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Correlation between annealing effects of damage and implanted deuterium release from graphite

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Abstract

In the present study the correlation between annealing effects of damage and release of implanted deuterium into graphite was investigated through the behavior of deuterium in the graphite during D_2^+ implantation. From the results of TDS experiments, the thermalized deuterium participated to form trapping sites. However the energetic deuterium would directly form CD_{x-1} ($x = 2$, 3, and 4) and simultaneously its kinetic energy was transferred to carbon atoms, and then this resulted in changing the electronic state of carbon from the sp^2 state to the sp^3 state. Those processes dominated during D_2^+ implantation at lower temperatures below 573 K. On the other hand, at higher implantation temperatures above 573 K, the disordered structure of the graphite was recovered to a crystalline graphite structure and then deuterium release was started. The effects of heating the sample, known as thermal annealing effects, were correlated with the hydrogen release from the graphite.

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1. Introduction

To evaluate the tritium safety in a fusion reactor, it is very important in case of an accident to know how tritium implanted into plasma facing materials (PFMs) behaves chemically at the operating temperatures. In PFMs, tritium behavior could be governed by chemical interactions with damage induced by ion implantation. The PFMs is exposed by energetic particles, such as deuterium and tritium, whose energy could be below keV [1]. It is assumed that the chemical reactions induced by ion implantation with high-energy (<keV), is specifically different from thermal chemical reactions. To understand the special chemical reaction known as a hot atom chemical reaction, the phenomenon when the energetic particles are implanted into materials should be distinguished between the reaction induced by the energetic particles and that by the thermalized particles.

Recently, a model of the chemical erosion induced by hydrogen irradiation was proposed [2–4]. This model is considered to be appropriate to study interactions of H atoms and the surfaces of partially or fully hydrogenated carbon materials [3]. From the viewpoint of the hot atom chemistry the behavior of the hydrogen implanted into graphite is very interesting. That model does not indicate whether the implanted hydrogen interacts directly under energetic condition or under thermalized conditions.

We have investigated the chemical interactions between the annealing effects of damage produced in, and release behavior of deuterium implanted in some candidates of PFMs [5,6]. In addition, we have studied the chemical reaction when the hydrogen isotopes were

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implanted into low Z materials at near liquid nitrogen temperature. These experimental results should be expected to provide us the new information on the reaction between the PFMs and energetic hydrogen isotopes, because the implantation at lower temperature could be expected to depress the annealing during the implantation, which means the rearrangement of disordered atoms by the energy provided by ion implantation, and by the interaction of thermalized particles. Takeuchi et al. reported that the structural change of graphite was induced by electron irradiation at lower temperature [7]. This result was very interesting from the viewpoint of material physics, and suggested that the experiments using the implantation at lower temperature were useful technique to understand the behavior of materials implanted by electrons and ions.

In the previous studies [8,9], we reported the construction of an apparatus for ion implantation at around 150 K equipped X-ray photoelectron spectroscopy (XPS) and thermal desorption spectroscopy (TDS), and suggested that the lower temperature ion implantation was very useful to study irradiation effects. In the present study, using the apparatus we investigate the damage process and the annealing effects during D_2^+ into graphite in detail. And then, we discuss the correlation between the annealing effects of the damage and the implanted deuterium release from the graphite by comparing the present results and with the previous ones [8].

2. Experimental

The sample was a pyrolytic graphite (PG) crystal provided by the Pechiney Co. The sample size was $10 \times 10 \times 1.5^{t}$ mm. The apparent density of the sample was 2.3 gcm^{-3}.

The pre-treatment of the sample was described as follows: the sample cleaved mechanically was degassed at ~1400 K in vacuum for 20 min. After the heating treatment, XPS measurements were performed to confirm the characteristics of the new cleavage surface. From XPS results, it was found that there were no impurities on the cleavage surface.

To investigate the change of the retention of deuterium, the D_2^+ implantation into the graphite sample was carried out, and then TDS experiments were performed. Deuterium ions were implanted into the graphite sample with an energy of 1.0 keV D_2^+, up to a flux of 1.0×10^{18} D^+ m^{-2} s^{-1}, and a fluence of 6.4×10^{21} D^+ m^{-2} at different temperatures from 153 to 773 K. The ion implantation area was 3×3 mm^2, and incident angle 90°. After D_2^+ implantation at different temperatures, TDS experiments were carried out by heating the sample from 150 to 1400 K with a constant heating rate of 0.5 K s^{-1}.

