Behaviors of Deuterium Retention and Microstructure Change of Tungsten Simultaneously Implanted with Carbon and/or Helium Ions

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Recent studies of deuterium (D) retention and microstructure behaviors of tungsten simultaneously implanted with carbon ion (C+) and/or helium ion (He+) are reviewed. Implantation of deuterium ion (D2+) was performed by simultaneous implantations with C+, He+ and a mixture of C+ and He+ using a triple-ion-implantation system, while D retention behavior was studied by thermal desorption spectroscopy. The D depth profile, microstructure changes, and chemical states of constituent atoms were observed by glow-discharge optical emission spectroscopy, transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy, respectively. D retention was observed to be enhanced by both C+ and He+ implantations. After the simultaneous implantation of D2+ and C+, substantial D2 desorption was observed at temperatures higher than 600 K. Following the simultaneous implantation of D2+ and He+, D retention increased to about five times that for D2+ implantation, while the D desorption temperature region was the same. However, in the case of triple-ion implantation, the accumulation of C on tungsten was suppressed, and the retention of D trapped by C was reduced. The D retention in triple-ion-implanted tungsten was considered to be suppressed by He+ implantation. TEM observations suggest that most of the deuterium would be retained at grain boundaries and lattice defects such as vacancy clusters. [doi:10.2320/matertrans.MG201205]

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1. Introduction

Plasma-facing materials research for fusion applications has recently focused on tungsten materials because of their low sputtering yield and low tritium retention.1-3 A key issue for the performance evaluation of plasma-facing materials is tritium retention and its recycling under fusion-relevant conditions. For tritium retention, the radiation damage effect, especially by neutron irradiation, and the surface modification effect are two important issues. It is thought that neutron irradiation can produce additional trapping sites, and tritium retention may dramatically increase.4-6 On the other hand, it is thought that surface modification is caused by the change in the surface chemical state by the reaction of tungsten with carbon, an impurity, which will enhance hydrogen isotope trapping and introduce irradiation damage structure by energetic ion implantation.3,7) In the International Thermo-nuclear Experimental Reactor, tritium retention may be underestimated if the tritium retention in the impurity deposition layer is not considered. In particular, carbon impurities will exist inside the vacuum vessel even if tungsten is used as a plasma-facing material throughout the first wall. In addition, many researchers have reported that the implantation of helium (He) produced by the fusion reaction could also enhance tritium retention5 and surface modification.8) The formation of He bubbles may also change the tritium retention behavior as well as the trapping state and desorption temperature. This study reviews the recent studies on the deuterium retention and microstructure change for tungsten simultaneously implanted with carbon and/or helium ions.9-13)

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2. Experimental

Disk-type tungsten (99.99% purity; Allied Material Co., Ltd.) samples with a diameter of 10 mm and a thickness of 0.5 mm were cut off from a tungsten rod that was swaged and heated for stress relief (1 h at 1173 K). These disk samples were mechanically polished using SiC abrasive papers and 1 and 3 μm diamond suspensions. The samples were preheated at 1173 K for 30 min under ultrahigh vacuum to remove surface impurities and damages introduced during the polishing process. After preheating, the samples were introduced into the simultaneous ion-implantation system.

The simultaneous triple-ion-implantation system, consisting of carbon ion (C+), helium ion (He+), and deuterium ion (D2+), combined with a thermal desorption spectroscopy (TDS) system was designed to investigate the effect of ion implantation on hydrogen isotope trapping. This system has three chambers: (1) an ion implantation chamber; (2) a sample introduction chamber; and (3) a TDS chamber. Samples can be easily transferred from the ion implantation chamber to the TDS chamber via the sample introduction chamber without air exposure. CO2 gas was used as the C+ source gas to exclude hydrogen impurities. The (electric field) E x (magnetic field) B mass separator was equipped at the head of the C+ gun, and the oxygen impurity in the C+ gun was evacuated by a turbomolecular pump. C+, He+ and D2+ were implanted using different individual ion guns equipped in the implantation chamber. Incident angles of He+ and D2+ guns were 30 degrees to the surface normal, while that of the C+ gun was 0 degrees. The implantation area was set to be 4 mm × 4 mm. The C+ acceleration energy was set to be 10 keV, and the maximum ion flux was 2.0 × 1018 C+ m-2 s-1, which was estimated by a Faraday
cup. The ion fluxes of 3 keV He$^+$ and 3 keV D$_2^+$ were $1.0 \times 10^{18}$ ions m$^{-2}$s$^{-1}$, respectively. After ion implantation, the sample was transferred to the TDS chamber, and the TDS experiment was performed. The sample holder was equipped with a ceramic heater to heat the samples up to 1300 K with a heating rate of 0.5 K s$^{-1}$.

