Hydrogen retention in self-damaged and He-irradiated tungsten for PFC: update on the recent results

Sabina Markelj, Anže Založnik, Primož Vavpetič,
Mitja Kelemen, Primož Pelicon, Iztok Čadež
Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia

In collaboration with:

Thomas Schwarz-Selinger, Klaus Schmid
Max-Planck-Institut für Plasmaphysik, Garching, Germany

Ethiene Hodille, Christian Grisolia
CEA, IRFM, F-13108 Saint Paul Lez Durance, France

This work has been carried out within the framework of the EUROfusion Consortium and has received funding from the Euratom research and training programme 2014-2018 under grant agreement No 633053. The views and opinions expressed herein do not necessarily reflect those of the European Commission.

Outline

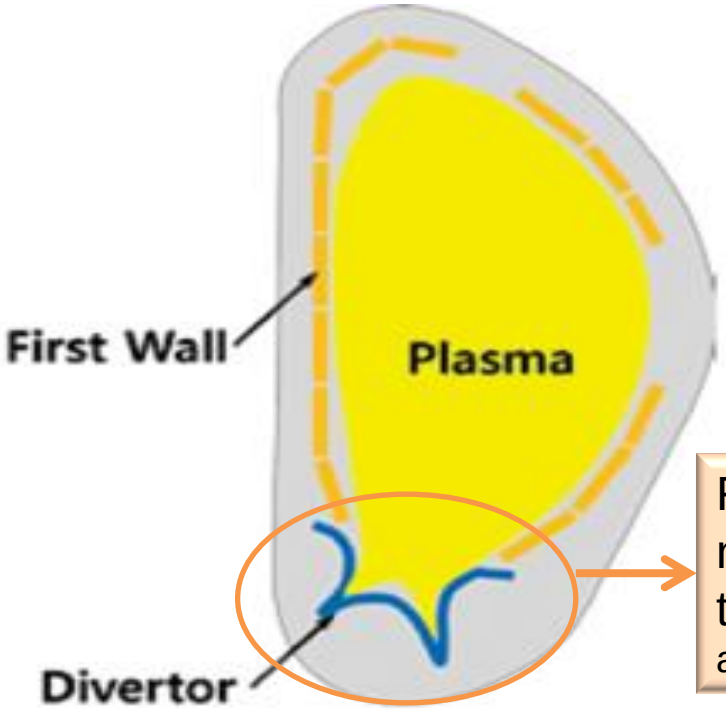
- Part 1: In situ benchmark experiments on hydrogen retention in self-damaged tungsten: Uptake, transport, dynamic retention, isotope exchange
- Part 2: Study of deuterium retention in tungsten simultaneously damaged by high energy W ions and loaded by D
- Part 3: Influence of He on deuterium retention
- Conclusions and motivation for further studies in each part

In situ benchmark experiments on hydrogen retention in self-damaged tungsten: Uptake, transport, dynamic retention, isotope exchange

CRP Objective 4: to perform coordinated experiments and computations to improve the knowledge base on the influence of tungsten microstructure on tritium retention and tritium transport properties

Motivation – Part 1

Plasma wall interaction involves molecular, atomic and ionic species with a broad energy range few eV - keV



Fluxes of low energy neutrals in divertor up to 10^{24} D/m^{2}s [Roth et al. JNM 390 (2009) 1]

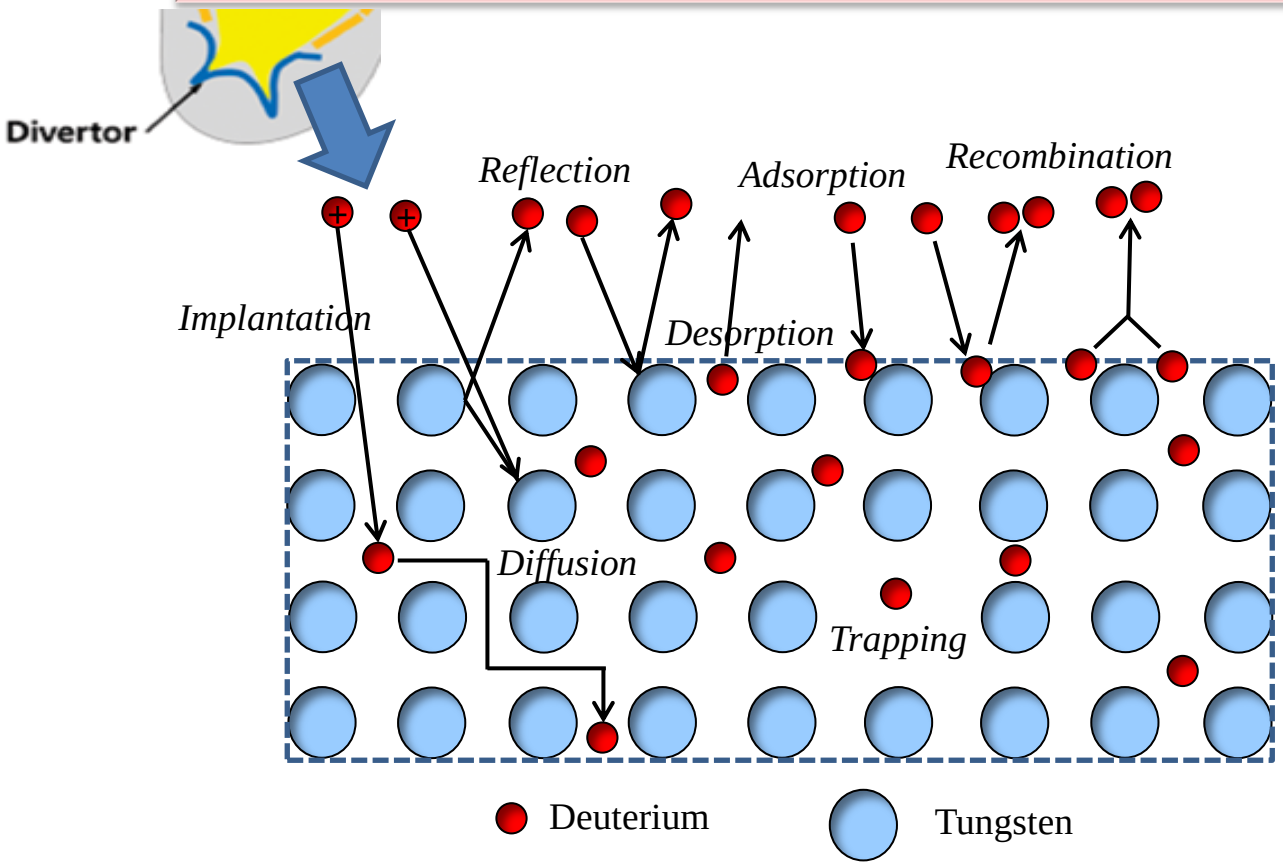
Tungsten interaction with neutrals - hydrogen isotope atoms

- The simplest possible specie
- Large fluxes of neutrals in divertor and remote areas
- Need to understand also atom/molecule interaction to predict tritium retention in fusion reactor

➢ **Goal: in depth understanding of tritium retention in W-based materials**

Motivation –Part 1

Plasma wall interaction involves molecular, atomic and ionic species with a broad energy range

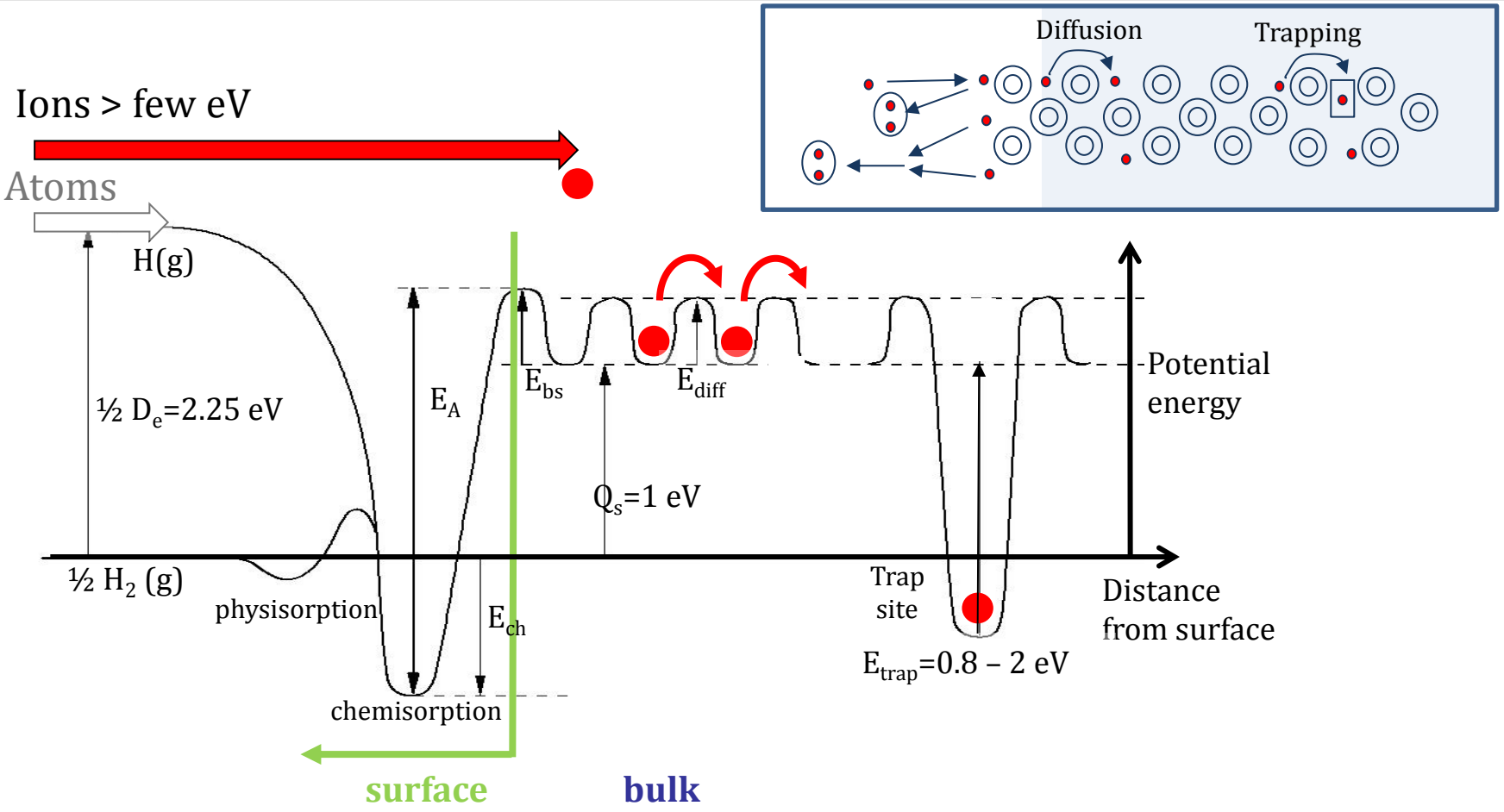


Tungsten interaction with neutrals - hydrogen isotope atoms

- Starting with low D atom flux in 10^{18}-10^{19} D/m^{2}s range
- Set-up a laboratory model system to benchmark modelling codes – extrapolating to large flux

➢ **Goal: in depth understanding of tritium retention in W-based materials**

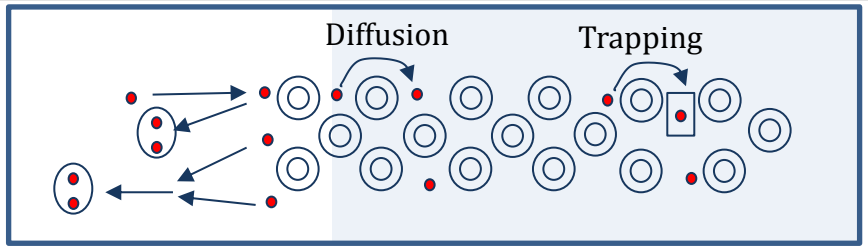
Processes: atoms versus ions

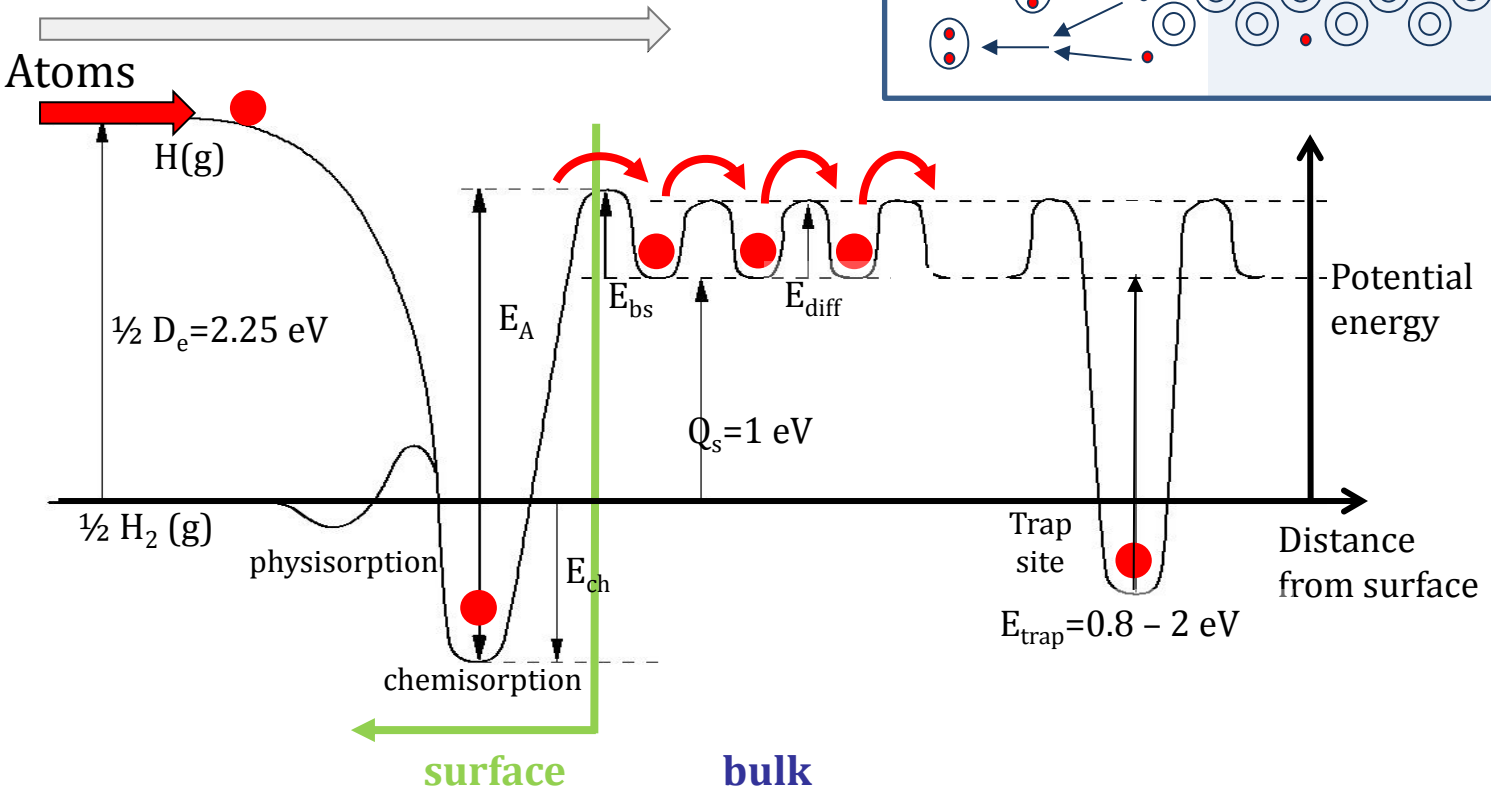


- Direct ion implantation
- Large hydrogen concentration in the lattice at implantation depth - possible defect creation due to local stress (ion-induced traps)

Processes: atoms versus ions

D atoms - most gentle way of loading





W bulk parameters

E_{diff} =0.39 eV

Q_s= 1.04 eV

$E_A = Q_S + E_{ch} + E_{bs}$

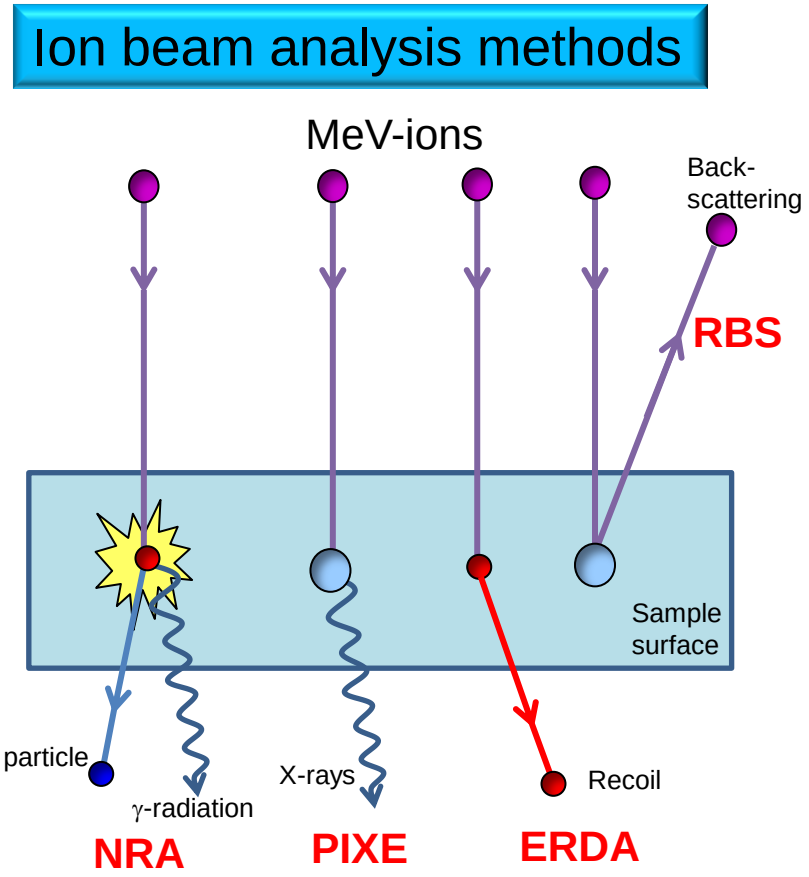
$E_A \approx 2$ eV

[Frauenfelder 1969 *J. Vac. Sci. Technol.*]

- No additional defect production
- Separate implantation effects from transport and trapping at defects
- High E_A → no transport of D atoms into bulk at low temperatures < 700 K

In situ studies by ion beam methods

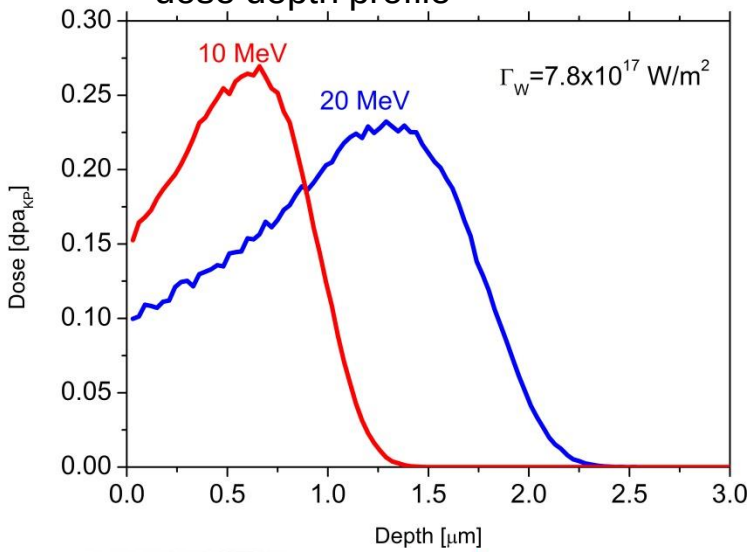
- *Möller et al. NIM B 136 (1998) 1203: Dynamic in situ diagnostics using high energy ion beam analysis* - "MeV ion beam is presented as a powerful tool for in situ, real-time process diagnostics…"
- No transport trough air between sample exposure and analysis – no contamination
- Possibility to study the dynamics of processes on the surface and in the bulk
- Measurements of all parameters - computer control of the system
- **Possibility of analysing beam effect** – damage production and He effect

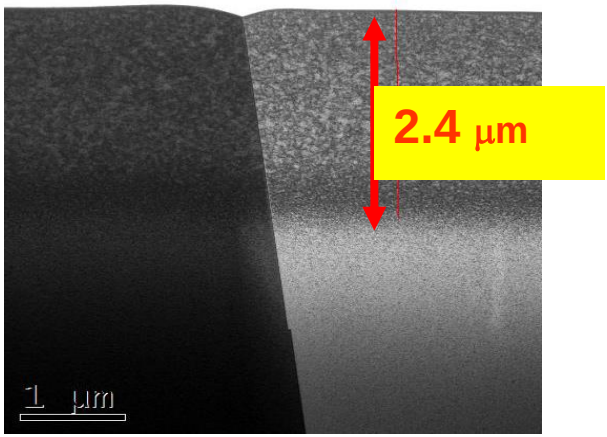


New: *in situ* study on **self-damaged tungsten** and exposure to deuterium **atoms**

Method: Use of self-damaged tungsten material + Nuclear reaction analysis (NRA) + HABS

SRIM calculation of damage dose depth profile





ScanningTransmission Electron Microscopy (STEM) [L. Ciupinski et al. NIM B 317 (2013) 159]

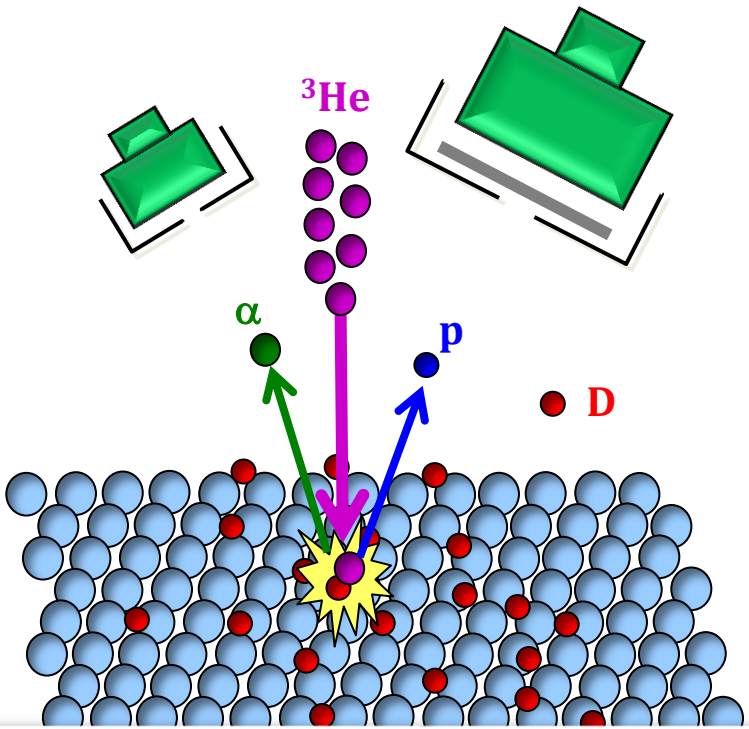
➢ High energy ion damaging

- High energy (20 MeV) W ion irradiation = self-damaging
- Surrogate for neutron damaging
- Damage creation - few μm
- Increased fuel retention in ion damaged W material from ~ 10^{-3} at. % ↗ ~ 1 at. %
- D retention saturated at ≥ 0.25 dpa
- Possibilities to study hydrogen isotope uptake/transport/isotope exchange in bulk

The damage layer serves as a "getter layer"
→ D retention - a way to determine the trap concentrations

Method: Use of self-damaged tungsten material + Nuclear reaction analysis (NRA) + HABS

Deuterium detection by ^{3}He NRA

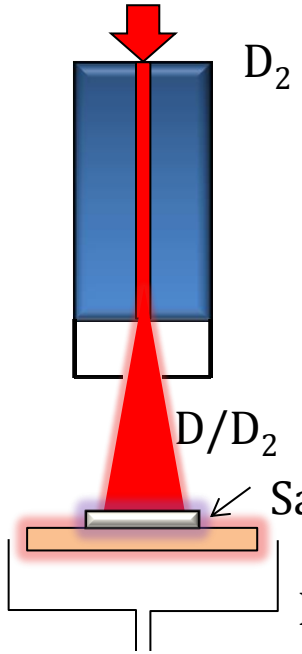


Nuclear reaction to probe ^{2}H = D:

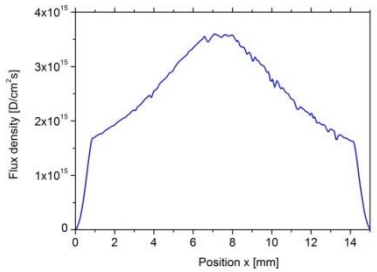
- ^{3}He + D → ^{4}He + p

(Q=18.352MeV; p energy 11-14 MeV)
Broad resonance peak near E(^{3}He) ≈ 0.63 MeV (FWHM 730 keV)

Hydrogen Atom Beam Source = HABS



D atom flux density profile



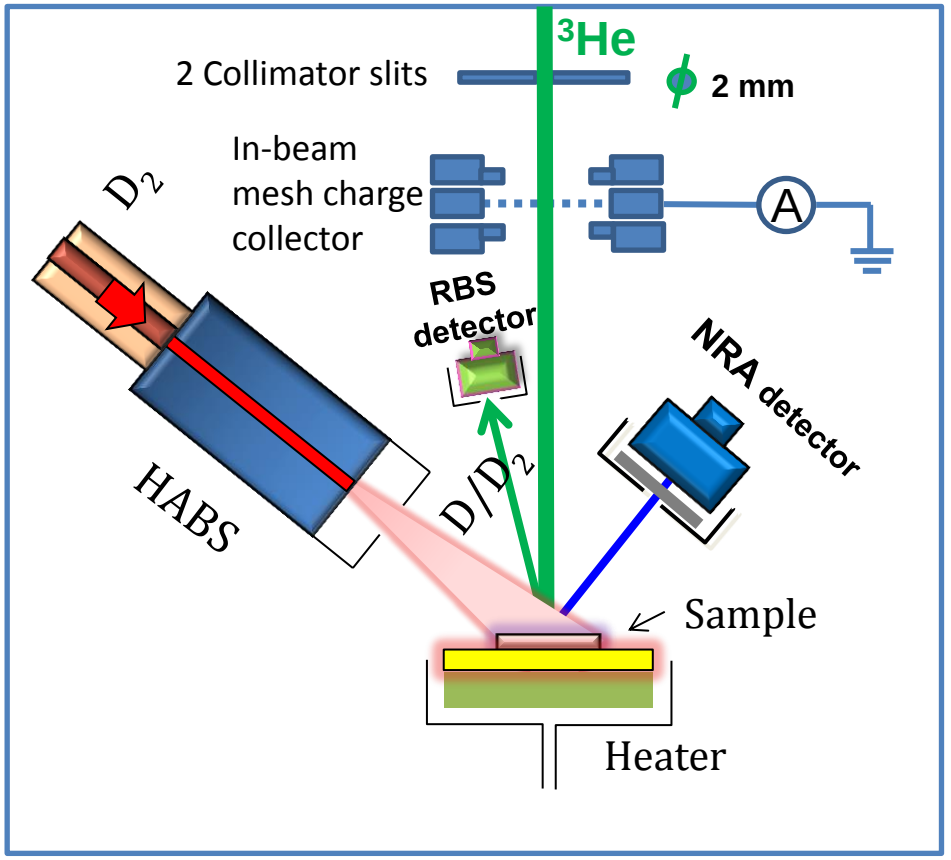
- Energy 0.28 eV/D (2150 K)
- Dissociation rate 30-50 %
- Atom flux: $4x10^{18}$ – $3x10^{19}$ D/m^{2}s
- Atom fluence: 10^{20}-10^{24} D/m^2

Studies with deuterium → extrapolation to tritium

Method: Use of self-damaged tungsten material + Nuclear reaction analysis (NRA) + HABS

- Recrystallized W sample damaged by 20 MeV W ions, Damage dose: 0.25 dpa_{KP}
- Exposure to D atom beam @ 600 K for 48 h.
- D atom beam flux density: 5.8×10^{18} D/m^2 s.

