1 Strongly reduced penetration of atomic deuterium in radiation-damaged tungsten

M.H.J. 't Hoen[1]**, M. Mayer**[2]**, A.W. Kleyn**[1,3] **and**
P.A. Zeijlmans van Emmichoven[1]

[1] FOM institute DIFFER, Association EURATOM-FOM, Partner in the Trilateral Euregio Cluster, PO Box 1207, 3430 BE Nieuwegein, The Netherlands
[2] Max-Planck-Institut für Plasmaphysik, Boltzmannstraße 2, D-85748 Garching, Germany
[3] Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, NL-1098 XH Amsterdam, The Netherlands, NL-1098 XH Amsterdam, the Netherlands
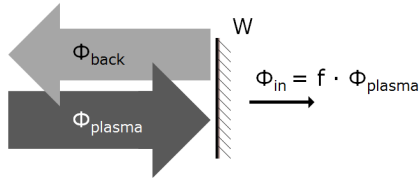
Abstract

Radiation-damaged tungsten is exposed to high-flux, low-energy deuterium plasmas at self-biased conditions. We observe that the fraction of deuterium that penetrates, is only $10^{-5} - 10^{-7}$ of the plasma flux and strongly dependent on the local surface temperature. We propose that deuterium does not directly penetrate bulk tungsten but that it thermalizes at the surface where it forms a protective chemisorbed layer. We find an energy barrier of 1–2 eV between surface and bulk, causing the influx of deuterium to be low as compared to the number of defects and leading to slow filling of the damaged layer.

Tungsten is foreseen as the main candidate material for use in the divertor of the experimental fusion reactor ITER. The divertor serves as the exhaust of the tokamak where the helium ash is removed. It is particular in this region where strong interaction of plasma with plasma facing components (PFC's) takes place. The plasma in the divertor region has a high electron density ($10^{20} - 10^{21}$ m^{-3}) and a temperature of 1–10 eV. This leads to extremely intense particle and energy flux densities of $\sim 10^{24}$ ions m^{-2} s^{-1} and ~ 10 MW m^{-2} respectively [1]. Its high thermal conductivity and melting point as well as its low erosion rate make tungsten favourable over many other materials. Another essential property of PFC's is that the uptake of tritium should be limited. For safety and efficiency reasons, the total tritium inventory in ITER should be kept below 700 g [2]. For tungsten it is known that the retention of hydrogen particles is low ($< 10^{-4}$ at.fr). However, radiation damage in a fusion reactor can lead to enhancement of the retention by orders of magnitude [3, 4].

In this Letter we present deuterium retention studies for radiation damaged tungsten targets, exposed to atomic deuterium plasmas under ITER-like conditions. For ion temperatures of a few eV it is known that 90–95% of the deuterium is directly reflected [5, 6]. However, the plasma flux is so high that there are large amounts of remaining deuterium atoms that interact with the tungsten surface. This results in a very complex plasma-surface interaction leading to adsorption of deuterium at the surface, recombination of atomic deuterium to molecules and release into the vacuum and/or back into the plasma [7, 8], penetration of deuterium in tungsten, etc. The situation is very schematically depicted in figure 1.1 with Φ_{plasma} the plasma flux and Φ_{back} the back flux containing directly reflected deuterium as well as thermalized deuterium leaving the surface as atoms and/or molecules. The effective ingoing flux, Φ_{in}, is the fraction f of the plasma flux that enters the tungsten material. In the present work we have monitored the diffusion of deuterium inwards from which we were able to directly determine Φ_{in} and thereby the fraction f. We obtain a value for f that is very small, 10^{-5}–10^{-7}. This fraction is strongly dependent on the local surface temperature and orders of magnitude lower than expected on the basis of the direct reflection mentioned above. We propose that this small value for f originates in the deuterium not directly entering bulk tungsten but thermalising and neutralising at the surface forming a protective chemisorbed layer. Before diffusing into the bulk, the atoms need to cross an energy barrier that strongly limits the influx. We will show that an activation energy for crossing the barrier of 1–2 eV is consistent with the temperature dependence of the influx.

Figure 1.1: The influx, Φ_{in}, is only a small fraction f of the incoming plasma flux, Φ_{plasma}.

