Blistering and Retention in the Near-Surface Region of Tungsten Exposed to High Flux Deuterium Plasmas of Tens of eV

W.M. Shu

Tritium Engineering Laboratory, Japan Atomic Energy Research Institute

Tokai-mura, Naka-gun, Ibaraki-ken 319-1195, Japan

Tungsten plates annealed at 1473 K were exposed to deuterium plasmas with incident energies ranging from 7 to 98 eV and a fixed flux of 10^{22} D/m^2/s, and the blistering and retention in the near-surface region were investigated with a variety of techniques, such as scanning and transmission electron microscopy (SEM and TEM), thermal desorption spectroscopy (TDS), nuclear reaction analysis (NRA), elastic recoil detection (ERD), secondary ion mass spectroscopy (SIMS) and X-ray diffraction (XRD),. Blisters with the maximum diameter of about 2 microns (comparable to grain size) were formed on the tungsten surfaces after plasma exposure, and small blisters with a diameter of around 30 nm and microcracks were formed in the near-surface region before the formation of larger blisters. Within the experimental error there was a zero change in the lattice parameter after the plasma exposure, implying that deuterium does not exist in the lattice interstitial sites, but instead forms a deuterium-vacancy complex and then clusters and further bubbles (predominantly in the form of molecules in vacancy clusters and voids) in the near-surface region. After deuterium plasma exposure, deuterium was retained in the depth up to a few microns from the surface, and the maximum atomic ratio of deuterium against tungsten reached as high as 1-2% in the near-surface region. These evidences suggest that crystal defects like vacancies should be generated due to lowering of the formation energy of vacancies by the intrusion of a great number of hydrogen isotope atoms into the near-surface region of tungsten.

Keywords: tungsten, retention, blistering, hydrogen isotopes

I. Introduction

Resent researches [1-8] revealed that blistering can occur on tungsten surface, even if the ion energy is too low to create displacement damage such as vacancies. Sze and co-workers observed macroscopic blisters with the diameters of a few to a few hundreds microns on the surfaces of tungsten foils exposed to high ion flux (10^{22} D^+/m^2/s) and low ion energy (about 110 eV) deuterium plasma at 400-500 K [1-2]. Haasz et al. found blisters with the diameters of a few to a few tens microns on the surfaces of tungsten pre-annealed at 1473 K after exposure to deuterium plasmas with the ion flux of about 10^{20} D^+/m^2/s and ion energy of 500 eV at 500 K [3]. Venhaus et al. reported that un-annealed samples and samples annealed to 1473 K revealed extensive blistering with many blister caps removed and minor blistering, respectively, while samples annealed to 1273 K showed no blistering, after exposure to deuterium and tritium ions with high ion flux of 1.7×10^{22} ions/m^2/s and low ion energy of 100 eV at 423 K [4]. Wang et al. [5] reported that the blister size increased and the number decreased with the deuterium fluence from 10^{19} to 10^{21} D^+/m^2 at the energy of 1 keV and room temperature and no blisters were found at elevated temperatures between 600 and 800^{o}C. Tokunaga et al. [6] found that blisters were formed on the powder metallurgy tungsten by deuterium irradiation with ion flux ranging from 4.8×10^{21} to 1.2×10^{22} $D^+/m^2/s$ and low ion energy of 100 eV at temperature of 708 to 843 K, and the amount of blisters and their average size increased with the increasing fluence from 7.5×10^{25} to 3.0×10^{26} D^+/m^2. Ye et al. [7] observed blister formation on tungsten surface under a low energy (about 90 eV) and high flux (2×10^{21} $H^+/m^2/s$) hydrogen plasma exposure at the surface temperature less than 950 K and the fluence higher than 3×10^{24} m^{-2}. Ueda et al. [8] investigated the impact of carbon impurities in hydrogen plasmas on tungsten blistering at a hydrogen ion flux of about 4×10^{21} $H^+/m^2/s$ and hydrogen ion energy of 100 to 1000 eV.

