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Deuterium trapping in ion-damaged tungsten single crystal

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Abstract

The trapping of plasma-induced deuterium in tungsten single crystal pre-irradiated with high-energy ions of H, D and He and then annealed at 1000 K has been studied by thermal desorption spectroscopy. Ion energies well higher and below the threshold of damage production were used for damage and probe irradiation, respectively. It has been shown that D retention in H and D-damaged tungsten crystals correlates with a damage level of these crystals that was calculated by using TRIM program. At the same time, at about the same damage level, D trapping in He-damaged tungsten was about 4 times more than in D-damaged tungsten. The results obtained are connected with some peculiarities of clustering and deuterium trapping in ion-damaged tungsten crystals.

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Keywords: Tungsten; Deuterium inventory; Helium; Thermal desorption; Ion–surface interactions

1. Introduction

Tungsten is one of promising candidate materials for divertor of the ITER. In the second phase of ITER operation divertor, first wall and limiters will be manufactured from tungsten [1]. Hence, behavior of hydrogen isotopes in tungsten will influence plasma parameters of fusion reactor. It is known that hydrogen can be trapped in metals at radiation-induced defects [2,3]. Moreover, helium can produce defects and be trapped on them [4,5]. It is expected that helium-induced defects will influence hydrogen behavior in tungsten leading to enhanced retention of hydrogen isotopes [4,6]. However, mechanism of this influence is not clear.

In the present work the trapping of plasma-induced deuterium in tungsten pre-irradiated with high-energy protium (H), deuterium (D) and helium (He) ions has been studied by thermal desorption spectroscopy (TDS). A tungsten single crystal (W) has been used to neglect the grain-boundary effects. Ions with energy well higher and below the threshold of damage production were used for damage and probe irradiations, respectively. It is known that D retention in tungsten strongly depends on a surface preparation and irradiation conditions [3,4]. Therefore, the detailed structure analysis of

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near-surface layer was carried out after each experimental procedure with using transmission electron microscopy (TEM), electron probe microanalysis (EPMA), and reflection high-energy electron diffraction (RHEED).

2. Experimental

The sequence of experimental procedures is presented in Fig. 1. All samples used of high purity (99.9 at.%) (100) oriented W single crystal with dimensions $3 \times 4 \times 0.2$ mm^3 were mechanically and electrochemically polished and then annealed at 1100 K for 10 min in high vacuum ($\sim 10^{-5}$ Pa). Then, the samples were implanted by mass-separated 20 keV H_2^+/D_2^+ or 12 keV $^4He^+$ ions. The projected ranges (R_p) of H, D and He ions were quite similar (about 50 nm). The irradiation temperature was equal to 350 K and determined by value of ion flux (5.6, 4.0 and 1.0×10^{18} ions/(m^{2}s) for H, D and He ions, respectively) and a way of holder cooling (by air or liquid nitrogen) as well. A three-electrode ion-plasma source with a heated cathode on the base of dc glow discharge was used for low-energy deuterium plasma irradiation at 500 K (see details in [7]). Ion energy was 100 eV/D, i.e., well below the threshold of damage production. Full flux of ions and atoms coming onto the sample was equal to 2×10^{20} D/(m^{2}s). Note that before D-plasma exposure the ion-damaged samples were annealed at 1000 K for 3 min or subjected to TDS procedure. Delay more than 24 h between D-plasma exposure and TDS was used to remove of dissolved deuterium. Then the samples were heated up to 1000 K with ramping rate 3.2 K/s by means of an electron bombardment. The temperature was measured by a W–Re thermocouple with a relative accuracy of ±20 K. During heating, the HD, D_2 and He molecules were detected by a quadrupole mass spectrometer (QMS) calibrated using of a special calibration bottle filled with gases (H_2, D_2 or He) to known pressure. An average value of H_2 and D_2 sensitivities was accepted as sensitivity for HD molecules. The amount of released deuterium was determined with accuracy of about 30% by integrating of D_2 and HD QMS signals.

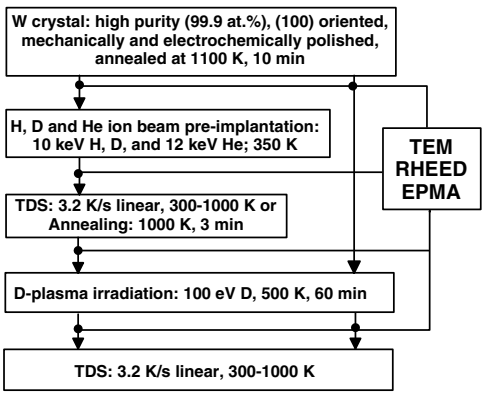

Fig. 1. Sequence of experiments.

