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Dependence of implantation temperature on chemical behavior of energetic deuterium implanted into tungsten carbide

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Abstract

Dependence of implantation temperature on chemical behavior of energetic deuterium implanted into WC was investigated by TDS and XPS. 1.0 keV D_2^+ ions were implanted into WC samples at the implantation temperature range of 323–873 K. It was found that the deuterium retention decreased as the implantation temperature increased. Above 573 K, most of the retained deuterium was bound to C, which was less than 20% of the total D retention after D_2^+ implantation at 323 K. Above 673 K, C was segregated on the WC surface and some of the implanted deuterium was retained in the segregated carbon layer. Additionally, it can be said that the D retention in WC was much less than that in other carbon-related materials, such as graphite and SiC. Hydrogen isotope retention can be reduced significantly when WC is formed on a divertor surface as a redeposited layer.

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Keywords: Chemical erosion; Divertor material; Tritium inventory; Tungsten; Thermal desorption

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1. Introduction

In ITER, both tungsten (W) and carbon (C) materials will be used as the plasma-facing materials (PFMs) [1]. It is expected that W and CFC are sputtered by energetic particles and then redeposited on the divertor surface as mixed materials [2]. Their composition is still unknown, while they could be carbon-rich due to the higher sputtering rate for C than that for W [3,4]. To understand chemical behavior of tritium in the redeposited layers, therefore, it is useful to investigate hydrogen isotopes behavior in carbon materials containing various concentration of W. As a fundamental study, we carried out the experiments for WC in the present paper.

It has been reported that there were four deuterium desorption peaks of the TDS spectrum for the deuterium implanted WC, when energetic deuterium was implanted at the temperature of 323 K: the two peaks observed at the lower temperature region were attributed to the desorption of deuterium retained in the interstitial sites, the third

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corresponded to that trapped by carbon vacancy, and the last was originated from the desorption of deuterium bound to carbon [5].

In this paper, implantation of energetic deuterium ion (D_2^+) into WC was carried out to understand temperature dependence on chemical behavior of hydrogen isotopes in temperature range from room temperature up to 873 K, which will almost covers the expected operating temperatures of fusion reactors. Thermal desorption processes of implanted deuterium from WC and the chemical structure of WC were studied by means of the thermal desorption spectroscopy (TDS) and X-ray photoelectron spectroscopy (XPS).

2. Experimental

The sample used in the present study was polycrystalline WC supplied by A.L.M.T. TUNGSTEN Corp. (Toyama, Japan). The size of the sample was $10\ \text{mm} \times 10\ \text{mm} \times 0.5\ \text{mm}^t$ and its density was $14.9\ \text{g/cm}^3$, which was almost same as that of $15.5–15.7\ \text{g/cm}^3$ for the single crystal. The sample was mounted on a sample holder equipped with a ceramic heater, whose details were described in Ref. [6].

To remove the impurities, such as H_2O, O_2, H_2 and so on, the samples were preheated at 1323 K for 10 min under ultrahigh vacuum ($\sim 10^{-8}$ Pa). Thereafter, the sample surface was sputtered by 1.0 keV argon ions (Ar^+), and its atomic composition ratio of W and C was determined to be almost unity according to the XPS measurement. The 1.0 keV D_2^+ ions were implanted into the WC samples at various temperatures in the range between 323 and 873 K, with the flux of $1.0 \times 10^{18}\ \text{D m}^{-2}\ \text{s}^{-1}$ and the fluence of $1.0 \times 10^{22}\ \text{D m}^{-2}$, which corresponded to the D saturation in WC. The chemical state of WC after the D_2^+ ion implantations at the various implantation temperatures was also analyzed by means of XPS using the AlKα source. To reveal the thermal desorption behavior of the implanted deuterium from the WC samples, the TDS experiments were carried out up to the temperature of 1323 K at a heating rate of $0.5\ \text{K s}^{-1}$.

3. Results and discussion

Fig. 1 shows the TDS spectrum for the D_2^+ ions implanted WC at the temperature of 323 K and the four analyzed peaks of D_2 desorbed from WC by using the Gaussian distribution function. These peaks were located at the temperatures of around 400, 490, 600 and 930 K, marked with Peak 1, Peak 2, Peak 3 and Peak 4, respectively. According to our previous study [5], Peaks 1 and 2 were assigned to the desorption of D retained in two interstitial sites of WC, Peak 3 was corresponded to that trapped by C vacancy, and Peak 4 was originated from the desorption of D bound to C.