Polycrystalline tungsten targets (PLANSEE, 99.96% purity, Ø 20 mm, 1 mm thick) were mechanically polished until mirror finish and subsequently heated for 1 h at 1273 K at a background pressure of 5×10^{-4} Pa. The targets were pre-irradiated at room temperature with 12.3 MeV W^{4+} ions at the 3 MV ion accelerator at IPP Garching to homogeneous lateral damage. The fluence of the pre-irradiations was taken such that a damage

level of 0.45 displacements per atom was reached (average displacement energy 90 eV). We have previously shown that this fluence is sufficient to saturate the damage level and that the damage extends to a depth of about 1.5 μm below the surface [3]. The surface cleanliness was checked by X-ray photoelectron spectroscopy. Since the targets were stored under ambient conditions, they were covered with nanometer-thick native layers of oxygen and carbon [3, 9]. During plasma exposure, most of these layers are removed within the first few seconds although the presence of in particular some oxygen cannot be excluded [10]. After plasma exposure, small amounts of Mo, Ca and F were found to be present on the surface. In most cases the concentrations were well below 10%. These impurities may slightly affect the protective layer and the energy barrier that we found in our measurements.

The pre-damaged tungsten targets were exposed to intense deuterium plasma beams at the linear plasma generator Pilot-PSI [11]. The plasma was created by a cascaded arc source and transported to the target by an axial magnetic field of 0.4 T. During the exposures, the targets were water-cooled and electrically floating. Electron density and temperature profiles of the plasma beam were determined by Thomson scattering [12]. The plasma beam has approximately a Gaussian profile with maximum electron density and temperature of about 4×10^{20} m^{-3} and 1 eV respectively. The ion flux on the targets can be estimated by applying the Bohm criterion [13] and ranges from 2×10^{24} ions m^{-2} s^{-1} in the centre of the target to 5×10^{23} ions m^{-2} s^{-1} at the edges. For our experimental conditions, the deuterium in the plasma predominantly consists of atomic ions [14, 15]. The kinetic energy of the ions arriving at the surface can be estimated by considering a drifting Maxwellian velocity distribution for the ions in the plasma and an acceleration over the plasma sheath towards the surface. Assuming equal electron and ion temperatures in the plasma [15], this leads to an ion kinetic energy of roughly 5 eV. The temperature profile of the tungsten surface during exposure was measured with a fast infrared camera (FLIR SC7500-MB) and varies between 560 K in the centre of the target to 470 K at the edges (the emissivity of the tungsten targets used was 0.06, a value verified ex situ with the help of a thermocouple measurement). The absolute uncertainty in the temperatures is of order 25 K and is mainly caused by the uncertainty in the emissivity and the transmission of the infrared radiation through the vacuum window. The relative uncertainty in the temperatures is a few K.

Deuterium depth profiles were measured one month after plasma exposure by nuclear reaction analysis (NRA) making use of the nuclear reaction D(^{3}He,p)^{4}He [16]. The ^{3}He beam spot of about 1 mm in diameter was positioned at six spots on the target: two close to the centre, two at 3 mm and two at 6 mm from the centre at opposite sides. In this way, we obtain deuterium depth profiles for three different exposure temperatures, i.e., 560 K, 530 K and 500 K. Differences between the measurements taken at the same temperature were small and only averages will be shown. At each position, the beam energy was scanned from 690 keV to 4.0 MeV to determine the deuterium concentration with a resolution of about 0.5 μm down to a depth of 6 μm. The depth profiles of retained deuterium were calculated from the measured proton energy distributions with the NRA-DC program [17]. The total amount of deuterium in the top 6 μm was obtained by integrating the depth profiles.
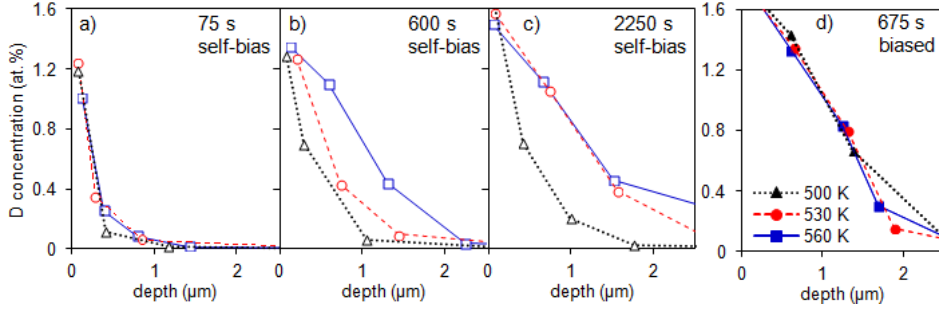
Figure 1.2: Deuterium depth distributions in damaged (0.45 dpa) tungsten targets exposed to high-flux deuterium plasmas at self-biased conditions (a-c) and biased at -40 V (d). The exposure times are as indicated. The deuterium depth profiles were measured at three positions on the target (centre at 560 K, squares; 3 mm off-centre at 530 K, circles; 6 mm off-centre at 500 K, triangles)

