INL/CON-10-20601
PREPRINT

Deuterium Depth Profile in Neutron-Irradiated Tungsten Exposed to Plasma

13th International Workshop on Plasma-Facing Materials and Components for Fusion Applications

Masashi Shimada
G. Cao
Y. Hatano
T. Oda
Y. Oya
M. Hara
P. Calderoni

May 2011

The INL is a
U.S. Department of Energy
National Laboratory
operated by
Battelle Energy Alliance

Deuterium Depth Profile in Neutron-Irradiated Tungsten Exposed to Plasma

Masashi Shimada*[,1], G. Cao[2], Y. Hatano[3], T. Oda[4], Y. Oya[5], M. Hara[3] and P. Calderoni[1]

[1]*Fusion Safety Program, Idaho National Laboratory, Idaho Falls, ID, 83415, USA*

[2]*Department of Engineering Physics, University of Wisconsin-Madison, Madison, Wisconsin, 53706,U.S.A.*

[3]*Hydrogen Isotope Research Center, University of Toyama, Toyama, 930-8555, Japan*

[4]*Department of Nuclear Engineering and Management, The University of Tokyo, Tokyo, 113-8656, JAPAN*

[5]*Radioscience Research Laboratory, Faculty of Science, Shizuoka University, Shizuoka, 422-8529, JAPAN*

Abstract

The tungsten samples (99.99 % purity from A.L.M.T. Corp., 6mm in diameter, 0.2mm in thickness) were irradiated by high-flux neutrons at 323K (50C) to 0.025 dpa in the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL). Subsequently, the neutron-irradiated tungsten samples were exposed to high-flux deuterium plasmas (ion flux: 10^{21}-10^{22} $m^{-2}s^{-1}$, ion fluence: 10^{25}-10^{26} m^{-2}) in the Tritium Plasma Experiment (TPE) at Idaho National Laboratory (INL). This paper reports the results of deuterium depth profiling in neutron-irradiated tungsten exposed to plasmas at 373K (100C), 473K (200C), and 773K (500C) via nuclear reaction analysis (NRA). The NRA measurements show that a significant amount of deuterium (> 0.1 at. % D/W) is still trapped in the bulk material (up to 5 μm) at 773K (500C).

Tritium Migration Analysis Program (TMAP) simulation results using the NRA profiles indicate that different trapping mechanisms exist for neutron-irradiated and unirradiated tungsten.

*Corresponding author tel: +1-208-533-4472

*Corresponding author E-mail: Masashi.Shimada@inl.gov

PACS : 61.80.Hg, 28.52.Fa, 52.40.Hf, 61.80.Jh, 61.82.Bg,

- Word count of the manuscript (3600 word limit):

3361 words

- Word count of the abstract (150 word limit):

148 words

- Total number of figures:

6 (Figures 1- 6)

- Total number of pages:

23

1. Introduction

Plasma-facing components (PFCs) will be exposed to 14 MeV neutrons from D-T fusion reactions, and tungsten, a candidate materials for the divertor PFC in ITER, is expected to receive a neutron dose of 0.7 displacement per atom (dpa) by the end of operation in ITER [1]. The effect of neutron-irradiation damage has been mainly simulated using high-energy ion bombardment [2-7]. While this prior database of results is quite valuable for understanding the behavior of hydrogen isotopes in PFCs, it does not encompass the full range effects that must be considered in a practical fusion environment. The ions are limited in range to only a few microns into the surface, PKA (the primary knock-on atom) energy (> MeV) from high energy ion-bombardment is much higher than that (< 300 keV) from 14 MeV neutrons, and the displacement rate (10^{-3}~10^{-4} dpa/sec) from high energy ion-bombardment are three to four orders of magnitude higher than that (10^{-7}~10^{-8} dpa/sec) from fission and fusion neutron environments [8]. In addition, the 14 MeV neutrons change the elemental composition via transmutations, and create a high radiation environment inside PFCs, which might have effects on the behavior of tritium in PFCs. Therefore, there still exists large uncertainty about the tritium retention in neutron-radiation damage from the 14 MeV fusion neutrons.

TPE is unique in that it combines four specialized elements: (a) the ability to handle tritium, (b) a divertor-relevant high-flux plasma, (c) the ability to handle radioactive materials, as well as (d) the ability to handle beryllium. First results of deuterium retention in neutron-irradiated tungsten exposed in TPE have been reported previously [9,10]. This paper reports the latest results of deuterium depth profiling in neutron-irradiated tungsten exposed to plasmas at 373K (100C), 473K (200C), and 773K

(500C) via nuclear reaction analysis (NRA). This work is collaborative research under the framework of US-Japan international collaboration, TITAN program.

2. Experimental Apparatus

The tungsten samples (ϕ 6mm x 0.2mm) were prepared by cutting polycrystalline tungsten rod (99.99 at. % purity, from A.L.M.T. Corp.) annealed at 1173 K for 0.5 hour in a hydrogen atmosphere to relieve internal stresses in the manufacturing process. The samples were mechanically polished to a mirror finish, and then annealed at 1173 K for 0.5 hour in ultra high vacuum (~10^{-6} Pa) prior to the plasma exposure. The grains are elongated along the direction normal to the plasma exposed surface, which is similar to ITER grade tungsten for the purpose of minimizing the large blister formation.

