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Effects of chemical states of carbon on deuterium retention in carbon-containing materials

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Abstract

Deuterium retention behavior in highly oriented pyrolytic graphite (HOPG), poly-crystalline diamond, poly-crystalline SiC, sintered WC, and converted B_4C were investigated to reveal tritium behavior in re-deposition and co-deposition layers. Such layers would contain carbon, when the first wall and/or divertor were made of graphite or carbon-containing materials. Furthermore, the employment of other materials such as tungsten, and first wall conditioning such as boronization would complicate the layers. No different deuterium trapping sites due to carbon from those in HOPG were found in all the samples, where two deuterium trapping processes were observed: hot atom chemical trapping of energetic deuterium by a dangling bond of carbon and thermochemical trapping of thermalized deuterium in a constituent atom vacancy surrounded by carbons. Additionally, the latter reaction could be easily counteracted by or competed with the other deuterium trapping reactions by constituent atoms.

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1. Introduction

Graphite is one of the most suitable candidate materials for plasma facing materials and has been studied extensively for its interaction with hydrogen isotopes [1–4]. However in fusion reactors, carbon can exist in various chemical structures, especially in re-deposition and co-deposition layers. Carbon fiber composite (CFC) and tungsten have been selected for employments as armor tiles in the ITER divertor region, which were exposed to the high heat flux due to energetic particles [5]. This means that complex re-deposition and co-deposition layers would be formed in ITER. It is, therefore, an important issue to reveal the effects of chemical states of carbon on deuterium retention in carbon-containing materials.

In our previous studies, chemical behavior of energetic hydrogen isotopes in carbon-containing materials such as highly oriented pyrolytic graphite (HOPG), poly-crystalline diamond, poly-crystalline silicon carbide (SiC), and sintered tungsten carbide

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(WC) have been systematically investigated [3,4,6–10].

In the present study, the effects of the chemical state of carbon on the retention of deuterium implanted with high energy was examined by means of thermal desorption spectroscopy (TDS) and X-ray photoelectron spectroscopy (XPS), both of which can be used to elucidate the trapping states of implanted deuterium and chemical states of carbon in carbon-containing materials.

2. Experimental

The samples used in the present study are HOPG, poly-crystalline diamond, poly-crystalline SiC and converted B_4C purchased from Pechiney Co., Element Six Co., Asahi Glass Co. Ltd. and Hitachi Ltd., respectively, and sintered WC provided by A.L.M.T. TUNGSTEN Corp. The samples were pre-heated at 1400 K at the maximum for 10 min to remove residual gases. The samples were characterized by XPS (ESCA-1600 system, ULVAC PHI Inc.). Thereafter, 1 keV D_2^+ implantation into each sample was performed with a fluence of 1×10^{22} D m^{-2} at ambient temperature. Additionally, the dependence of deuterium behavior on ion implantation temperature was investigated for HOPG and SiC to reveal commonality in deuterium trapping behavior of carbon. The temperature range of the samples during ion implantation was from 150 K up to 1173 K. After the implantation, TDS experiments were performed with the heating rate of 0.5 K s^{-1} up to the temperature of 1423 K to reveal deuterium desorption behavior. Desorbed gases were analyzed by a quadrupole mass spectrometer. An XPS measurement was also carried out at each step to reveal the change of chemical states of carbon during the deuterium ion implantation. It should be noted about experimental apparatus in Shizuoka University used in the present study that the XPS apparatus was connected with TDS experimental apparatus under a same vacuum of 10^{-8} Pa. Additional ion implantation installations were attached to both apparatuses. All experimental procedure could, therefore, be performed without air exposure. The details were described in our previous paper [3,4,6–10].