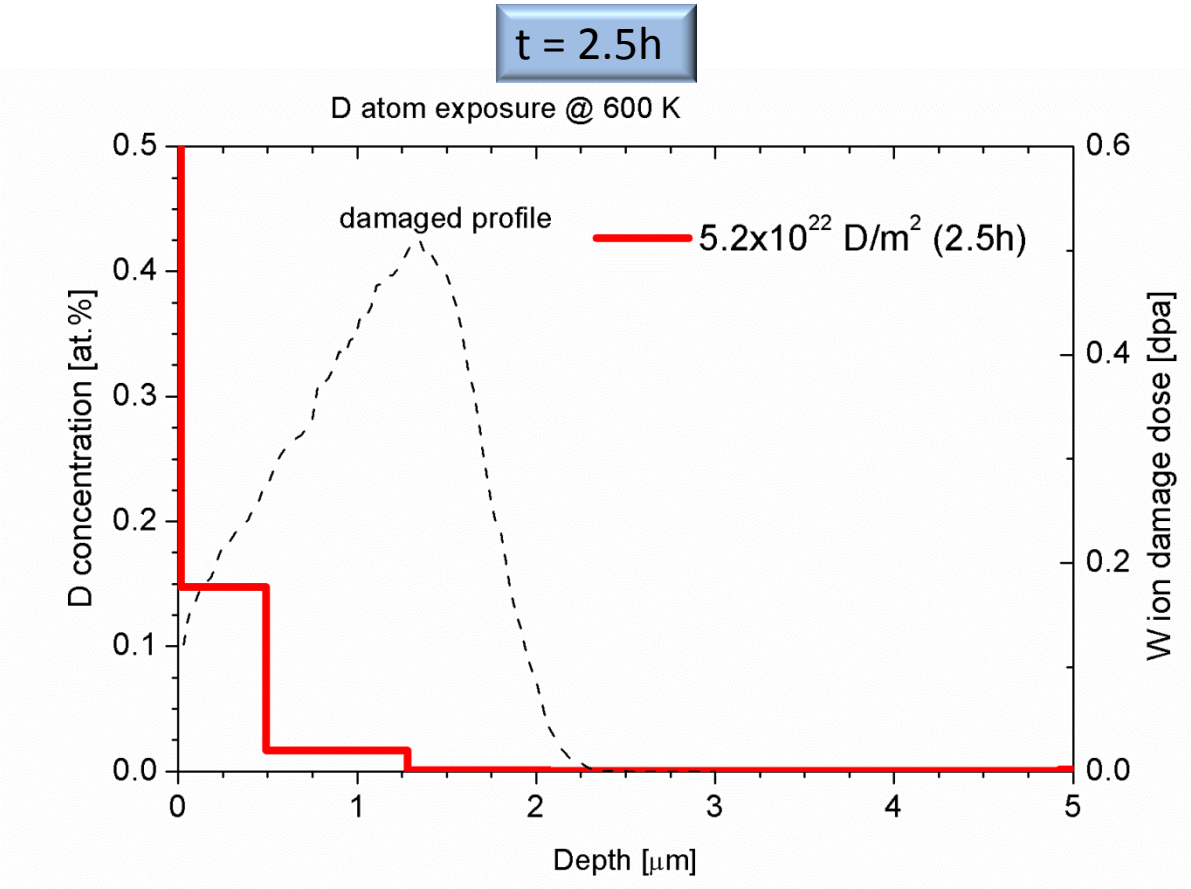
In situ studies by ^{3}He NRA



Deuterium depth profiles - Analyzing protons from nuclear reaction D(^{3}He,p)^{4}He at different ^{3}He energies from 700 keV up to 4.3 MeV

D loading of self-damaged W by D atom exposure

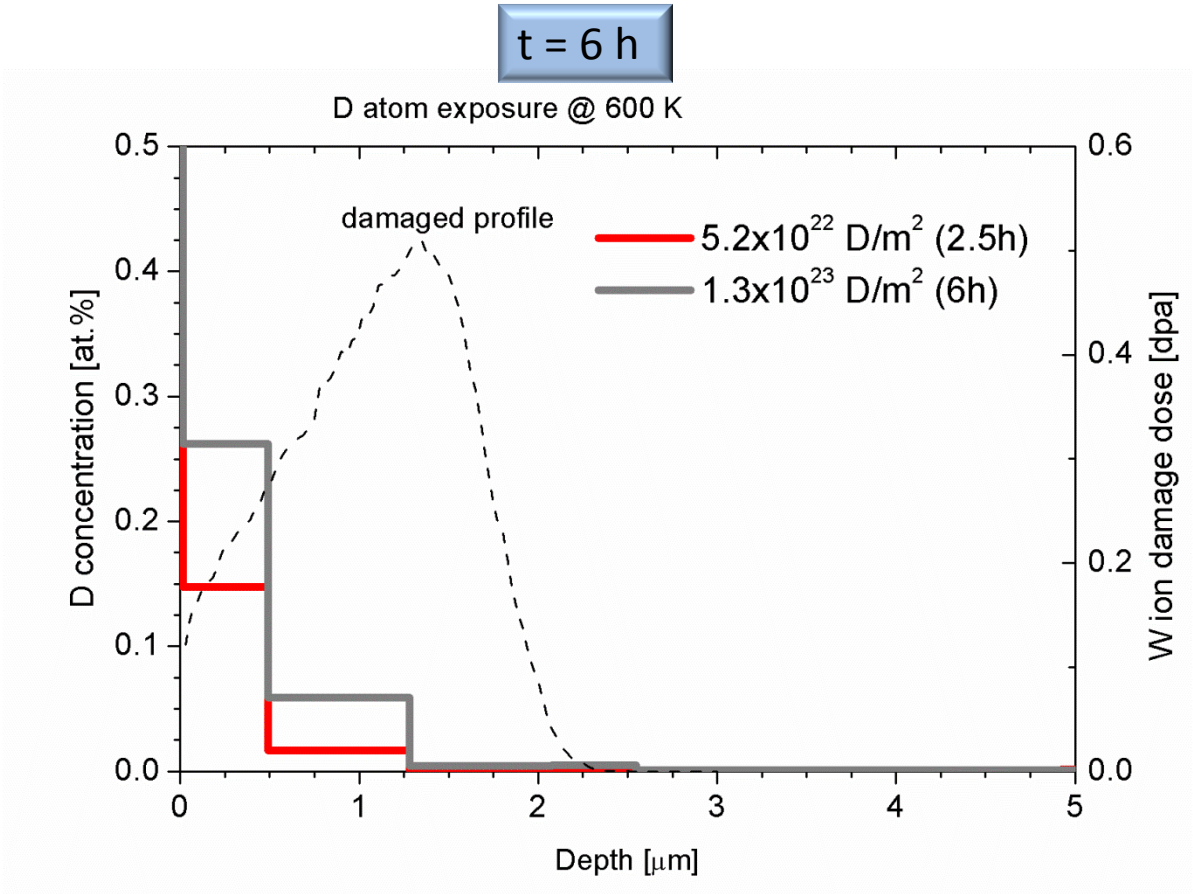
- **D atom loading - filling of damaged area by D atoms.**



For more information see: Markelj et al. JNM 469 (2016) 133

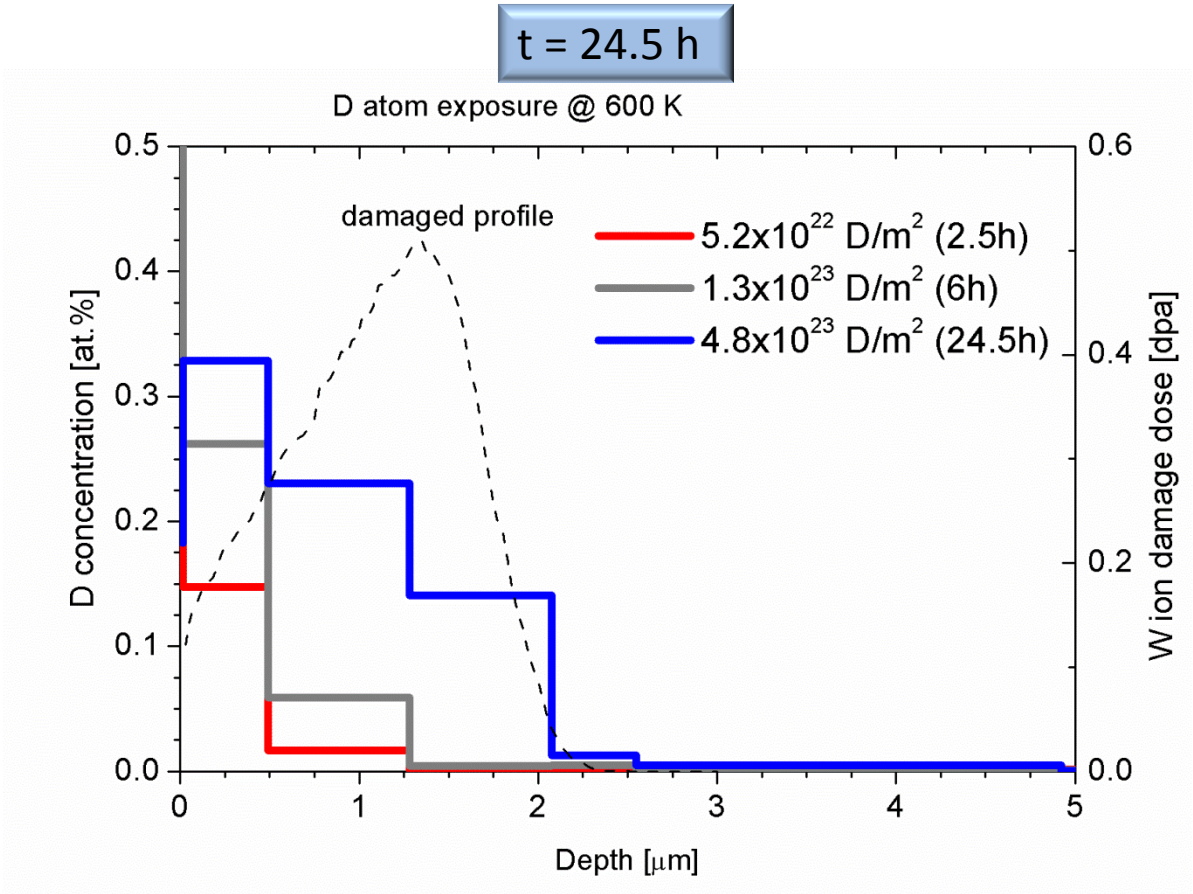
D loading of self-damaged W by D atom exposure

- **D atom loading - filling of damaged area by D atoms.**



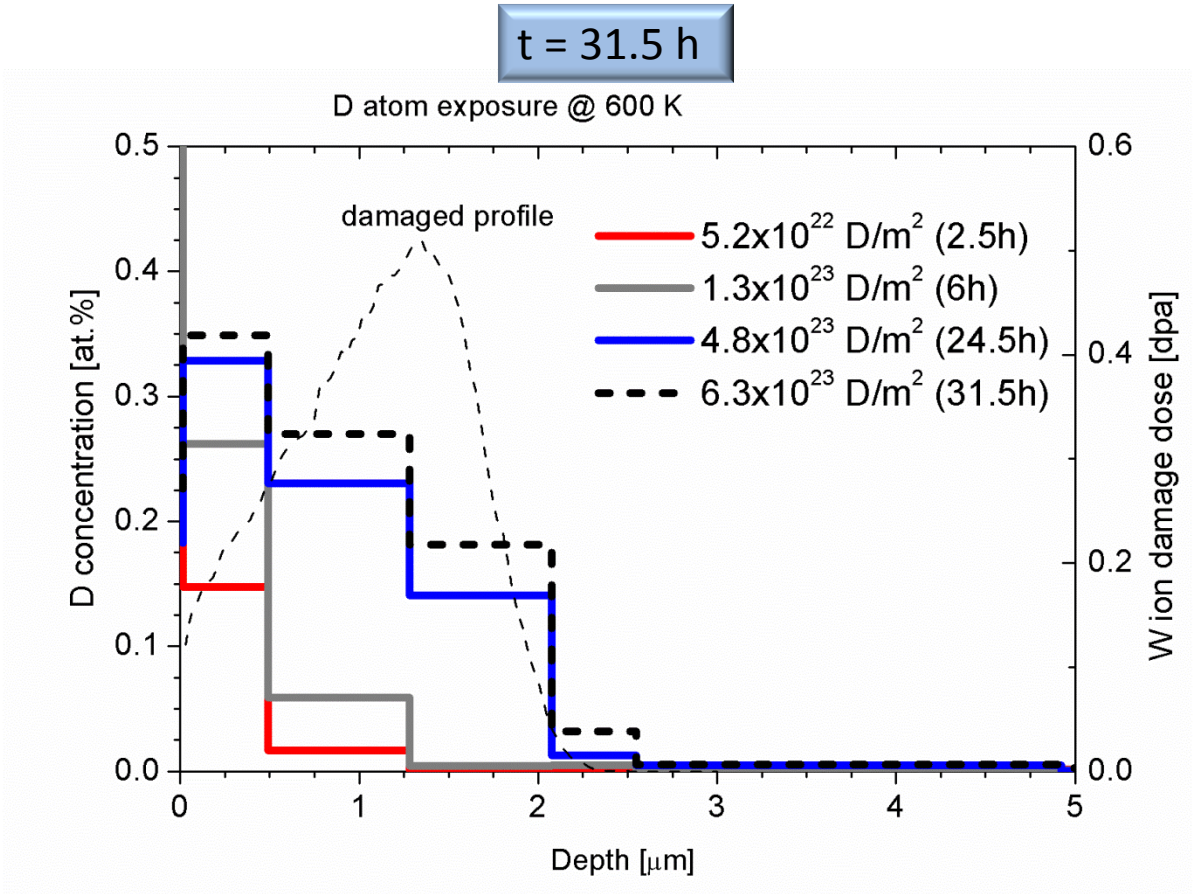
D loading of self-damaged W by D atom exposure

- **D atom loading - filling of damaged area by D atoms.**



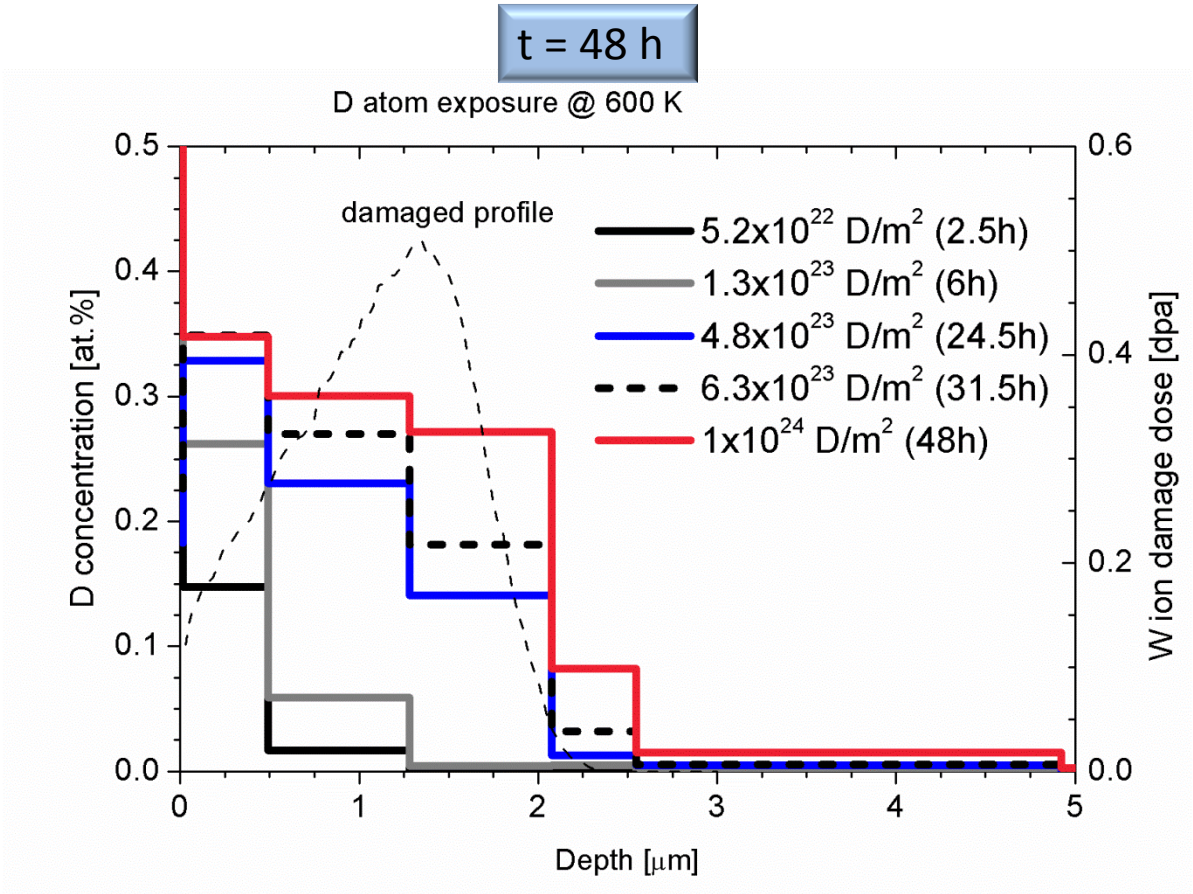
D loading of self-damaged W by D atom exposure

- **D atom loading - filling of damaged area by D atoms.**



D loading of self-damaged W by D atom exposure

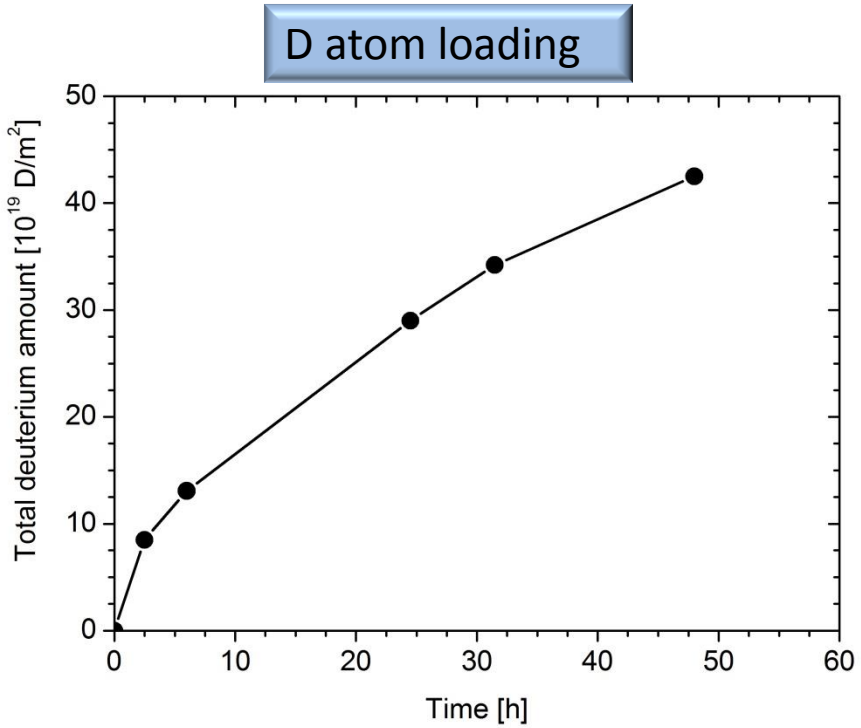
- **D atom loading - filling of damaged area by D atoms.**



D loading of self-damaged W by D atom exposure

D atom loading - filling of damaged area by D atoms.

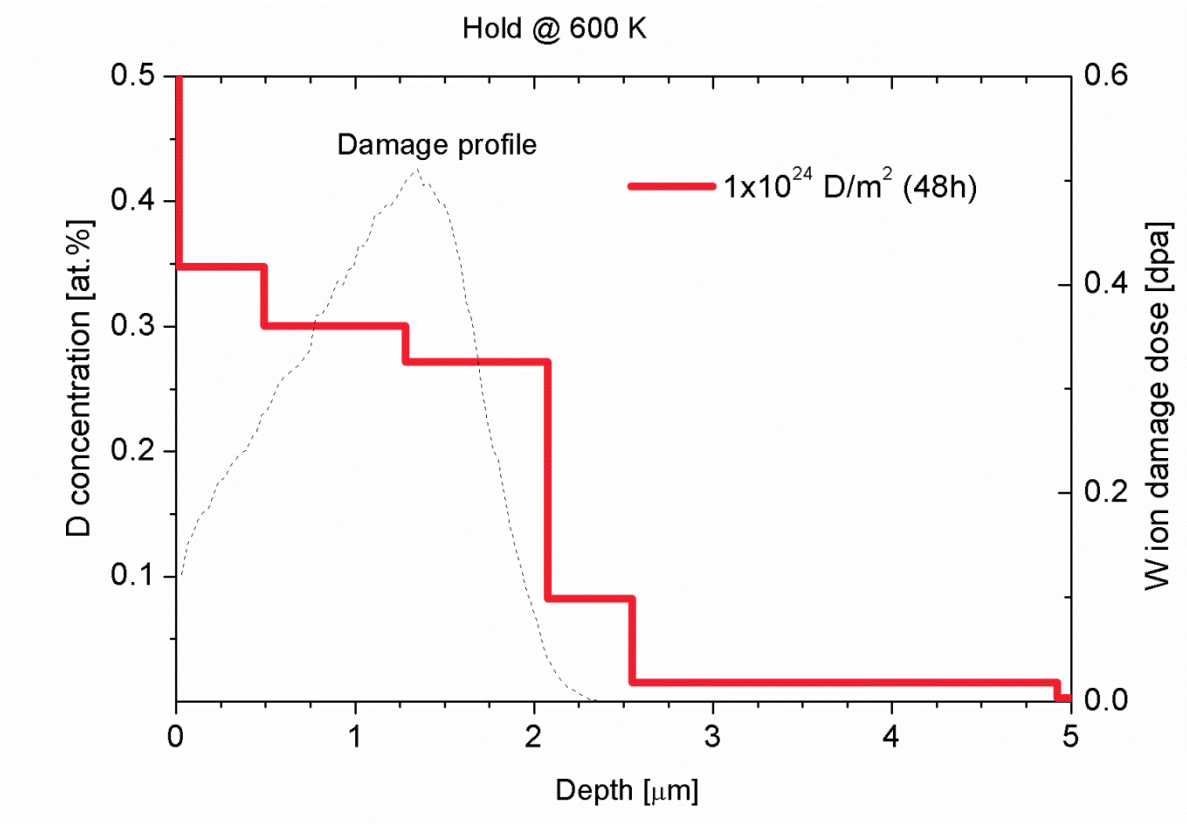
- Total fluence 1.0×10^{24} D/m^2
- D total amounts in damaged layer



- Atoms do penetrate into the bulk
- Deuterium transport is dominated by trapping into traps created by W ion damaging

Dynamic retention @ 600 K

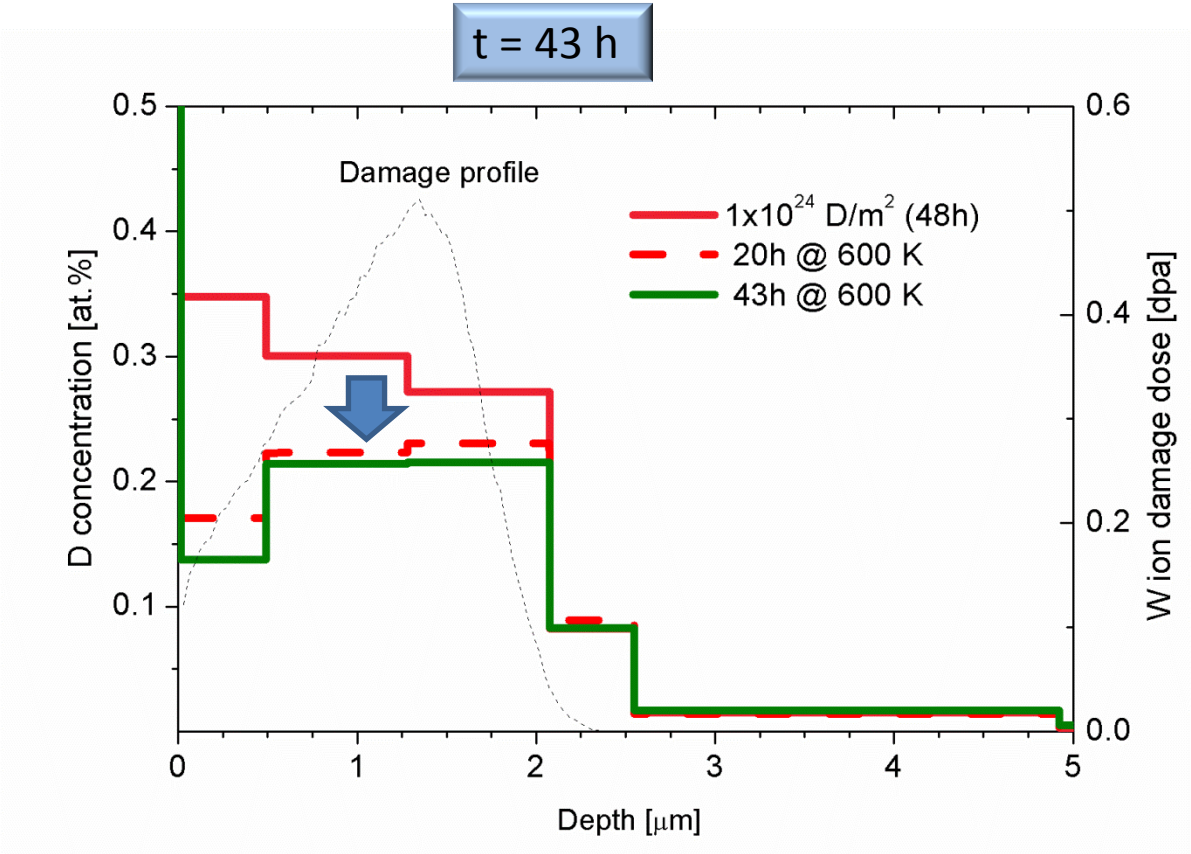
How much of D is dynamically released during the exchange at 600 K?