The above researches have clearly demonstrated that hydrogen isotope exposure with energy as low as 100 eV can definitely produce blistering on tungsten surface. However, the mechanism of blistering is not well understood yet and requires future investigations. In this work, tungsten plates annealed at 1473 K were exposed to deuterium plasmas with incident energies ranging from 7 to 98 eV and a fixed flux of 10^{22} $D^+/m^2/s$, and the blistering and retention in the near-surface region were investigated with a variety of techniques, such as scanning and transmission and scanning electron microscopy (SEM and TEM), thermal desorption spectroscopy (TDS), nuclear reaction analysis (NRA), elastic recoil detection (ERD), secondary ion mass spectroscopy (SIMS) and X-ray diffraction (XRD).

II. Experimental

II. A. Samples and Linear Plasma Generator

Tungsten plates were prepared by powder-metallurgy and hot-rolled reduction, and then annealed at 1473 K for 30 minutes. The plates were subsequently cut and double-sided

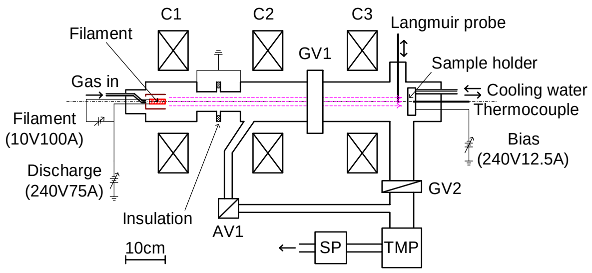

Fig. 1 The schematic view of the linear plasma generator.

polished into samples of 10 × 10 × 2 mm. The tungsten material has a purity of 99.99 wt% and principal impurities (in weight ppm) of Mo and Fe ~10, C and O <30. The polished samples were cleaned in an acetone ultrasonic bath prior to placing into the deuterium exposure chamber.

The schematic view of the linear plasma generator used in this study is shown in Fig. 1. The apparatus consists of sections of vacuum chamber and pumping, cooling water, gas admittance, power supply, plasma generation, plasma delivery, sample holder, and plasma diagnosis. The vacuum system was composed of two turbo molecular pumps (TMP1, 300 l/s and TMP2, 70 l/s), a scroll pump (SP, 250 l/min), two gate valves (GV1 & 2), an angle valve (AV1), and tubing. The achievable background pressure is lower than 5×10^{-6} Pa. The plasma is ignited by an electron-emitting filament and maintained by an arc discharge power supply applied between the filament (cathode) and the grounded chamber wall (anode), being assisted by the confinement coils (C1~C3). The filament element is made of LaB_6 shaped into a hollow dual-spiral, and heated directly with a low voltage and high current power supply. The coils (C1~C3) are not only necessary to transport the plasma onto the sample holder, but also helpful to the plasma ignition and stability. The water-cooled sample holder is isolated from the grounded chamber wall so that the sample can be negatively biased to adjust the energy of ions impinging onto the sample. And a single

Langmuir probe is equipped to obtain basic plasma parameters. The ion species can be controlled by adjusting the operational parameters of the plasma generator. With suitable adjustment, we can achieve plasma beams highly enriched with a single species of D^+, D_2^+, or D_3^+, to a ratio over 80%. A fixed flux of 1×10^{22} $D^+/m^2/s$ and varying incident energies from 7 to 98 eV were used in the experiments. The comparison between this work and the previous researches [1-8] is made in Figure 2, in which the ion flux is plotted against ion energy, and the coverage of both flux and energy for ITER divertor dome, baffle and liner [9] is also shown.