3. Results and discussion

The XPS spectra revealed that almost all the samples before deuterium implantation showed an atomic composition comparable with their stoichiometry, except for B_4C which is well-known as a non-stoichiometric compound. The normalized TDS spectra of deuterium desorbed from deuterium-implanted HOPG and SiC are shown in Fig. 1 with their peak analyses by numerical calculations of the Redhead equation [11] for HOPG and by the Gaussian distribution function for SiC. The numerical calculations show that each spectrum was analyzed into two peaks, named Peak 1 and Peak 2 for HOPG, and Peak A and Peak B for SiC. It was reported that Peak A and Peak B were attributed to the desorption of deuterium bound to Si and C by forming Si—D and C—D bonds, respectively [8,9]. The temperature of Peak B was almost the same as that of Peak 1. The deuterium retention of each peak was normalized by the total retention following the implantation at 150 K for graphite and 300 K for SiC as shown in Fig. 2(a) and (b). It should be noted that another peak named Peak C appeared at somewhat higher implantation temperature for SiC, which is considered to be comparable with Peak 2 for HOPG. The total deuterium retention in HOPG and SiC decreased as implantation temperature increased. For graphite, this result agreed with the previous reports that the saturated concentration of hydrogen in pyrolytic graphite decreased with increasing the implantation temperature [12] and that retained amount of implanted deuterium into polycrystalline graphite increased with decreasing temperature below RT [13]. However, the results of the peak analyses for all TDS spectra indicated that the deuterium retention

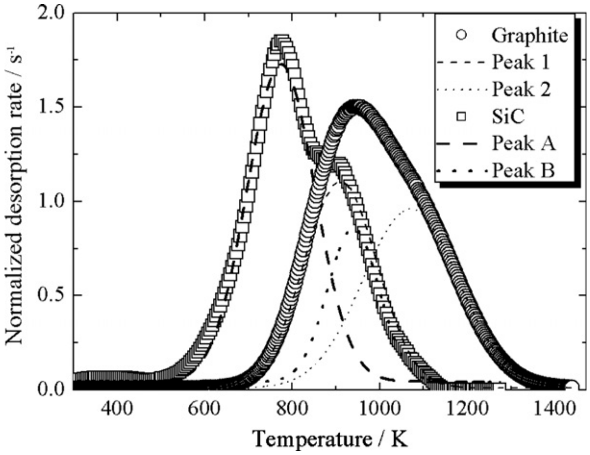

Fig. 1. Normalized TDS spectra of deuterium implanted into HOPG and SiC with their analyses by the Redhead equation and Gaussian distribution function, respectively.

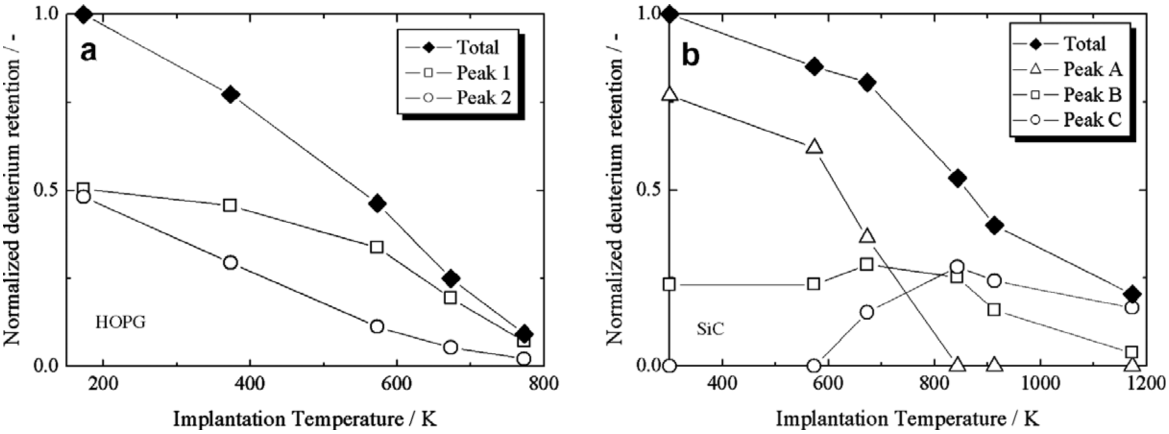

Fig. 2. Dependence of deuterium retention by each process of HOPG in (a) and of SiC in (b) on temperature during deuterium ion implantation.

resulting in Peak 1 and Peak B were little dependent on implantation temperatures, in contrast with the dependence of other peaks. The latter process would, therefore, be governed by thermal equilibrium chemistry, although the former would not. The trapping state of Peak 1 would be less stable than that of Peak 2 from the viewpoint of their activation energies [14] and their peak temperatures. Vietzke and Philipps discussed that the direct hot atom chemical reaction of energetic hydrogen with carbon would not proceed, but the energetic hydrogen give rise to a damaged rather reactive carbon structure [15]. Assuming a non-thermal equilibrium process which is so-called hot atom chemical process, however, the reason why the behavior of only Peak 1 was independent of thermal equilibrium could be explained.