3. Results and discussion

Fig. 1 shows TDS spectra of D_2 (a) and CD_x (b) after D_2^+ implantation at 173 K, which are typical TDS spectra after D_2^+ implantation at lower temperature. It can be found from the figures that two peaks were observed in the D_2 TDS spectra and one peak in the CD_x ($x = 2$, 3, and 4) TDS spectra. In addition it was suggested that the D_2 peak in the higher temperature region could consist of two peaks because of the peak shape with a shoulder peak with increasing implantation temperature. Here, we represent those three peaks as peak 1, peak 2, and peak 3. Peak 1 of D_2 released at the temperature around 230 K has not been reported yet. Peak 1 was not observed in the TDS spectrum of the sample after exposure to D_2 gas at 173 K [8]. Therefore, the appearance of peak 1 could be attributed to D_2^+ implantation at lower temperature. (More experiments are necessary to discuss the details of the desorption process of peak 1.) In the present study, our attention will be focused on peaks 2 and 3 appeared at the higher temperature region of the TDS spectrum. The peak temperature of peaks 2 and 3 were observed around 900 and 1100 K, respectively. Ashida et al. reported that the release peak of D_2 was attributed to the desorption of deuterium trapped by carbon atoms in a graphite sample [10]. Therefore the release processes for D_2 for peaks 2 and 3 could be attributed to detrapping from the

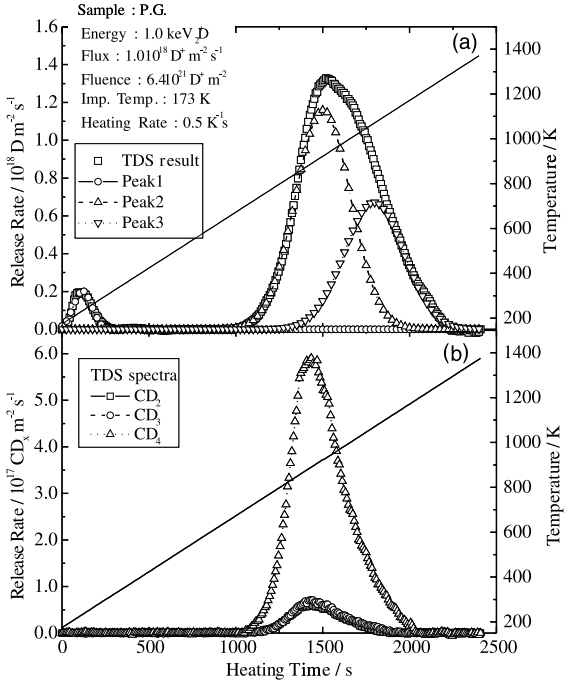

Fig. 1. TDS spectra of D_2^+ (a) and CD_x (b) released from the graphite.

trapping site where deuterium could interact strongly with carbon. The desorption of CD_4 species was explained in detail in Refs. [2–4]. In these reports, it was proposed that trapped D was explained to form a precursor, i.e. CD_3, and to be desorbed through forming CD_4. In the case of the present study the CD_2, CD_3 and CD_4 released peaks were observed [9]. The cracking pattern of CD_4 should be considered to estimate the released amount of CD_2 and CD_3. In Fig. 1(b) the cracking pattern was considered. To understand the desorption of CD_2 and CD_3, we extended the model described in Refs. [2–4] for CD_4 to the other CD_x species by assuming that their release could progress in the same manner of that for CD_4. The pre-cursor of CD_{x-1} is adsorbed deuterium on the trapping site and then the CD_x species are desorbed from the graphite.

Table 1 shows the ratio of retained deuterium against the number of the carbon atoms. Here, the number of carbon atoms was estimated using the density and ion range calculated by the TRIM code. The H/C ratio for the graphite is typically 0.4 at RT [11]. In the present study, however, the H/C value increased above 0.4 with decreasing D_2^+ implantation temperature, and reached to 0.53 at 153 K. To compare with the published data, the amount of peak 1 was not included in this value. It can be seen that the amount of D released in the formation of CD_x was found to be almost constant up to around 573 K as shown in Table 1. The amount of released CD_x decreased in the temperature region above 573 K. In addition, the D_2 release of peak 2 also indicated the same behavior for that of CD_x. There seemed to be a threshold of the implantation temperature at 573 K where the deuterium retention quickly decreased. Fig. 2 shows the hydrogen retention in the graphite sample after D_2^+ implantation at different temperatures. Doyle et al. reported that the saturated concentration of hydrogen in PG decreased with increasing the implantation temperature [12]. Our results agreed with their report except the part with temperatures lower than RT. The D/C ratio increased to more than 0.4 in our data when the hydrogen retention at temperatures lower than RT. These results were reported for the first time and suggested that there is a potential for the increase of the hydrogen retention at lower temperatures.