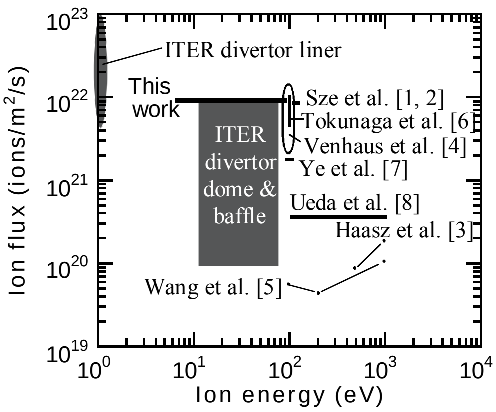

Fig. 2 A summary of flux and energy used in recent researches on W blistering. For comparison, the design values of ITER divertor are also shown.

II. B. Observations and measurements

Blister formation on the surface of tungsten exposed to deuterium plasmas was observed by a scanning electron microscopy (Real Surface View Microscope, KEYENCE VE-7800) at a tilt angle of 45º.

Thin foils for transmission electron microscopy (TEM) were prepared with a focused ion beam (FIB) microsampling system (HITACHI FB-2000A). The system enabled not only the broad cross-sectional TEM observation, but also the detailed study of irradiated microstructure. Procedures to prepare thin foils for TEM observation are: (a) W deposition (to reduce damage during the specimen fabrication in the region for observation), (b) removal of material with a fine Ga^+ (20 keV) beam to obtain a foil, (c) welding of a W needle to the foil by W deposition, (d) cutting to separate the foil from the irradiated disk, (e) welding the foil to a mesh by W deposition, and (f) removal of the damaged layer near the foil surface formed during FIB processing by an Ion Miller (GENTILE MILL, TECHNOLOGY LINDA). These efforts successfully enabled a TEM (JEOL JEM-2000FX) examination of plasma exposure-induced microstructural defects.

Patterns of X-ray diffraction (XRD) were measured to examine the crystallographic change in the near surface region of tungsten before and after deuterium plasma exposure. XRD patterns were recorded by an X-ray diffractometer (Phillips PW1700, Toyama University). The probe was the Cu Kα line at 0.1572 nm operated with 1200 W power. The incident angle of X-rays was fixed at 1.5° to the surface of the sample to measure the lattice constant in the near-surface region, and the scanned 2θ ranged from 30° to 136°.

Thermal desorption spectroscopy (TDS) was used to evaluate the deuterium retention in the tungsten samples after deuterium plasma exposure via integrating the deuterium release rate with respect to time. A standard deuterium leak with an inaccuracy lower than 10% was employed to calibrate the quadrupole mass spectrometer (QMS) prior to each TDS analysis so that the calibrated release rate during TDS could be obtained. During TDS, an infrared heater was used to heat the irradiated samples at a ramp rate of 5 K/s and the sample temperature was raised to ~ 1500 K and then held for 2 min, being monitored by a type R thermocouple.

Depth profile of deuterium in the near-surface region of tungsten after plasma exposure was measured by nuclear reaction analysis (NRS) and elastic recoil detection (ERA). In the NRS measurement, a beams of 2 MeV $^3He^+$ ions with a current of 5 nA (250 nA/cm^2) from a Pelletron 5SDH-2 accelerator (Kobe University) were incident on the sample with an incident angle of 60° to the surface normal through an aperture with diameter of 1.0 mm. A solid state detector (SSD) with solid angle of 2.1×10^{-3} sr located at 50° to the surface normal was used to detect alpha (α) particles produced by the nuclear reaction D(^{3}He,α)H. Before the SSD, an aluminum film 8 mm thick was placed to prevent the scatted $^3He^+$ ions from intervention. The output signals from the SSD were analyzed with a multi-channel analyzer (MCA). On the other hand, in the ERD measurements, a beams of 4 MeV $^4He^+$ ions with a current of 0.5 nA (25 nA/cm^2) from the same accelerator were incident on the sample with an incident angle of 75° to the surface normal and the recoiled hydrogen isotopes were detected with the SSD at a forward angle of 60° to the surface normal.