Dynamic retention @ 600 K

Study of dynamic release

- Sample held at 600 K for 43 h

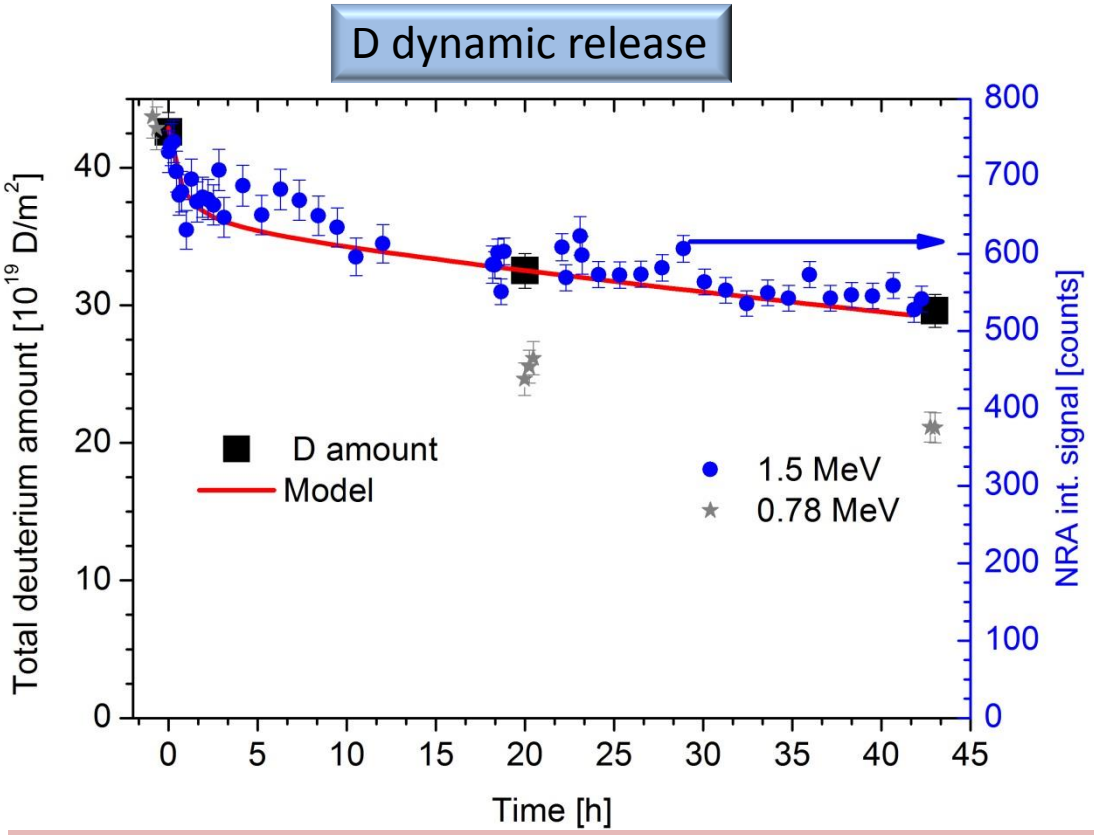


Dynamic retention @ 600 K

- Atomic beam switch off; Study of dynamic release for 43 h at 600 K

➢ 30% decrease in total D amount in damaged layer after 43h

➢ 68% decrease during the isotope exchange @ 43h

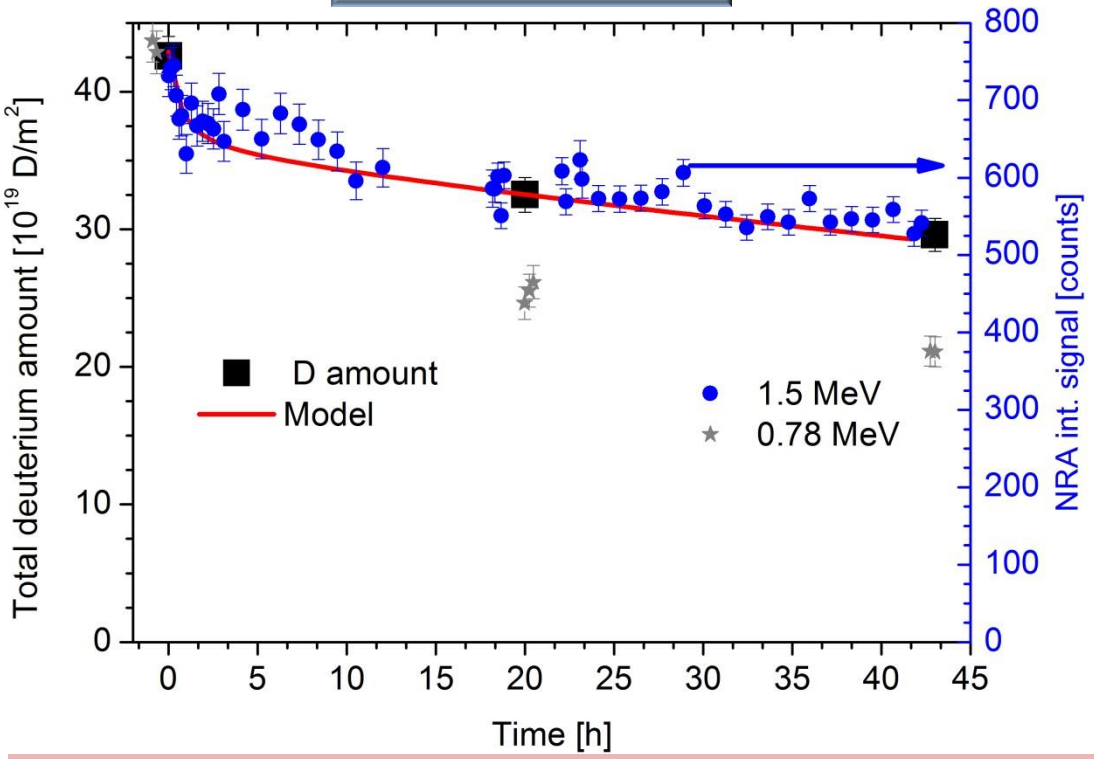


For more information see: Markelj et al. JNM 469 (2016) 133

Dynamic retention @ 600 K

- Atomic beam switch off; Study of dynamic release for 43 h at 600 K
- ➢ 30% decrease in total D amount in damaged layer after 43h
- ➢ 68% decrease during the isotope exchange @ 43h

D dynamic release



Can we model what was observed in the experiment?

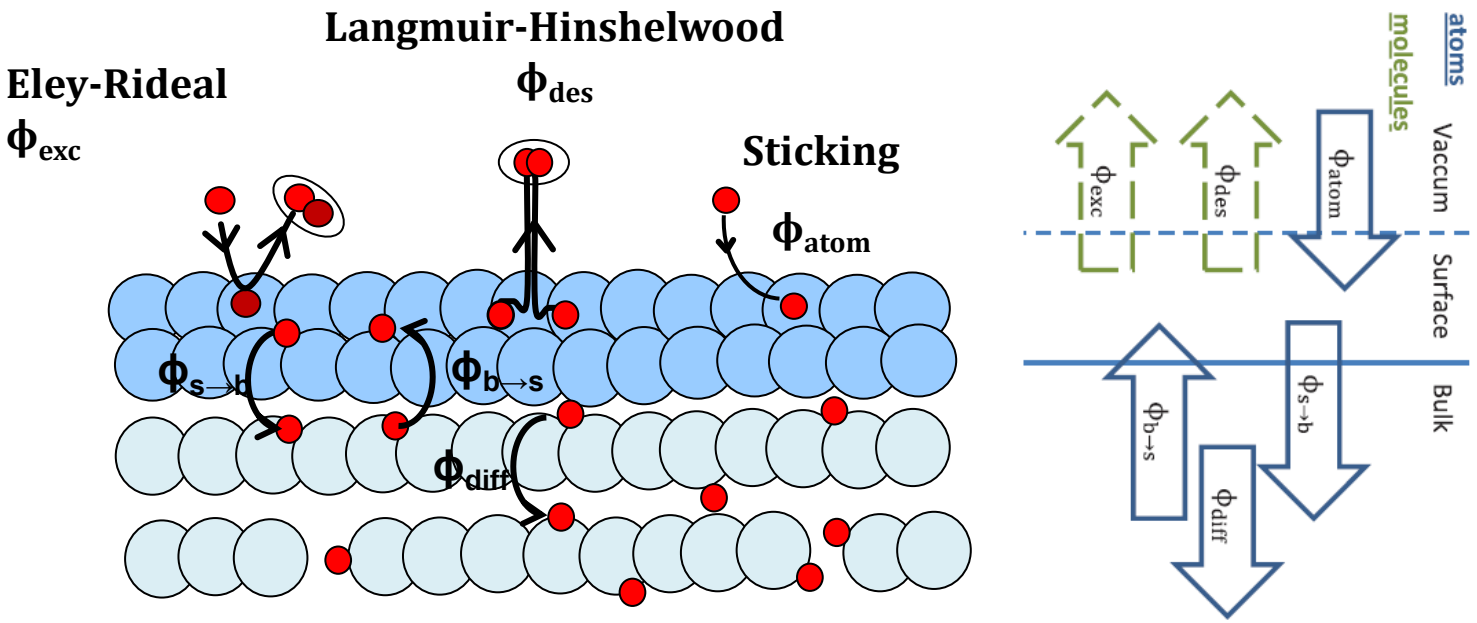
Do we understand all the mechanisms?

For more information see: Markelj et al. JNM 469 (2016) 133

Modelling experimental results by rate equation model

Rate equation model

- ➢ The MHIMS code – developed at CEA (C. Grisolia, E. Hodille) to model bulk H trapping/detrapping and diffusion [Hodille at al., JNM 467 (2015) 424]
- ✓ New: Included surface processes
- ➢ Determination of parameters by modelling the experimental data



Modelling experimental results by rate equation model

- The MHIMS code - surface processes + bulk trapping/detrapping and diffusion

Modelling results:

- ✓ **Trap concentration and trapping energy obtained from the annealing study (D depth profile and TDS spectra)** [Založnik et al. Phys. Scripta T167 (2015) 014031]
- Surface parameters determined by varying the parameters and from literature
- ✓ Simulation of depth profiles shown before

D atom loading

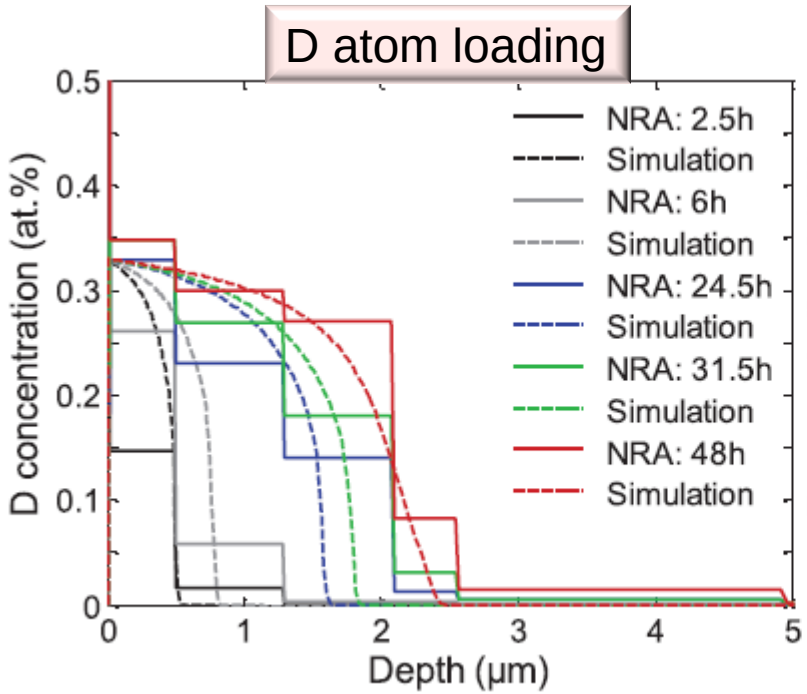
Dynamic release

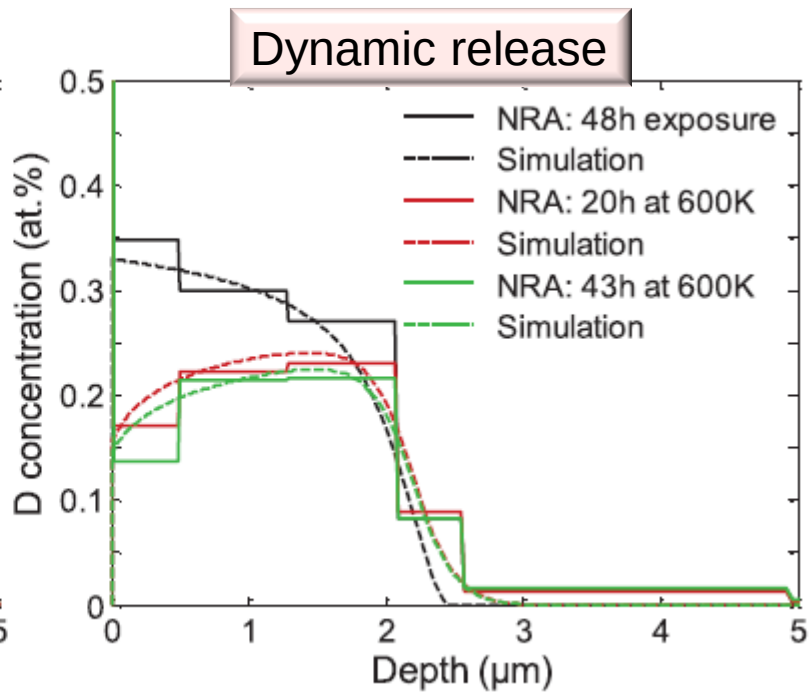
Modelling experimental results by rate equation model

- The MHIMS code - surface processes + bulk trapping/detrapping and diffusion

Modelling results:

- ✓ **Trap concentration and trapping energy obtained from the annealing study (D depth profile and TDS spectra)** [Založnik et al. Phys. Scripta T167 (2015) 014031]
- Surface parameters determined by varying the parameters and from literature
- ✓ Simulation of depth profiles shown before - Good agreement





Details in: Hodille et al. Nucl. Fus. 57 (2017) 056002

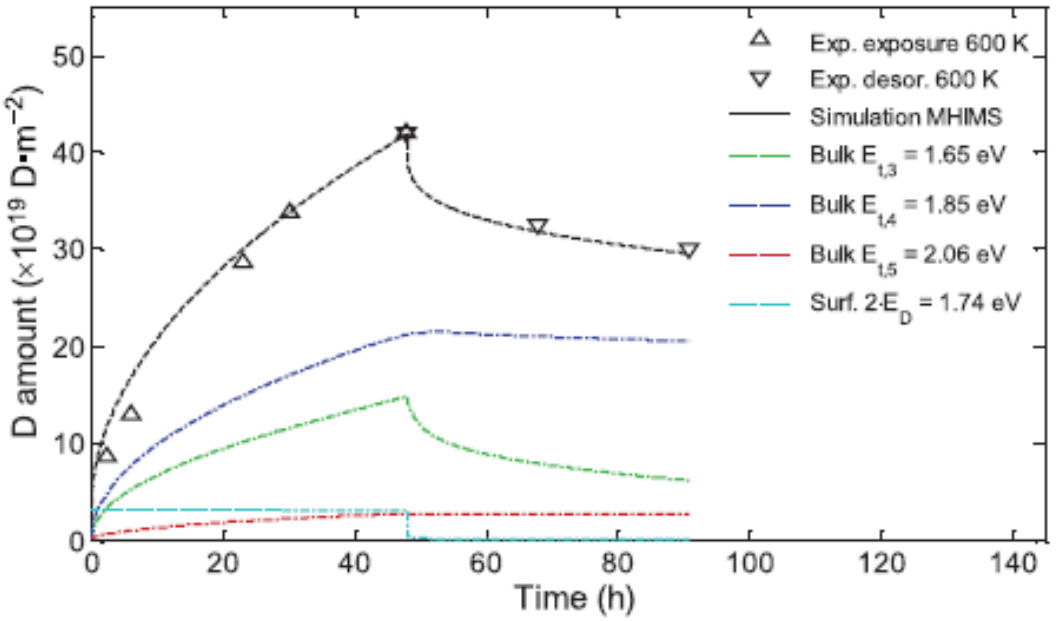
Modelling experimental results by rate equation model

- The MHIMS code - surface processes + bulk trapping/detrapping and diffusion

Modelling results:

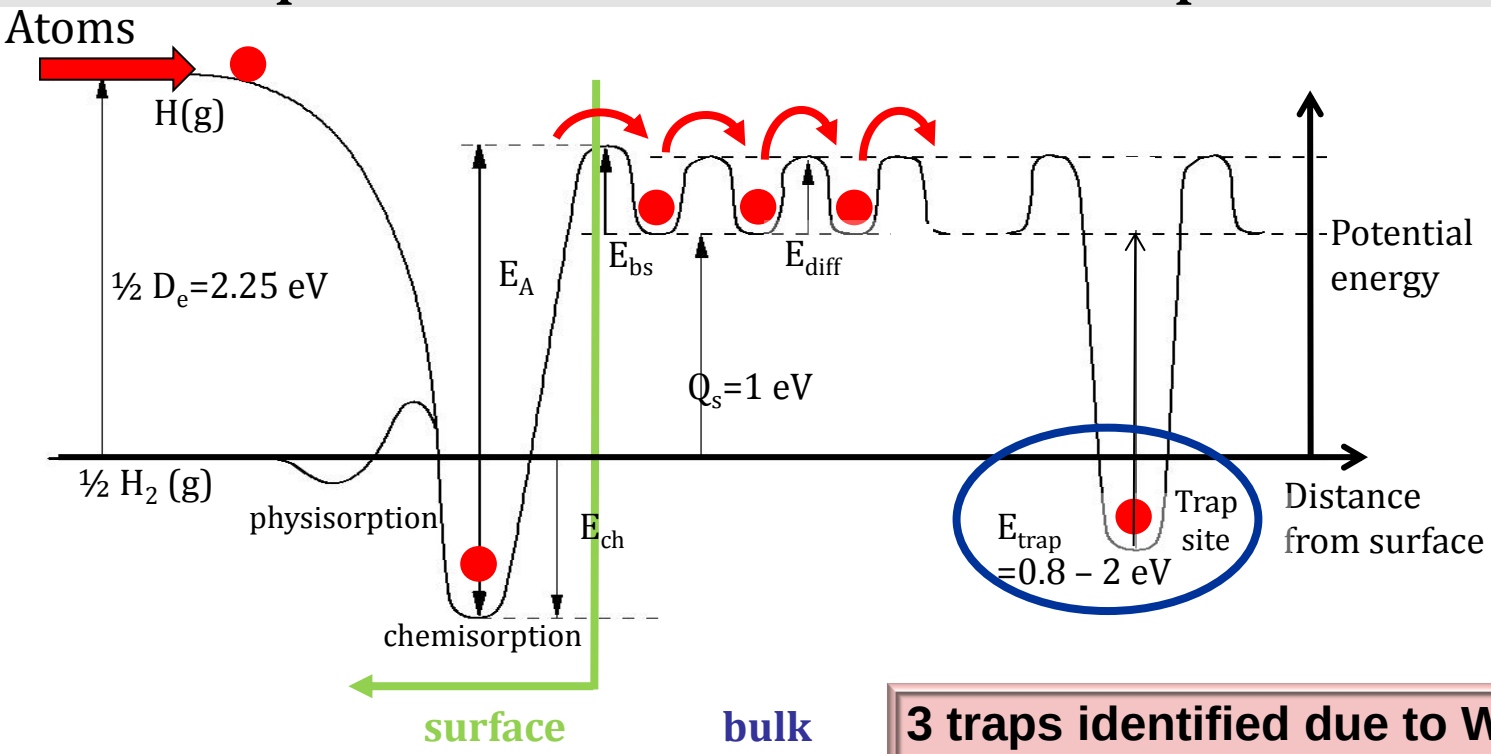
- ✓ **Trap concentration and trapping energy obtained from the annealing study (D depth profile and TDS spectra)** [Založnik et al. Phys. Scripta T167 (2015) 014031]
- Surface parameters determined by varying the parameters and from literature
- ✓ Extraction of D total amount from loading + dynamic release - Good agreement

Total amounts



Details in: Hodille et al. Nucl. Fus. 57 (2017) 056002

Modelling experimental results by rate equation model – determined parameters



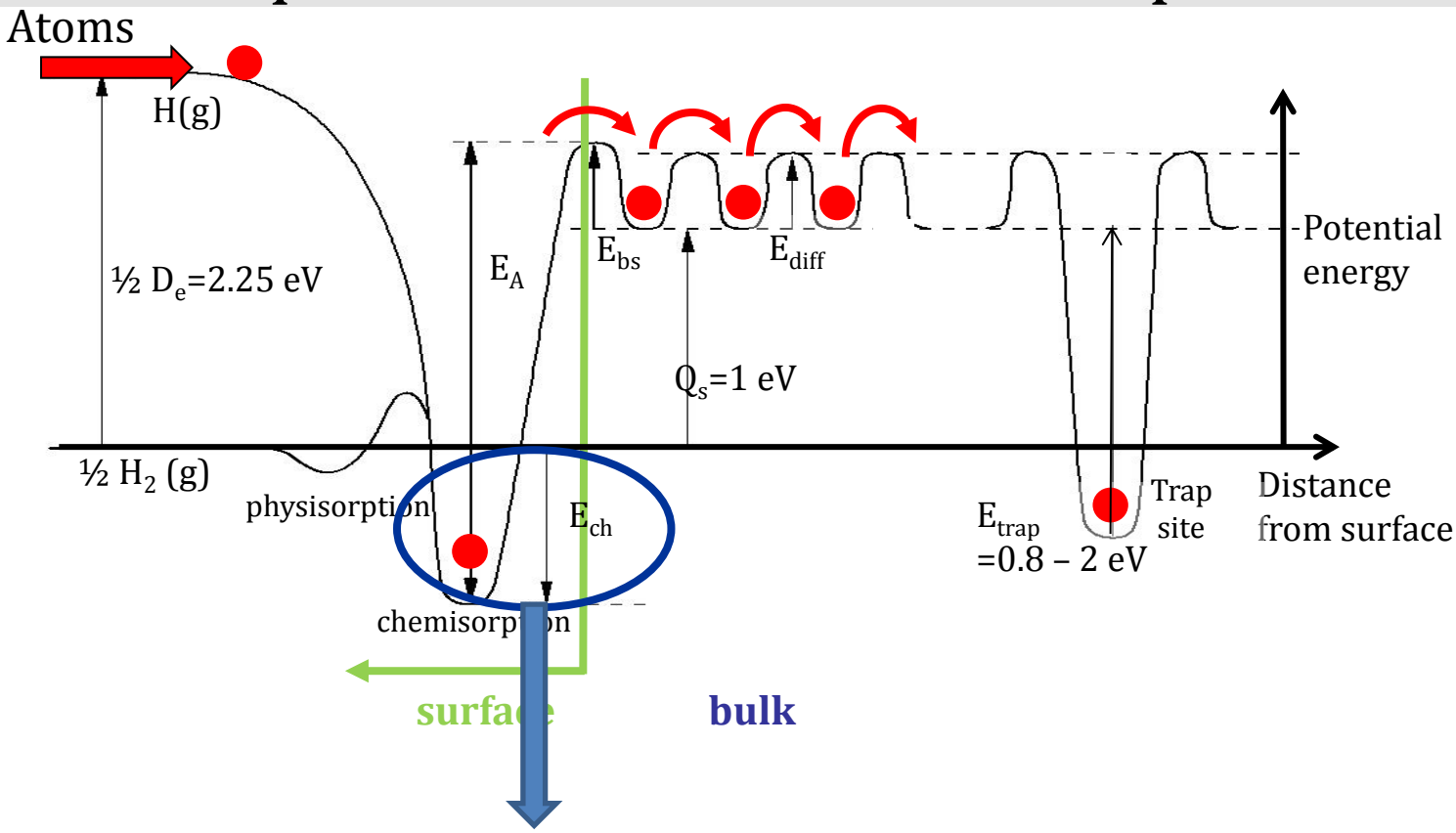
E$_{diff}$ =0.2 eV
[DFT - Fernandez et al. 2015 *Acta Mater.* **94** 307]
E$_{bs}$= E$_{diff}$

3 traps identified due to W ion damaging

E$_t$ = 1.65 eV jogged dislocation line
E$_t$ = 1.85 eV dislocation loop
E$_t$ = 2.06 eV cavity

- **In agreement with literature** ['t Hoen et al. NF 53 (2013); Ogorodnikova et al. JAP 118 (2015), JAP 119 (2016)]