Five identical tungsten targets were exposed to deuterium plasma. The plasma fluxes and the corresponding surface temperatures were very similar in all experiments. The difference between the targets was the exposure time that was varied over almost two orders of magnitude, from 30 s to 2250 s. This means a variation in fluence in the centre of the targets from about $6 \times 10^{25}\,\mathrm{m}^{-2}$ to $4.5 \times 10^{27}\,\mathrm{m}^{-2}$ deuterium ions (fluence equals time integrated flux).

The NRA results for three of the targets are shown in figures 1.2a–c. For the one but shortest exposure time (figure 1.2a), the deuterium is retained mostly within 0.5 μm from the surface for all three temperatures. At longer exposure times (figure 1.2b) it is clear that, in particular for the highest temperature, deuterium penetrates deeper in the material. This penetration continues for the longest exposure time as shown in figure 1.2c. The observations qualitatively agree with a process that is determined by diffusion: deeper penetration of deuterium for longer exposures and higher temperatures. For comparison, we also show the NRA results for a target that was exposed for 675 s to deuterium plasma at similar plasma conditions but biased at a potential of -40 V (figure 1.2d). In contrast to the self-biased experiments, for all three temperatures the damaged slab has been filled with deuterium as result of direct penetration of tungsten. This clearly different result will be discussed in more detail later.

In figure 1.3, we show the integrated, total amounts of deuterium in the top 6 μm for the self-biased experiments. It is clear that for the highest temperature of 560 K, deuterium retention saturates after approximately 1000 s. The deuterium inventory at saturation corresponds to the damaged layer (thickness about 1.5 μm) being completely filled with deuterium (1.2 at.%). For 530 K, it seems that saturation is reached for the longest exposure time of 2250 s. For the lowest temperature of 500 K, full saturation is never obtained.

The experimentally observed durations for complete saturation of the damaged layer with deuterium are long as compared to what would be expected on the basis of the large plasma flux and the diffusion of deuterium in tungsten. Using the Frauenfelder
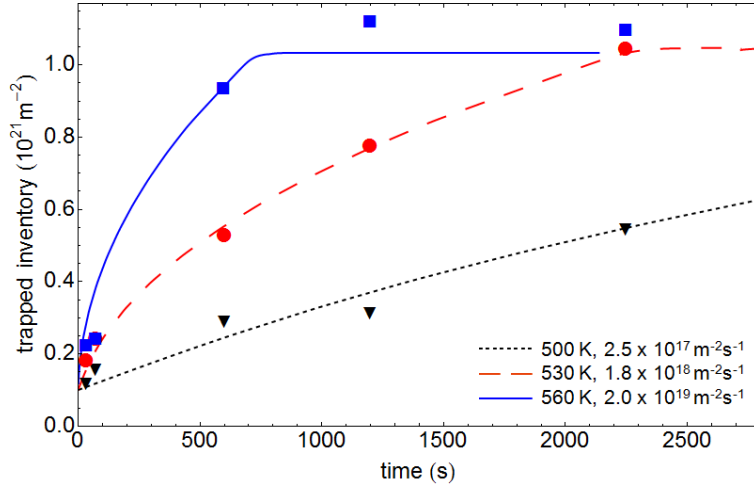
Figure 1.3: The integrated, total amounts of deuterium in the top 6 μm for the self-biased experiments. The lines show the results of the TMAP7 simulations.

diffusion coefficient of deuterium in tungsten of $D_F = D_0 \exp[-0.39/(k_B T)]$ with $D_0 = 2.9 \times 10^{-7} \mathrm{m^2\,s^{-1}}$ [18], shows that for temperatures of 500–560 K deuterium diffuses in less than a second through the damaged layer. The damaged layer has an areal density of trapped deuterium of $\sim 10^{21}\,\mathrm{m^{-2}}$. The plasma flux, after correction for the direct reflection of deuterium from tungsten, amounts to $\sim 10^{23}\,\mathrm{m^{-2}\,s^{-1}}$. This means that in one second plasma exposure there is ample deuterium available to fill the traps. This simple estimate thus yields a timescale that is more than three orders of magnitude faster than the experimentally observed saturation times. Uncertainties in the Frauenfelder diffusion coefficient [19] cannot explain this.