The TDS spectrum of each sample normalized by the total amount of deuterium retention is shown in Fig. 3. This figure indicates that there are one or two types of chemical states of deuterium trapped by carbon. These are comparable with Peak 1 and Peak 2, and may be common to all carbon-containing materials. In the TDS spectrum of deuterium implanted into diamond, a sharp deuterium desorption peak at higher temperature would be attributed to deformation of deuterium bubbles, as in the previous study [7], rather than to deuterium trapped by carbon. In other words, there are only two trapping processes of deuterium by carbon; a hot atom chemical one and thermal equilibrium one independent of the chemical state, the chemical structure, or the chemical composition of the carbon-containing material. Table 1 lists the abundance of deuterium trapped by carbon of each sample. This indicates

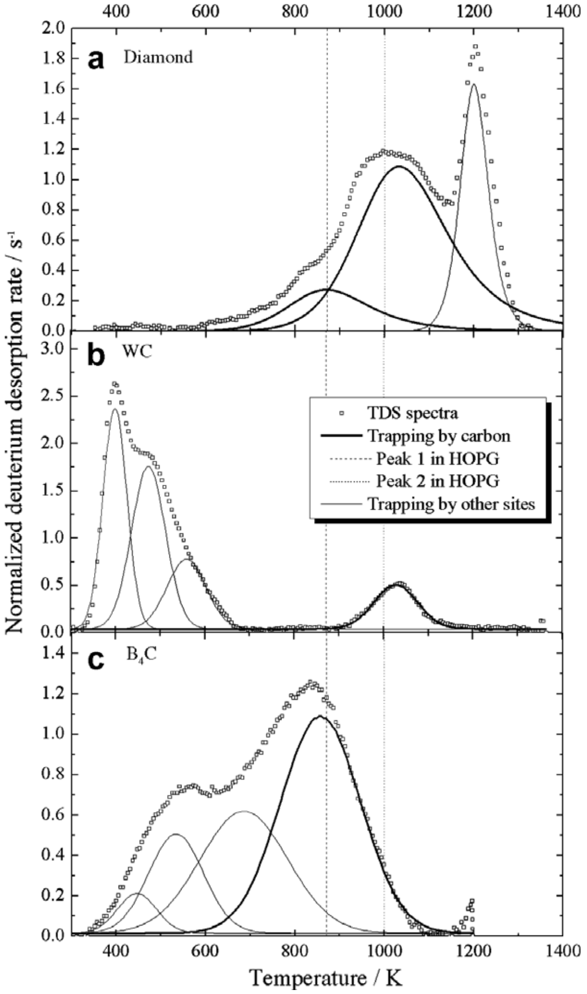

Fig. 3. TDS spectra of deuterium implanted into diamond, WC, and B_4C in (a), (b), and (c), respectively, with their analyses by Gaussian distribution function, focusing on the deuterium trapping by carbon.

that the deuterium trapping processes by carbon in SiC and B_4C are dominated by Peak 1, and those in diamond and WC by Peak 2. The difference between SiC and diamond, both of which have diamond structure, indicates that the deuterium trapping processes by carbon would not be controlled by the crystal structure. The C1s peak energy of the XPS spectrum of each sample in the initial state shown in Table 1 has no correlation with the deuterium trapping processes by carbon. The deuterium trapping processes by carbon, therefore, would not be related to the chemical states, the chemical structure, and the chemical composition of carbon-containing materials, although they are different for each sample.

