

Effect of Deuterium Fluence on Deuterium Retention in Tungsten with Fibrous Nanostructured Layer in a Compact Plasma Device APSEDAS^{*)}

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The formation of helium (He) induced “fuzz layer” significantly changes the deuterium (D) retention in tungsten (W). In this study, the D retention in W with an identical fuzz layer is investigated using thermal desorption spectroscopy, with various D ion fluences. It is found that the D retention substantially decreases by ~80% at relatively low fluence of $\sim 10^{24}$ D/m², and ~40% at the higher fluence of 6×10^{25} D/m². A new broad desorption peak at ~650 K appearing at the higher D ion fluences of $> 10^{25}$ D/m² originates from the interior of the fuzz layer, not the W bulk space. This suggests that the fuzz layer can force D ions to stay near the surface of W regardless of the D ion fluence, working as a diffusion barrier of hydrogen isotope fuels.

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1. Introduction

During the operation of a fusion reactor, a large amount of hydrogen ions flow from the surrounding plasma to the plasma facing material (PFM) in the divertor region. The fuel hydrogen isotopes then collide with PFM, while some amounts of particles are retained beneath the surface of the PFM. In research of the plasma-wall interactions, the retention of hydrogen fuels in PFM is one of the most important issues when considering the particle balance in the reactor as well as radioactive safety requirements due to tritium inventory [1].

Tungsten (W) possesses several favorable characteristics, such as high melting point, high thermal conductivity and low sputtering yield, thus has been considered as the plasma facing material (PFM) in the ITER divertor [2]. In recent study, it is suggested that the formation of helium (He) defects, such as He nanobubbles and fiber form nanostructure, so-called fuzz, may reduce the retention of hydrogen isotopes in W.

Thus far, previous studies have shown that He bubbles may contribute to reducing the deuterium (D) retention in W by acting as a diffusion barrier, desorption path, and by preventing the formation of blistering [3–7]. It has been observed that W with a fuzz layer reduced the D retention by one order of magnitude, acting as a diffusion barrier and enhancing the re-emission owing to its large surface area [8–10]. On the other hand, there is ambiguity

on the retention of D inside of a fuzz layer, where the effective particle reflectance decreases by 50% compared to a smooth W surface [11, 12], which may increase the trapping probability of the reflected particles within the layer. In some cases, D retention in W with a fuzz layer slightly increased compared to a He-untreated W [10, 13], showing that the D fluence affects the total retention amount.

In this research, we investigated the D ion retention properties using thermal desorption spectroscopy (TDS). The dependence of D retention on the ion fluence was compared between untreated W samples and the He pre-exposed samples with a fuzz layer on the surface. In addition, separated TDS measurements with fuzz-removed surfaces were performed with the aim of clarifying the effect of a fuzz layer on the properties of diffusion and trapping of D atoms into W bulk area.

2. Experimental Setup

W samples (99.95%, $10 \times 10 \times 0.2$ mm³, Nilaco Co.) were prepared to expose to He plasmas. The samples were ultrasonic cleaned for 5 min in ethanol and ultrapure water bath before the plasma exposures.

Helium plasma pre-exposure and consecutive D plasma irradiations were performed in the RF plasma device APSEDAS (Advanced PWI Simulation Experimental Device and Analysis System). The plasmas were generated by RF discharge with 13.56 MHz radio frequency applied to an RF antenna. The schematics for the plasma exposures are shown in Fig. 1. The configuration of the

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APSEDAS device can be seen elsewhere [14]. Fig. 1 (a) shows a schematic for the He plasma pre-exposure. At first, a W sample was spot-welded with a $\phi = 0.5$ mm W rod at the tip of a reciprocating sample manipulator, then placed at the center of a He plasma column. To fulfill the conditions for fuzz growth, the sample was located without any active cooling equipment, and the He plasma was generated with the helicon mode, where a high density plasma could be maintained at the central region with the typical electron density of $\sim 10^{19}$ m⁻³. Typical operational pressure was ~ 4.6 Pa. The sample temperature was measured by using a radiation pyrometer with the wavelength of 1.6 μ m. The He plasma was operated in a pulsed mode (100 Hz, Duty 50%) to deliver a better temperature control. The sample was negatively biased via a bipolar DC power supply, so that the sample temperature and the incident energy were ~ 1450 K and 70 - 85 eV, satisfying the fuzz growth conditions [15]. The He ion fluence was kept the same at 5×10^{25} He/m². In this process, a fuzz layer was formed on the W surface.