Why then is the experimentally observed filling of traps with deuterium three orders of magnitude slower than expected on the basis of plasma flux and diffusion? The assumption in the above considerations is that the high-flux plasma, after correction for reflection, directly penetrates into the outermost layers of the target. This seems to be a realistic assumption since the introduction of atomic deuterium in tungsten is known to be exothermic [20] and since the incoming ions in addition have a kinetic energy of 5 eV. However, our results strongly suggest that the assumption is <u>not</u> valid. We propose that instead of directly penetrating tungsten, the deuterium ions thermalize and neutralize at the surface where they form a chemisorbed layer. Presence of this layer in fact plays an important role in the thermalization process: deuterium-deuterium collisions cause energy pooling, thereby decreasing the energy of the incoming ions preventing direct penetration. This interpretation is supported by other experiments where it was shown that a chemisorbed deuterium layer on a barium surface actively decreases the interaction between incoming deuterium and barium atoms [21]. The contribution of the chemisorbed layer to the thermalization of deuterium means that it 'protects' tungsten from direct penetration by deuterium. To diffuse from this protective chemisorbed layer at the surface into bulk tungsten, deuterium needs to be activated over an energy barrier of a few eV

[20, 22]. This energy barrier reduces the effective influx of deuterium by many orders of magnitude to values so low that the filling of the damaged layer with deuterium is limited by the amount of traps and not by the diffusion coefficient. We will show that this interpretation leads to a consistent picture explaining the filling of the damaged layer being orders of magnitude slower than initially expected.

To determine values for Φ_{in} that are consistent with our experimental observations, we carried out TMAP7 simulations. TMAP7 is a one-dimensional program that solves the diffusion equation for deuterium in materials [23]. The program includes trapping of deuterium and recombination to molecules at the surface. Following our previous results [9], we assume three different trap sites for deuterium in tungsten with trap densities of 2×10^{-1} at.%, 4.5×10^{-1} at.%, and 6.5×10^{-1} at.% for trapping energies of 1.2 eV, 1.4 eV, and 1.85 eV respectively. For the diffusion coefficients of deuterium in tungsten, the above mentioned Frauenfelder values were used. For recombination of two atoms at the surface to a molecule, a coefficient of 3.2×10^{-15} m^4 s^{-1} exp$[-1.16/(k_{\text{B}}T)]$ was taken [24]. The simulations were run with the flux varied until good agreement with the experiments was obtained. The results of the simulations are shown in figure 1.3. The deuterium influxes, Φ_{in}, used were 2×10^{19} m^{-2} s^{-1} (560 K), 1.8×10^{18} m^{-2} s^{-1} (530 K), and 2.5×10^{17} m^{-2} s^{-1} (500 K), which means that f is in the range of 10^{-5} to 10^{-7}. Note that Φ_{in} is the deuterium influx in the first nanometer of the material. Part of this influx leaves the surface again via recombination. To fit the experimental data, the simulated curves have slightly been shifted upwards by 1×10^{20} m^{-2}. The kinks in the simulated curves for the two highest temperatures at 750 s and 2200 s correspond to the times where the damaged layer is filled with deuterium. The simulations reproduce the experiments well. The effective influx turns out to be strongly dependent on temperature: almost two orders of magnitude variation is obtained in the temperature range of only 60 K. This dependence is much stronger than the variation in plasma flux, which varies only by about 30%.

In figure 1.4, the simulated influx is plotted as function of the inverse temperature. The data-points follow quite well a straight line showing that the process has Arrhenius-type behaviour ($\Phi_{\text{in}} = \Phi_{\text{in}}(T_\infty)$ exp$[-E_a/k_{\text{B}}T]$) with Φ_{in} the influx of deuterium, k_{B} Boltzmann constant and T the local temperature of the surface during plasma exposure. The activation energy E_a directly follows from the slope and amounts to 1.6 eV. The pre-exponential factor, $\Phi_{\text{in}}(T_\infty)$, represents the surface coverage of chemisorbed deuterium, $(1-2 \times 10^{19}$ m$^{-2})$ [25] multiplied by the attempt frequency, typically in the order of 10^{13} s^{-1}. We fixed this value at 10^{32} m^{-2} s^{-1}. Taking into account the uncertainties in the experimental values for the temperature, the results become $E_a = (1-2)$ eV. E_a is close to reported energy barriers of around 2 eV for diffusion of chemisorbed deuterium from surface to bulk [20, 22].