Tungsten samples were irradiated to three different damage levels (0.025, 0.3, and 1.2 dpa) under the TITAN program. The first set of tungsten samples were irradiated for 33 hours by high-flux neutrons at 323K (50C) to 0.025 dpa in HFIR, ORNL in January 2009. The thermal neutron flux and fluence at the irradiation location are 2.5×10^{19} $m^{-2}s^{-1}$, and 3.0×10^{24} m^{-2} respectively. The fast neutron (>0.1MeV) flux and fluence are 8.9×10^{18} $m^{-2}s^{-1}$, and 1.1×10^{24} m^{-2} respectively.

The set of tungsten samples were sealed in a molybdenum envelope to prevent cooling water leakage onto the samples but allowing enough heat conduction for the sample to be cooled down to the cooling water temperature during the neutron irradiation. The molybdenum envelope was installed in a perforated aluminum rabbit capsule allowing contact with the flowing coolant in the hydraulic tube to maintain the specimen temperature at 323 K (50C).

TPE at INL was used to implant low energy (100eV) deuterons in both the neutron-irradiated tungsten and unirradiated tungsten. Three neutron-irradiated tungsten and three unirradiated tungsten samples were exposed to identical high-flux deuterium

plasma conditions (ion flux: $5x10^{21}$ $m^{-2}s^{-1}$, ion fluence: $(5\text{-}7)x10^{25}$ m^{-2}) at the same sample temperature of 373 K (100 C), 473 K (200 C), and 773 K (500 C) in TPE. Incident ion energy of 100 eV was achieved by adjusting the target bias voltage. For the sample exposed at 373K (100C) and 473K (200C), the sample temperature was kept below the stage III recovery temperature of 550 K (0.15 T_m, where T_m is the melting temperature of tungsten, 3695 K) to prevent recovery of neutron-irradiated damage during the deuterium plasma exposure, and the effect of diffusion on the deuterium depth profile is evaluated [11]. For the sample exposed at 777K (500C), the sample temperature was above the stage III recovery temperature, and the effects of the stage III recovery, which is attributed to the migration of self-interstitial atoms, on deuterium depth profile is evaluated. The sample temperature was monitored by the ungrounded K-type (chromel–alumel) thermocouple that was attached on the back of the sample.

A 3.5 MeV ^{3}He beam was carried out to measure the deuteron retention and depth profile using D(^{3}He,p) ^{4}He nuclear reaction at the Ion Beam Laboratory at University of Wisconsin-Madison. The ^{3}He beam was bombarded normal to the tungsten sample and the proton signal was detected with a deep depletion depth (2000 μm) silicon detector at 135^o detection angle [12]. A 10 μm thick Ni foil was used to block ^{4}He particles. The SIMNRA program was used to obtain the depth profile up to 5 μm [13].

3. Simulation

The Tritium Migration Analysis Program version 7 (TMAP7) [15] was used to simulate the previously reported TDS spectra at 200C [9], and only the thermal desorption was simulated in this study to avoid the difficulty of simulating the hydrogen isotope exposure process that is a dynamic and non-equilibrium process [14]. In the simulation we chose the hydrogen diffusivity formula by Frauenfelder [16] (corrected for deuterium) as the review paper by Causey [17] suggested ($D=2.9\times10^{-7}\exp(-0.39\text{eV}/kT)$ [m^2/s]). Recombination coefficients vary by several orders of magnitude in the literature, but we chose to use the recombination coefficient formula by Anderl at al [18] ($K_r=3.2\times10^{-15}\exp(-1.16\text{eV}/kT)$ [m^4/s]).

From the literature of the detrapping energy in tungsten [19-21], the low-energy (0.8-1.1 eV) trap is associated deuterium atoms trapping with impurities or dislocations, the 1.3-1.5 eV trap is associated with deuterium atoms trapping at vacancies in tungsten and deuterium molecules desorbed from voids, and the high-energy (1.7-2.1 eV) trap is associated with dissociation and release of deuterium atoms decorating a void.

Unfortunately, the deuterium depth profile via NRA alone was not able to reproduce the higher deuterium retention measured by TDS. This could be due to the desorption of deuterium atom after the deuterium plasma exposure. It is important to note that TDS was performed a day after the deuterium plasma exposure [9], whereas NRA was carried out several months after the deuterium plasma exposure. Therefore, it is reasonable to assume that the NRA measurement might underestimate the deuterium concentration in this study. Therefore, an approach to adjust the peak deuterium concentration in the normalized NRA spectrum profile was used to fit the experimental

TDS spectrum. For the NRA profiles at 200C, similar profiles with uniform concentration up to 3μm and gradual drop to zero around 5 μm are obtained from both 0 dpa and 0.025 dpa.