Figure 2 shows the scanning electron microscope (SEM) images of (a) surface and (b) cross section of a W sample after the He plasma exposure. A 3.1 μ m-thick fuzz layer was formed on the W surface. The conditions for the He plasma pre-exposures were maintained the same, hence the identical expected fuzz layer thicknesses.

W-fuzz samples were exposed to the air once after the He pre-exposure, and then were placed on a copper stage

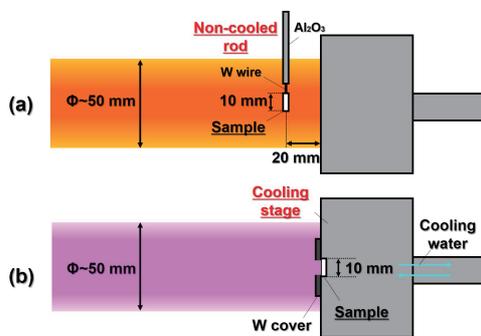


Fig. 1 Schematic diagrams of (a) He plasma pre-exposure and (b) D plasma exposure. W samples were exposed to the He plasma at 1450 K without cooling to form a fuzz layer on the surface, then to the D plasma with water cooling.

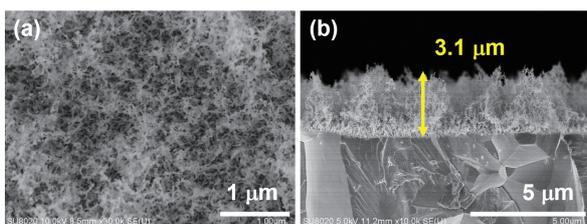


Fig. 2 SEM images of (a) surface and (b) cross section of a W sample after He pre-exposure.

and fixed with a W cover to be exposed to a D plasma. The D plasma was operated with the inductive coupled mode, with the typical plasma density and temperature of 1.7×10^{17} m⁻³ and 10 eV, respectively. The sample stage was conducted to the ground voltage, thus giving the incident ion energy of ~ 30 eV, same as the plasma potential. The sample temperature was 650 K. Throughout the experiments, W samples were exposed to five different D fluences (1.5, 6.0, 8.0, 20, 60×10^{24} D/m²). For comparison, other W samples were kept without the He pre-treatment and exposed only to the D plasma at the same D ion fluences.

After the exposures, W samples were taken out to the air and delivered to the thermal desorption spectroscopy (TDS) chamber. The samples were heated up to 1540 K with the rate of 1 K/s. At this moment, we used two quadrupole mass spectrometers simultaneously, one of which measured H₂, HD and D₂ + He ($m = 2 - 4$), and the other separated D₂ ($m = 4.028$) and He ($m = 4.003$). The pressures of the gases were then calibrated by He and D₂ calibrated leaks.

3. Results and Discussion

Figure 3 (a) shows the D desorption spectra of W samples exposure only to D plasmas. The D ion fluences were altered to 1.5×10^{24} , 6.0×10^{24} , and 6.0×10^{25} D/m². The sample exposed only to the D plasma at the fluence of 1.5×10^{24} D/m², a desorption peak appeared around 400 K,

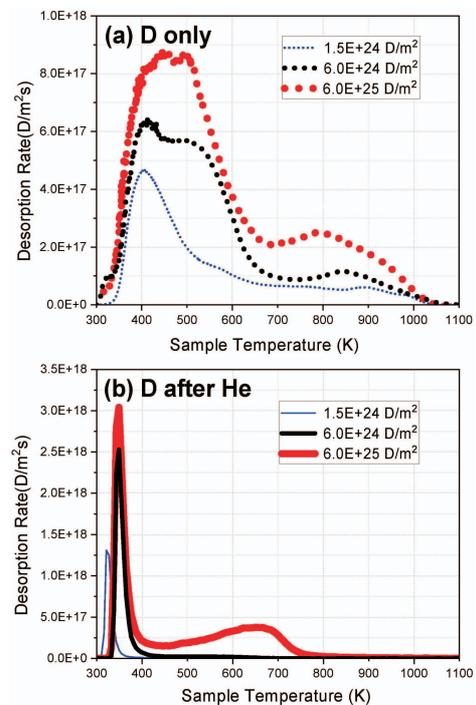


Fig. 3 Deuterium desorption spectra of (a) W exposed only to D plasmas (D only) and (b) W with fuzz layer exposed to D plasmas after He pre-exposures (D after He), with the D ion fluences of 1.5, 6.0×10^{24} , and 6.0×10^{25} D/m².

and a weak and consecutive desorption were observed till 1000 K. As the fluence increased, the peaks at 400 K became greater, and also new peaks appeared around 500 and 800 K. Also, the desorption rate for each peaks increased as D ion fluence increased. The previous study has suggested that the peaks at the different temperatures may be derived from internal defects in the bulk W body like dislocation loops (400 K), vacancies (500 K), and nano-voids (800 K) [16]. This suggests that the diffusion of D ions is enhanced and the trapping rates in the internal defects increased with the fluence increases.