In conclusion, we have shown that the experimentally observed, slow diffusion of deuterium in pre-irradiated tungsten is consistent with the deuterium atomic ions not directly penetrating in bulk tungsten but forming a chemisorbed layer at the surface. This leads to a reduction in the effective influx of deuterium by many orders of magnitude as compared to the plasma flux. Obviously, at self-biased conditions, the kinetic energy of the atomic ions arriving at the surface of roughly 5 eV is not sufficient for penetration
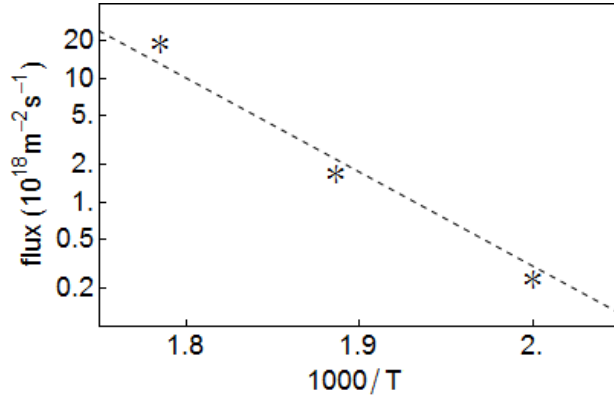
Figure 1.4: The simulated influx as a function of $1000/T$ with T the local target temperature.

of the surface with its protective layer. For a target biased at a potential of -40 V, on the other hand, we observed that the damaged layer is filled on a much shorter timescale. This suggests that, upon their acceleration towards the surface by the bias potential, the ions directly penetrate the bulk, leading to high concentrations of deuterium and fast filling of the damaged layer. Our results are to some extent reminiscent of what has been observed by others on the diffusion of deuterium in tungsten containing considerable amounts of defects ([26]. Also in these experiments the trapping of deuterium per unit time was the limiting factor for diffusion. However, the kinetic energy of the deuterium ions was so high that direct penetration occurred. Our observations are furthermore qualitatively consistent with the molecular dynamics simulations of [5], where it was shown that individual hydrogen atoms incident on perfect tungsten at kinetic energies up to 3 eV either reflect from or stick at the surface whereas at 10 eV a small fraction directly penetrates. In a comparison with these simulations, one should realize that our high-flux plasma leads to the presence of large amounts of deuterium in the neighbourhood of the surface including a chemisorbed layer. As discussed, this chemisorbed layer can act as a protective layer preventing direct penetration. Finally, our results shed light on previously reported strong surface modifications of tungsten during exposure to deuterium plasmas at biased conditions [27, 28] as opposed to the absence of such modifications for self-biased conditions. The surface modifications can be related to an oversaturation of tungsten with deuterium originating in the direct penetration. The absence of surface modifications at self-biased conditions can readily be understood in terms of the absence of direct penetration, as was shown in the present Letter.

Bibliography

[1] G. Federici et al, *Plasma-material interactions in current tokamaks and their implications for next step fusion reactors*, Nucl. Fusion **41** (2001) 1967–2137.

[2] J. Roth et al, *Recent analysis of key plasma wall interactions issues for ITER*, J. Nucl. Mater. **390-391** (2009) 1–9.

[3] M. H. J. 't Hoen et al, *Saturation of deuterium retention in self-damaged tungsten exposed to high-flux plasmas*, Nucl. Fusion **52** (2012) 023008.

[4] M. Shimada et al, *The deuterium depth profile in neutron-irradiated tungsten exposed to plasma*, Phys. Scr. **2011** (2011) 014051.

[5] K. O. E. Henriksson et al, *Sticking of atomic hydrogen on the tungsten (001) surface*, Surf. Sci. **600** (2006) 3167–3174.

[6] S. Markelj et al, *Temperature dependence of D atom adsorption on polycrystalline tungsten*, Appl. Surf. Sci. **282** (2013) 478– 486.