Following ion implantations, the chemical states of W and C were evaluated by X-ray photoelectron spectroscopy (XPS) (ESCA1600 system, ULVAC-PHI Inc.) using an Al-K$\alpha$ X-ray source (1486.6 eV) and a hemispherical electron analyzer. The measurement was carried out in the center of the implanted area. To evaluate D desorption and retention behaviors, TDS was performed at a heating rate of 0.5 K s$^{-1}$ up to 1173 K using two quadrupole mass spectrometers: a high-resolution mass spectrometer and a wide range one. The D depth profile was evaluated by glow-discharge optical-emission spectroscopy (GD-OES) (GD-Profiler2, Horiba Inc.) at University of Toyama. Transmission electron microscopy (TEM) (JEM2000EX, JASCO Inc.) experiments were performed at Kyushu University.

3. Results and Discussion

3.1 Effect of C$^+$ implantation on D retention

Figure 1 shows the D$_2$ TDS spectra of D$_2^+$-implanted tungsten with a fluence of $1.0 \times 10^{22}$ D$^+$ m$^{-2}$. The major desorption species was D$_2$, and no other species were observed by TDS. D$_2$ desorption stages consisted of two stages, characterized by Peaks 1 and 2, respectively, found in the temperature range between 350–750 K. A large amount of D was desorbed at the lower-temperature region of 400 K as Peak 1. The TEM images of D$_2^+$-implanted tungsten with a fluence of $1.0 \times 10^{22}$ D$^+$ m$^{-2}$ as a function of post-implantation annealing temperature are shown in Fig. 2. Comparing with that of unimplanted tungsten, the TEM image showed that dislocation loops (black-dot-like structures) were introduced throughout the sample, which partly disappeared by annealing at 973 K. The formation of dislocation loops is attributed to the aggregation of interstitial tungsten atoms that were simultaneously introduced with vacancies. In addition, the trapping energy of hydrogen isotopes by dislocation loops was much lower than that by vacancy. Hence, the first stage (Peak 1) is considered to be initiated by the desorption of D trapped at the surface, intrinsic defects, and/or dislocation loops. The second stage (Peak 2) can be attributed to the detrapping from the other irradiation defects, such as vacancies, which will be discussed later.

The D$_2$ TDS spectrum of tungsten implanted simultaneously with D$_2^+$ and C$^+$ is shown in Fig. 3. The C$^+/D_2^+$ ratio was set to 0.2. The shape of the TDS spectrum is obviously different from that of D$_2^+$-implanted tungsten. The D$_2$ desorption stage consisted of three stages characterized by Peaks 1, 2 and 3, respectively. Substantial desorption was observed at 750 K (Peak 2). From Figs. 1 and 3, the
temperature region of the D desorptions at Peaks 1 and 2 for the C\(^+\)-D\(_2^+\)-implanted sample were observed to be shifted to about 100 K toward the higher-temperature side. This suggests that deuterium trapped by dislocation loops and possibly vacancies in C\(^+\)-D\(_2^+\)-implanted tungsten needs a higher temperature for desorption compared to the tungsten sample implanted with D\(_2^+\) only. The first and second desorption stages were expected to be the same as the case of only D\(_2^+\) implantation. The peak shift toward higher temperatures can be explained in terms of the growth of vacancy clusters. The third desorption stage (Peak 3) was caused by the existence of carbon, which would lead to the trapping of D by C. The TEM observation results of C\(^+\)-D\(_2^+\)-implanted tungsten are summarized in Fig. 4. The diffraction patterns of D\(_2^+\)-implanted tungsten and that for unimplanted tungsten were similar, i.e., no structure change was observed, as also shown in Fig. 2. In contrast, spots and halo rings were observed in the diffraction pattern of C\(^+\)-D\(_2^+\)-implanted tungsten, indicating the formation of second phases and amorphization in the near-surface layer. In the TEM images of both D\(_2^+\)- and C\(^+\)-D\(_2^+\)-implanted tungsten, dislocation loops (black dots) were observed after ion implantation. The number density and size of the irradiation defects of C\(^+\)-D\(_2^+\)-implanted tungsten were higher and larger, respectively, than those of D\(_2^+\)-implanted tungsten. The density of irradiation defects produced by C\(^+\) implantation was more than 20 times higher than that produced by D\(_2^+\) implantation. Further, the implantation fluence of C\(^+\) is one-fifth that of D\(_2^+\). The hydrogen isotope is known to be stabilized by trapping by vacancy clusters and mono vacancies.\(^8\) Therefore, the substantial D retention is likely to be due to trapping by vacancies. Figure 5 summarizes D retention as a function of the fluences of C\(^+\) and D\(_2^+\) during simultaneous C\(^+\)-D\(_2^+\) implantation.\(^13\) Both Peak 2 and the D\(^+\) fluence increased, indicating that it would have a significant correlation with the amount of vacancies. The D retention that occurred as Peak 3 was the highest at the fluences of 0.5 \(\times \) \(10^{22}\) D\(^+\) m\(^{-2}\) and 0.1 \(\times \) \(10^{22}\) C\(^+\) m\(^{-2}\). C\(^+\) implantations into tungsten at room temperature have been reported to result in the formation of two principal regimes: (1) regimes for the sputtering of tungsten with the formation of the W–C mixture; and (2) carbon deposition where the layer of the C–C bond forms over the W–C mixture.\(^14\) In this case, the effect of C\(^+\) changed at the C\(^+\) fluence of 0.1–0.2 \(\times \) \(10^{22}\) C\(^+\) m\(^{-2}\), where the major process changed from the sputtering of tungsten with the formation of the W–C mixture to the formation of the C–C layer. In addition, the deuterium trapped as the C–D bond would be sputtered through the formation of CD\(_x\), since the C–C bond can be broken more easily than the W–C bond, leading to a reduction in D retention.
3.2 Effect of He⁺ implantation on D retention