The near-surface layer structure (about 10 nm thick) was analyzed by RHEED at electron beam acceleration voltage of 50 kV and spot size 0.1 mm in diameter. All EPMA measurements for analyses of carbon and oxygen were performed with a fully automated microanalyzer CAMEBAX. Characteristic X-ray was generated by electron beam bombardment at 15 kV and 100 nA from area of 50×50 μm^2. TEM investigation was carried out by transmission electron microscope Philips EM400T at acceleration voltage of 100 kV.

3. Results

Irradiation conditions and TDS results are summarized in Table 1. Note that D trapping for H, D, and He-damaged W crystals at probe D-plasma irradiation is presented with correction on D trapping in undamaged W crystal.

Thermal desorption spectra of deuterium and helium implanted in W crystals for damage creation are shown in Fig. 2(a) and (b). In both cases gas release starts at about 650 K and has a peak at about 800 K. However, if almost all trapped deuterium is removed before 1000 K that helium release is observed at the temperatures higher 1000 K both at first and at repeated heating of the W crystal (see Fig. 2(b)).

Thermal desorption spectra of plasma-induced deuterium for ion-damaged W crystals are presented in Fig. 3. D release from both H and D-damaged W crystals starts at the same temperature of 730 K. Shift of peak maximum towards higher temperatures for D-damaged W crystal can be connected with deuterium release from radiation defects located in deeper layers. D release from He-damaged W crystal is started at the temperature of 650 K, i. e., early then in D-damaged W crystals.

For understanding of a difference between D trapping in tungsten damaged by hydrogen (H or D) and helium ions, structure analysis is very useful. TEM micrographs, diffraction and RHEED

Table 1
Irradiation conditions, TRIM data and TDS results for damage and probe irradiations ('Damage' and 'Probe' trapping)

Irradiation	Energy (keV)	Fluence	'Damage' trapping	Damage (dpa)	'Probe' trapping ($\times 10^{19}$ D/m^2)
D plasma	0.1	72×10^{22} D/m^2	1.0×10^{19} D/m^2	0	–
H ions	10	3×10^{22} H/m^2	–	6.1	1.7
D ions	10	3×10^{22} D/m^2	2.6×10^{20} D/m^2	21.3	7.4
He ions	12	0.5×10^{22} He/m^2	0.1×10^{22} He/m^2	21.8	27

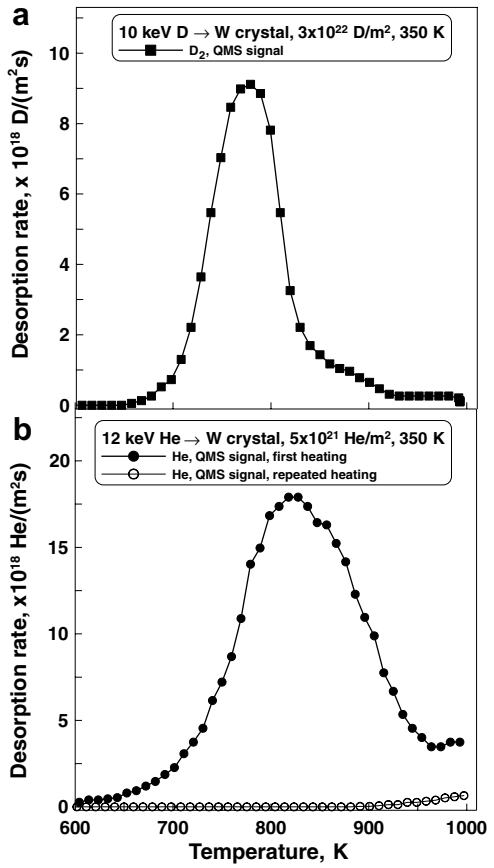

Fig. 2. The thermal desorption spectra of deuterium (a) and helium (b) from W samples implanted at 350 K by D and He ions with energies of 10 and 12 keV to fluences of 3 and 0.5×10^{22} ions/m^2, respectively. After the first heating of He-damaged W crystal the repeated heating was carried out (b). Heating rate was 3.2 K/s.