The peak deuterium concentration was varied in the range 10^{-1} <D/W<10^{-3} in the normalized profile. TMAP7 allows us to vary the fraction of traps sites filled, but we assumed the saturable trap (all traps are filled with deuterium) from the surface. Very low trap concentration (trap/W<10^{-5}) of empty traps (no traps are filled with deuterium) was assumed in deeper bulk tungsten (x > 5 μm) beyond the detection range of NRA measurements for simplicity.

The TMAP7 has a capability of simulating with three trap sites (with different detraping energies). In our previous study [9], we were not able to simulate the experimental result of 0.025 dpa at 200C with three trap sites alone. A new approach to combine two TMAP7 spectra with three trap sites (total of six trap sites) was developed to simulate the TDS spectrum with six trap sites (with different detrapping energies). Through this combination of these two spectra might not be perfect simulation for the TDS spectrum from six trap sites, this approach can provide reasonable representation of the TDS spectrum with six trap sites for the simulation condition used in this study as shown in the next section.

4. Results and Discussion

Figure 1 shows the optical microscope images of the plasma exposed area for 0 dpa and 0.025 dpa tungsten after the plasma exposure at 373 K (100 C), 473 K (200 C), and 773 K (500 C). A noticeable difference was observed only for 0.025 dpa at 773K (500C), which shows the significant increase in the number density of small (<5 μm) blisters, and a few large (>5 μm) blisters. Detailed investigation of surface morphology in neutron-irradiated tungsten is beyond the scope of this study, and will be discussed in the subsequent publication under the TITAN collaboration.

Figure 2(a), (b), and (c) show the deuterium depth profiles up to 5 μm in depth via NRA at 373K (100C), 473K (200C), and 773K (500C), respectively. Figure 2(a) shows that deuterium atoms are trapped up to 3 μm with (0.1-0.2) at. % D/W in 0.025 dpa and similar D/W concentrations are observed from 0 dpa to 0.025 at 373K (100C). Figure 2(b) also illustrates that deuterium atoms are trapped up to 3μm with (0.2-0.4) at. % D/W in 0.025 dpa and (x2~4) higher D/W concentration was observed in 0.025 dpa at 473K (200C). The deuterium depth profile of (0.2-0.4) at. % up to 3 μm depth in this study agrees well with the profile (~0.5 at. % up to 3 μm depth) of Wampler and Doerner [8], however the deuterium concentration is much higher in this study considering the factor of 25 difference in damage level (0.025 dpa vs. 0.6 dpa).

The deuterium depth profiles at 773K (500 C) shows a significant amount (>0.1 at. % D/W) of deuterium is still trapped up to 5 μm in 0.025 dpa as shown in Figure 2(c). This observation of deuterium depth profile of (0.1-0.3) at. % up to 5 μm depth in this study is different from the results from high-energy ion-damage studies, which show the

decreasing trends of deuterium retention above 773K (500C) [2-5]. The result indicates that different trapping mechanisms exist for neutron-irradiated and unirradiated tungsten.

Figure 3 shows the comparison of deuterium retention from NRA with that from previously obtained TDS spectrum [9]. Note that the deuterium retention from NRA is partial deuterium retention within 5 μm, whereas that from TDS is total deuterium retention. For the NRA results from 0 dpa tungsten (shown in the open circles), the deuterium retention increases from 373K (100 C) to 473K (200 C), and then decreases significantly from 473K (200 C) to 773K (500 C), agreeing with the trend observed for the unirradiated tungsten in the literature [2-5]. This decrease is due to the detrapping from low energy trap sites during the plasma exposure.

For the NRA results from 0.025 dpa tungsten (shown in the solid circles), the deuterium retention increases significantly from 373K (100 C) to 473K (200 C), and then continue increasing from 473K (200 C) to 773K (500 C), indicating that different trapping mechanisms exist for neutron-irradiated and unirradiated tungsten. Through the deuterium retention from NRA agrees with that from TDS within an order of magnitude, the deuterium depth profile via NRA alone cannot represent the higher deuterium retention from TDS. Therefore, an attempt to adjust the peak deuterium concentration in the normalized NRA profile was used to fit the experimental TDS spectrum in this study.

Figure 4 shows the thermal desorption spectra and overlay of TMAP modeling data with 1.1 and 1.3 eV traps for unirradiated tungsten (0 dpa). The TMAP simulation using two traps (1.1 eV and 1.3 eV) with 0.17 and 0.15 at. % D/W concentration give a reasonable fit to the experimental TDS spectrum of 0 dpa at 200C and the combined trap

concentration (0.32 at.%) is higher than the experimental D/W concentration (0.1-0.2 at.%) determined by NRA.