The depth profiles of deuterium, hydrogen and impurities (oxygen and carbon) in the near surface region of tungsten before and after deuterium plasma exposure were analyzed by secondary ion mass spectroscopy (SIMS) (ULVAC-PHI ADEPT1010 Dynamic SIMS System, JT-60 Facilities Division II), using cesium ion (Cs^+) as the primary ion with an energy of 5 keV and a beam current of 100 nA at 45° to the surface normal. The beam size was about 32 μm and the rastering area was set at 400×400 μm^2. Depth profiling with a profilometer showed the sputtering rate to be around 0.55 μm/h. In order to eliminate the effect of crater edges, the signal of the secondary ion was collected only from the center of the rastered area. The negative secondary ion intensities of deuterium and hydrogen were normalized by that of tungsten for comparison.

III. Results and Discussion

III. A. Blistering

A typical SEM image is shown in Fig. 3, where blisters with diameters of 0.1 to about 2 μm are observed. This sample was exposed to deuterium plasma with the energy of 98 eV and the fluence of 10^{25} D/m^2 at room temperature. Subsequently, a cross-section of a large blister with a diameter of about 2 μm on this sample was fabricated by FIB technique. Before removing the material with Ga^+ ions, a protection thin layer of tungsten was deposited on the blister. The cross-sectional SEM image of this blister is shown in Fig. 3, where the thickness of the blister cap was determined to be about 0.4 μm.

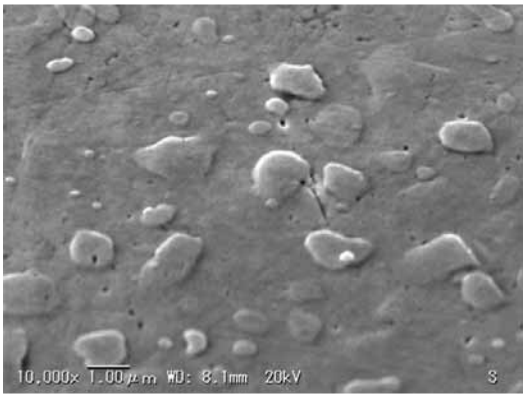

Fig. 3 Blisters formed on W surface (SEM image at a tilt angle of 45°).

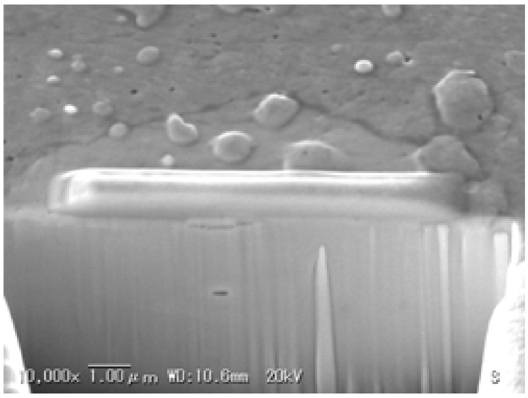

Fig. 4 Cross-sectional SEM image of a blister viewed at a tilt angle of 45°.

The maximum blister size observed in this study is 1-2 orders smaller than that of blisters formed on tungsten exposed to 100-1000 eV hydrogen isotope plasmas reported before [1-8]. Fore instance, Sze and co-workers observed much larger blisters with the diameters up to a few hundreds microns on tungsten foils exposed to high ion flux (10^{22} $m^{-2}s^{-1}$) and low ion energy (about 110 eV) deuterium plasma at 400-500 K [1-2], and Ye et al. observed blisters with the size of a few tens to a few hundreds microns formed on tungsten surface under a low energy (about 90 eV) and high flux (2×10^{21} $H^+/m^2/s$) hydrogen plasma exposure at the surface temperature less than 950 K [7]. It seems that the maximum size of blisters is independent of the incident energy and the exposure temperature, but instead it must be strongly influenced by the microstructures like grain size.