Simultaneous He⁺–D₂⁺ implantation was performed to study the He effect on D retention in tungsten. Figure 6 compares TDS results of He⁺–D₂⁺-implanted and D₂⁺-implanted tungsten. The He⁺ fluence was set to \(0.2 \times 10^{12}\) He⁺ m⁻². The flux ratio of He⁺/D⁺ was 0.2. D retention was observed to increase in simultaneous He⁺–D₂⁺-implanted tungsten in comparison with that of D₂⁺-implanted tungsten by a factor of five, although the D₂ desorption temperature region was almost the same as that for D₂⁺-implanted tungsten. The irradiation defects produced by He⁺ implantation can be said to induce D trapping in tungsten. The Stopping and Range of Ions in Matter (SRIM) calculation showed that the six vacancies were produced by one 3 keV He⁺ particle and that the vacancy concentration should be at least two times that of D₂⁺-implanted tungsten. These findings indicate that D retention enhancement cannot account for the concentration of vacancies produced by He⁺ implantation. Figure 7 depicts the TEM images of He⁺–D₂⁺-implanted tungsten after annealing at 1073 K for 20 min. By comparing the focus images, it was clearly observed that He bubbles were formed and retained in tungsten. This suggests that the He atoms diffused and aggregated in the matrix by annealing, and the He bubbles grew. To elucidate the detailed behavior of He-vacancy clusters and D retention, the flux ratio of He⁺/D⁺ was changed from 0.2 to 1.8, although the D⁺ fluence was set to be constant at \(1.0 \times 10^{22}\) D⁺ m⁻². The microstructure changes as a function of the He⁺/D⁺ ratio observed by TEM are summarized in Fig. 8. Dislocation loops were formed in all samples. The density of He bubbles increased without annealing as the He⁺/D⁺ ratio increased, indicating that the amount of He-vacancy clusters increased with the He⁺/D⁺ ratio (Fig. 8). By comparing the D₂ TDS spectra of He⁺–D₂⁺-implanted tungsten and D₂⁺-implanted tungsten, as shown in Fig. 9, enhancement of D retention by He⁺ implantation can be observed, but no correlation with the He⁺/D⁺ ratio was found. The D depth profiles of He⁺–D₂⁺-implanted tungsten observed by GD-OES show that the D depth profiles were almost the same among these samples (Fig. 10). This illustrates that D retention within the implantation depth should be saturated.

3.3 D retention of triple ion (C⁺, He⁺, D₂⁺)-implanted tungsten

In the above sections, it was described how D retention behavior under the effect of C⁺ or He⁺ implantation can be
significantly affected by accompanying ion species. By the simultaneous implantation with $C^+$, D trapping behavior clearly changed. Major desorption stages shifted toward higher temperatures, indicating that D was stably trapped by tungsten, which is in contrast to the case of $D_2^+$ implantation. For simultaneous $He^+$ implantation, total D retention was enhanced by the presence of He bubbles, but no change in the D desorption temperature was observed.