Figure 5(a)-(c) also illustrates the thermal desorption spectra and overlay of TMAP modeling data with six traps (0.9, 1.1, 1.3, 1.5, 1.75, and 2.0 eV) for neutron-irradiated tungsten (0.025 dpa). The lower temperature part of the TDS spectrum is fitted with three lower detrapping energies (0.9, 1.1, and 1.3 eV) as shown in Figure 5(a), and the higher temperature part is analyzed with three higher detrapping energies (1.5, 1.75, and 2.0 eV) as shown in Figure 5(b). The solid lines denote the combined spectrum, and the dotted lines correspond to the spectrum from each trap site in Figure 5(a) and 5(b). The two TDS spectra in Figure 5(a) and 5(b) were combined to fit the entire temperature range of the experimental TDS spectrum as shown in Figure 5(c). The solid lines denotes for the combined spectrum, and the dotted lines correspond to the spectra from lower energy(0.9-1.3 eV) and higher energy (1.5-2.0eV). For the TDS spectrum of 0.025 dpa at 473K (200 C), six traps (0.9 ~ 2.0 eV) with (0.14~0.45) at.% D/W concentration are required to fit the experimental TDS and the combined trap concentration (1.3 at.%) is higher than the experimental D/W concentration (0.2-0.4 at.%) by NRA for 0.025 dpa at 473K (200C). Figure 6 shows deuterium retention from six different traps in 0 dpa and 0.025 dpa tungsten. The results show that the contribution from 1.1 and 1.3 eV did not change from 0 dpa to 0.025 dpa, and the remaining four (0.9, 1.5, 1.75, 2.0 eV) traps are induced by neutron-irradiation, confirming that different trapping mechanisms exist for neutron-irradiated and unirradiated tungsten.

5. Conclusions

The deuterium depth profiles in neutron-irradiated tungsten show deuterium trapping up to 3μm with (0.1-0.2) at. % D/W in 0.025 dpa and similar D/W concentrations from 0 dpa to 0.025 dpa at 373K (100 C), deuterium trapping up to 3μm with (0.2-0.4) at. % D/W in 0.025 dpa and (x2~4) higher D/W concentration in 0.025 dpa at 473K (200 C), and deuterium trapping up to 5 μm with (0.1-0.3) at. % D/W in 0.025 dpa at 773K (500C). A significant amount of deuterium (>0.1 at. % D/W) is still trapped in the bulk material in 0.025 dpa at 773K (500C), which differs from the high-energy ion damage results in the literature. The results indicate that different trapping mechanisms exist for neutron-irradiated and unirradiated tungsten.

Further investigation with TMAP7 simulation reveals that two traps (1.1 eV and 1.3 eV) with 0.17 and 0.15 at. % D/W concentration give a reasonable fit to the experimental TDS spectrum of 0 dpa at 473K (200 C) and the combined trap concentration (0.32 at.%) is higher than the experimental D/W concentration (0.1-0.2 at.%) by NRA. For the TDS spectrum of 0.025 dpa at 473K (200 C), six traps (0.9 ~ 2.0 eV) with (0.14~0.45) at.% D/W concentration are required to fit the experimental TDS and the combined trap concentration (1.3 at.%) is higher than the experimental D/W concentration (0.2-0.4 at.%) by NRA for 0.025 dpa at 473K (200C). Four (0.9, 1.5, 1.75, 2.0 eV) traps are induced by neutron-irradiation, confirming that different trapping mechanisms exist for neutron-irradiated and unirradiated tungsten.

This paper illustrates the difference in trapping mechanisms between high-energy ion bombardment and neutron-irradiation, suggesting the effort to correlate among high-energy ions, fission neutrons, and fusion neutrons is crucial for accurately estimating

tritium retention under neutron-irradiation environment along with detailed microstructure analysis such as TEM observations and positron analysis.

Acknowledgement

This work was prepared for the U.S. Department of Energy, Office of Fusion Energy Sciences, under the DOE Idaho Field Office contract number DE-AC07-05ID14517. This work is a part of the collaborative research between Japan and the U.S. with TITAN (Tritium, Irradiation and Thermofluids for America and Nippon) project.

References

[1] Iida, H., Khripunov, V., Petrizzi, L., and Federici, G., *2004 ITER Nuclear Analysis Report* G 73 DDD 2 W 0

[2] Wampler, W.R., and Doerner, R., *Nucl. Fusion* **49** (2009) 115023

[3] Tyburska, B., Alimov, V.Kh., Ogorodnikova, O.V., Schmid, and K., Ertl, K., *J. Nucl. Mater*. **395**, (2009) 1150

[4] Fukumoto, M., Kashiwagi, H., Ohtsuka, Y., Ueda, Y., Taniguchi, M., Inoue, T., Sakamoto, K., Yagyu, J., Arai, T., Takagi, I., and Kawamura, T., *J. Nucl. Mater.* **390-391** (2009) 572

[5] Wright, G.M., Mayer, M., Ertl, K., de Saint-Aubin, G., and Rapp, J., *Nucl. Fusion* **50** (2010) 075006

[6] van Veen, A., Filius, H.A., De Vries, J., Bijkerk, K.R., Rozing, G.J., and Segers, D., *J. Nucl. Mater.* **155-157** (1988) 1113

[7] Oliver, B.M., Causey, R.A., and Maloy, S.A., *J. Nucl. Mater.* **329-333** (2004) 977

[8] Ishino, S., Schiller, P., and Rowcliffe, A.F., *J. Fusion. Energy.* **8** (1989) 147

[9] Shimada, M., Hatano, Y., Calderoni, P., Oda, T., Oya, Y., Sokolov, M., Zhang, K., Cao, G., Kolasinski, R.D., and Sharpe, J.P., *J. Nucl. Mater., doi:10.1016/j.jnucmat.2010.11.050*