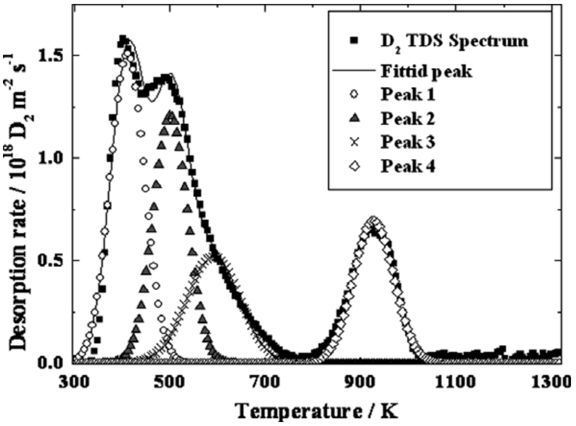

Fig. 1. TDS spectra of D_2 for D_2^+ ion implanted WC with fitted peaks.

Fig. 2 shows the TDS spectra for D_2^+ ion implanted WC at the various implantation temperatures between 323 and 873 K. It was found that the total D retention decreased as implantation temperature increased. No Peak 1 was observed in the TDS spectrum for the WC irradiated at 423 K. Peak 2 and Peak 3 did not also observed in the TDS spectrum at the implantation temperature of 573 K. The saturated retention of D bound to C was determined to be almost $3.0 \times 10^{20}\ \text{D m}^{-2}$ at 573 K. Above 573 K,

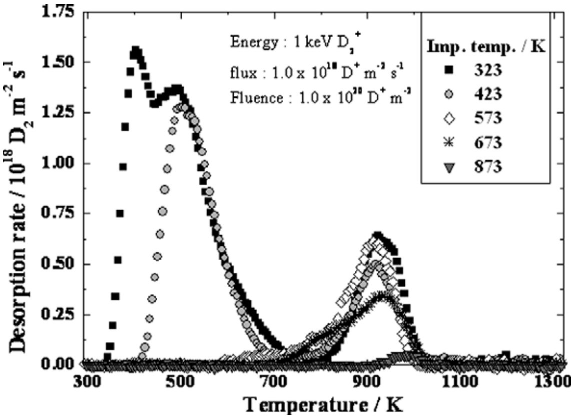

Fig. 2. TDS spectra of D_2 for D_2^+ ion implanted WC with various implantation temperatures.

it was found that most of D bound to C was desorbed. The desorption temperature for D bound to C has elevated as implantation temperature increased above 573 K as shown in Fig. 2, which was attributed to the fact that the D desorption was refrained by a re-combination process [7].