The $D_2$ TDS spectrum of triple-ion-implanted tungsten was compared with those of $C^+-D_2^+$- and $He^+-D_2^+$-implanted tungsten (Fig. 11). The $D_2$ desorption for only $D_2^+$-implanted tungsten takes place at temperatures lower than 600 K. The shape of the $D_2$ TDS spectrum of $C^+-D_2^+$-implanted tungsten differed from those of the other TDS spectra. The large amount of D desorbed at a higher temperature of 800–1000 K, and the spectra consisted of three stages, one of which can be seen in Fig. 3. For $He^+-D_2^+$-implanted tungsten, the $D_2$ desorption stage was concentrated at a lower-temperature side of less than 700 K. For triple-ion implantation, the $D_2$ desorption temperature is almost the same as that for $D_2^+$-implanted tungsten and $He^+-D_2^+$-implanted tungsten. The mixture of $C^+$ and/or $He^+$ with $D_2$ resulted in the enhancement of D retention as compared with that for $D_2^+$-implanted tungsten by about three times. By triple-ion implantation, D retention was reduced in comparison with $C^+-D_2^+$ and $He^+-D_2^+$ implantations. Similar to $He^+-D_2^+$ implantation, the $D_2$ TDS spectrum of triple-ion-implanted tungsten differs from that of $C^+-D_2^+$-implanted tungsten as mentioned above, indicating that $C^+$ implantation would enhance sputtering, and $He^+$ implantation would introduce irradiation damages. To evaluate the microstructure change induced by $C^+-D_2^+$ implantation and triple-ion implantation, TEM micrographs are summarized in Fig. 12. Large amounts of micro irradiation defects were introduced by $C^+-D_2^+$ implantation, and dislocation loops did not anneal after heating at 1073 K. In the case of triple implantation, a higher density of dislocation loops with the size of a few nanometers was produced by ion implantation, suggesting that $C^+$ and $He^+$ implantations introduce irradiation damages that accompany D sputtering.

To evaluate the interaction with carbon, which was implanted into tungsten, XPS measurements were performed. In Fig. 13, the C-1s XPS spectra of $C^+-$, $C^+-D_2^+$-, and triple-ion-implanted tungsten showed that the amount of C–C bond for triple-ion-implanted tungsten was lower than that for $C^+-D_2^+$-implanted tungsten, indicating $He^+$ implantation prevented C accumulation, particularly the formation of C–C bonds, on tungsten. Therefore, the major chemical state of C on tungsten surfaces would be C–W bonds, and the C concentration was lower than that for $C^+-D_2^+$-implanted tungsten. These facts indicate that the trapping of D by C was limited for triple-ion-implanted tungsten, and no D desorption was observed at a higher temperature of 800 K, although a majority of deuterium for $C^+-D_2^+$ implantation should be trapped as C–D bonds. For $He^+-D_2^+$ implantation, He retention would introduce additional irradiation defects and produce He bubbles, which prevents D diffusion toward the deep area and/or enhances D desorption, reducing D accumulation beneath the surface. Therefore, D retention was limited, and most of the deuterium would be retained at the irradiation defects, indicating that D desorption proceeded at lower temperatures. For triple-ion-implanted tungsten, $C^+$ and $He^+$ were retained during the implantation process. However, $He^+$ implantation also induces the removal of a C layer and interferes with C and D accumulation. Some residual C would be bound to tungsten during the formation...
of C–W bonds. The retained He would also prevent D trapping and diffusion toward the deep area, leading to the suppression of D retention. For triple-ion implantation, the five potential D trapping sites are as follows: (1) grain boundaries; (2) interstitial sites; (3) C–D bond; (4) vacancy clusters produced by C\(^+\) implantation; and (5) He-vacancy clusters produced by He\(^+\) implantation. In addition, the desorption of hydrocarbons by the dissociation of C–W bonds by D\(_2^+\) implantation would be accompanied by the formation of these trapping sites. He\(^+\) also dissociates C–C bonds by physical sputtering, leading to the reduction of C–D bonds. He also diffuses inside tungsten and is trapped by vacancy clusters, which were produced by C\(^+\) implantation, stopping D retention. It can be concluded that major D trapping sites in tungsten by triple-ion implantation would be the grain boundaries, interstitial loops and He-vacancy clusters.

### 4. Conclusion

Investigation of D retention and microstructure change in tungsten following simultaneous C\(^+\)–D\(_2^+\) and He\(^+\)–D\(_2^+\) and triple-ion implantations showed that D retention was enhanced by each of these implantations. The D desorption behaviors of C\(^+\)–D\(_2^+\) - and He\(^+\)–D\(_2^+\)-implanted tungsten differed from that of D\(_2^+\)-implanted tungsten. Substantial D\(_2^+\) desorption of C\(^+\)–D\(_2^+\)-implanted tungsten was observed at temperatures higher than 600 K. By simultaneous He\(^+\)–D\(_2^+\) implantation, D retention increased to about five times that for D\(_2^+\) implantation, although the D desorption temperature was the same. However, for triple-ion implantation, the accumulation of C on tungsten was suppressed, and the retention of D trapped by C decreased. These findings indicate that the D retention of triple-ion-implanted tungsten is limited by He\(^+\) implantation and that most of deuterium would be retained at the grain boundaries, interstitial loops, and vacancy clusters under simultaneous triple-ion implantation.

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