[10] Oda, T., Shimada, M., Zhang, K., Calderoni, P., Oya, Y., Sokolov, M., Cao, G., Kolasinski, R.D., Sharpe, J.P., and Hatano, Y., *in the proceedings of TRITIUM 2010 conference (2010)*

[11] Keys, L.K., and Moteff, J., *J. Nucl. Mater.* **34** (1970) 260

[12] Mayer, M., Gauthier, E., Sugiyama, K., and von Toussaint, U., *Nucl. Instr. and Meth B* **267** (2009) 506

[13] Mayer, M., SIMNRA User's Guide, Tech. Rep. IPP 9/113, Garching, 1997. <http://www.rzg.mpg.de/~mam>.

[14] Poon, M., Haasz, A.A., and Davis, J.W., *J. Nucl. Mater.* **374** (2008) 390

[15] Longhurst, G.R., *TMAP7: "Tritium Migration Analysis Program", User Manual, Idaho National Laboratory,* INEEL/EXT-04-02352, Rev. 2 (2008)

[16] Frauenfelder, R., *J. Vac. Sci. Technol.* **6** (1969) 388

[17] Causey, R.A., *J. Nucl. Mater.* **300** (2002) 91

[18] Anderl, R.A., Holland, D.F., Longhurst, G.R., Pawelko, R.J., Trybus, C.L., and Sellers, C.H., *Fusion Technol.* **21** (1992) 745

[19] Ogorodnikova, O.V., Roth, J., and Mayer, M., *J. Appl. Phys.* **103** (2008) 034902

[20] Eleveld, H., and van Veen, A., *J. Nucl. Mater.* **191-194** (1992) 433

[21] Eleveld, H., and van Veen, A., *J. Nucl. Mater.* **212-215** (1994) 1421

Figure Captions

Figure 1: Optical microscope images of 0 dpa and 0.025 dpa tungsten

Figure 2: Deuterium depth profiles in 0 dpa and 0.025 dpa tungsten

Figure 3: Comparison of deuterium retention between NRA and TDS

Figure 4: TMAP simulation of TDS spectrum for 0 dpa at 200C

Figure 5: TMAP simulation of TDS spectrum for 0.025 dpa at 200C, (a): simulation with the lower three traps (0.9, 1.1, 1.3 eV), (b): simulation with the higher three traps (1.5, 1.75, 2.0 eV), (c): combined simulation spectrum of (a) and (b)

Figure 6: Deuterium retention from six different traps in 0 dpa and 0.025 dpa tungsten

Figures

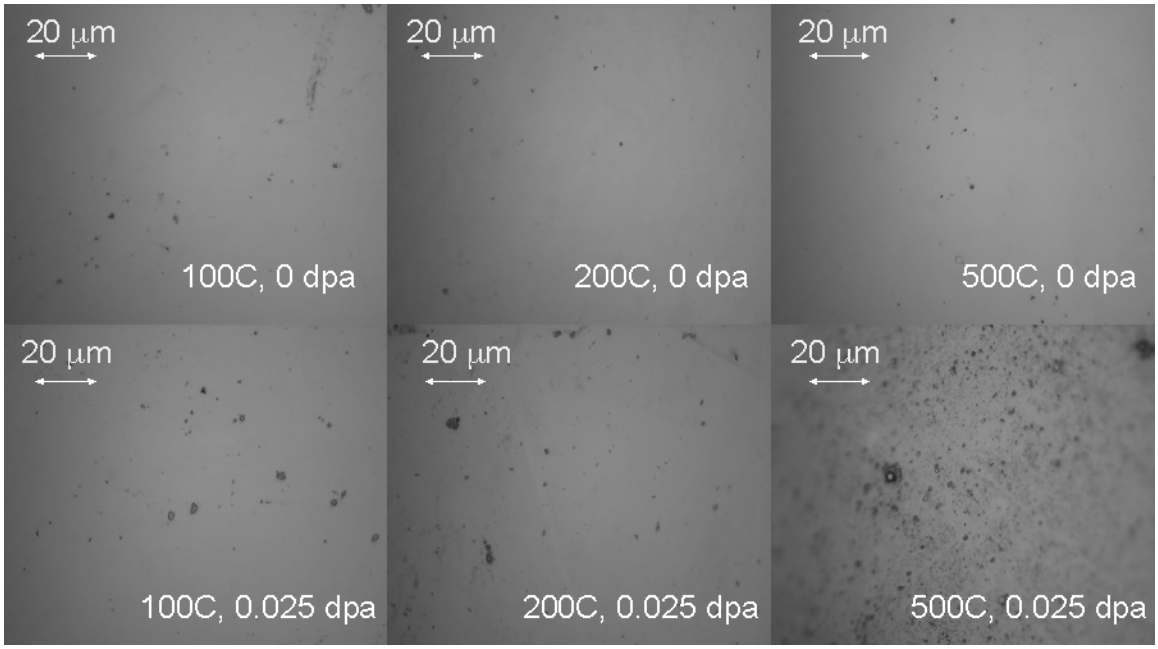

Figure 1 (M. Shimada et al, PFMC13, Physica Scripta)