Table 1
Abundance of deuterium trapped by carbon via hot atom chemical process and thermal equilibrium process of each sample deuterium implanted at ambient temperature with the initial value of C1s peak of each sample

	Hot atom chemical process (%)	Thermal equilibrium process (%)	C1s (eV)	XPS
HOPG	51	49	9	284.09
Diamond	18	82	6	285.86
SiC	100	0	0	283.40
WC	0	100	0	282.60
B_4C	100	0	3	283.23

A model proposed to describe this scenario is shown in Fig. 4. In this model, the trapping of implanted energetic deuterium is described as following three processes: (1) generation of defects such as vacancies and dangling bonds by the energetic deuterium implanted into the sample during thermalizing the deuterium through physical scattering process, (2) the direct trapping of energetic deuterium of which a part of energy have lost in a dangling bond of carbon atom, and (3) thermalized deuterium trapping in the vacancy occupied by carbon atoms through thermal equilibrium chemical process. It should be noted that, in this model, only the energetic deuterium can interact with the dangling bond which has high energy potential wall. According to this model, the hot atom chemical trapping of deuterium by carbon would not proceed unless the production of dangling bonds was prevented as in semimetal such as WC, and perhaps in metals. The thermochemical trapping could be prevented in materials in which a vacancy surrounded by carbon atoms could not be produced such as B_4C, or competitively reduced by other thermochemical trapping reactions of deuterium.

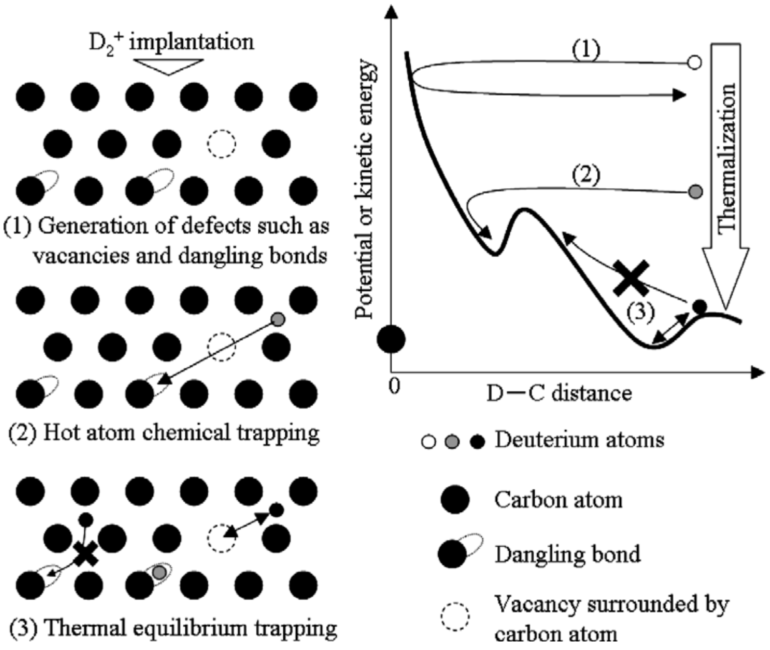

Fig. 4. A sequential model of implanted deuterium trapping behavior as: (1) generation of defects such as vacancies and dangling bonds generated during thermalization of high energy deuterium; (2) hot atom chemical trapping in dangling bonds; and (3) thermal equilibrium trapping in vacancy surrounded by carbon atoms, with suggested potential curve as a function of D–C distance (‘0’ means the position of carbon atom of steady states). Color gradation means kinetic energy level of deuterium: the lighter the color is, the higher the energy is.

This model is supported by the study reported by Mayer that the D_2 TDS spectrum for deuterium-implanted B_4C does not seem to have Peak 2, while that for boron doped graphite does, and there seems to be no other trapping states of deuterium than that in pure graphite and pure boron in either case [16].

4. Conclusion

The behavior of deuterium in some carbon-containing materials such as HOPG, poly-crystalline diamond, poly-crystalline SiC, sintered WC, and converted B_4C were investigated in the present study. It is suggested that two deuterium trapping processes by carbon would occur in carbon-containing materials. One is the hot atom chemical process involving trapping at dangling bonds, and the other a thermochemical reaction with vacancies. These could occur without any concern with the chemical states, chemical structure, and chemical composition of carbon-containing materials. The former could not proceed in semimetals such as WC, or perhaps in metals, because the dangling bonds of carbon would not form in them, and the latter would be counteracted by or competed with trapping at other trapping sites and the annealing of the defects which act as the deuterium trapping site.

These results indicate that the basic retention processes of hydrogen isotopes by carbon atom in re-deposition and co-deposition layers with the other carbon-containing materials would be no different from those in graphite.

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