Modelling experimental results by rate equation model – determined parameters



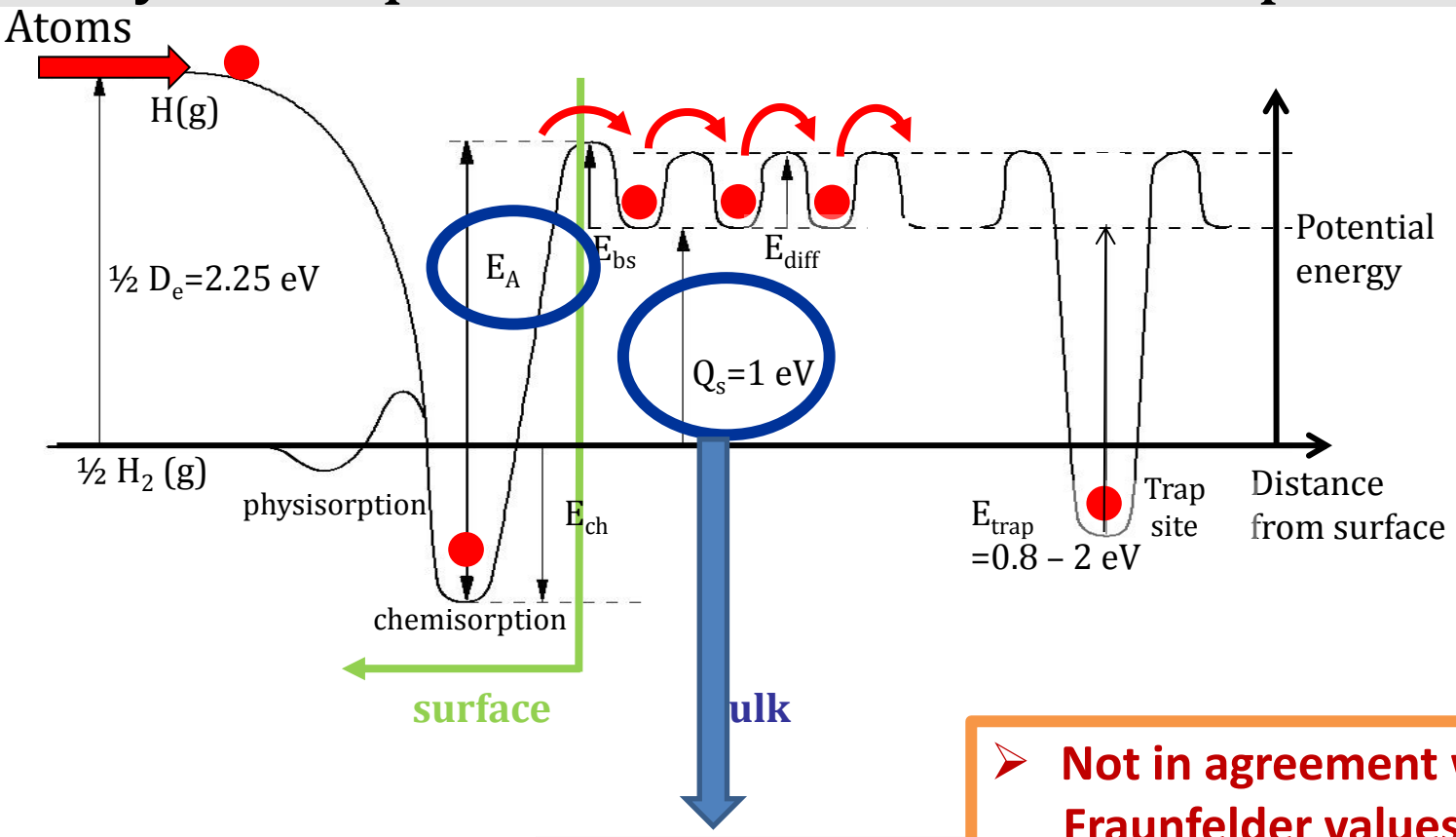
E$_{diff}$ =0.2 eV
[DFT - Fernandez et al. 2015 *Acta Mater.* **94** 307]

E$_{bs}$= E$_{diff}$

E$_{ch}$ = 0.69 eV & 0.87 eV

➢ **In agreement with literature**
[Tamm & Schmid JCP 45 (1971) 4775; Markelj et al. ASS 282 (2013) 478]

Modelling experimental results by rate equation model – determined parameters



E$_{diff}$ =0.2 eV
[DFT - Fernandez et al. 2015 *Acta Mater.* **94** 307]
E$_{bs}$= E$_{diff}$

E$_A$ = 1.33 /1.55 eV
→ Q$_s$ = 0.44/0.48 eV

- **Not in agreement with Fraunfelder values**
  E$_A$≈ 2 eV → Q$_s$=1.04 eV
- **Experiment: Gas loading of tungsten at high temperatures**
  [Frauenfelder R. 1969 *J. Vac. Sci. Technol.* **6** 388]

Modelling experimental results by rate equation model – conclusions

What have learned

- We "understand" and can model the experimental results - the agreement is very good

✓ **For more details see: Markelj et al. JNM 469 (2016) 133 - experiment**
Hodille et al. Nucl. Fus. 57 (2017) 056002 - modelling

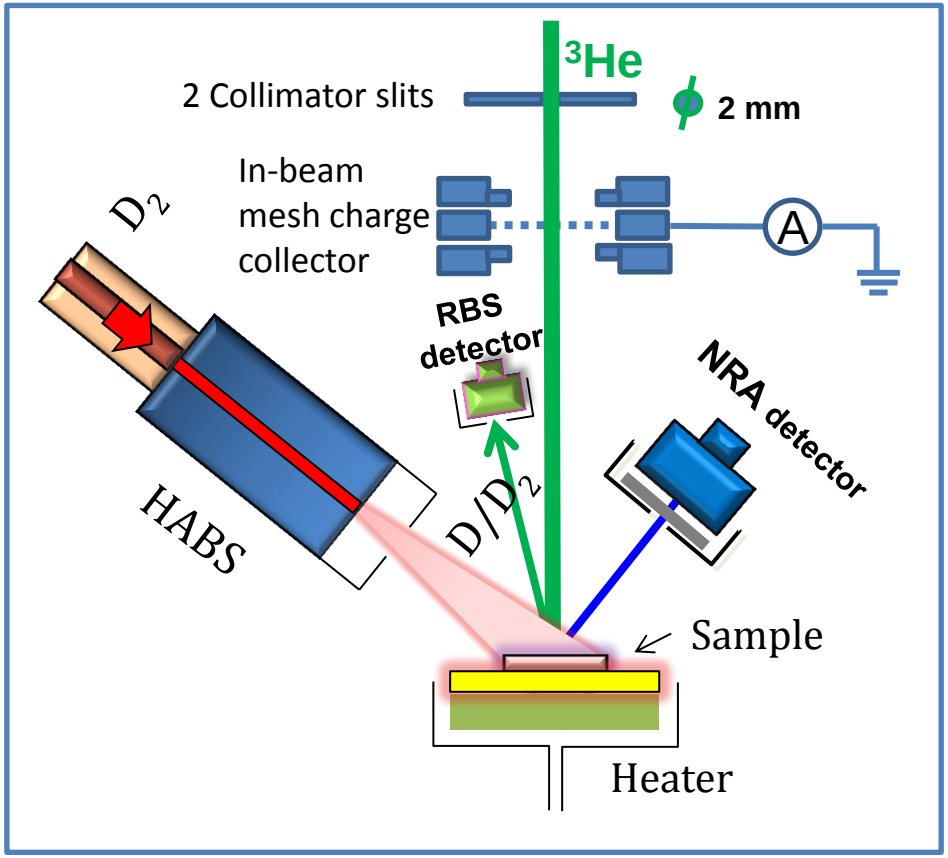
Questions that we still need to address:

- Reason for lower activation energy → lower Q_s as compared to Fraunfelder

More detailed look by second benchmark experiment: D-atom loading study at different temperatures

D atom loading of self-damaged W at different temperatures

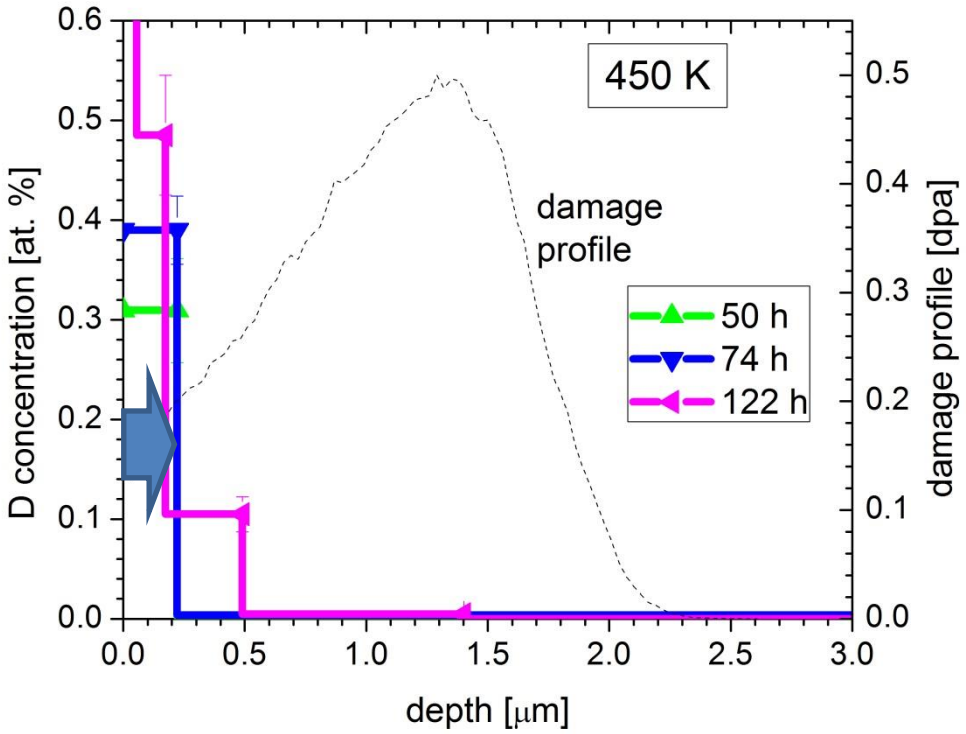
- Recrystallized W sample damaged by 20 MeV W ions, Damage dose: 0.25 dpa_{KP}
- D atom exposure 122 h ≈ 5 days; j = 4.2×10^{18} D/m^2s
- Fluence = 1.8×10^{24} D/m^2
- Each sample different temperature – depth profile measurement at different times/fluences
- **Exposure at low temperature where defect annealing has minor role.**



D atom loading of self-damaged W at different temperatures

The D atom loading experiment at 450 K

- Max D concentration 0.49 at % - range 0.2 μm

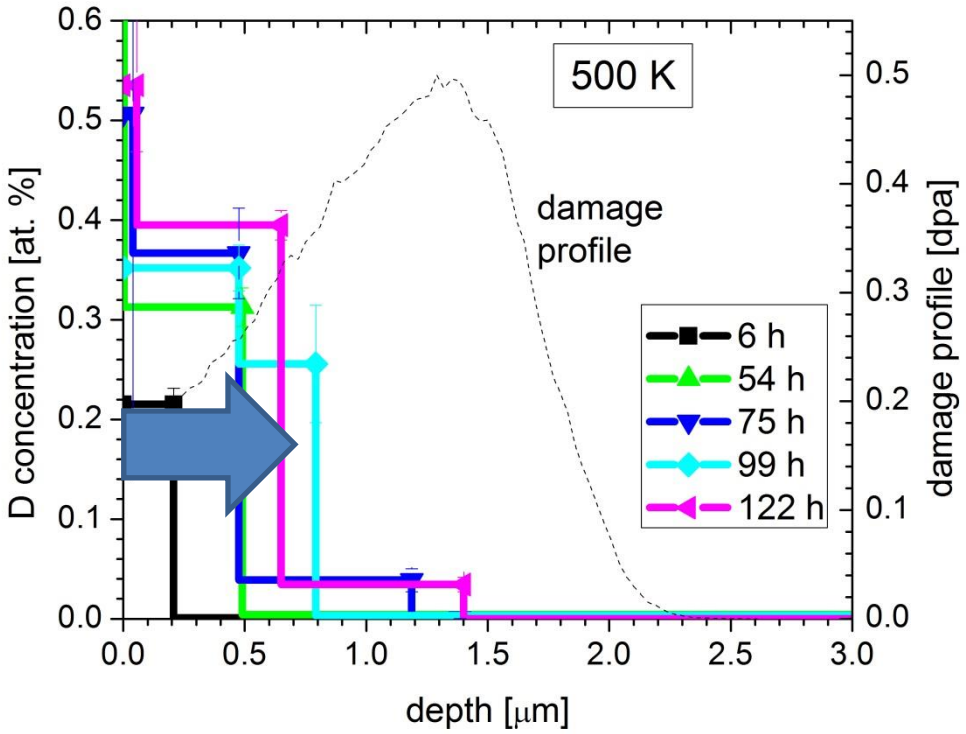


[Založnik et al., submitted to JNM]

D atom loading of self-damaged W at different temperatures

The D atom loading experiment at 500 K

- Max D concentration 0.4 at % - range 0.65 μm

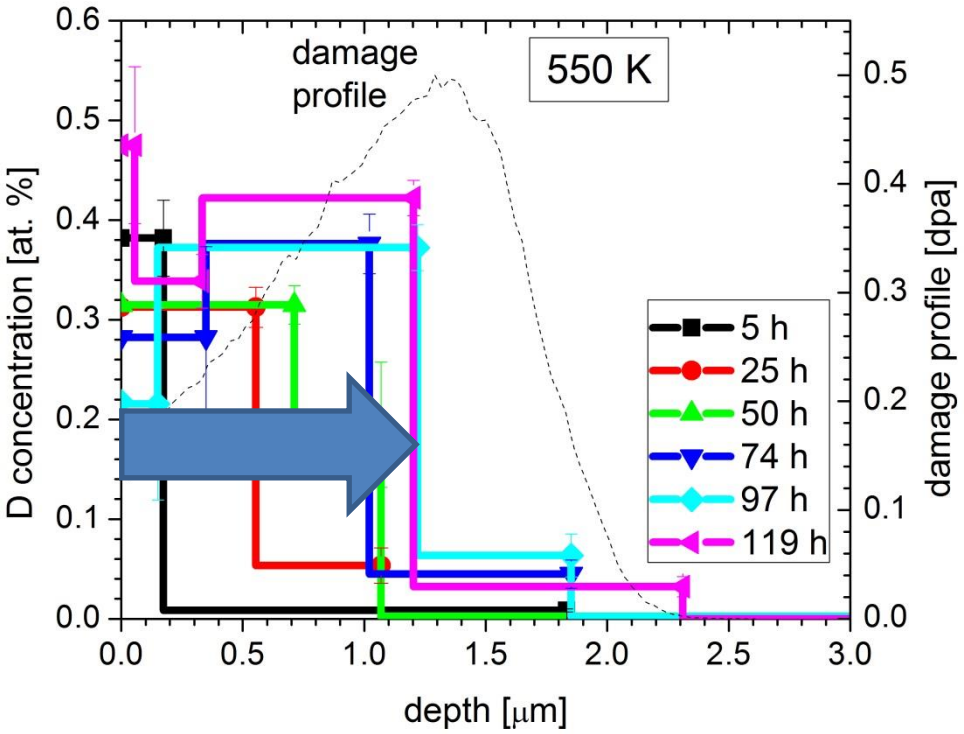


[Založnik et al., submitted to JNM]

D atom loading of self-damaged W at different temperatures

The D atom loading experiment at 550 K

- Max D concentration 0.42 at % - range 1.2 μm

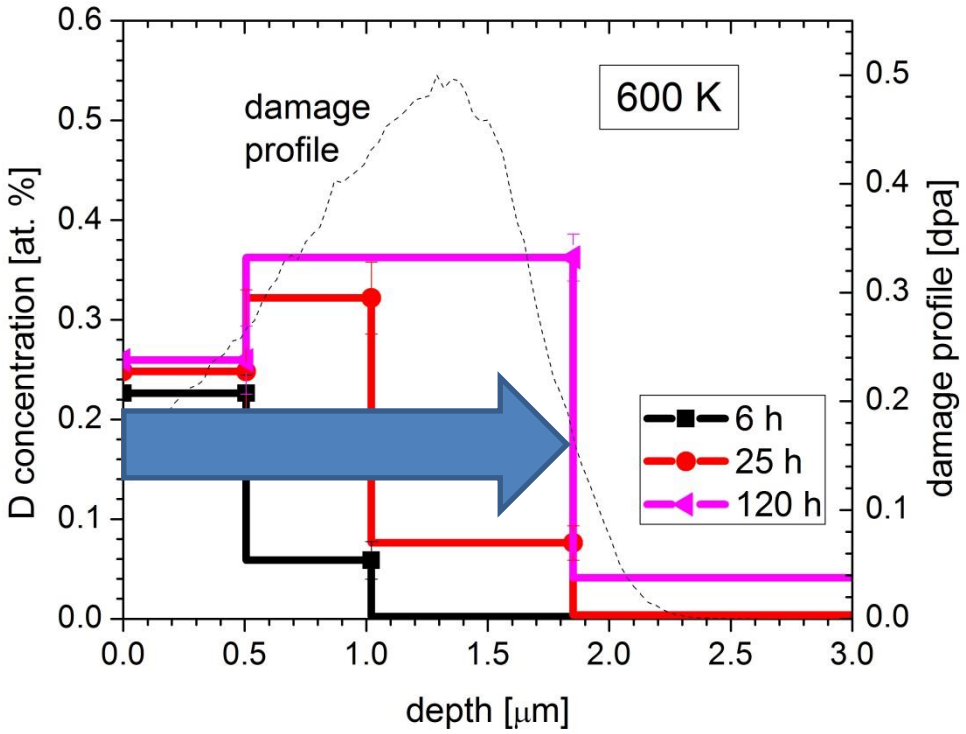


[Založnik et al., submitted to JNM]

D atom loading of self-damaged W at different temperatures

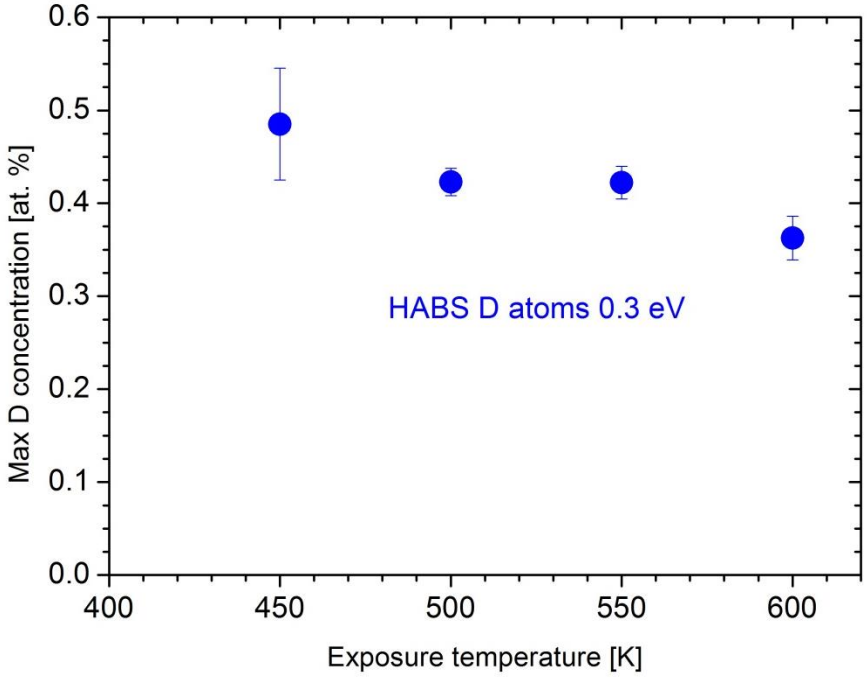
The D atom loading experiment at 600 K

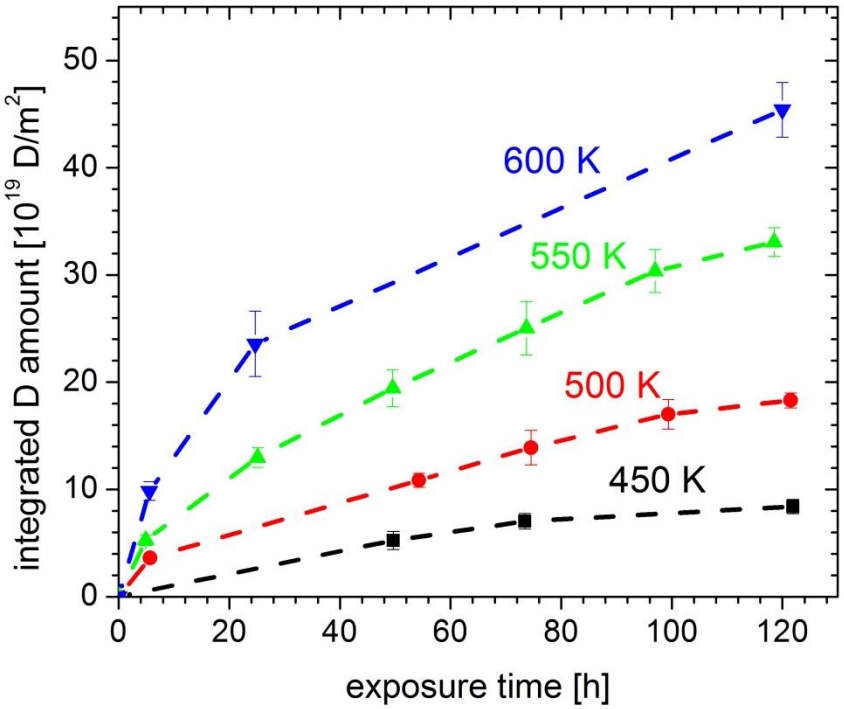
- Max D concentration 0.36 at % - range 1.9 μm



[Založnik et al., submitted to JNM]

D atom loading of self-damaged W at different temperatures





- **Smaller penetration depth but higher D conc. @ lower temperatures**
- Higher the temperature less time/fluence needed to saturate damaged layer
- Large temperature dependence of D uptake

D atom loading of self-damaged W at different temperatures – modelling results

The TESSIM code (developed by K. Schmid, IPP) – "the same" as the MHIMS code

- **Bulk de-trapping energies and trap concentration from TDS spectra**

- ✓ **Fitting of the total amount for all four temperatures – the same surface/bulk parameters**

Total D amount from NRA

Thermodesorption spectra

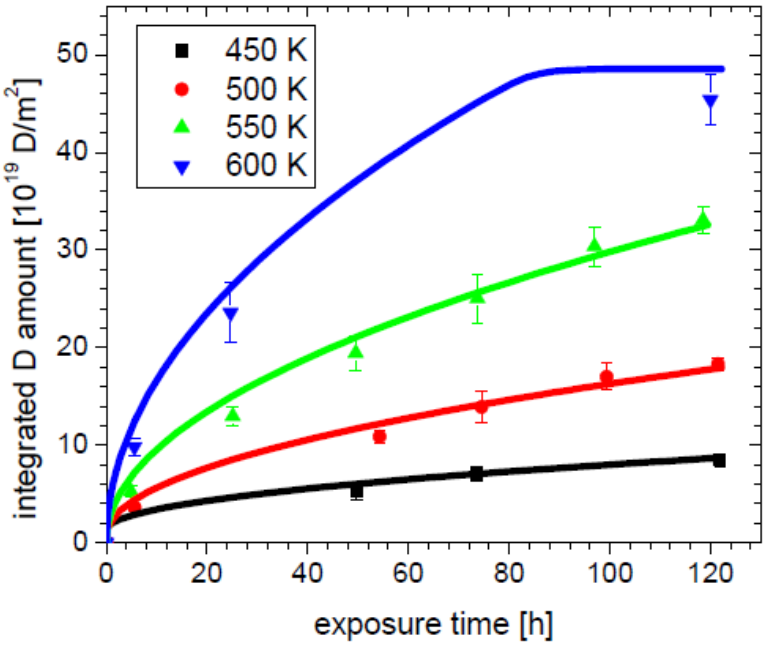
D atom loading of self-damaged W at different temperatures – modelling results

The TESSIM code (developed by K. Schmid, IPP) – "the same" as the MHIMS code

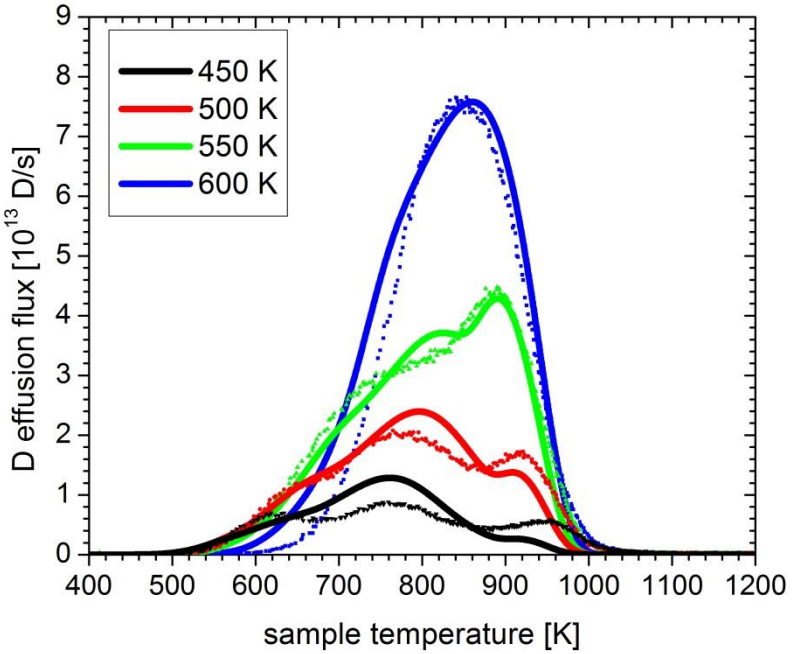
- **Bulk de-trapping energies and trap concentration from TDS spectra**

- ✓ **Fitting of the total amount for all four temperatures – the same surface/bulk parameters**