Figure 3 (b) shows the D desorption spectra of W samples with fuzz layers by the pre-exposure of He plasmas. Different from the case for W with the D plasma exposure, the highest desorption peak appeared at 320 or 350 K. These temperatures are slightly higher than the room temperature, implying that the D ions are trapped near the surface or just adhered to the surface, and both of the cases were with relatively weak trapping energy. Therefore, these results may indicate that most of D ions are trapped within a fuzz layer, rather than a W bulk body. As the D ion fluence increased, the intensity of the desorption peak also increased, slightly shifting to higher temperature. It should be noted that several previous studies [8, 17] which adopted surface polishing and pre-annealing treatment have shown no or weak D desorption at <400 K. Thus, it is likely that deuterium was adsorbed on the surface of fuzz layer, which was desorbed at ~350 K. In addition, one can consider some of the absorbed D diffuse from the surface into body of each fuzz nanofiber. A preliminary experiment conducted using two tungsten samples, one of which experienced pre-annealing treatment at 1423 K for 1 hour and the other as received, showed a significant decrease by 70% in desorption at ~350 K, while small amount of desorption still existed on the pre-annealed sample. Therefore, it is conjectured that the D desorption at the low temperature than that of D plasma exposure is attributed to surface adsorption and subsequent diffusion into the body of fuzz, while affected by the history of thermal treatment and residual internal defects of W bulk.

There were no additional desorption peaks at higher temperature, while a broad peak appeared at ~650 K when the ion fluence increased to $6.0 \times 10^{25} \text{ D/m}^2$. It is likely that the D ions diffused into the body of W fuzz as the fluence increases, and were trapped in the defects formed due to He-bubbles with slightly higher trapping energy. The desorption peak at ~650 K is more or less consistent with the previous research [10], where a peak appeared around 700 K after He pretreatment was performed. However, different from the previous study, the desorption peak at 330 K appeared with a great intensity. This difference might result from the preparation process before plasma exposures. The W samples were ultrasonically cleaned, but not polished. This could have led to an enhanced surface adhesion of D. Nevertheless, it would be good news that the most of desorption occurred at relatively low tem-

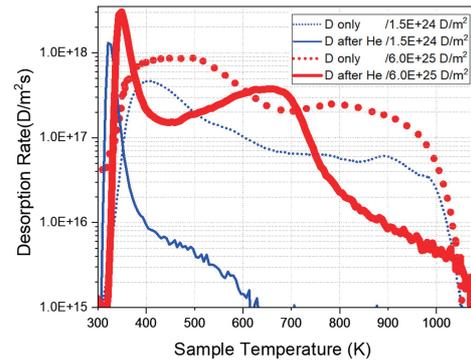


Fig. 4 Deuterium desorption spectra of W exposed only to D plasmas (D only) and W with fuzz layer exposed to D plasmas after He pre-exposures (D after He) for comparison. The vertical axis is taken as the logarithmic scale.

peratures, meaning that hydrogen removal can be conducted with ease.

At the relatively low fluences as seen in Fig. 3 (b), desorption spectra above 400 K are hardly detected compared to the peak intensities at lower temperatures. Therefore, it is better to compare the desorption tendency with the logarithmic scale. Figure 4 shows the comparison of D desorption spectra of W exposed only to D plasmas and W exposed to D plasmas with He pre-exposures, at the lowest ($1.5 \times 10^{24} \text{ D/m}^2$) and the highest fluences ($6.0 \times 10^{25} \text{ D/m}^2$). At the lowest fluence, the desorption above 400 K, which may be derived from internal defects, significantly decreased. This result is consistent with the results in previous studies [8, 10], supporting the hypotheses that a fuzz layer prevents D ions from diffusing into a W bulk body, working as a diffusion barrier.