Thus, the behavior of blistering on tungsten exposed to high flux and low energy plasma was firstly investigated by FIB/TEM in this study.

Fig. 5 XTEM image of W sample after 7 eV deuterium plasma exposure.

The cross-sectional TEM images are shown in Fig. 5 to Fig. 8 for a sample exposed to 7 eV deuterium plasma with a fluence of 10^{25} D/m^2. At the exposure conditions, visible blisters could not be observed by the SEM with a solubility of about 0.1 μm.

As shown in Fig. 5, the microstructures of tungsten are almost isotropic with a maximum grain size of about 2 μm, and a deformation layer around 0.1 μm thick is formed in the near-surface region.

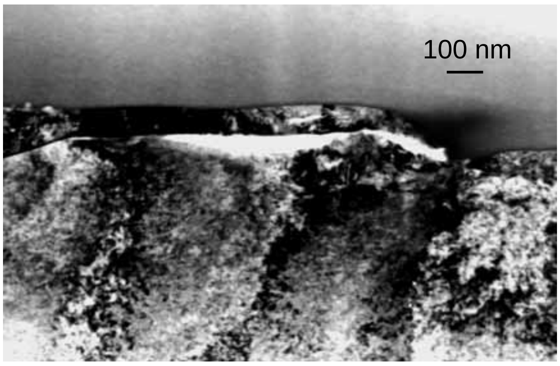

Fig. 6 XTEM image of microcrack/void along grain boundary.

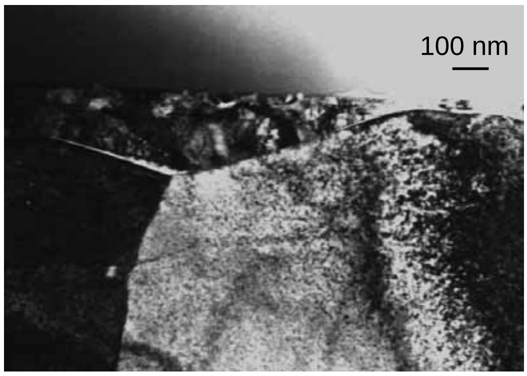

Fig. 7 XTEM image of microcrack along grain boundary and void at grain corner.

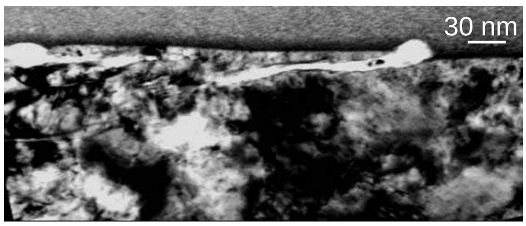

Fig. 8 XTEM image of small blisters (around 30 nm) and microcrack.

Microcrack/void was generated at the depth of about 100 nm along the grain boundary parallel almost to the surface (Fig. 6), and void was generated at the grain corner at the depth of about 300 nm and microcrack extended along the grain boundary (Fig. 7). Besides, small blisters with a diameter of around 30 nm and microcracks formed in the near-surface region before the formation of larger blisters with diameters of up to a few microns (Fig. 8).

The observations indicate that the maximum size of blisters (about 2 μm) is limited by microstructures, especially by grain size. Much larger blisters observed by the previous researchers like Sze et al. [1-2] should be caused by the crystal texture of the tungsten foils used in their study.

III. B. Retention

The deuterium retention in the exposed samples was measured using thermal desorption spectrometer (TDS). The TDS spectrum of deuterium shows a peak around 770-970 K at a heating rate of 5 K/s, implying a predominant release in its molecular form from the blisters. The relationship between the amount of retained deuterium and the fluence shows a sudden drop at a certain fluence, indicating that deuterium retention is limited by rupture of blisters. The maximum retention in samples exposed to the plasma at room temperature is around 10^{20} D/m^2. In addition, the relationship between the amount of retained deuterium and the plasma exposure temperature shows the maximum retention at around 400~500 K. Above 700 K, the retention decreased to a quite low level, and blisters disappeared at the exposure of 900 K.