Total D amount from NRA



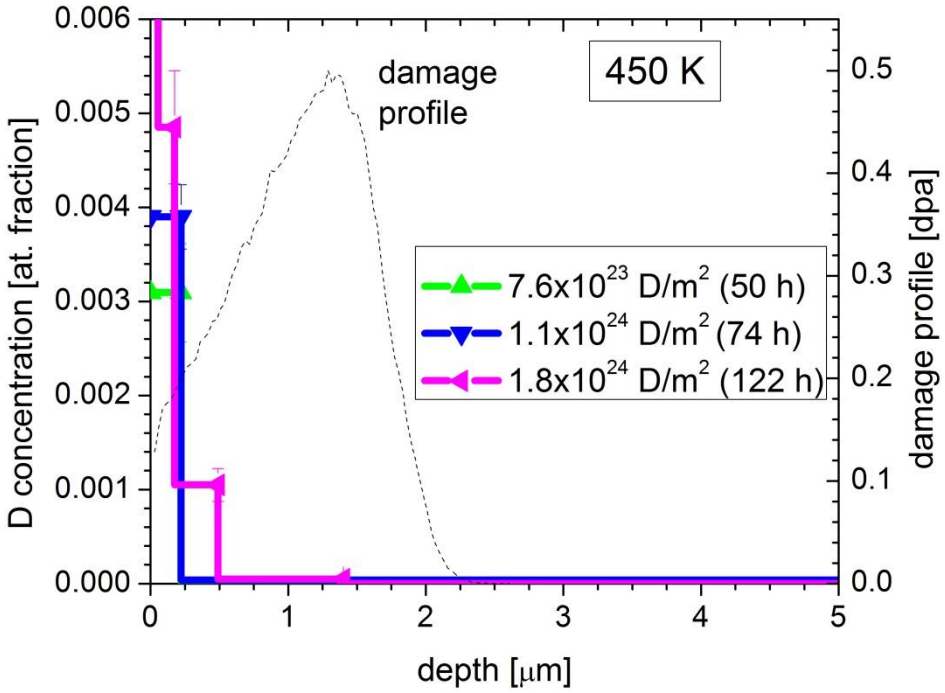
Thermodesorption spectra

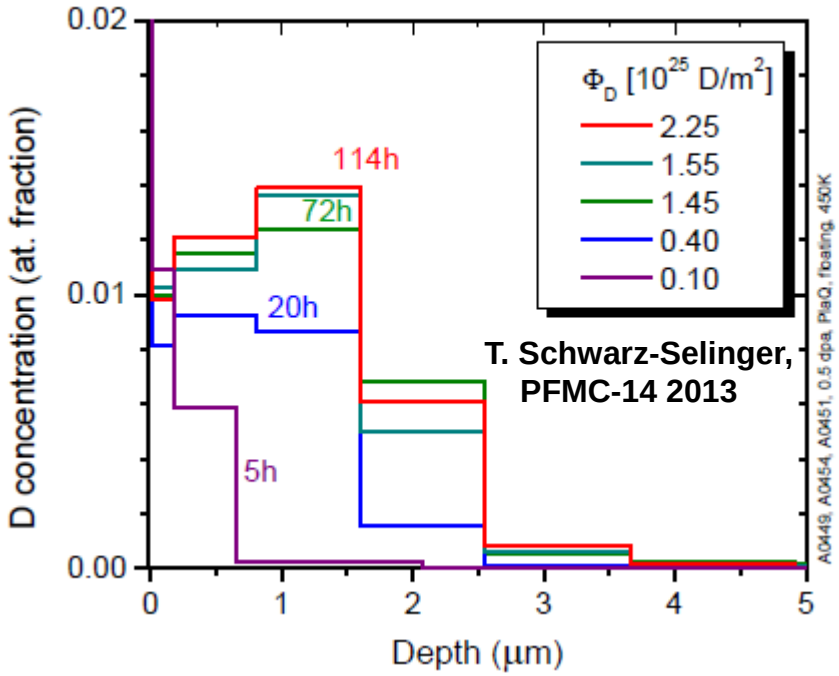


D atom loading of self-damaged W at different temperatures – comparison to plasma

Hydrogen Atom beam source
Energy: 0.3 eV - thermal energy
Ion flux: 4.2×10^{18} D/m^{s}s
Temperature: 450 K

Low-temperature ECR plasma (PlaQ)
Energy: "<5 eV/D" (floating target)
Ion flux: 5.6×10^{19} D/m^{s}s
Temperature: 450 K



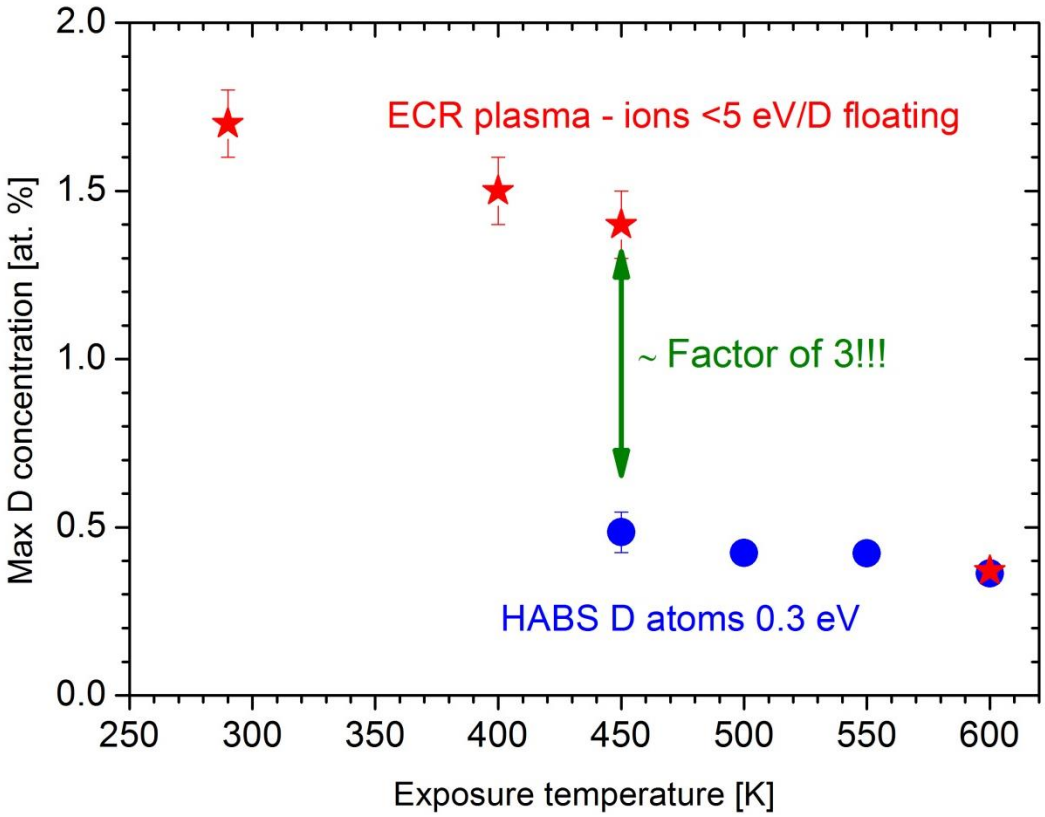


Small penetration depth = reason why low energy neutrals can be ignored at plasma exposures at temperatures ≤ 450 K

D atom loading of self-damaged W at different temperatures – comparison to plasma

Hydrogen Atom beam source
Energy: 0.3 eV - thermal energy
Ion flux: 4.2×10^{18} D/m^{s}s
Temperature: 450 K

Low-temperature ECR plasma (PlaQ)
Energy: "<5 eV/D" (floating target)
Ion flux: 5.6×10^{19} D/m^{s}s
Temperature: 450 K



Further work needed to understand the difference – fill level dependence

Plasma data by courtesy of T. Schwarz-Selinger, IPP

D atom loading of self-damaged W at different temperatures - modelling results

- **Activation energy from surface to bulk** $E_A = 1.43$ eV → $Q_s = 0.34$ eV **in good agreement with Hodille et al. (E_A=1.33 eV/1.55 eV)**

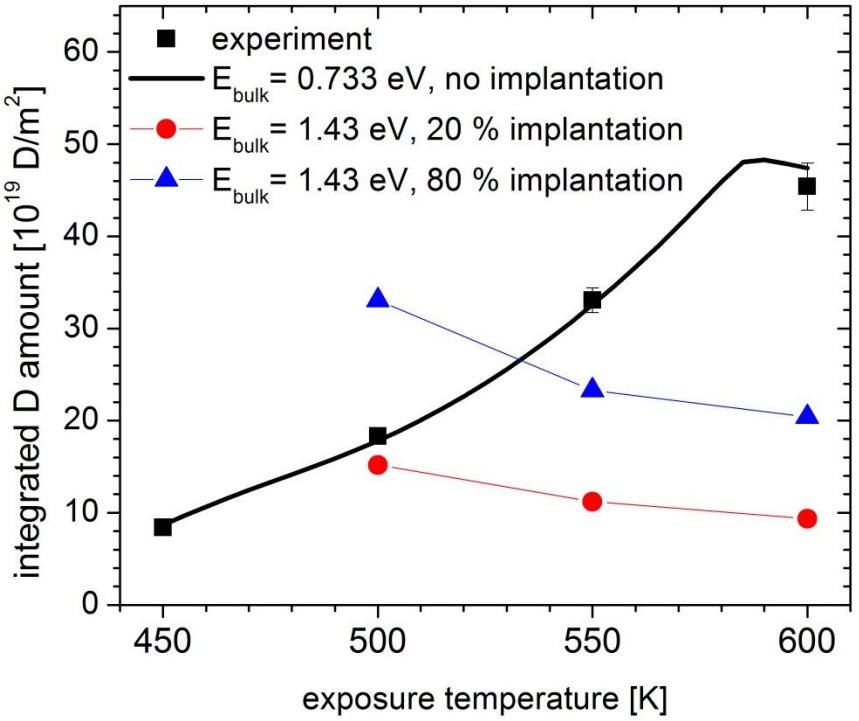
Possible explanations?

D atom loading of self-damaged W at different temperatures - modelling results

- **Activation energy from surface to bulk E_A = 1.43 eV → Q_s = 0.34 eV in good agreement with Hodille et al. (E_A=1.33 eV/1.55 eV)**

Possible explanations?

- **No D uptake in the case of the Fraunfelder value of Q_S**
- **Direct implantation + Q_s Fraunfelder value** – from MD calculations 0.3 eV D atoms penetrate 0.2 nm deep [Ogorodnikova et al. JAP 119 (2016) 054901]

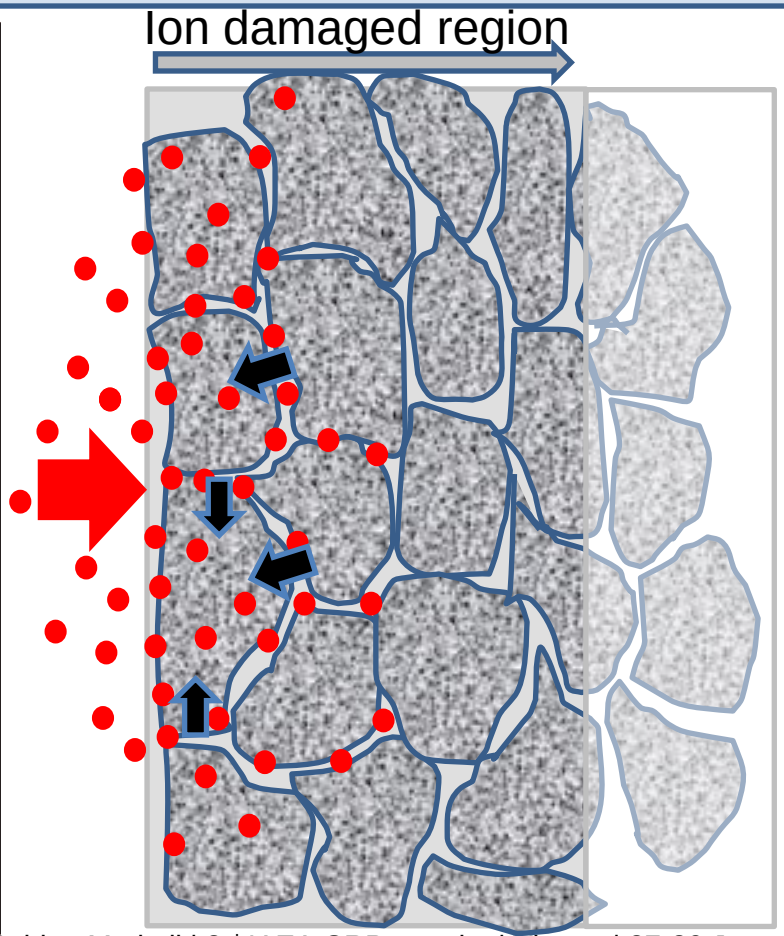


D atom loading of self-damaged W at different temperatures - modelling results

- **Activation energy from surface to bulk E_A = 1.43 eV → Q_s = 0.34 eV in good agreement with Hodille et al. (E_A=1.33 eV/1.55 eV)**

Possible explanations?

- **No D uptake in the case of the Fraunfelder value of Q_S**
- ~~**Direct implantation + Q_s Fraunfelder value** – from MD calculations 0.3 eV D atoms penetrate 0.2 nm deep [Ogorodnikova et al. JAP 119 (2016) 054901]~~
- **Diffusion through grain boundaries** – additional access to grains yields faster effective uptake and lower effective Q_S [von Toussaint et al. Phys Scr. T159 (2014) 014058, Oda Fus. Eng. Des. 112 (2016) 102]

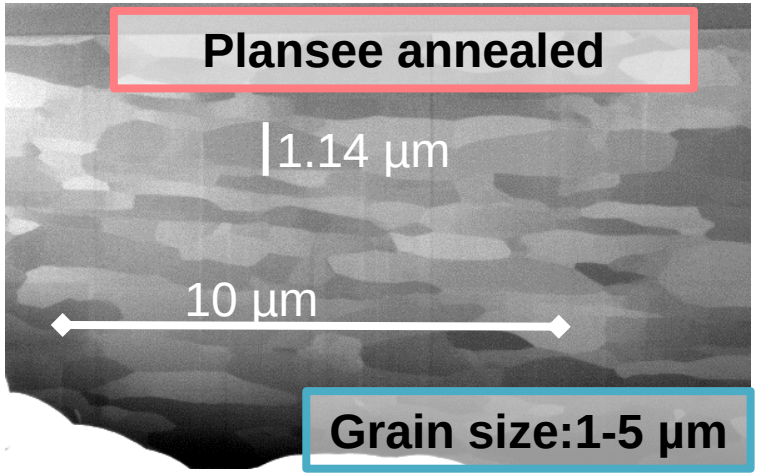


D atom loading of self-damaged W with different grain size

Exposure of four self-damaged samples W at 600 K

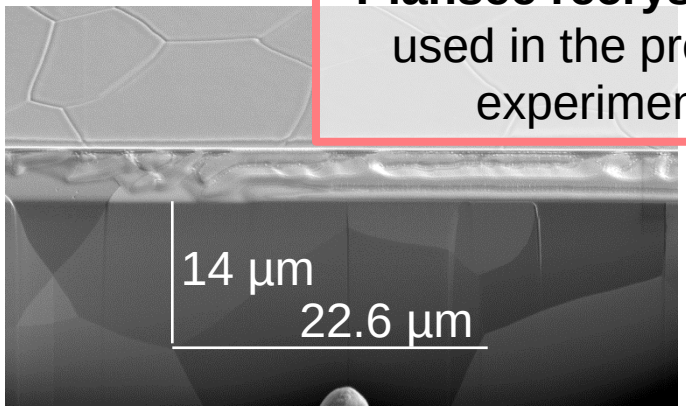
- D atom exposure 70 h – 4 days; j = $4.2 \times 10^{14} D/m^2 s$
- **Each sample different grain size** - FIB cut figures

Plansee annealed



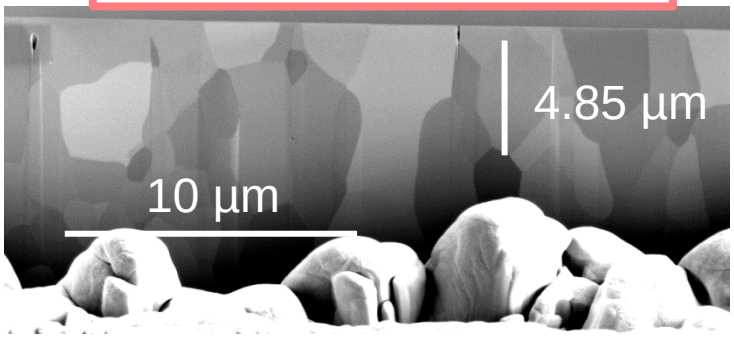
Grain size:1-5 µm

Plansee recrystallized used in the previous experiments



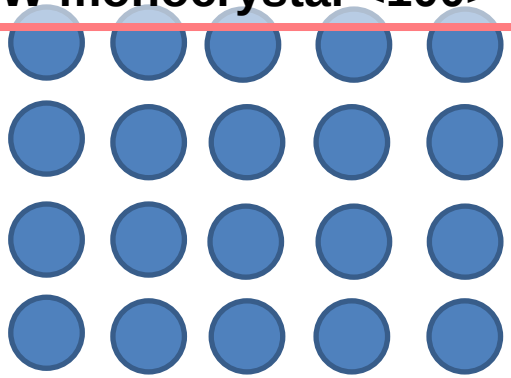
Grain size:10-50 µm

ITER grade



Grain size:5-10 µm

W monocrystal <100>

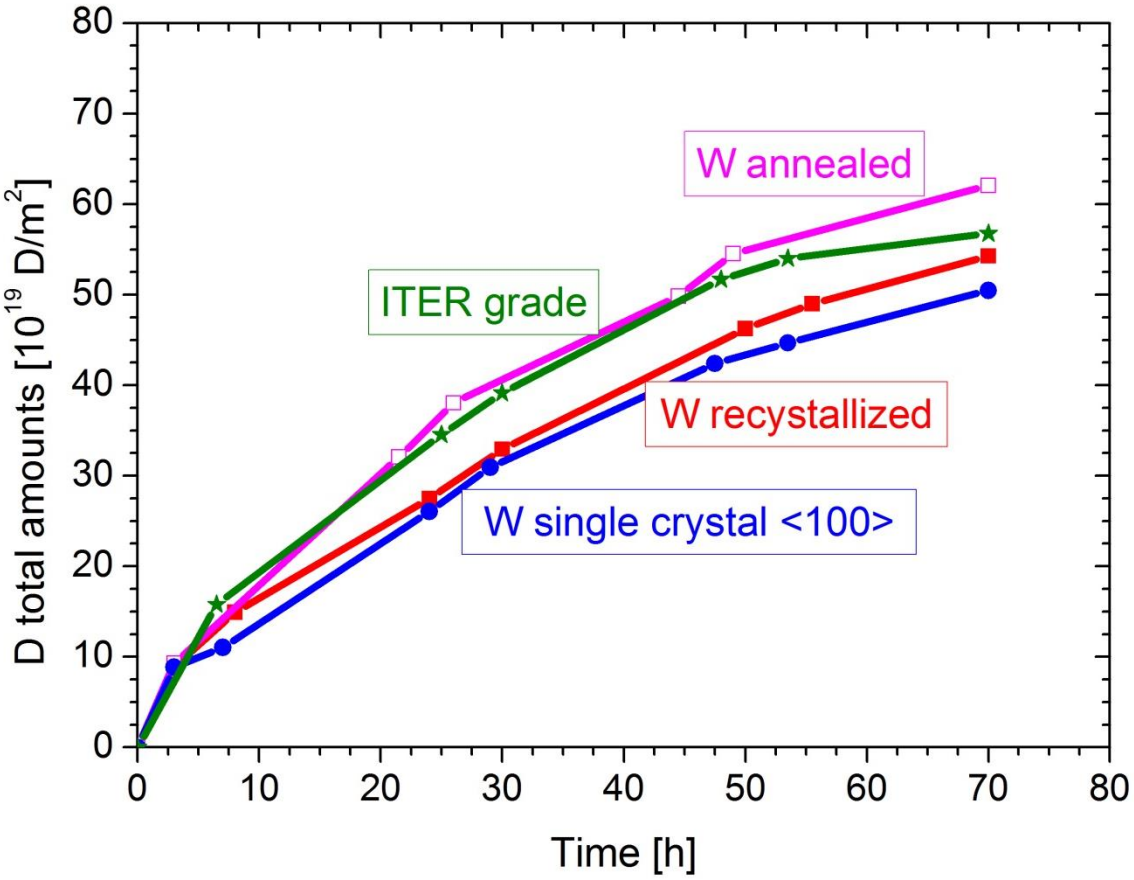


D atom loading of self-damaged W with different grain size

- We do observe a difference in the transport BUT is small
- **Smaller the grains the faster uptake of D**

BUT:

- Recrystallized W and single crystal W – very much similar
- Q_s previously determined in the loading study was performed on recrystallized W



The diffusion in grain boundary does not explain the lower solution energy.

Conclusions Part 1

- In situ NRA used for benchmark experiments to study D uptake, transport and dynamic retention and isotope exchange in self-ion damaged W by D atom exposure
- Rate equation models can explain the experimental data – determining the free parameters needed for modelling

➢ **Difference between atom and plasma loading:**

✓ **Small penetration depth of atoms at low temperature – reason why neutrals can be ignored at plasma exposures ≤ 450 K**

✓ **Difference in D concentration – further work - fill level dependence**

➢ **Lower solution energy Q_S as compared to Fraunfelder value:**

✓ **No uptake when the Fraunfelder value would be used – but we do observe it**

✓ **Direct implantation of D atoms does not explain the experimentally observed temperature dependence of D total amounts**

✓ **Diffusion through grain boundary does not explanation for lower Q_S BUT we did observed difference in D transport in samples with different grain size**

✓ **Further work needed to reveal the reason for lower solution energy**

Study of deuterium retention in tungsten simultaneously damaged by high energy W ions and loaded by D

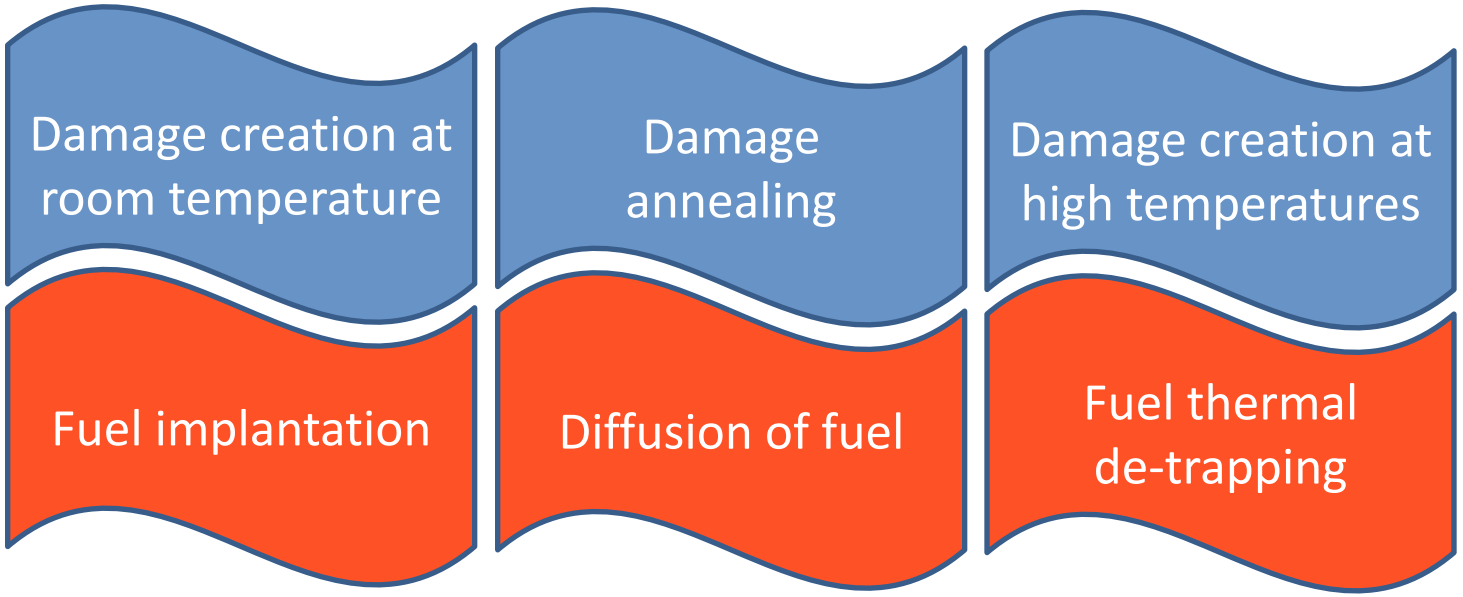
CRP objective 1: to inventories knowledge about effects of neutron irradiation and charged particle surrogate irradiation on the microstructure of tungsten based plasma facing materials

CRP objective 2: to inventories knowledge about the relation between tungsten microstructure after irradiation and plasma material interaction properties for erosion, tritium retention and tritium migration

Motivation – Part 2

In depth understanding of tritium retention in neutron-like irradiated W-based materials

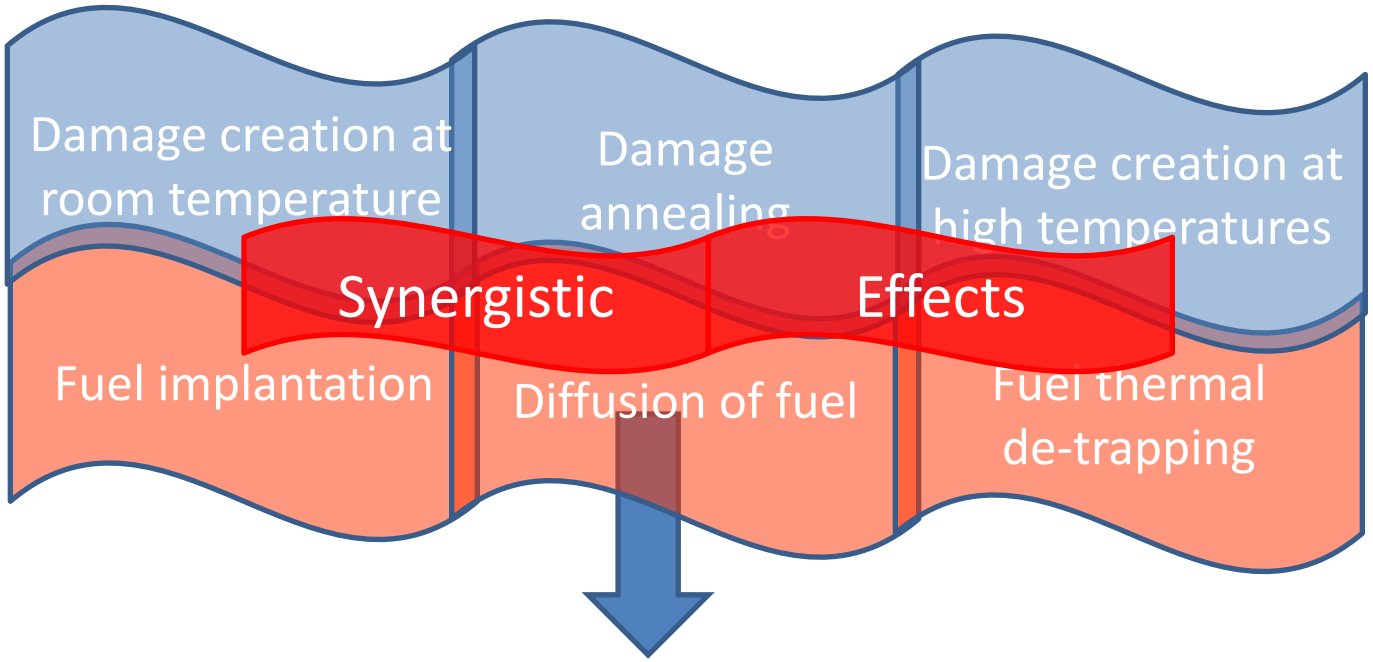
- Increased fuel retention in neutron damaged W material [e.g. Hatano et al. NF 53 [2013] 073006] – more significant in DEMO (2-6 dpa/fpy)



