desorption by sample heating. This tendency was similar to the graphitization of diamond structure. Heating brought about extension of graphite network formation.

FWHM of C 1s peaks of diamond became wider with increasing the heating temperature as shown in Fig. 4. In general, the width of FWHM broadened, as there are some chemical states. Hence, it was considered that the existing states of carbon atoms in diamond were increased with increasing heating temperature. In contrast, the existing states of carbon in HOPG were decreased because the FWHM narrowed in HOPG. In short, disordered graphite recovers to original graphite structure with heating. These results also suggest that chemically trapped deuterium desorbed and the configuration of carbon came to sp^2 states. From these XPS data, it was clarified that the diamond disordered structure by

deuterium implantation formed graphite network as disordered HOPG recovered to original graphite structure, but still remains in a variety of carbon states.

The thermal desorption behavior of deuterium chemically trapped by carbon was quite similar in diamond and HOPG. The trapping of deuterium, however, was dominated by the original carbon structures. The original carbon structures led the difference of the amount of deuterium retention between diamond and HOPG.

4. Conclusion

Thermal desorption behavior of deuterium implanted into diamond and HOPG was investigated using TDS and XPS techniques. These results were compared with each other.

Most of all deuterium implanted into diamond and HOPG was desorbed by forming D_2 . In diamond, two deuterium desorption peaks were observed in the temperature range from 700 to 1100 K and from 1100 to 1300 K, respectively. The desorption peak at lower temperature corresponded with that from HOPG. These results indicate that there are similar trapping sites for deuterium in diamond and HOPG. The desorption would be attributed to detrapping of deuterium caused by breaking sp^3C -D bonds, which were made by ion implantation. However, the amount of retained deuterium in diamond was almost half of that in the HOPG. The D/C value of the diamond was estimated to be approximately 0.2. The difference of the amount of retained deuterium was caused by the original carbon structures.

After deuterium ion implantation, the diamond and HOPG samples were heated up to 1333 K with intervals of 200 K, and XPS measurements were performed at each temperature. The C 1s peak shifted toward lower binding energy with heating samples at 773 K. At this temperature, a π - π^* transition peak was observed in both samples. This suggested that disordered diamond started reconstruction not to original diamond structure, but to graphite-like structure. After heating at 1173 and 1333 K, it was observed that a new peak appeared in the higher binding energy of the C 1s peak in the diamond, which resulted from the formation of a graphite network. The disordered diamond structure was reconstructed by annealing of defects and distortion induced by ion implantation, in the same way of the disordered HOPG recovered to original graphite structure.

Above 1173 K, an abrupt deuterium desorption was also observed in TDS experiment for diamond. Implanted deuterium was desorbed abruptly, and the graphite network grew up appreciably in the diamond. This desorption would be induced by structure annealing such as rupture of bubbles.

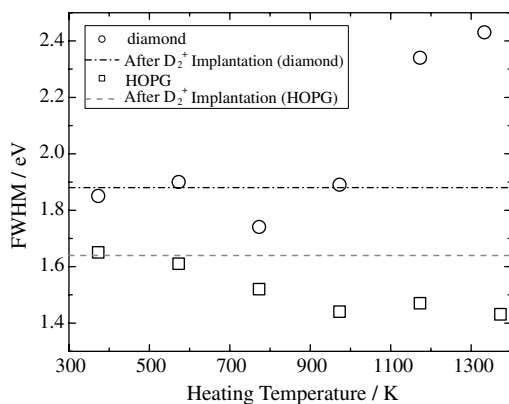


Fig. 4. Evolution of C 1s FWHM with heating after D_2^+ implantation.

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