The NRA/ERD results are summarized in Fig. 9, where averaged values of NRA data were plotted for 3 sets of the data measured at the center, and at 2 mm above/below the center. The results show that deuterium diffuses to the depth deeper than around 1 μm. The maximum atomic ratio of D/W reaches as high as 1-2% in the near-surface region.

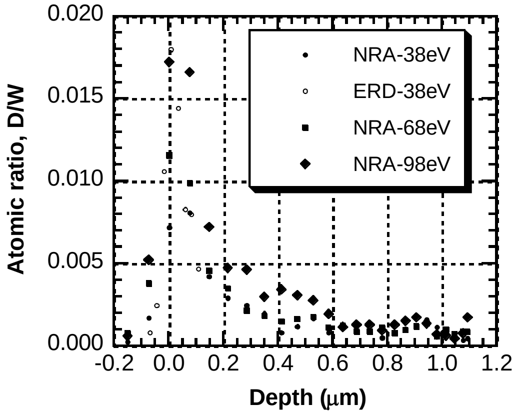

Fig. 9 Depth profile of D/W measured by NRA and ERD.

A preliminary SIMS result is shown in Fig. 10. As pointed out by Alimove et al. [10], the appearance of the SIMS D^- signal is attributed to the existence of separate D atoms within the matrix. In other words, SIMS only detects the atomic hydrogen isotopes in the material. Since the efficiency transferred to negative ions for deuterium is almost the same as that of hydrogen, deuterium retains in atom form with a very small fraction. It is also seen in this figure that the background of hydrogen signal is mach larger than that of deuterium. On the other hand, in comparison with the un-exposed sample, deuterium in tungsten exposed for 1000 seconds at the flux of 10^{22} D/m^2/s, the energy of 98 eV and room temperature diffuses to the depth deeper than around 1 μm.

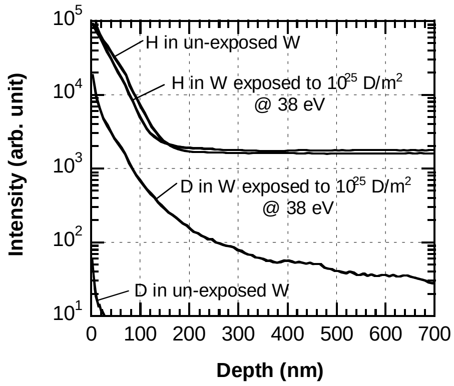

Fig. 10 Depth profiles of H^- & D^- intensities in exposed and un-exposed samples.

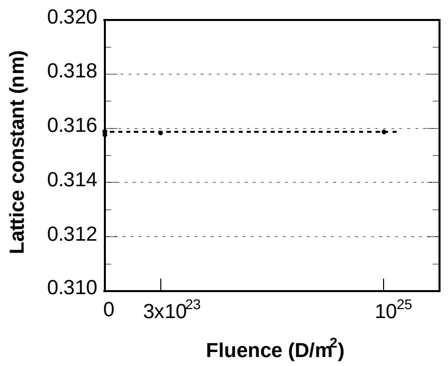

Fig. 11 Lattice constants of un-exposed and exposed W samples.

The results of small angle XRD at a fixed incident angle of 1.5^o are summarized in Fig. 11 for the W samples un-exposed and exposed to fluence of 3×10^{23} and 10^{25} D/m^2 at 38 eV. The lattice constant was determined to be 0.31584±0.00008 nm, indicating that within the experimental error there was a zero change in the lattice parameter after the plasma exposure. This implies that deuterium does not exist in the lattice interstitial sites, but instead forms a deuterium-vacancy complex and then clusters and further bubbles (deuterium molecules in vacancy clusters and voids) in the near-surface region.