- Different damaging/exposure scenarios to understand the mechanisms of damage creation and annihilation and deuterium trapping/diffusion

Motivation – Part 2

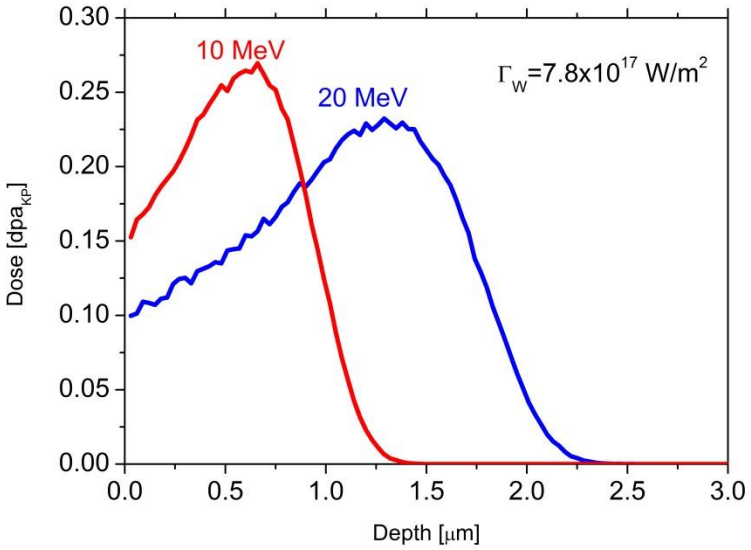
Fusion device scenario
neutron damaging and D/T ion bombardment simultaneously at high temperature



Theory predicts defect stabilization in presence of hydrogen
[Kato NF 55 (2015) 083019 & Middleburgh et al. JNM 448 (2014) 270]

Method: Use of high energy W beam for self-damaging + HABS + Nuclear reaction analysis (NRA)

- Neutron irradiated samples– activation of the samples



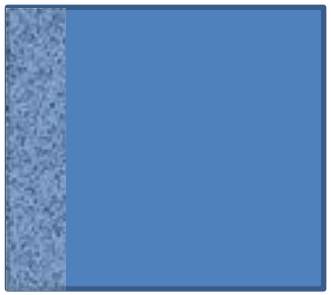
SRIM calculation of damage dose depth profile

The same D retention at saturation level ≥ 0.25 dpa

➢ High energy ion damaging

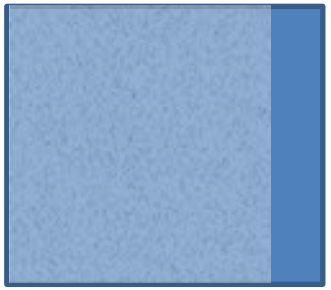
- Surrogate for neutron irradiation
- High energy (10-20 MeV) W ion irradiation = self-damaging
- Dense cascades and no chemical effect
- Shallower damage creation few μm

Ion damaging



Few μm

neutron damaging

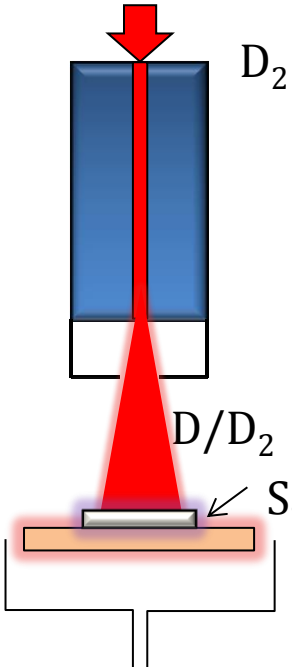


Few cm

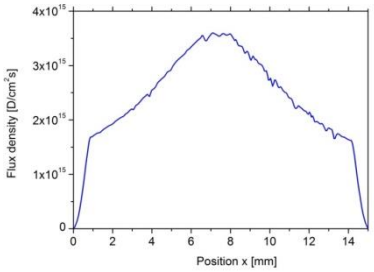
Method: Use of high energy W beam for self-damaging + HABS + Nuclear reaction analysis (NRA)

WP PFC

Hydrogen Atom Beam Source = HABS



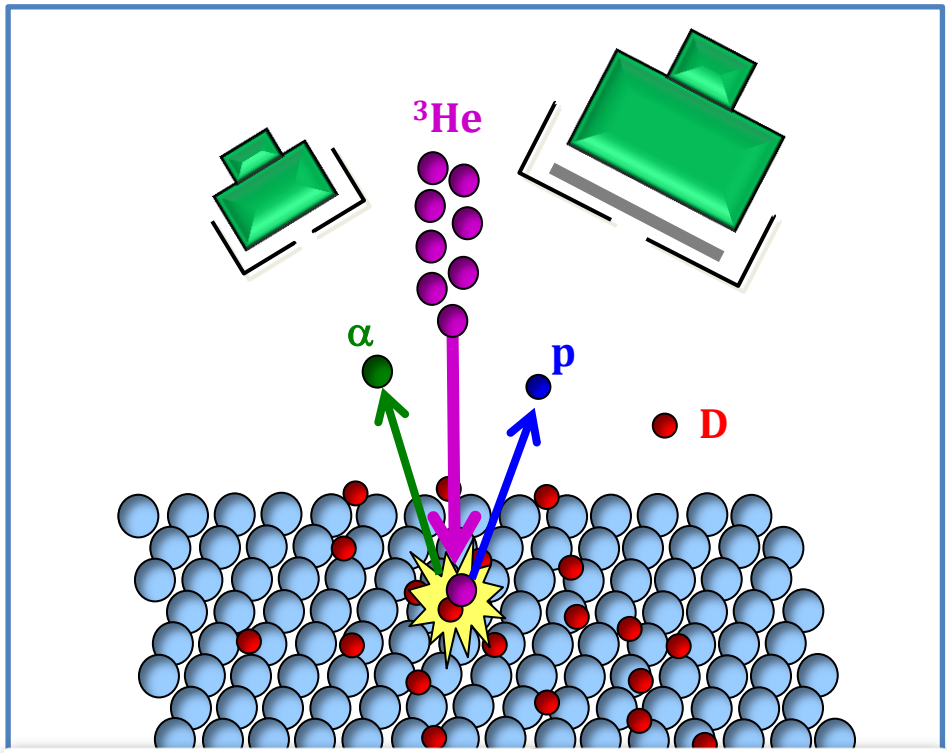
D atom flux density profile



- Energy 0.28 eV/D (2150 K)
- Dissociation rate 30-50 %
- Atom flux: $4x10^{18} – 3x10^{19}$ D/m²s
- Atom fluence: 10^{20}-10^{24} D/m²

Studies with deuterium → extrapolation to tritium

Deuterium detection by ^{3}He NRA



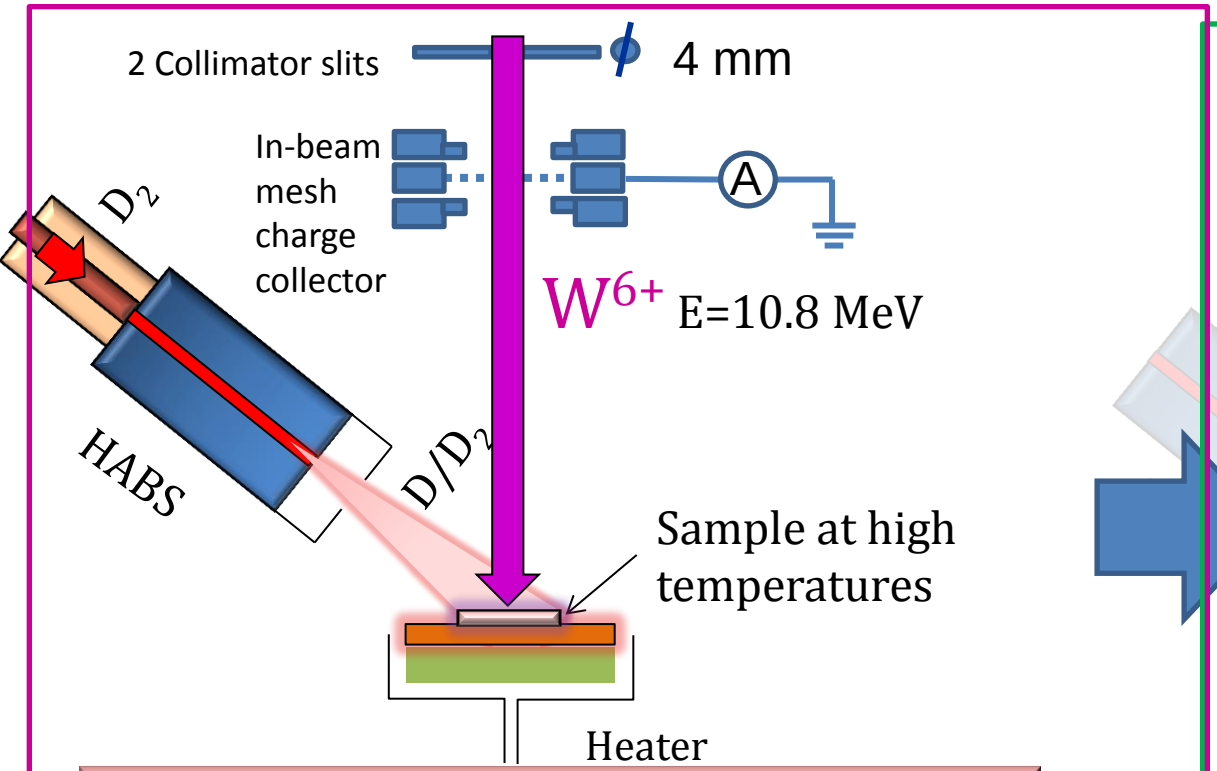
Nuclear reaction to probe ^{2}H = D:

- $^3He + D \rightarrow {}^4He + p$

(Q=18.352MeV; p energy 11-14 MeV)
Broad resonance peak near E(^{3}He) ≈ 0.63 MeV (FWHM 730 keV)

Simultaneous W irradiation and D loading

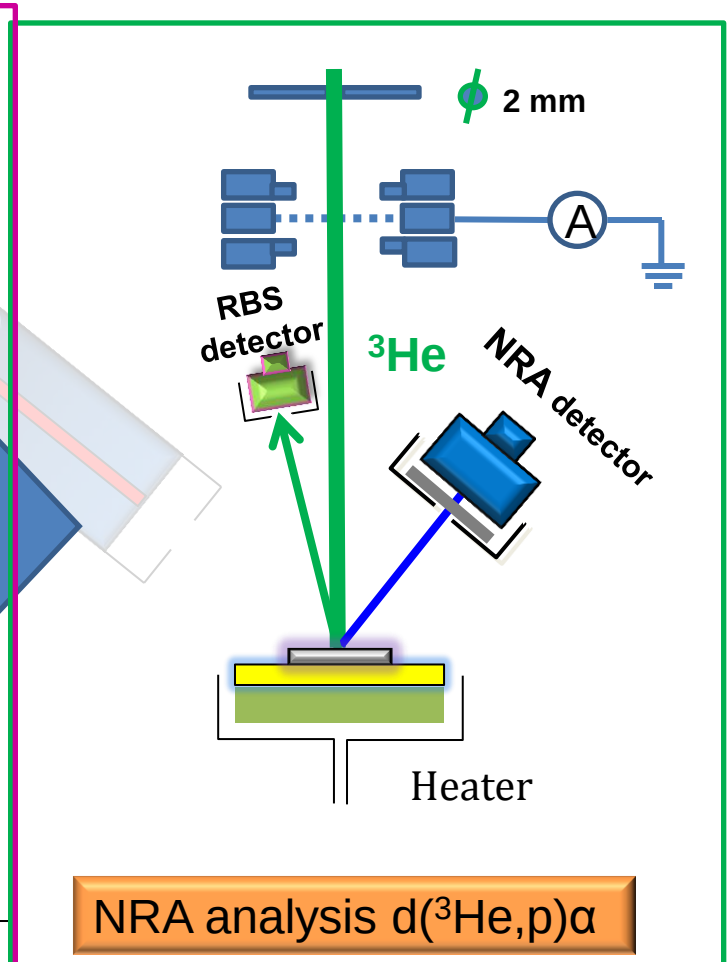
Experimental set up



Simultaneous W irradiation and D atom exposure at high temperatures for 4 h

Atom flux=5.4x10^{18} D/m^{2}s
Γ_D=8x10^{22} D/m^2

W fluence = 1.4x10^{18} W/m^2
Dose→ 0.47 dpa$_{KP}$
Displ. Rate = 3*10^{-5} dpa/s

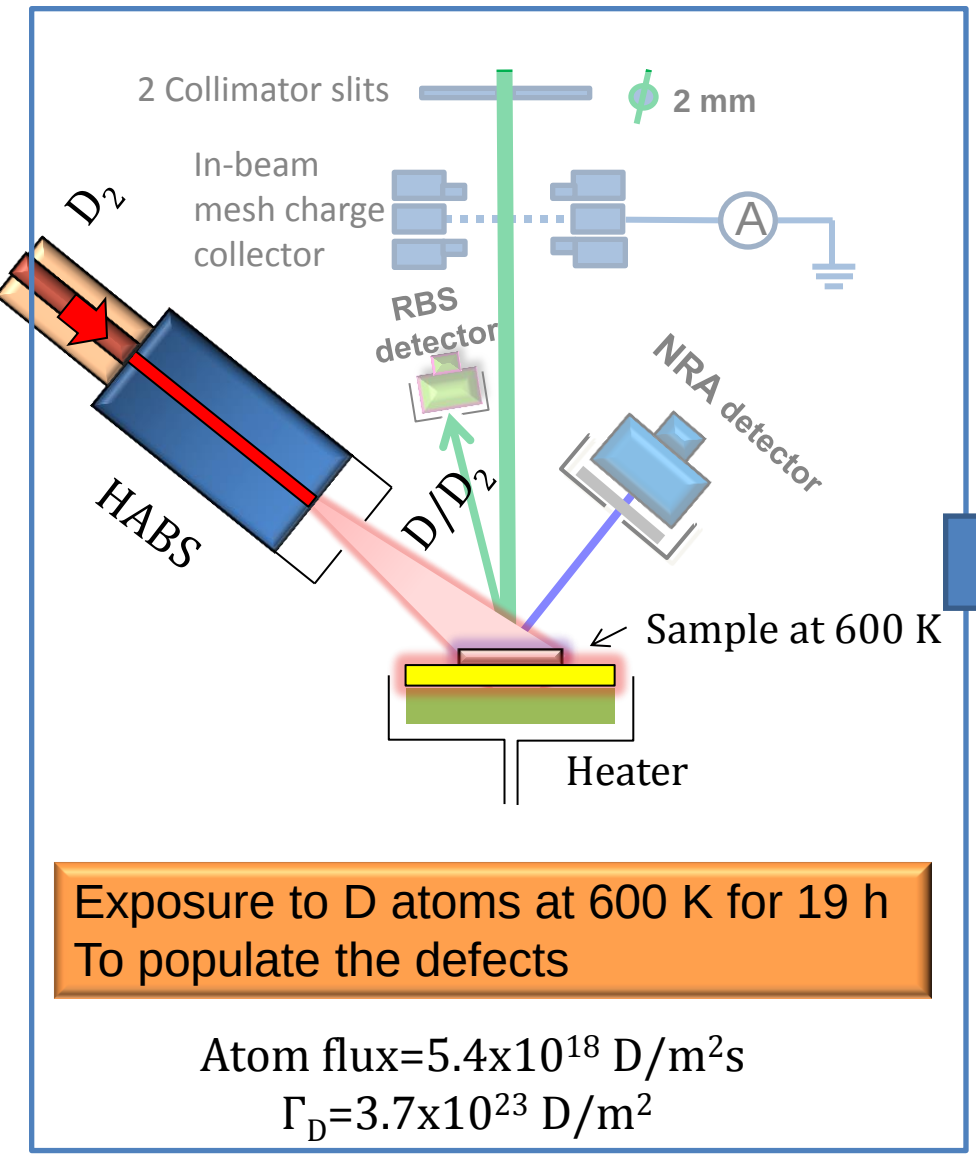


NRA analysis d(^{3}He,p)α

Depth profile deconvolution with SIMNRA and NRADC [K. Schmid et al., NIM B 281 (2012) 64]

Simultaneous W irradiation and D loading

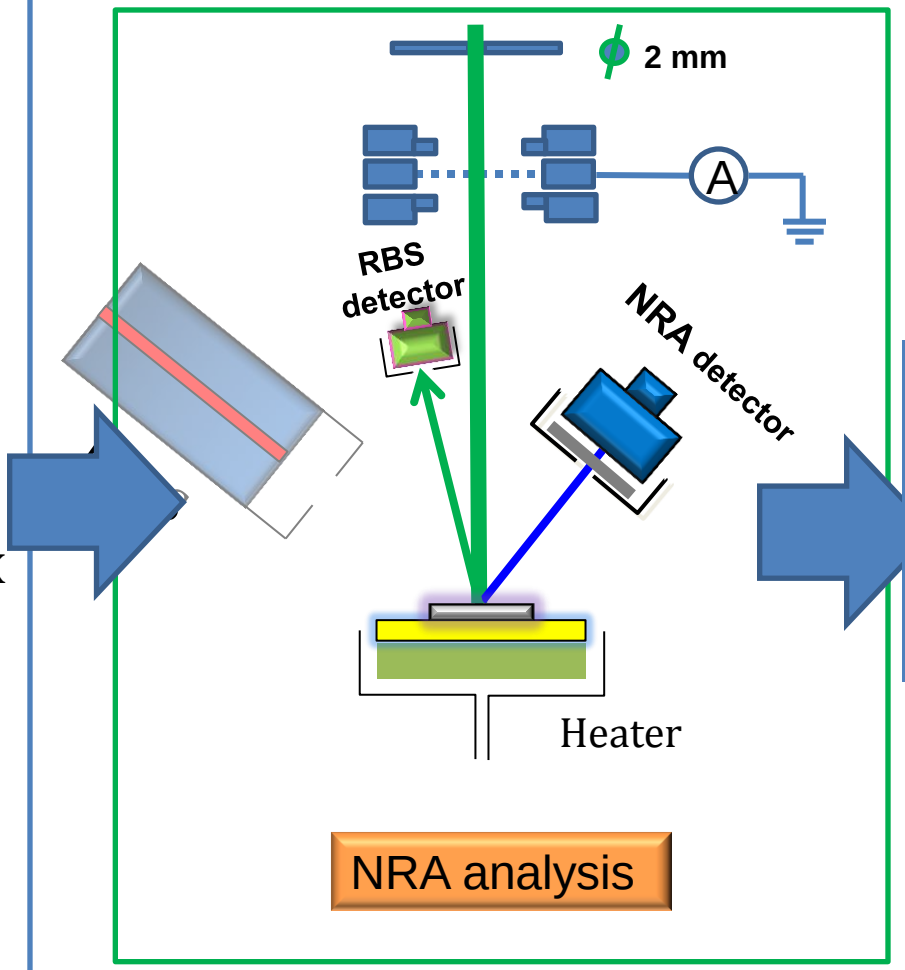
Trap population with D atoms at 600 K



Exposure to D atoms at 600 K for 19 h
To populate the defects

Atom flux=5.4×10^{18} D/m^{2}s

$\Gamma_D = 3.7 \times 10^{23}$ D/m^2



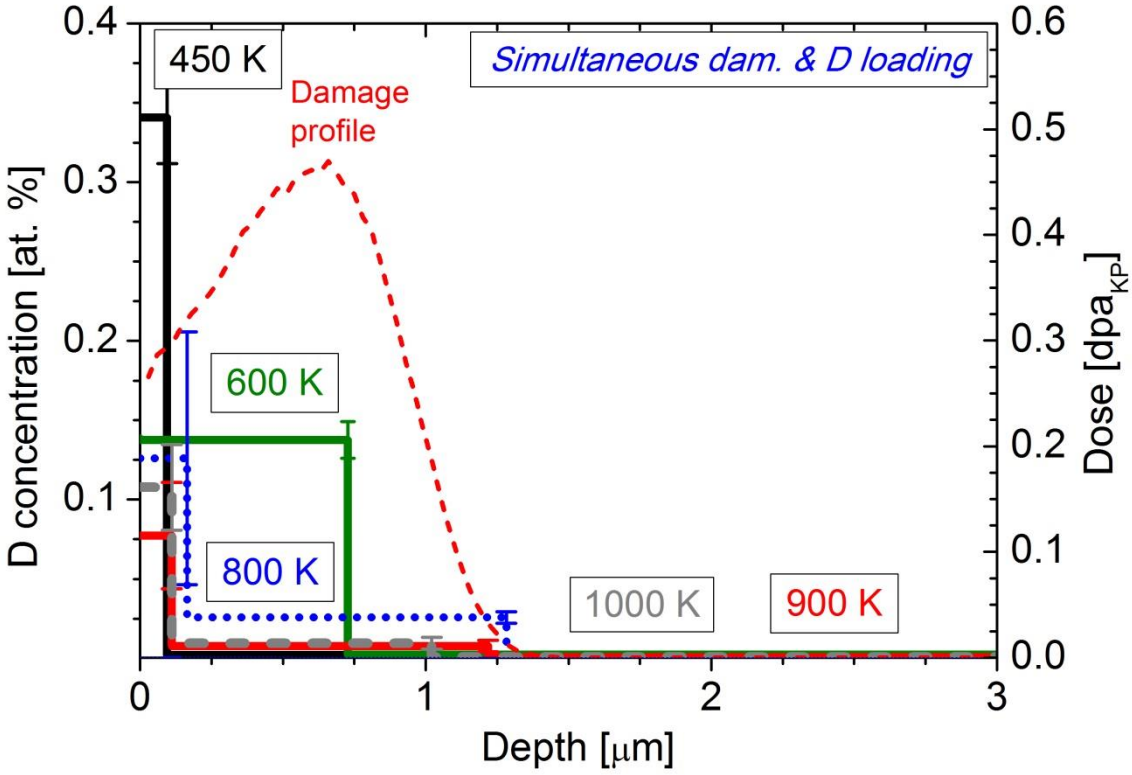
Simultaneous W irradiation and D loading

D depth profiles after 4 h damaging and exposure

- Terminal D conc. depth profiles for different damaging + D loading temperatures

✓ D concentration determined by balance between D flux into the bulk and flux out due to D thermal de-trapping

✓ <u>At lower temperatures higher fluence needed to populate traps deeper in bulk</u>



- Retention decreases with exposure temperature similar to the sequential damaging at RT and exposure at high temperatures" [Ogorodnikova et al., Appl. Phys 119 (2016) 054901 & Markelj et al. NENE proceedings 2015]

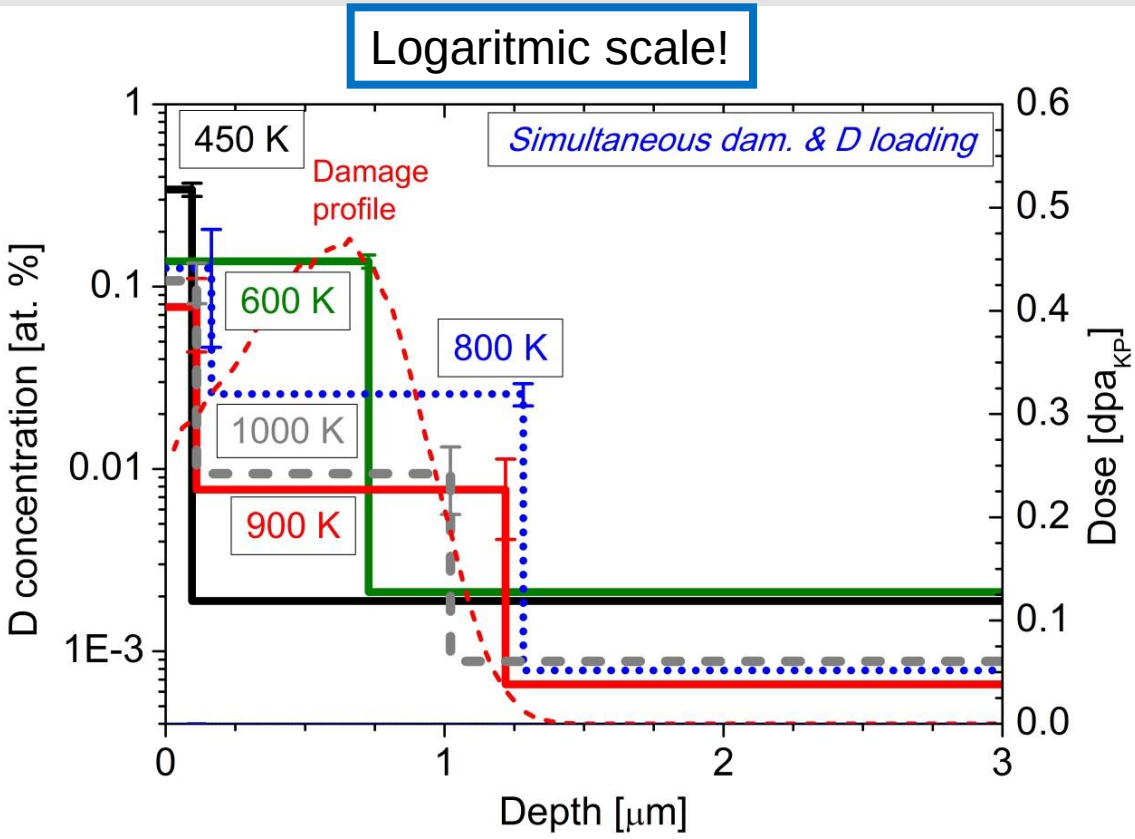
Simultaneous W irradiation and D loading

D depth profiles after 4 h damaging and exposure

- Terminal D conc. depth profiles for different damaging + D loading temperatures

- ✓ D concentration determined by balance between D flux into the bulk and flux out due to D thermal de-trapping

- ✓ <u>At lower temperatures higher fluence needed to populate traps deeper in bulk</u>