Table 1
The ratio of retained deuterium against the number of carbon[a]

Imp. temp.	D/C	(Peak 2/C	Peak 3/C	CD_x/C)
153	0.53	(0.17	0.21	0.15)
223	0.48	(0.14	0.20	0.14)
273	0.43	(0.14	0.16	0.13)
373	0.39	(0.11	0.15	0.13)
573	0.25	(0.10	0.06	0.09)
673	0.11	(0.05	0.02	0.03)
773	0.03	(0.02	0.01	0.00)

D means the total amount of released deuterium expect that of peak 1. $D/C = ([\text{peak 2}] + [\text{peak 3}] + 4[CD_4] + 3[CD_3] + 2[CD_2])/C$. [peak 2], [peak 3], $[CD_4]$, $[CD_3]$ and $[CD_2]$ are the amount of released D_2 (peak 2), D_2 (peak 3), CD_4, CD_3 and CD_2, respectively.

[a] The number of carbon was estimated with the density and the ion range calculated by the TRIM code.

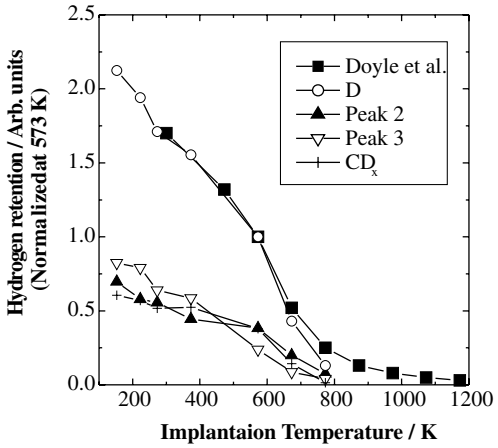

Fig. 2. The change of deuterium retention in the graphite after D_2^+ implantation at different temperatures. Total D was not including the released amount of peak 1. The amount of deuterium retention was normalized with that of 573 K.

In the lower temperature region below 573 K, the released amount of CD_x did not depend on the implantation temperature as shown in Fig. 2. However, the ratio of CD_x against total retained deuterium increased up to the implantation temperature of 573 K [8]. On the other hand, the behavior of the deuterium retention indicated the difference between those of peaks 2 and 3. In the case of peak 2, the amount of retention of D decreased slightly in the temperature region up to 573 K and then it decreased rapidly above 573 K. This suggests that there is a threshold around 573 K. In the case of peak 3, the retention decreased with increasing implantation temperature and the threshold was not observed. It was suggested that the deuterium released eventually via peak 3 would be affected by heating the sample more than those via peak 2 and CD_x peak. Moreover, thermalized deuterium would take part in the formation of the trapping site that resulted in peak 3. However, the deuterium via CD_x did not depend on the implantation temperature, and that via peak 2 only very weakly. This suggests that almost the same process would form the trapping site of the deuterium via peak 2 and CD_x during D_2^+ implantation. In addition, it was considered that the thermalized deuterium ions would not take part in the formation of CD_{x-1} and the trapping site of peak 2. Therefore, it was considered that CD_{x-1} and the trapping site of peak 2 was directly formed by D_2^+

implantation, and then the internal energy of carbon transferred from energetic deuterium would be used to change the electron state of carbon from the sp^2 state to the sp^3 state. From this reason, the sp^3 state appeared in graphite in spite of the sp^2 state being more stable than the sp^3 state from the viewpoint of thermodynamics.

In the higher temperature region above 573 K, the released amount of all species decreased as shown in Fig. 2. The graphite structure damaged by D_2^+ implantation began to recover at 573 K, because the π–π^* transition on the C1s XPS spectrum appeared, which was disappeared with D_2^+ implantation at the temperature below 573 K [8]. The π–π^* transition is characteristic of C1s XPS spectra of a graphite crystal. Release of the implanted deuterium from the graphite took place at 573 K for the recovery of the graphite structure. If the behavior induced by thermalized deuterium is one of the thermal annealing effects during D_2^+ implantation, the dominating the thermal annealing effect was shifted from the formation of a trapping site such as peak 3 to the recovery of the structure at 573 K. On the other hand, although the trapping site of peak 2 and CD_{x-1} would be formed by energetic deuterium up to 573 K, the recovery of the graphite structure dominated above 573 K. It was suggested that the desorption behavior of implanted deuterium would be correlated closely with the recovery of the graphite structure, in other words, the annealing effects of damage.

4. Conclusion

We investigated behaviors of deuterium during the implantation into graphite with different implantation temperature and its thermal desorption. The experimental results showed as follows.

The thermalized deuterium contributed to form the trapping site of deuterium via peak 3. The trapping site of peak 2 and CD_{x-1} was formed by the energetic deuterium. The trapping site corresponding to peak 2 and CD_{x-1} is sp^3 state. The sp^3 state of carbon would be formed by the internal energy transferred from energetic deuterium ions when CD_{x-1} was formed. Above 573 K, the recovery of the graphite disordered by D_2^+ implantation dominated, and then the release of the implanted deuterium from the graphite was started during D_2^+ implantation. The release behaviors of implanted deuterium would be strongly correlated with the recovery of the graphite structure.

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