Ogorodnikova et al. [11] introduced two kinds of traps to describe the deuterium retention in tungsten exposed to high-flux and low-energy plasmas. One is low-temperature traps: intrinsic defects (dislocations, grain boundaries, some impurities, presence of bulk oxide) with a trapping energy of 0.85 eV distributed over the whole sample thickness; and another is high-temperature traps: "ion-induced" traps associated with deuterium agglomeration in molecules and bubbles near the implanted surface and deuterium trapping in vacancies with a trapping energy of 1.45 eV which fom and grow during implantation, distributed near the surface and correlated with the implantation range. Many of the other studies such as those by van Veen et al. [12, 13] and Sakamoto et al. [14] have shown that hydrogen decorates pre-existing voids and can create new ones if they do not already exist. Deuterium implanted into tungsten will diffuse back to the surface or deeper into the material. The hydrogen diffusing deeper into the material will eventually find vacancies, dislocations, and voids into which they are trapped (unless the temperature is maintained at a temperature above which the traps are thermally depopulated). Creating areas of high pressure voids in the very near-surface region may create microcracks to release this hydrogen to the surface. In this case, bubbles would be created deep into the material leading eventually to blister formation.

Causey [15] argued that using tungsten in a plasma-facing application may eventually result in moderate inventories of hydrogen isotopes in the bubbles and blisters (unless the tungsten is maintained at very high temperatures). Note that the bubble formation may also eventually result in tungsten being released into the plasma. Tungsten can be released into the plasma either through grain ejection [1] or by evaporation due to the creation of open blister caps that lose their thermal contact with the material below.

Even many researches have been carried out, some questions about the mechanisms of blistering and retention still remain. For instance, how the "ion-induced" traps are generated? And why could blistering occur in annealed tungsten and even single crystal tungsten [16] exposed to deuterium plasmas with energies much smaller than that required for generating displacements? In a future work, we will propose a new model to describe the generation of vacancies due to lowering of the formation energy of vacancies by the intrusion of a great number of hydrogen isotope atoms into the near-surface region in tungsten, and the formation of hydrogen isotopes-induced vacancies in the near-surface region of tungsten will be further confirmed directly by positron lifetime and Doppler broadening measurements with slow positron beams.

IV. Conclusions

(1) Blisters with the maximum diameter of about 2 microns (comparable to grain size) were formed on the tungsten surfaces after plasma exposure, and small blisters with a diameter of around 30 nm and microcracks were formed in the near-surface region before the formation of larger blisters. The maximum size of blisters is limited by the microstructures, especially by the grain size.

(2) After deuterium plasma exposure, deuterium was retained in the depth up to a few microns from the surface, and the maximum atomic ratio of deuterium against tungsten reached as high as 1-2% in the near-surface region. There was a zero change in the lattice constant after the plasma exposure, implying that deuterium does not exist in the lattice interstitial sites, but instead is trapped by vacancy clusters and voids in the near-surface region predominantly in the form of molecules. These evidences suggest that crystal defects like vacancies should be generated due to lowering of the formation energy of vacancies by the intrusion of a great number of hydrogen isotope atoms into the near-surface region of tungsten.

Acknowledgements

The author would like to appreciate the contributions of Dr. G.-N. Luo (JAERI) for plasma exposure experiments and TDS measurements, Dr. T. Sawai (JAERI) for FIB and TEM observations, Mr. Y. Aihara (KEYENCE) for SEM observations, Drs. N. Kubota and K. Ochiai (JAERI) for NRA and ERD measurements, Drs. Y. Ishimoto and N. Miya (JAERI) for SIMS measurements and Dr. M. Hara and Prof. M. Matsuyama (Toyama University) for XRD measurements. Special thanks are due to Drs. M. Seki, S. Seki, H. Takatsu, M.F. Nishi and T. Yamanishi (JAERI) for their continuous encouragement and support of this study.