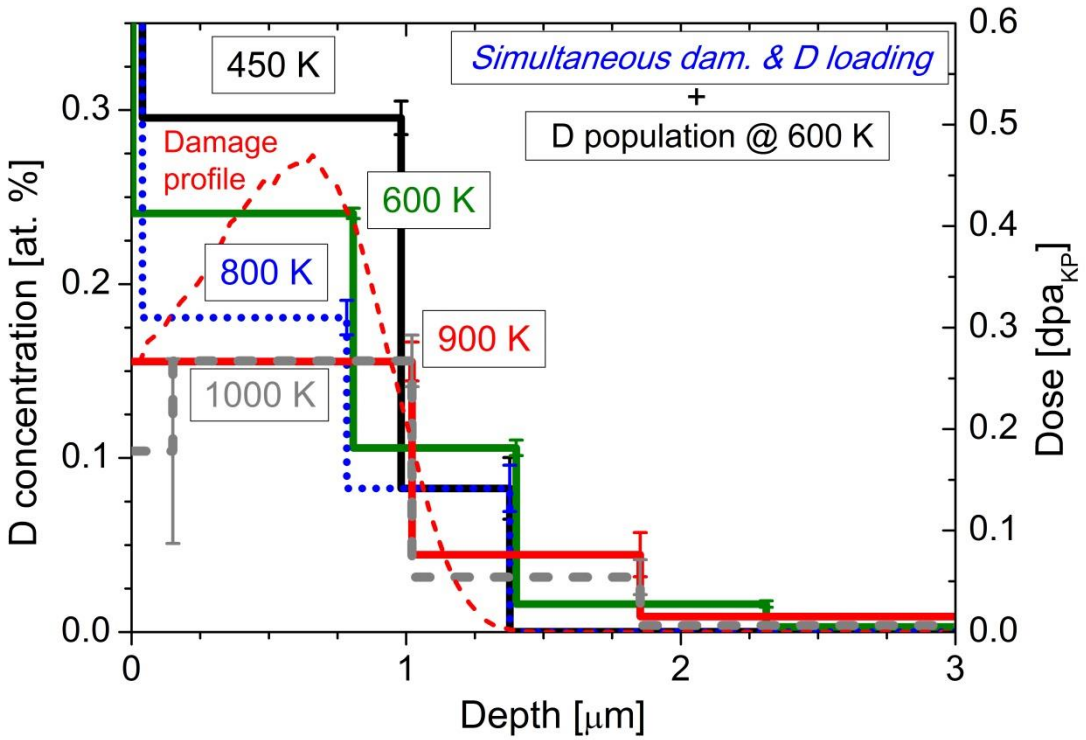
Markelj et al. NME in press, 2017

- Retention decreases with exposure temperature similar to the sequential damaging at RT and exposure at high temperatures" [Ogorodnikova et al., Appl. Phys 119 (2016) 054901 & Markelj et al. NENE proceedings 2015]

Simultaneous W irradiation and D loading

Final D depth profiles to obtain trap population

- D conc. depth profiles after additional D atom exposure at 600 K
- Indicated temperatures apply for damaging + D loading temperatures
- ✓ D concentration in the damaged zone decreases with temperature

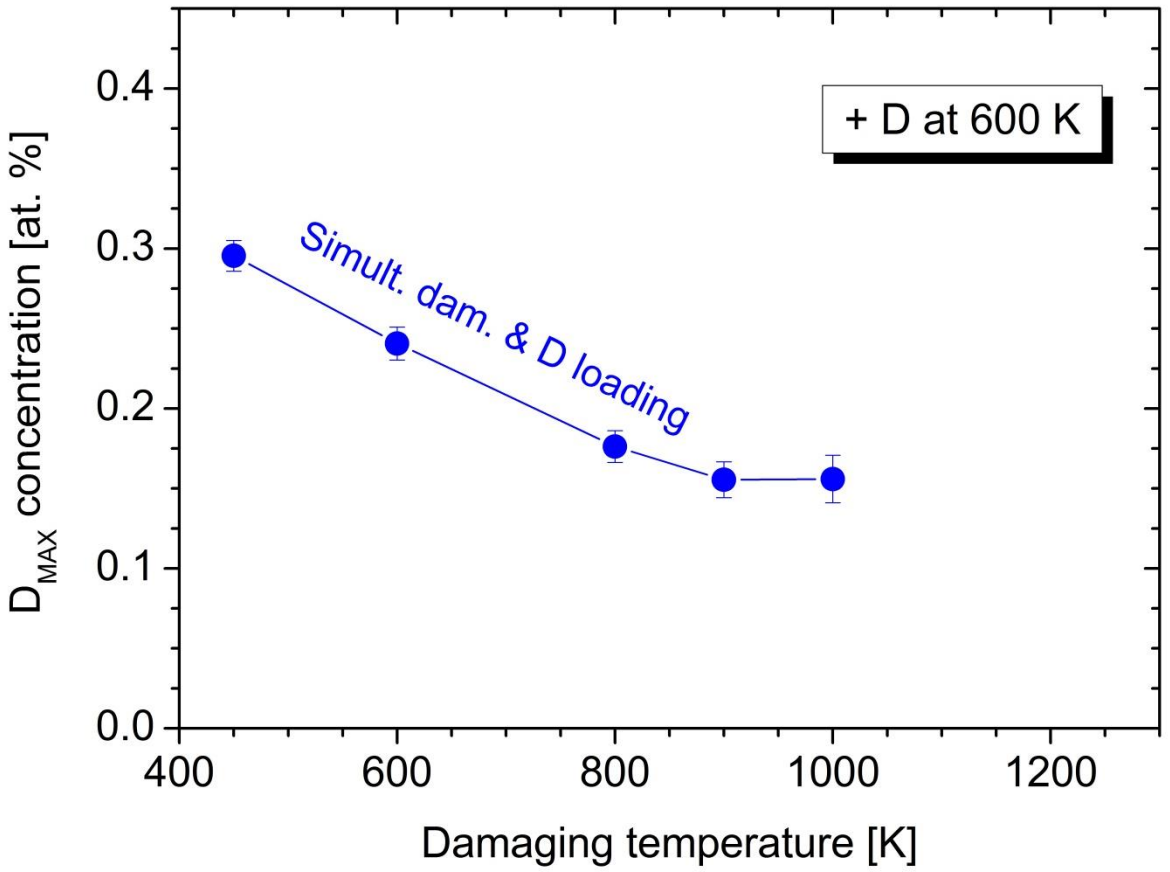


Simultaneous W irradiation and D loading

Maximum D concentration at damaging temperatures

Simultaneous damaging and D loading at T^{EXP}

- ➢ Maximum D concentration in the damaged zone versus damaging temperature
- ✓ Concentration decreases with damaging temperature
- ✓ Stabilization of concentration > 900 K

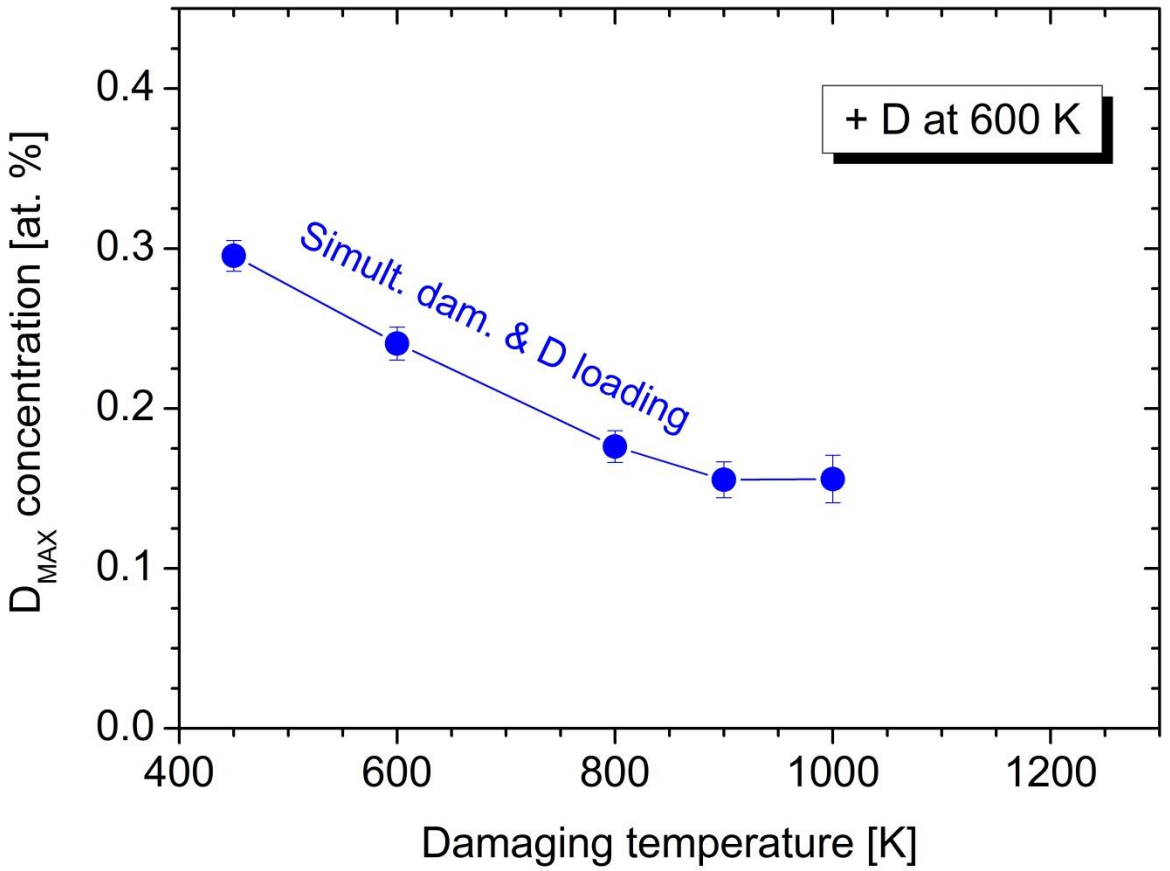


Simultaneous W irradiation and D loading

Maximum D concentration at damaging temperatures

Simultaneous damaging and D loading at T^{EXP}

- ➢ Maximum D concentration in the damaged zone versus damaging temperature
- ✓ Concentration decreases with damaging temperature
- ✓ Stabilization of concentration > 900 K

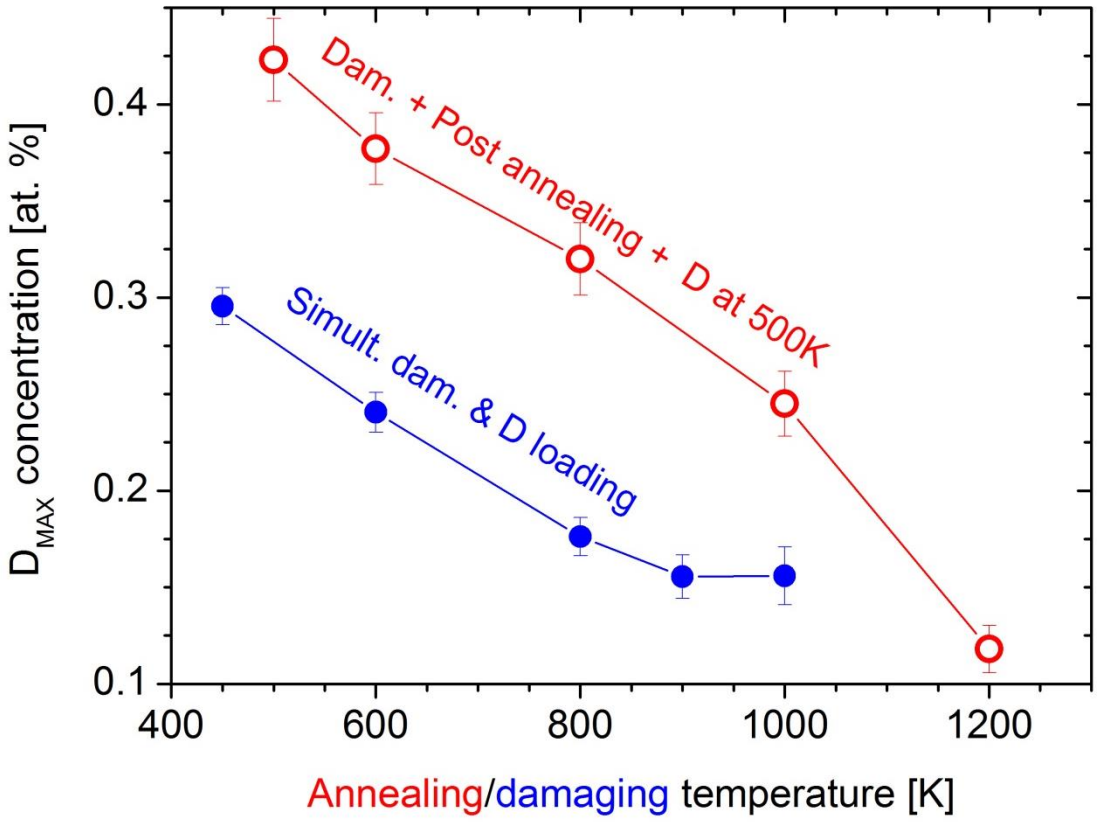


Comparison to sequential procedures of damage formation and loading?

Comparison of different damaging procedures

Different Damaging procedures

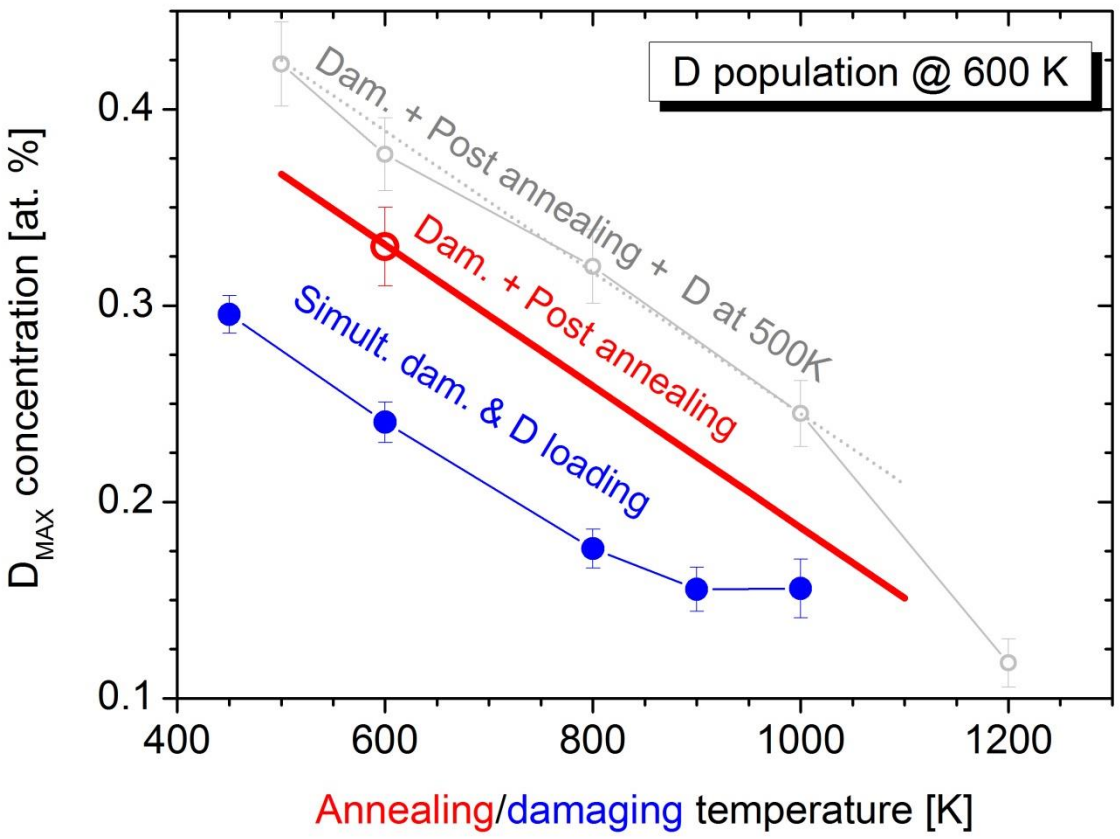
- **Damage at 300 K + anneal at T^{EXP}; D population at 600 K (extropolation)**
- **Damage & D exposure at T^{EXP}; D population at 600 K**



Comparison of different damaging procedures

Different Damaging procedures

- Damage at 300 K + anneal at T^{EXP}; D population at 500 K
- **Damage at 300 K + anneal at T^{EXP}; D population at 600 K (extrapolation from 500 K)**
- **Damage & D exposure at T^{EXP}; D population at 600 K**

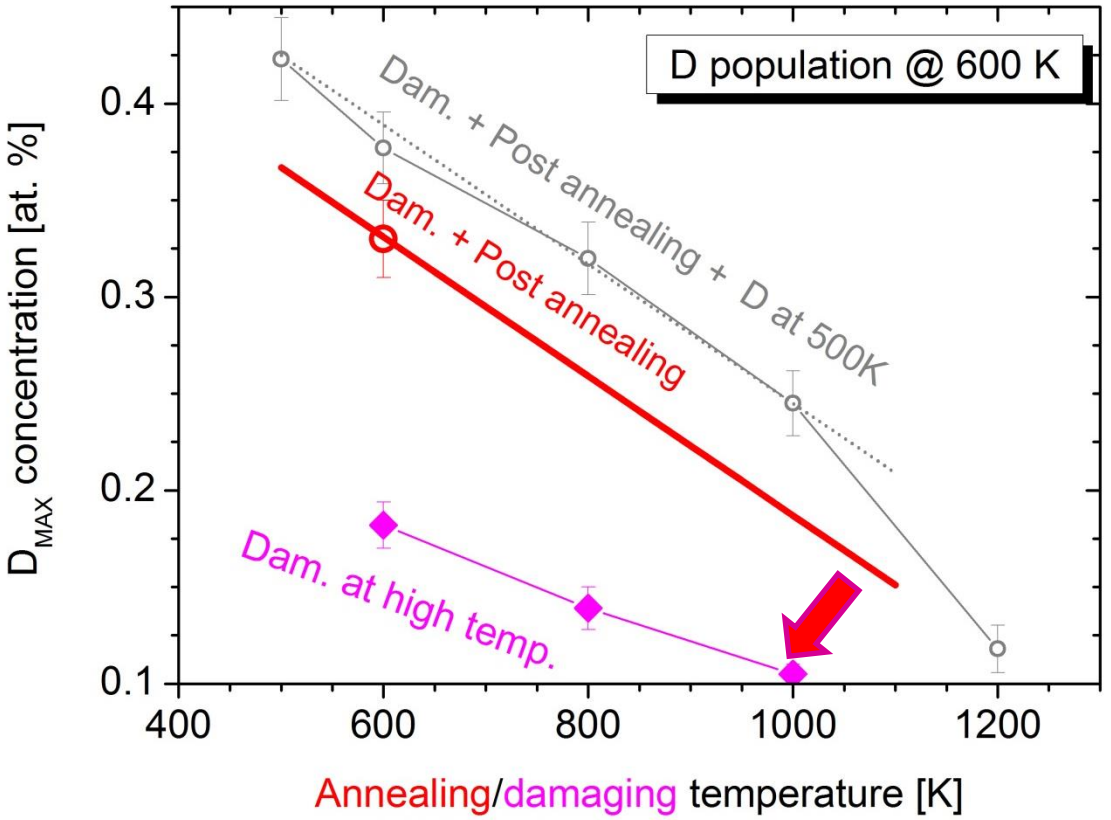


➢ Lower D retention in simultaneous case as compared to sequential post annealing

Comparison of different damaging procedures

Different Damaging procedures

- **Damage at 300 K + anneal at T^{EXP}; D population at 600 K (extropolation)**
- **Damage at T^{EXP}; D population at 600 K**



Damaging at elevated temperatures

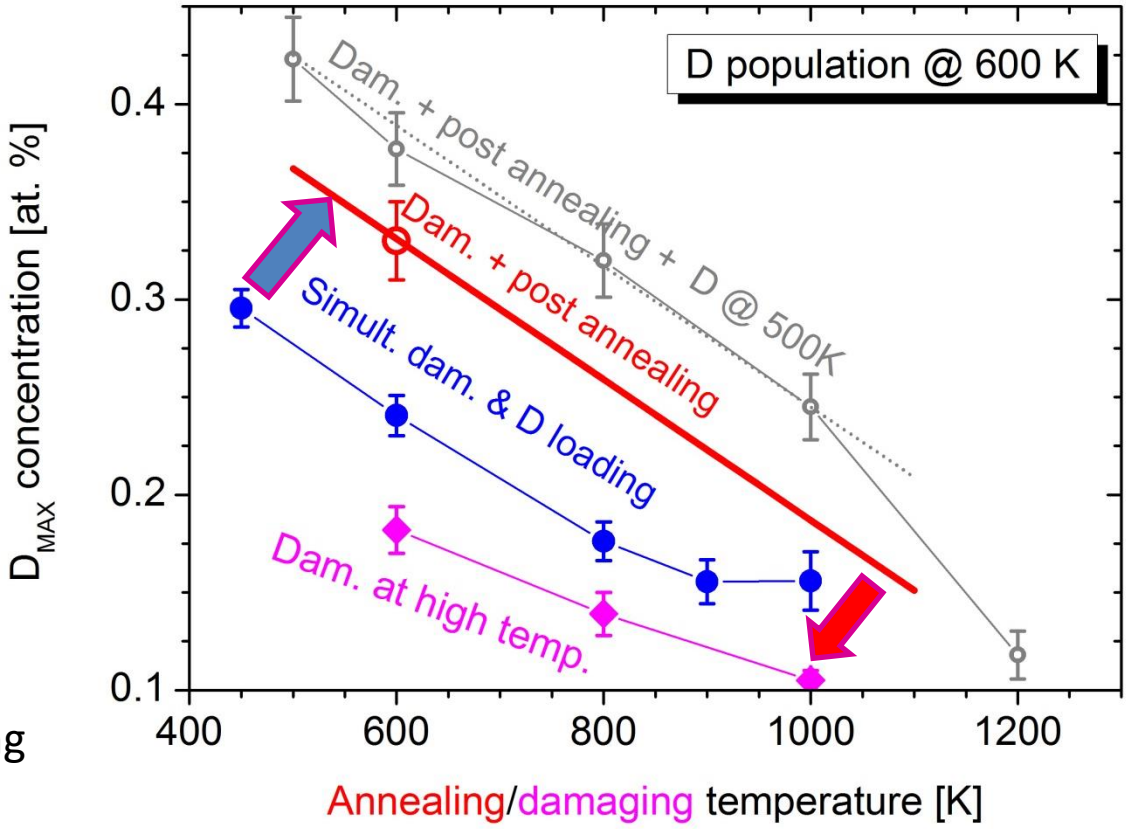
~ factor of 2 less D compared to post annealing

Comparison of different damaging procedures

Different Damaging procedures

- **Damage at 300 K + anneal at T^{EXP}; D population at 600 K (extropolation)**
- **Damage at T^{EXP}; D population at 600 K**
- **Damage & D exposure at T^{EXP}; D population at 600 K**

✓ Despite high T during damaging, simultaneous damaging and loading results in more trap sites (higher D retention) than damaging at high T.



➢ ***Simultaneous damaging and D exposure***

⇒ competition: defect annihilation at elevated temp. and defect stabilization by D = presence of D stabilizes the defects

Conclusions and outlook for part 2

- D retention in self-ion damaged studied by D atom loading
- Simultaneous W ion damaging and D atom exposure
  - ✓ Comparison to other damaging/exposure procedures
  - ✓ Competition between defect annihilation and defect stabilization with D
  - ✓ Synergies are present but not dramatic
- Decrease in D retention when exposure at higher temperatures but faster D diffusion in depth

For more details see: Markelj et al. NME in press (2017)

- ***Modelling ongoing***
- ***STEM analysis - under way***
- ***Simultaneous W ion damaging and ion exposure - in progress***
- ***Effect of simultaneous He irradiation and D loading***
- ***Comparison to neutron damaged material***

Influence of He irradiation on D retention

IOP Publishing | International Atomic Energy Agency
Nuclear Fusion
Nucl. Fusion 57 (2017) 064002 (5pp)
https://doi.org/10.1088/1741-4326/aa6b27

Letter

Hydrogen isotope accumulation in the helium implantation zone in tungsten

S. Markelj[1], T. Schwarz-Selinger[2] and A. Založnik[1]

[1] Jožef Stefan Institute (JSI), Jamova cesta 39, 1000 Ljubljana, Slovenia
[2] Max-Planck-Institut für Plasmaphysik (IPP), Boltzmannstrasse 2, D-85748 Garching, Germany

E-mail: sabina.markelj@ijs.si

Received 5 December 2016, revised 8 March 2017
Accepted for publication 4 April 2017
Published 28 April 2017

Abstract

The influence of helium (He) on deuterium (D) transport and retention was studied experimentally in tungsten (W). Helium was implanted 1 μm deep into W to a maximum calculated concentration of 3.4 at.%. To minimize the influence of displacement damage created during the He implantation on D retention, so-called self-damaged W was used. W was damaged by 20 MeV W ion bombardment and defects were populated by low-temperature D plasma at room temperature before He implantation. Deuterium depth profiling was performed *in situ* during isochronal annealing in the temperature range from 300 K to 800 K. It is shown for the first time unambiguously that He attracts D and locally increases D trapping. Deuterium retention increased by a factor of two as compared to a non-He implanted W reference after sample annealing at 450 K. Rate equation modelling can explain the measured D depth profiles quantitatively when keeping the de-trapping parameters unchanged but only increasing the number of traps in the He zone. This bolsters the confidence in the theoretical calculations predicting that more hydrogen isotopes can be stored around a He cluster zone.

Keywords: tungsten, helium, deuterium retention, displacement damage, NRA

(Some figures may appear in colour only in the online journal)

Reduced retention in He-D mixed plasma experiments – He diffusion barrier?

Influence of He as an analyzing beam?