[7] R. Gat and J. C. Angus, *Hydrogen atom recombination on tungsten and diamond in hot filament assisted deposition of diamond*, J. Appl. Phys. **74** (1993) 5981–5989.

[8] M. Rutigliano and M. Cacciatore, *Eley-Rideal recombination of hydrogen atoms on a tungsten surface*, Phys. Chem. Chem. Phys. **13** (2011) 7475–7484.

[9] M. H. J. 't Hoen et al, *Reduced deuterium retention in self-damaged tungsten exposed to high-flux plasmas at high surface temperatures*, Nucl. Fusion **53** (2013) 043003.

[10] S. Xu and L. Diao, *Study of tungsten oxidation in $O_2/H_2/N_2$ downstream plasma*, J. Vac. Sci. Technol. **26** (2008) 360–364.

[11] G. J. van Rooij et al, *Extreme hydrogen plasma densities achieved in a linear plasma generator*, Appl. Phys. Lett. **90** (2007) 121501.

[12] H. J. van der Meiden et al, *High sensitivity imaging Thomson scattering for low temperature plasma*, Rev. Sci. Instrum. **79** (2008) 013505.

[13] D. Bohm. *The Characteristics of Electrical Discharges in Magnetic Fields, chapter 3.* ed A Guthrie and R K Wakerling (NewYork: McGraw-Hill) (1949).

[14] R. C. Wieggers, P. W. C. Groen, H. J. de Blank and W. J. Goedheer, *Simulation of the Neutral Inventory in the Pilot-PSI Beam*, Contrib. Plasma Phys. **52** (2012) 440–444.

[15] A. E. Shumack et al, *Rotation of a strongly magnetized hydrogen plasma column determined from an asymmetric Balmer- β spectral line with two radiating distributions*, Phys. Rev. E **78** (2008) 046405.

[16] M. Mayer, E. Gauthier, K. Sugiyama and U. von Toussaint, *Quantitative depth profiling of deuterium up to very large depths*, Nucl. Instrum. Methods Phys. Res. B **267** (2009) 506–512.

[17] K. Schmid and U. von Toussaint, *Statistically sound evaluation of trace element*

depth profiles by ion beam analysis, Nucl. Instrum. Methods Phys. Res. B **281** (2012) 64–71.

[18] R. Frauenfelder, *Solution and Diffusion of Hydrogen in Tungsten*, J. Vac. Sci. Technol. **6** (1969) 388–397.

[19] R. A. Causey, *Hydrogen isotope retention and recycling in fusion reactor plasma-facing components*, J. Nucl. Mater. **300** (2002) 91–117.

[20] A. van Veen et al, *Hydrogen exchange with voids in tungsten observed with TDS and PA*, J. Nucl. Mater. **155-157** (1988) 1113–1117.

[21] R. M. A. Heeren, D. Ćirić, H. J. Hopman and A. W. Kleyn, *Enhanced preferential sputtering of a hydrogenated barium surface*, Appl. Phys. Lett. **59** (1991) 158–160.

[22] D. F. Johnson and E. A. Carter, *Hydrogen in tungsten: Absorption, diffusion, vacancy trapping, and decohesion*, J. Mater. Res. **25** (2010) 315–327.

[23] G. R. Longhurst. TMAP7 User Manual. Technical report, INEEL/EXT-04-02352 (Idaho: Idaho National Engineering and Environmental Laboratory) (2004).

[24] R. A. Anderl et al, *Deuterium transport and trapping in polycrystalline tungsten*, Fusion Technol. **21** (1992) 745–752.

[25] B. Feuerbacher and B. Fitton, *Electronic Energy Levels of Hydrogen Adsorbed on Tungsten*, Phys. Rev. B **8** (1973) 4890–4892.

[26] R. Causey et al, *Defects in tungsten responsible for molecular hydrogen isotope retention after exposure to low energy plasmas*, J. Nucl. Mater. **390-391** (2009) 717–720.

[27] A. Manhard, K. Schmid, M. Balden and W. Jacob, *Influence of the microstructure on the deuterium retention in tungsten*, J. Nucl. Mater. **415** (2011) S632–S635.

[28] H. Xu et al, *Observations of orientation dependence of surface morphology in tungsten implanted by low energy and high flux D plasma*, J. Nucl. Mater. **443** (2013) 452–457.