Fig. 3 shows the XPS spectra C-1s and W-4f of WC normalized at the various implantation temperatures. The initial binding energies of C-1s and W-4f were located at 282.9 eV and 31.4 eV, respectively. A positive peak shift of C-1s to 283.0 eV was observed after the D_2^+ ion implantation at 323 K. This suggests that C–D bonds are formed in D_2^+ ion implantation. On other hand, no distinct chemical shifts of W-4f were observed by D_2^+ ion implantation at 323 K. The additional peak shift of C-1s toward the lower energy side was observed as the implantation temperature increased, and at the temperature of 873 K, it was reached to 282.7 eV, which was consistent with a typical binding energy of C-1s for WC [8]. It was suggested that the amount of D bound to C decreased as implantation temperature increased [9]. For the binding energy of W-4f, a positive chemical shift was observed as the implantation temperature increased. The binding energy of W-4f at the implantation temperature of 423 K was 0.2 eV higher than that at 323 K, which was consistent with the result of the TDS measurement that D bound to one of the interstitial sites was detrapped. The trapped D is affected by two vertical atoms of W because the distance between the trapped D and planate three atoms was longer than that between the trapped D and the vertical two W atoms. The distinct chemical shift of C-1s between the implantation temperature of 323 K and 423 K was not observed, indicating the trapped D was influenced by not C but W. It is known that there are two different interstitial sites in WC, namely Interstitial I, where arranges three W atoms on planate and the other two C atoms on vertically located, and Interstitial II which is opposite configuration with Interstitial I. According to these experimental results, it was thought that the D trapped by Interstitial II would be energetically more stable than that by Interstitial I, and Peak 1 of the TDS spectrum was attributed to the D desorption from Interstitial I, and Peak 2 to that from Interstitial II. At the temperature of 573 K, the binding energy of W-4f was 0.3 eV lower than that of 423 K, which corresponded to the D desorption from Interstitial II and carbon vacancies. Especially, the D desorption from the carbon vacancies induced negative peak shift of W-4f, as the D trapped by carbon vacancies were surrounded by only W atoms. Furthermore, a shoulder appeared on the higher energy side of C-1s peak after the D_2^+ ion implantations. The shoulder shifted to the higher energy side and the FWHM value of the C-1s peak increased as implantation temperature increased. Consequently, the C-1s XPS spectra were found to be divided into two peaks; the lower one (282.7 eV) was attributed to C–W bond, and the higher one (284.6 eV), C–D bond and/or C–C bond [4,7,9]. Fig. 4 shows the peak areas of C–W bond and 'C–D + C–C' bonds, which estimated from C-1s spectra. Fig. 5 indicates the peak areas of W-4f and C-1s XPS spectra as a function of implantation temperature. Below 673 K, both peak areas in Fig. 4 and C-1s in Fig. 5 were not changed significantly. However, above 673 K, the peak area of 'C–C + C–D' in Fig. 4 and C-1s in Fig. 5 increased as implantation temperature increased, although the total D

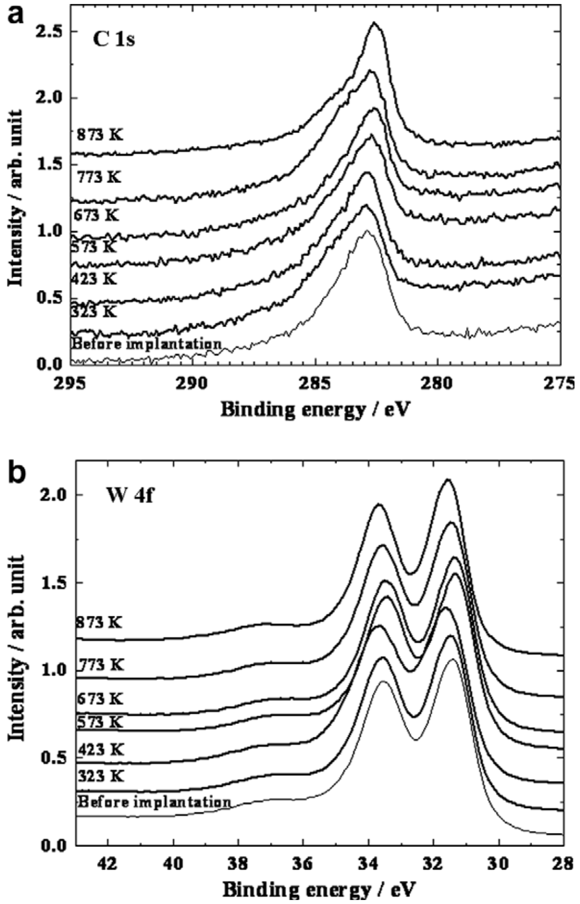

Fig. 3. XPS spectra for D_2^+ ion implanted WC with various implantation temperatures. (a) C-1s (b) W-4f. These were normalized to equalized these intensities.

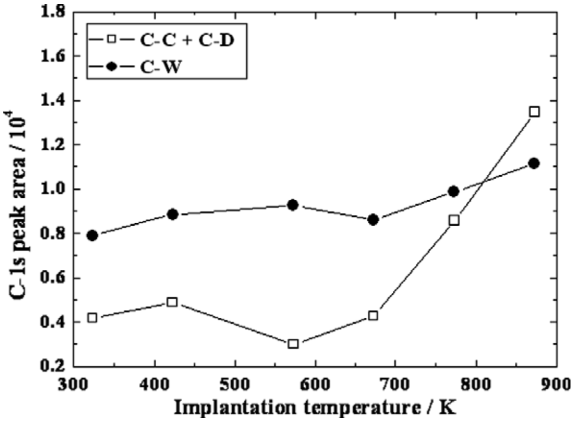

Fig. 4. Implantation temperature dependence of peak areas of C-1s XPS spectra.