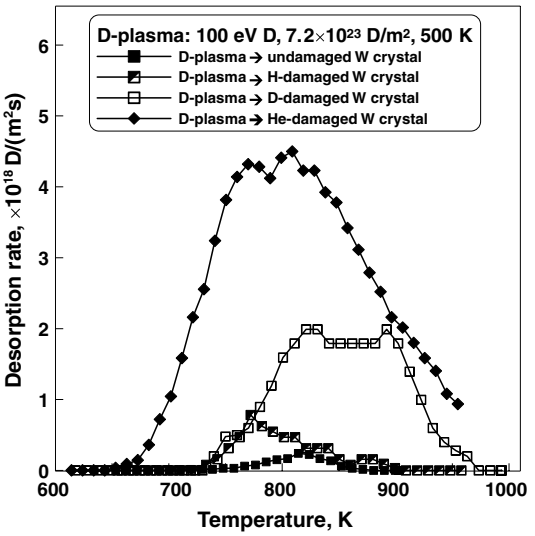

Fig. 3. Dependence of thermal desorption spectra of plasma-induced deuterium on pre-irradiation of W samples at 350 K by H, D, and He ions with energies of 10, 10 and 12 keV at fluences 3.0, 3.0 and 0.5×10^{22} ions/m^2, respectively. After ion implantation all the samples were annealed at 1000 K for 3 min. D release spectrum of undamaged W sample is presented for comparison. D-plasma exposure was carried out at 500 K for 1 h to fluence of 7.2×10^{23} D/m^2. Heating rate was 3.2 K/s.

patterns of H and He-damaged W surface are presented in Fig. 4(a–e). Initial (1 0 0) W surface is presented in Fig. 4(a). Perfect structure of W crystal with single dislocations only was found out. RHEED pattern of the sample at glancing beam angle less 0.7° has shown one or two haloes associated with tungsten oxide 2–3 nm thick. This result was confirmed by EPMA measurements of oxygen content (about 10^{20} at.O/m^2) for the same sample. TEM investigation of D-plasma irradiated tungsten did not find out radiation loops and dislocation network (Fig. 4(b)). However, the specific diffraction contrast points out to the strong post-radiation lattice deformation. H-ion irradiation at 350 K leads to a high level of radiation damage in the near-surface layer including dislocation loops and strong lattice deformation of material (Fig. 4(c)). Moreover, on the surface of H-damaged W crystal an amorphous (tungsten oxide, a-W:O) and crystalline (tungsten carbide, WC_{1-x}) films were formed. Average thickness of the films estimated by EPMA is equal to about 10 nm. TEM study of He-damaged layer of W crystal performed after annealing at 1000 K revealed the presence of such radiation defects like blisters and dislocation loops (Fig. 4(d)). Moreover, a high density (1.6×10^{25} m^{-3}) of tiny (~2 nm in diameter) He-filled bubbles