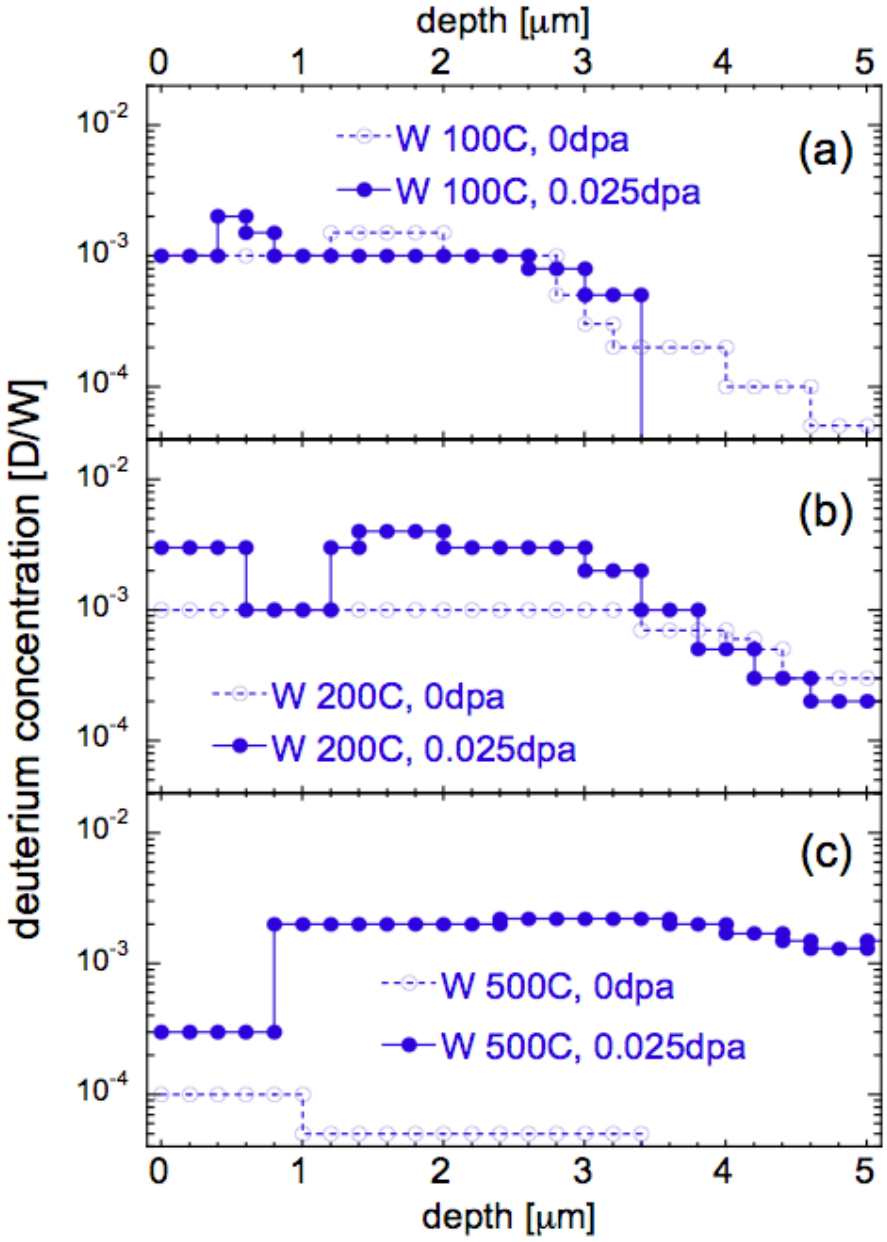

Figure 2 (M. Shimada et al, PFMC13, Physica Scripta)