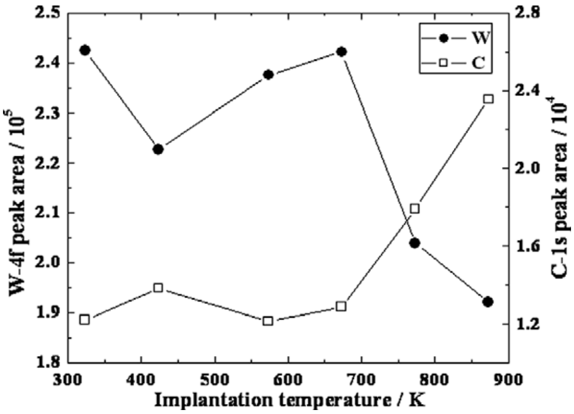

Fig. 5. Implantation temperature dependence of peak areas of C-1s and W-4f XPS spectra.

retention in WC decreased. It was suggested that C–C bond was the major chemical form on the WC surface above 673 K, expecting that C was segregated on the surface by heating treatment during D_2^+ ion implantation. Coincidentally, peak area of W-4f in Fig. 5 was decreased as implantation temperature increased whereas C–W in Fig. 4 was not widely changed. It was suggested that deuterium desorbed by heating above 673 K and, thereafter, C–W bonds were recovered. However some disordered C were remained and easily diffused toward the surface. These facts induced the C segregation on the WC surface.

The D retention in WC per one component atom (D/WC × 0.5) as a function of implantation temperature is summarized in Fig. 6, in which the D retention in pyrolytic graphite (D/C) and SiC (D/SiC × 0.5) are also shown [10,11]. The D retention in WC was decreased significantly up to 573 K, and the reduction became almost gradual above 573 K, where the amount of D bound to C was less than 20% of the D retention at 323 K. It should be noted that the D retention in WC was much less than those in the other materials, one fifth of that in pyrolytic graphite and one sixth in SiC. In addition, the D retention would be lowered if the temperature of WC layer could be high during discharge in fusion reactors. However, it is thought that the D retention would increase when the C concentration in the re-deposition layer increased. Further studies, therefore, will be required to reveal C concentration dependence on hydrogen isotope retention in redeposition layers of tungsten–carbon mixtures on divertor region of fusion reactors.

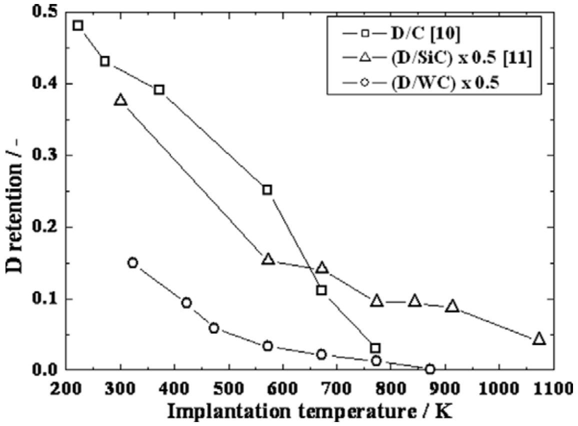

Fig. 6. D retention for D_2^+ ion implanted graphite, SiC and WC at various temperatures.

4. Conclusion

Dependence of implantation temperature on chemical behavior of energetic deuterium implanted into WC was investigated by using TDS and XPS.

There were four D desorption stages for the D_2^+ ion implanted WC according to TDS results. It was suggested that D was trapped mainly by two different interstitial sites and carbon vacancies in WC below 423 K. Above 573 K, most of D was bound to C, which was less than 20% of the total D retention at 323 K. Above 673 K, C was segregated on the WC surface.

The present experimental results imply that possibility for the reduction of tritium inventory in WC redeposition layer in the divertor region for ITER compared to the C redeposition layer when the surface temperature was increased. In the operating temperature of divertor ITER, therefore, a significant reduction of tritium inventory in the WC deposited layer could be achieved. For more detailed estimation of tritium inventory in redeposited layers of W and C mixtures in ITER, however, further studies will be required to reveal C concentration dependence on hydrogen isotopes retention.

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