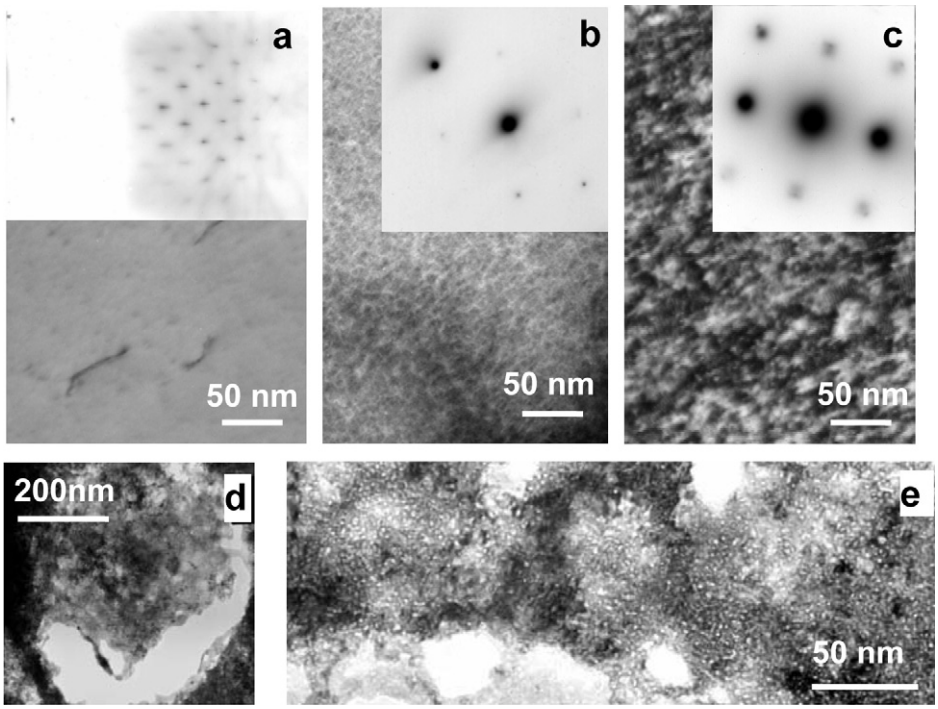

Fig. 4. TEM, diffraction and RHEED (glancing angle 4°) patterns of W crystal surface: initial (a); exposed to D-plasma (100 eV/D, 7.2×10^{23} D/m^2, 500 K) only (b); irradiated by H ions (10 keV/H, 3×10^{22} H/m^2, 350 K) (c); as well as TEM micrographs of blister with exfoliated cap (d) and dense bubble structure of He-irradiated (12 keV, 0.5×10^{22} He/m^2, 350 K) W crystal after annealing at 1000 K for 3 min (e).

was observed (Fig. 4(e)). Note that the exposure of H and He-damaged W samples in D-plasma does not lead to any significant changes in near-surface layer, whereas post-radiation annealing of W samples leads to partial or complete removal of lattice deformation.

4. Discussion

It is known that the strong tungsten lattice deformation found out by TEM after damage implantation by H ions can be caused by hydrogen-vacancy complexes which were formed during irradiation [3,4]. A heating up to 1000 K leads to decomposition of these complexes, gas release and formation of clusters containing from 11 to 16 vacancies [8]. Similar processes of helium-vacancy complexes decomposition, He release and clustering with voids formation occur in He-damaged W crystals [3]. Some amount of He can be also released from He-filled bubbles. Thus, the annealed ion-damaged W crystals will contain vacancy type defects.

At irradiation temperature above 475 K dislocation loops and individual vacancies do not work as trapping sites for deuterium [4]. However, deuterium can be trapped by vacancy clusters, voids, and He bubbles [4,8,9]. Decoration with deuterium of V_{11-16} clusters results in to the deuterium desorption at 800 K [9]. Thus, D retention in H and D-damaged W crystals can be attributed mainly to trapping by the clusters.

He bubbles release a trapped deuterium at temperature about 650 K [4,8]. However, in our case, the He bubbles were annealed before D plasma influence and to our opinion should be similar to voids as traps for deuterium. Note that D release from voids takes place in a wide temperature range from 400 to 1200 K [2]. Therefore, we believe that D trapping in He-damaged W crystals can be connected with a special defect void-He bubble structure formed during the annealing.

The damage level for H, D and He-irradiated W crystals was evaluated with using of TRIM program ('Full Damage Cascade' option, SRIM-2003.26) and presented in Table 1. A total number of displacements per W atom (dpa) minus a number of replacement collisions were taken as a damage level. One should note (Table 1) that at the same fluence a

ratio between damage level produced by D and H ions is approximately equal to a ratio between D trapping in D and H-damaged W crystals (3.5 and 4.3, respectively). It means that trapping of plasma-induced deuterium in H and D-damaged W crystals correlates with damage level of the crystals.

D trapping in He-damaged W is about 4 times higher than that in D-damaged W at about the same damage level (see Table 1). The amount of deuterium trapped by He-damaged W crystal is equal to 27×10^{19} D/m^2. Assuming homogeneous distribution of bubbles on depth of 70 nm ($\sim 2 R_p$) and volume bubble density is 1.6×10^{25} m^{-3}, a He bubble can trap about 240 deuterium atoms. This value is higher than value for trapping obtained in [4] (about 150 D atoms) for unannealed He bubbles. The enhanced D trapping can be attributed to a void-He bubble structure formed in the crystal during annealing.

5. Conclusions

The trapping of plasma-induced deuterium in ion-damaged W single crystals after annealing at 1000 K has been studied by TDS. It has been shown that D trapping in ion-damaged W crystals can be significantly (in 27 times) higher than in undamaged W crystals. If D retention in H and D-damaged W crystals correlates with damage level produced by ion implantation that D trapping in He-damaged W was about 4 times higher than in D-damaged W at about the same level of damage. The enhanced D retention in He-damaged W can be connected with a special void-He bubble structure formed at the annealing. The data obtained indicate that interaction between hydrogen isotopes and helium-induced defects should be taken into account using tungsten as a plasma facing material for ITER.

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