At the highest fluence, D desorption amount in the W fuzz sample decreased compared to W with D plasma exposure. Peak intensity around 400 - 500 and 800 K significantly decreased, indicating that trapping at the internal defects of the W bulk body was suppressed. But the presence of the desorption peak around 650 K means that some of D ions could diffuse inside and be trapped in other internal defects. The peak intensity was even greater than that of the case of 'D-only', implying that this peak would be desorbed from other trapping sites, which would be formed newly by the He plasma exposure, than the aforementioned internal defects in the W bulk body shown in Fig. 3 (a). For the D ion fluence of $6.0 \times 10^{25} \text{ D/m}^2$, the D plasma exposure time was 25000 s, which was sufficient for D ions to diffuse into the W bulk body. As will be discussed later, the desorbed D ions for the sample 'D after He' was mostly retained within the fuzz layer, not the W bulk.

Figure 5 shows the change of total amount of D retention in the samples depending on the D ion fluences for both cases of 'D only' and 'D after He', the D retention increased as the fluence increased, while the rate of increase lessened above 10^{25} D/m^2 . This suggests that trapping rate of D ions gets closer to saturation. With the He plasma

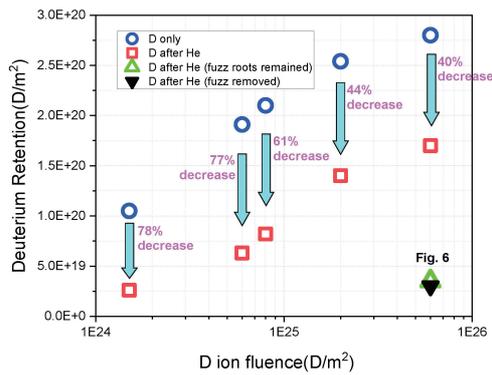


Fig. 5 The changes of total depending on the D ion fluence for W samples. For comparison, the surface where fuzz layers were removed are shown, more detailed in Fig. 6.

pre-exposures, the total retention decreased by 40–80%, showing larger decrement at lower fluence. These results indicate that the suppression effect of D retention resulting from the He-bubble induced diffusion barrier and/or re-emission of D ions owing to enlarged effective surface area at a fuzz layer surpass potential enhancement of retention due to new trapping sites formed on the fuzz layer.

While showing drastic decrements of the D retention after the He pre-treatment, it is still vague where the trapping sites activating the peak at ~ 650 K are located. As mentioned before, it is not peculiar to conjecture that some D ions may reach to a W bulk and be trapped in the internal defects considering the exposure time of 25000 s. Therefore, additional experiments were designed for clarifying the location of trapping sites for the ‘D after He’ sample. A fuzz layer was similarly formed with identical conditions to the previous ‘D after He’ samples, then the fuzz layer was wiped off by Kimwipes to fully remove the layer, or scratched by a metallic bar for making a partially remained fuzz surface.

Figure 6 shows D desorption spectra at the highest D ion fluence of 6.0×10^{25} D/m² with D plasma exposure after He pretreatment. Two of the samples were wiped off (W with fuzz removed), or scratched (W with fuzz roots remained). As shown in the inlets of Fig. 6, nanofibers remained departed, but fuzz structures were not observed for the sample ‘fuzz removed’, while it seemed that a part of the fuzz basement still remained pressed. The D desorption peak at ~ 330 and 650 K significantly decreased compared to the undamaged ‘D after He’ sample. This result indicates that the most of D ions stayed within the fuzz layer, barely traveling into the W bulk space. This result is consistent with the previous report, where a fuzz layer was totally wiped off with the color recovered by naked eyes, and almost no desorption was measured at the D fluence of 2.0×10^{25} D/m² [10].

For further understanding to the trapping property inside the fuzz layer, we deliberately leaved the root parts of the fuzz layer by scratching the surface softly, and the

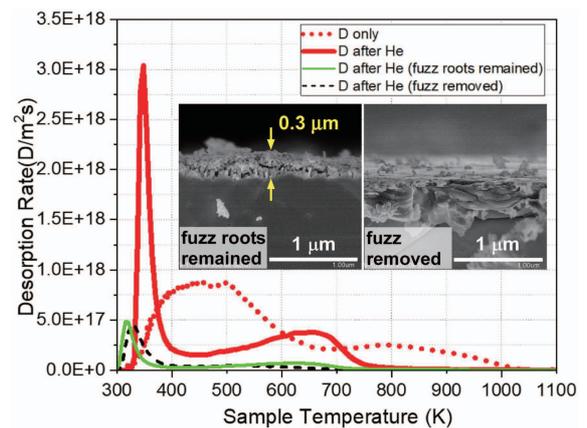


Fig. 6 Deuterium desorption spectra of W samples with D plasma exposure after He pretreatment while two of the samples were wiped off by Kimwipes (fuzz removed), or by a metallic bar (fuzz roots remained). The inlets show SEM images for cross sections of the two damaged samples.

cross section in Fig. 6 revealed the remained thickness was 0.3 μm . In this case, the D desorption peaks decreased similarly to the sample ‘fuzz removed’, but a slightly increased desorption peak at ~ 650 K appeared. These results indicate that most of desorption at ~ 650 K originates from upper interior of the fuzz layer, not from the W bulk space.