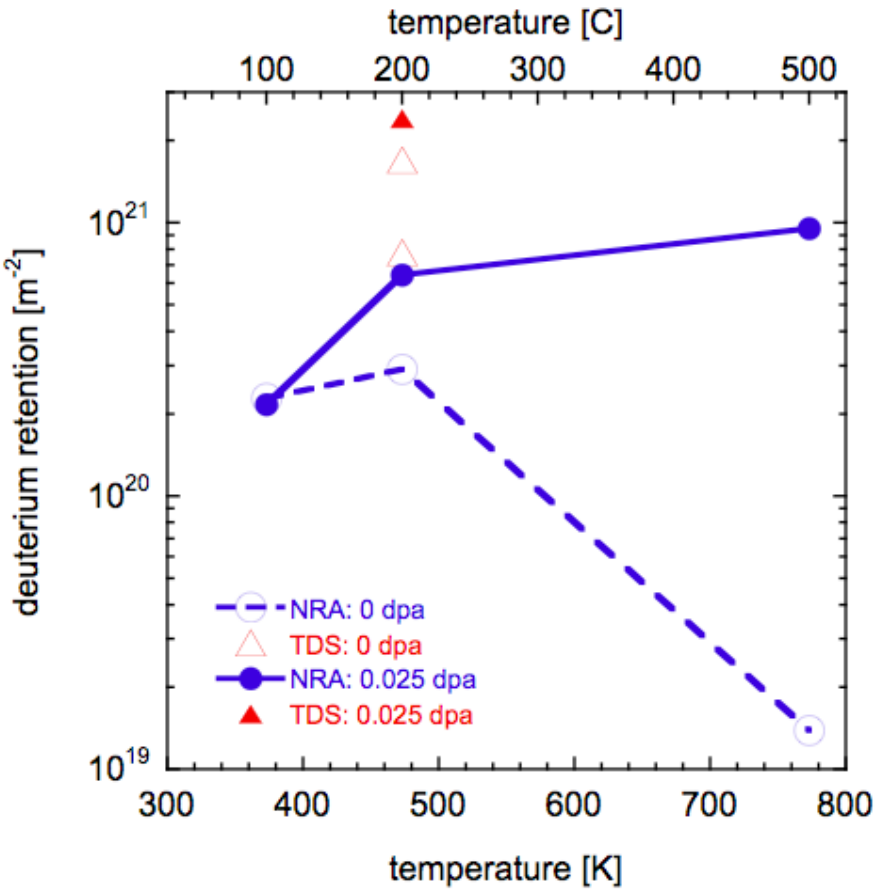

Figure 3 (M. Shimada et al, PFMC13, Physica Scripta)

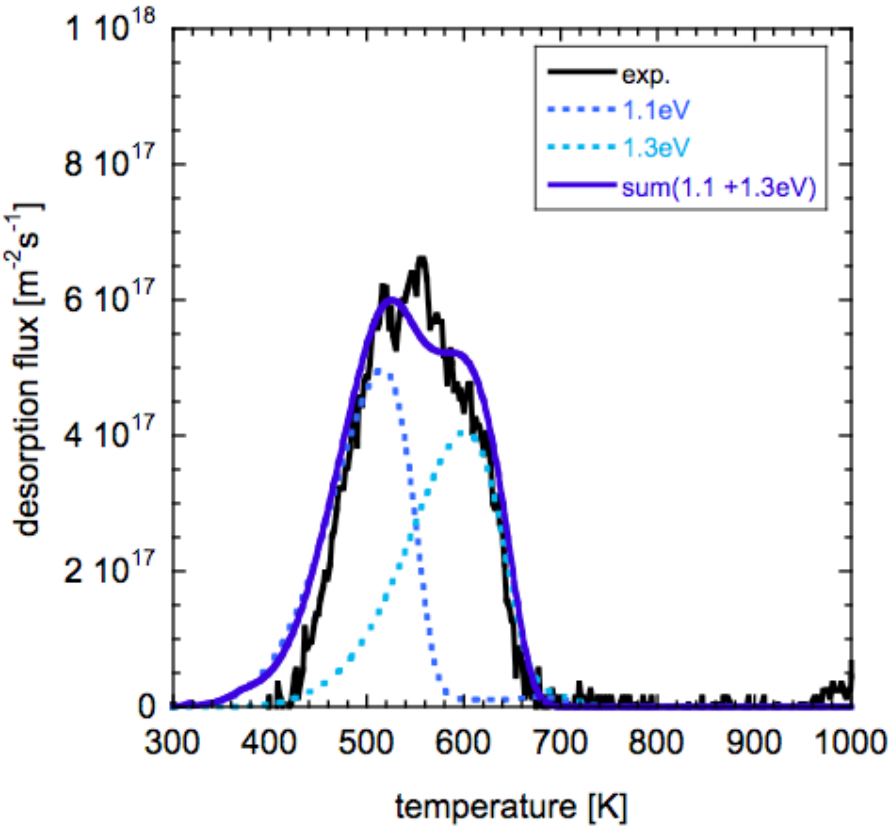

Figure 4 (M. Shimada et al, PFMC13, Physica Scripta)