References

[1] F.C. Sze, R.P. Doerner and S. Luckhardt, “Investigation of plasma exposed W-1% La_2O_3 tungsten in a high ion flux, low ion energy, low carbon impurity plasma environment for the International Thermonuclear Experimental Reactor,” J. Nucl. Mater., **264**, 89 (1999).

[2] F.C. Sze, L. Chousal, R.P. Doerner and S. Luckhardt, “Growth of redeposited carbon and its impact on isotope retention properties on tungsten in a high flux deuterium plasma,” J. Nucl. Mater., **266-269**, 1212 (1999).

[3] A.A. Haasz, M. Poon and J.W. Davis, “The effect of ion damage on deuterium trapping in tungsten,” J. Nucl. Mater., **266-269**, 520 (1999).

[4] T. Venhaus, R. Causey, R. Doerner and T. Abeln, “Behavior of tungsten exposed to high fluences of low energy hydrogen isotopes,” J. Nucl. Mater., **290-293**, 505 (2001).

[5] W. Wang, J. Roth, S. Lindig and C.H. Wu, “Blister formation of tungsten due to ion bombardment,” J. Nucl. Mater., **299**, 124 (2001).

[6] K. Tokunaga, R.P. Doerner, R. Seaydarian, N. Noda, N. Yoshida, T. Sogabe, T. Ko and B. Schedler, “Modification of tungsten coated carbon by low energy and high flux deuterium irradiation,” J. Nucl. Mater., **307-311**, 126 (2002).

[7] M. Y. Ye, H. Kanehara, S. Fukuta, N. Ohno and S. Takamura, “Blister formation on

tungsten surface under low enrgy and hgh flux hydrogen plasma irradiation in NAGDIS-I," J. Nucl. Mater., **313-316**, 72 (2003).

[8] Y. Ueda, T. Shimada and M. Nishikawa, "Impact of carbon impurities in hydrogen plasmas on tungsten blistering," Nucl. Fusion, **44**, 62 (2004).

[9] G. Federici, C.H. Skinner, J.N. Brooks, J.P. Coad, C. Grisolia, A.A. Haasz, A. Hassanein, V. Philipps, C.S. Pitcher, J. Roth, W.R. Wampler and D.G. Whyte, "Plasma-material interactions in current tokamaks and their implications for next step fusion reactors," Nucl. Fusion, **41**, 1967 (2001).

[10] V. Kh. Alimov, K. Ertl and J. Roth, "Deuterium retention and lattice damage in tungsten irradiated with D ions," J. Nucl. Mater., **290-293**, 389 (2001).

[11] O.V. Ogorodnikova, J. Roth and M. Mayer, "Deuterium retention in tungsten in dependence of the surface conditions," J. Nucl. Mater., **313-316**, 467 (2003).

[12] A. Van Veen, H.A. Filius, J. De Eries, et al., "Hydrogen exchange with voids in tungsten observed with TDS and PA," J. Nucl. Mater., **155-157**, 1113 (1988).

[13] H. Eleveld and A. Van Veen, "Deuterium interaction with impurities in tungsten studied wit TDS," J. Nucl. Mater., **191-194**, 433 (1992).

[14] R. Sakamoto, T. Muroga and N. Yoshida, "Retention and desorption of implanted deuterium of high-Z plasma facing materials," J. Nucl. Mater., **233-237**, 776 (1996).

[15] R.A. Causey, "Hydrogen isotope retention and recycling in fusion reactor plasma-facing components," J. Nucl. Mater., **300**, 91 (2002).

[16] K. Tokunaga, M.J. Baldwin, R.P. Doerner, et al., "Blister formation and deuterium retention on tungsten exposed to low energy and high flux deuterium plasma," J. Nucl. Mater., **337-339**, 887 (2005).