Previous research has shown that the D retention in W with porous structures like fuzz layer decreases by a factor of 2–4 compared to a smooth W at the incident D ion fluence of 10^{22-24} D/m², resulting from the fuzz layer providing a kind of ‘release channels’ for D ions [18]. On the other hand, the effect of fuzz layer may vary with the fuzz thickness, suggested by the previous research where a 4.0 μm -thick fuzz layer may promote the total retention [10]. Considering that most of D retained in this research was placed at < 400 K for the fuzz samples, the potential enhancement of retention may be related to the surface area. In our preliminary experiment, D retention in a fuzz sample slightly increased by $\sim 30\%$ as the thickness of fuzz layer increased from 1.9 to 2.7 μm . Therefore, it would be important to investigate the D ion fluence dependence on D retention with various thicknesses of fuzz layers for evaluating the effect of the fuzz layer on the hydrogen fuel inventory in PFMs.

4. Summary

In this study, the D fluence dependence on the D retention in W with an identical fuzz layer was surveyed to clarify the effect of fuzz layer formation by He pre-exposures. From the TDS results, D desorption peak derived from the internal defects in a W bulk space significantly decreased with substantial decrement in total D retention when a fuzz layer was formed, and the D ions were mainly desorbed at around 320–350 K. At the highest fluence of 6×10^{25} D/m², a new broad peak appeared at 650 K, and

the retention did not originate from the W bulk, but the interior of the fuzz layer. Most of D ions still stayed in the upper interior of the fuzz layer above 0.3 μm from W bulk, even at relatively higher D ions fluence (6×10^{25} D/m²). This hints that the number of released D ions can increase regardless of the ion fluence, owing to porous morphology of the fuzz layer. Therefore, it seems clear that fuzz can contribute to reducing the accumulation of hydrogen isotopes in PFMs, working as a diffusion barrier.

Acknowledgments

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- [1] T. Loarer *et al.*, *J. Nucl. Mater.* **337-339**, 624 (2005).
- [2] R.A. Pitts *et al.*, *J. Nucl. Mater.* **438**, 48 (2013).
- [3] Y. Ueda *et al.*, *J. Nucl. Mater.* **386-388**, 725 (2009).
- [4] Y. Nobuta *et al.*, *Fusion Sci. Technol.* **77**, 76 (2021).
- [5] M. Miyamoto *et al.*, *Nucl. Fusion* **49**, 065035 (2009).
- [6] V.Kh. Alimov *et al.*, *J. Nucl. Mater.* **415**, 628 (2011).
- [7] M. Reinhart *et al.*, *J. Nucl. Mater.* **463**, 1021 (2015).
- [8] M.J. Baldwin *et al.*, *Nucl. Fusion* **51**, 103021 (2011).
- [9] O.V. Ogorodnikova *et al.*, *J. Nucl. Mater.* **515**, 150 (2019).
- [10] L. Liu *et al.*, *J. Nucl. Mater.* **539**, 152327 (2020).
- [11] K. Doi *et al.*, *Fusion Eng. Des.* **136**, 100 (2018).
- [12] D.H. Liu *et al.*, *Nucl. Fusion* **60**, 056018 (2020).
- [13] M. Yajima *et al.*, *J. Nucl. Mater.* **438**, S1142 (2013).
- [14] A. Rusinov *et al.*, *Plasma Fusion Res.* **7**, 1405105 (2012).
- [15] S. Kajita *et al.*, *Nucl. Fusion* **49**, 095005 (2009).
- [16] Z. Harutyunyan *et al.*, *J. Nucl. Mater.* **548**, 152848 (2021).
- [17] M. Oya *et al.*, *J. Nucl. Mater.* **438**, S1052 (2013).
- [18] Z. Tian *et al.*, *J. Nucl. Mater.* **399.1**, 101 (2010).