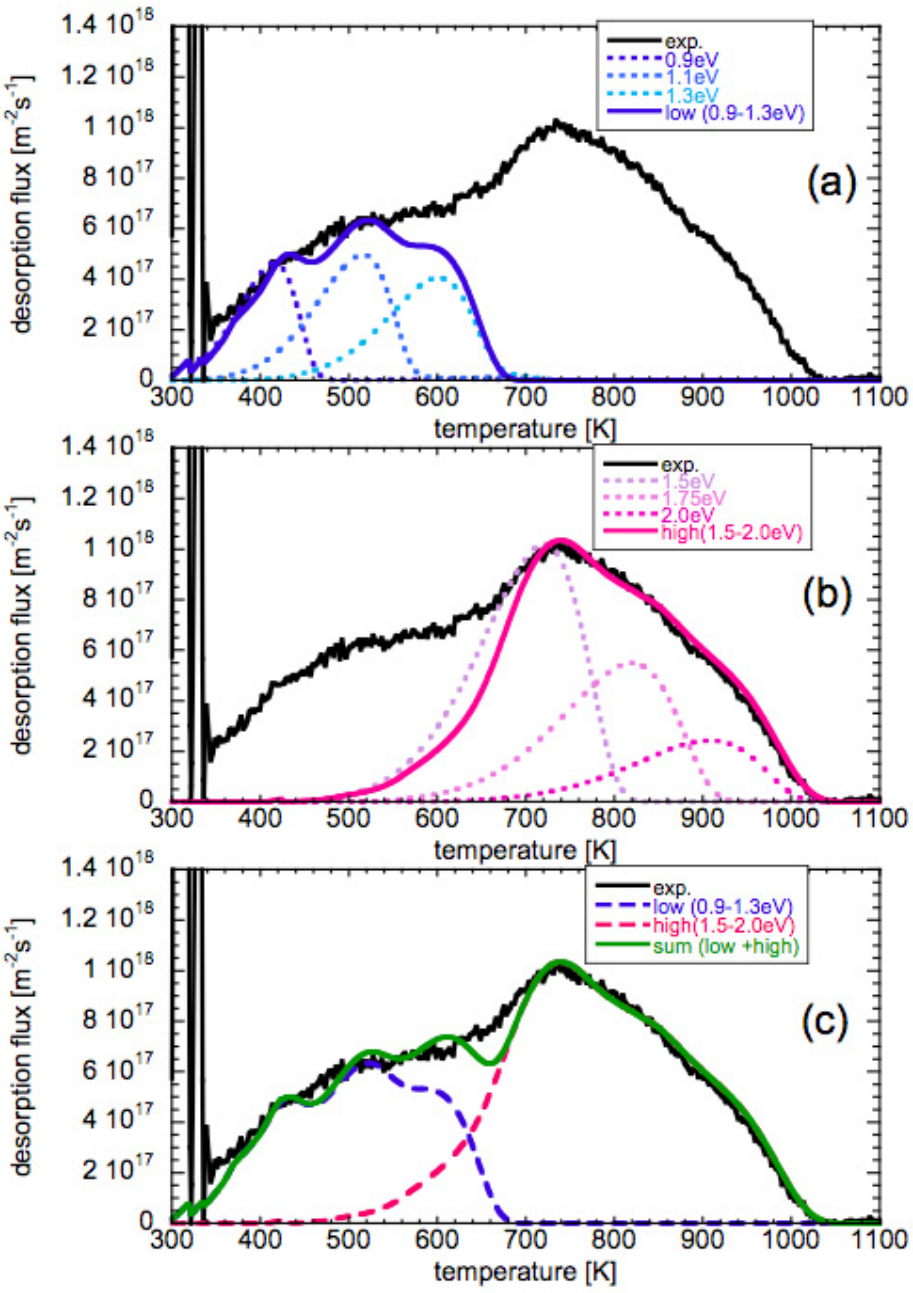

Figure 5 (M. Shimada et al, PFMC13, Physica Scripta)

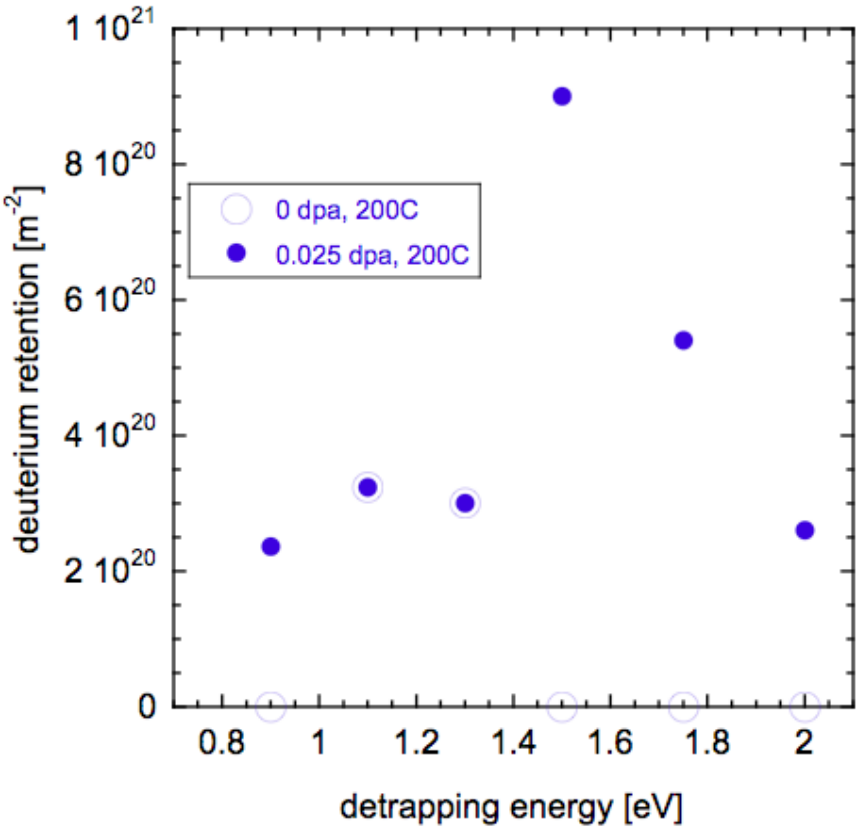

Figure 6 (M. Shimada et al, PFMC13, Physica Scripta)