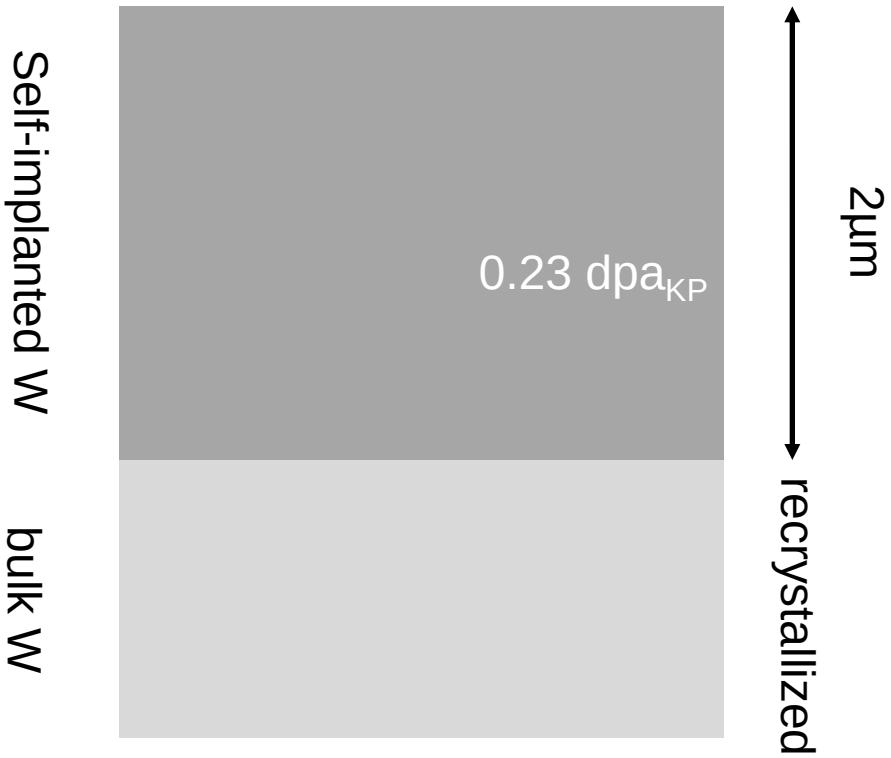
CRP Objective 4: to perform coordinated experiments and computations to improve the knowledge base on the influence of tungsten microstructure on tritium retention and tritium transport

Sample preparation

W self damaging until saturation

20 MeV

7.9×10^{17} W/m^2

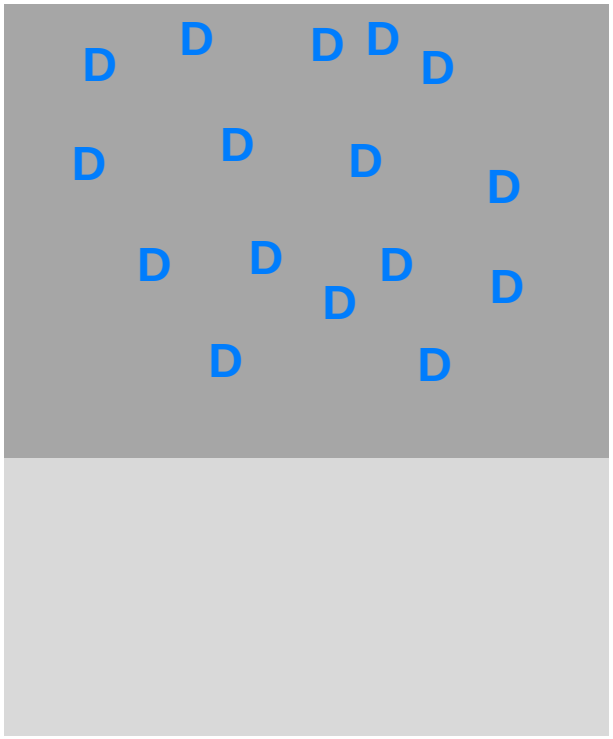


Sample preparation

D plasma loading at 290K

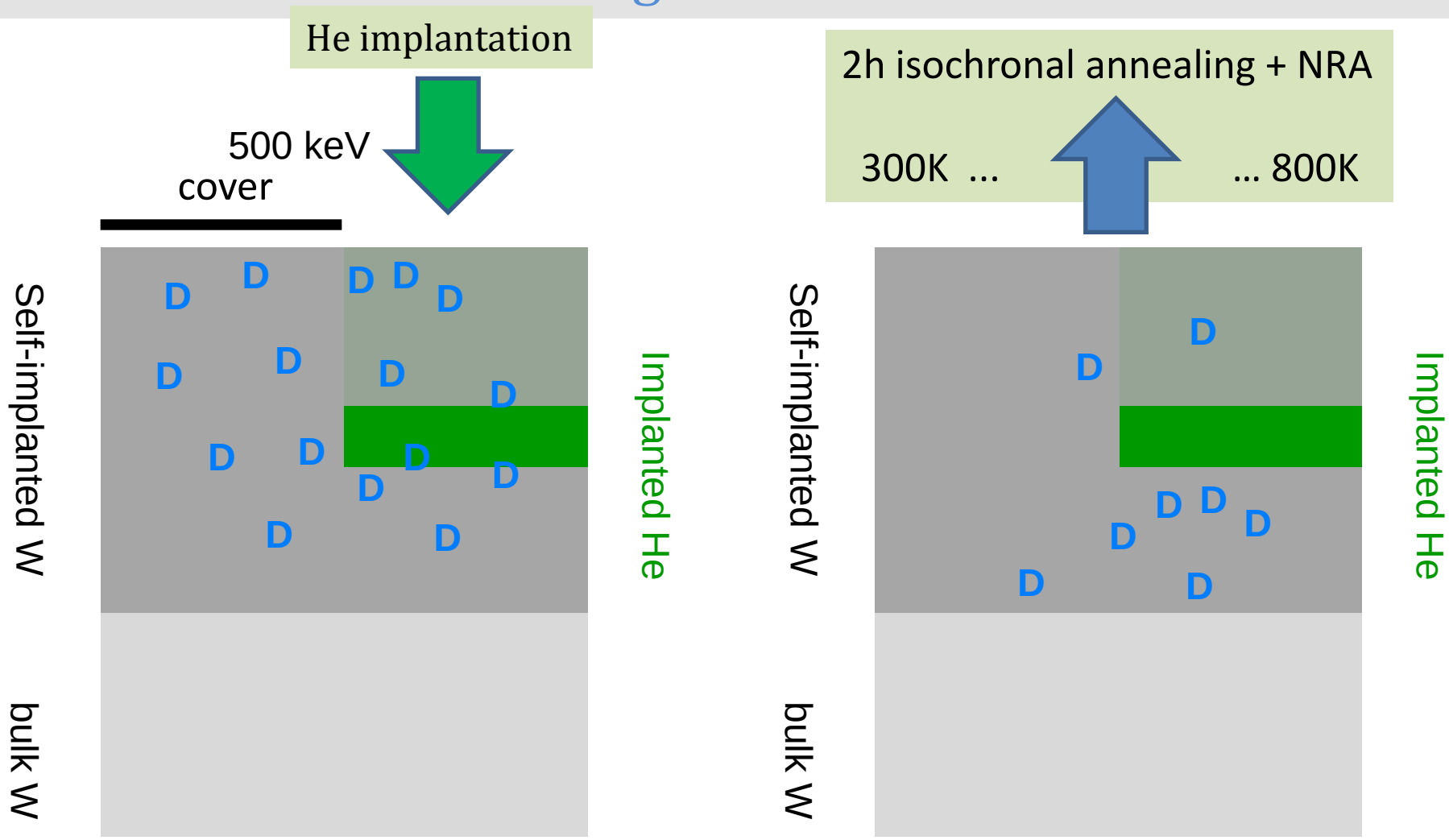
< 5eV/D

1.5×10^{25} D/m^2



< 2 at.%

First experimental series: In situ annealing + NRA



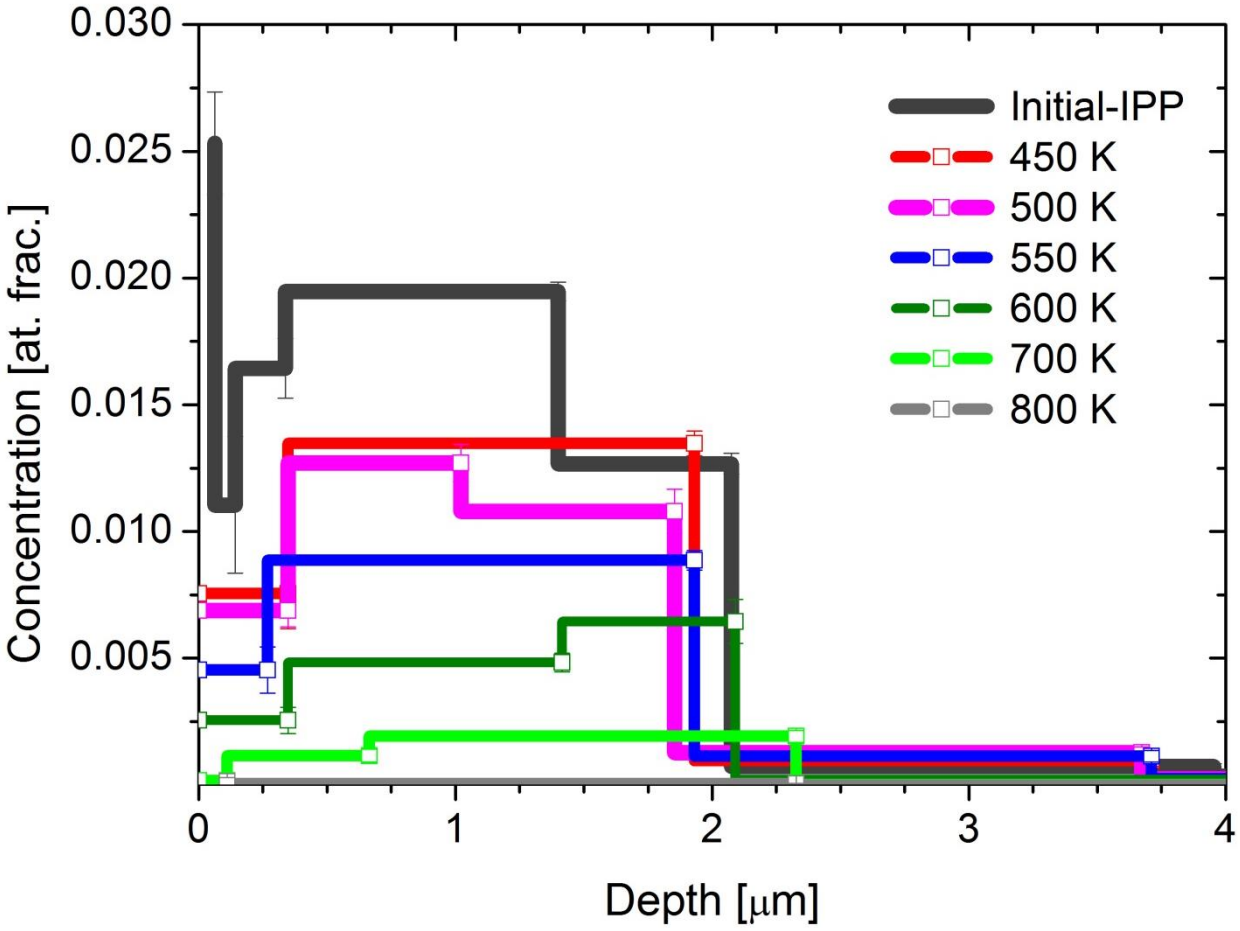
The experiment: Isochronal annealing

Depth profiles on the self-damaged part

- Heating for 2h at each temperature
- In-situ NRA after cool down

Observations:

Only **self-damaged** part of the sample:



The experiment: Isochronal annealing

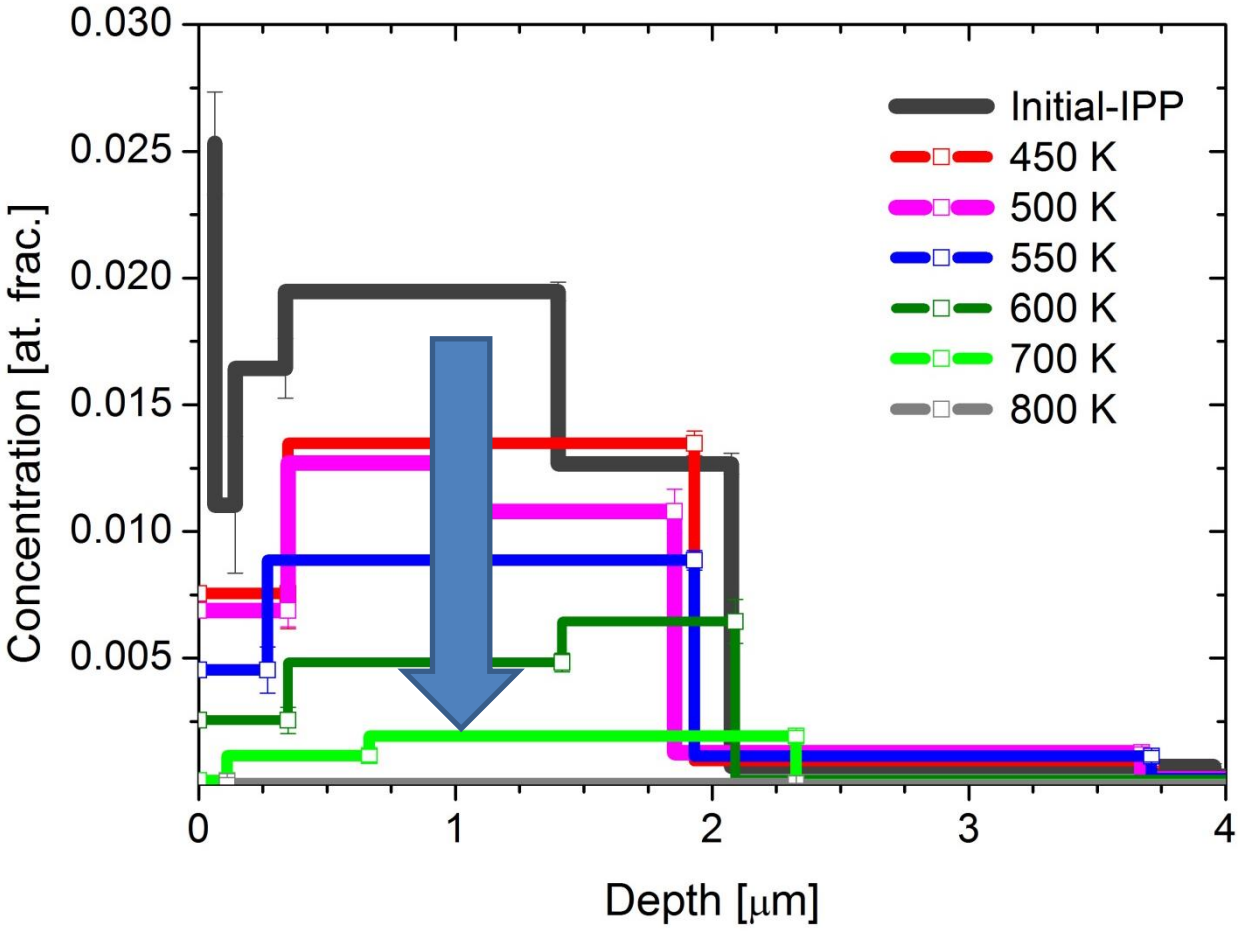
Depth profiles on the self-damaged part

- Heating for 2h at each temperature
- In-situ NRA after cool down

Observations:

- ✓ D content drops continuously with temperature
- ✓ No D left after heating at 800 K

Only **self-damaged** part of the sample:



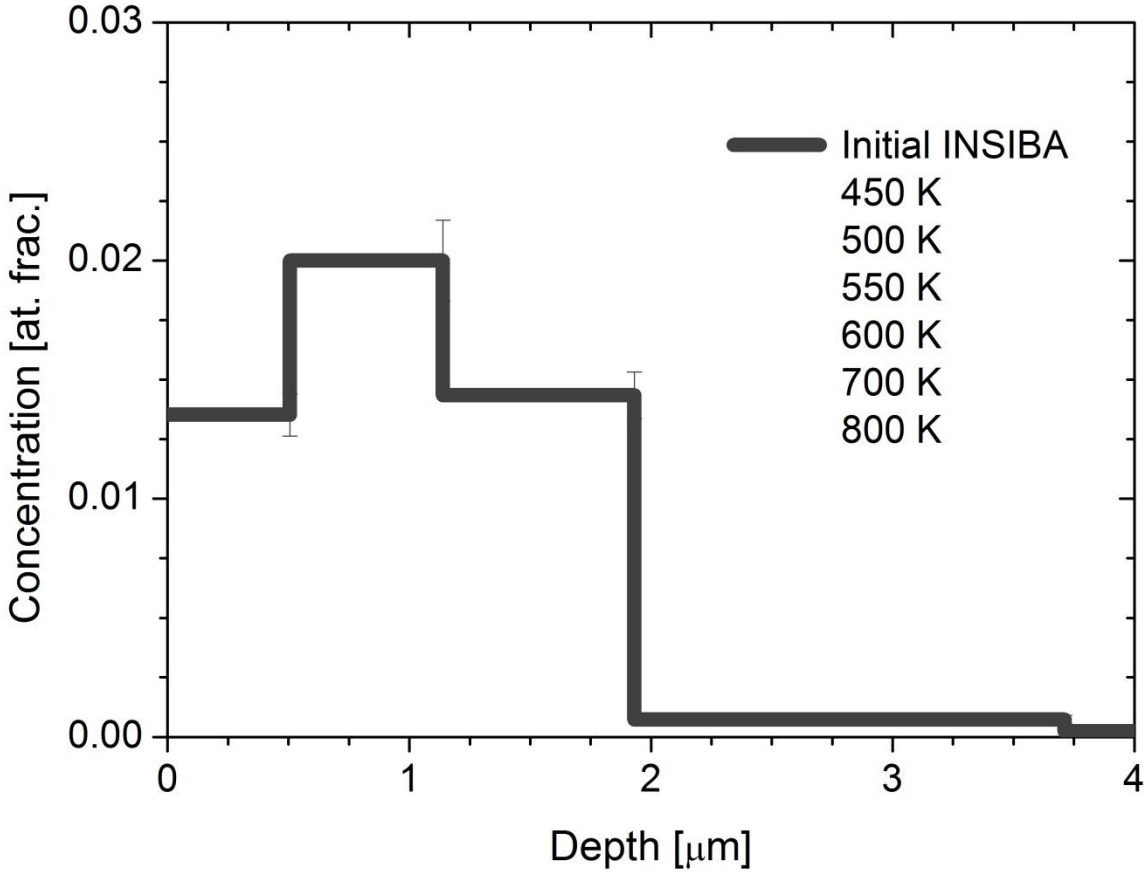
The experiment: Isochronal annealing

Depth profiles on the He irradiated part

- Heating for 2h at each temperature

Observations:

He implanted part of the sample:



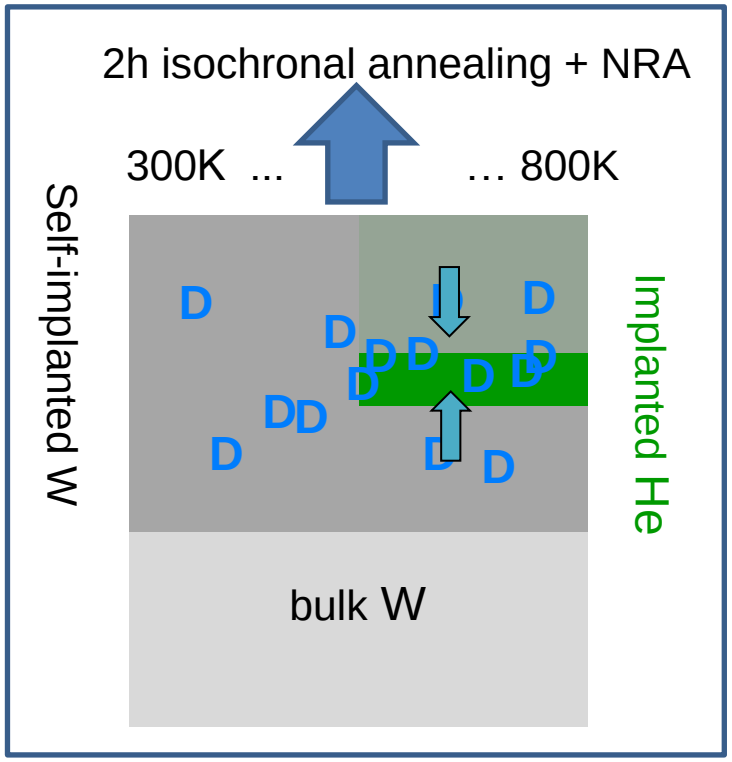
The experiment: Isochronal annealing

Depth profiles on the He irradiated part

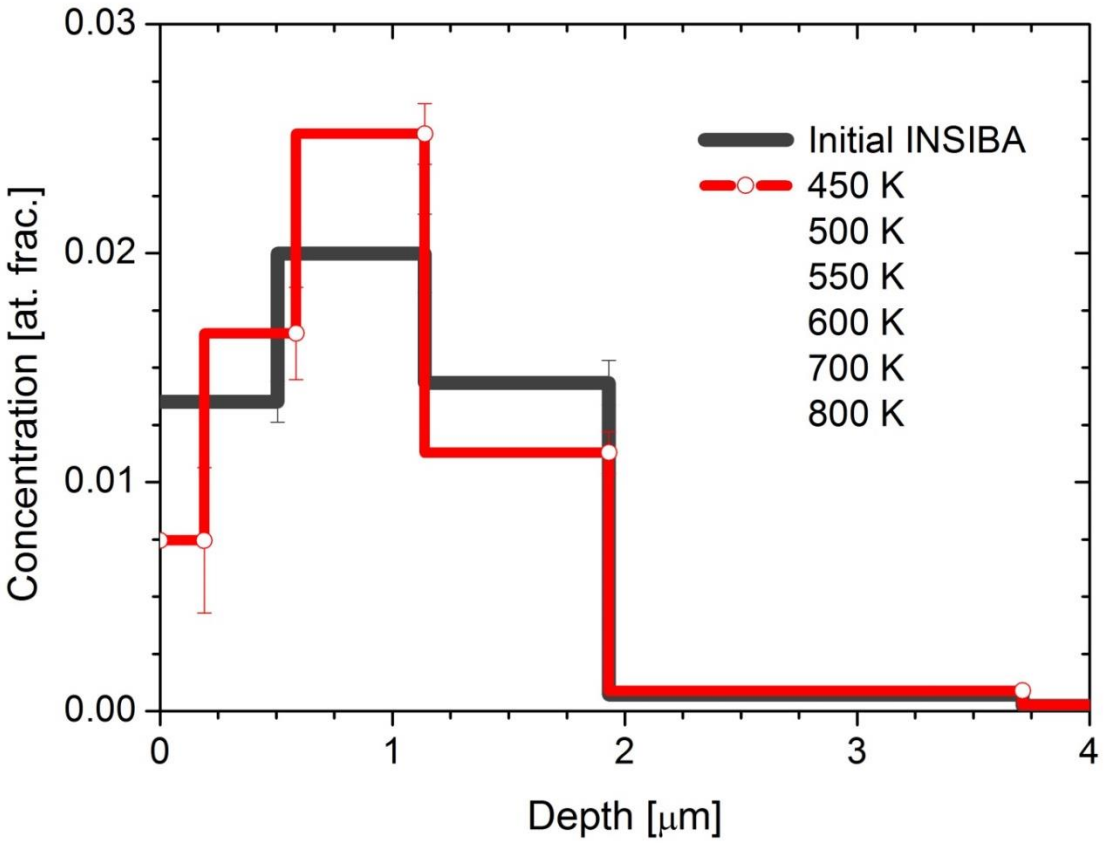
- Heating for 2h at each temperature

Observations:

✓ **D increases in the He zone!!!**



He implanted part of the sample:



The experiment: Isochronal annealing

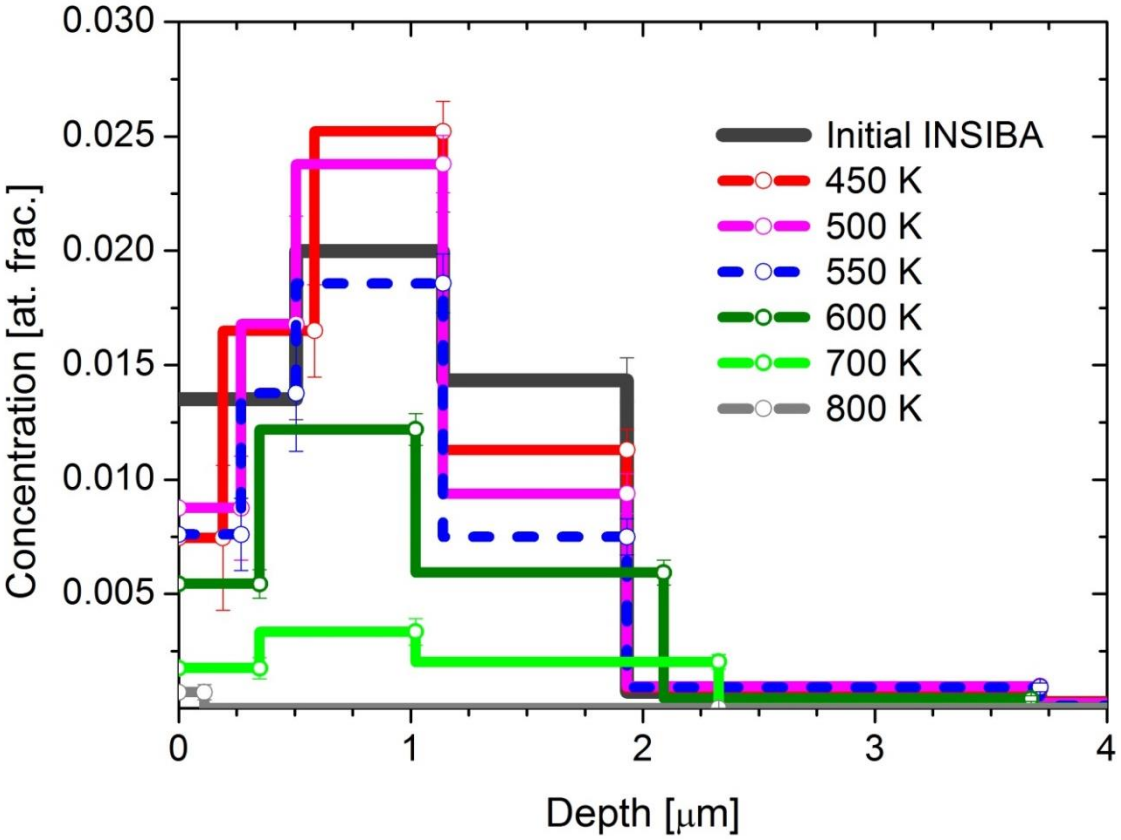
Depth profiles on the He irradiated part

- Heating for 2h at each temperature

Observations:

- ✓ **D increases in the He zone!!!**
- ✓ D content beyond the He layer drops in the same way as in the non-He-exposed part!
- ✓ **Total D desorption at 800 K** as for the non-He-exposed part

He implanted part of the sample:

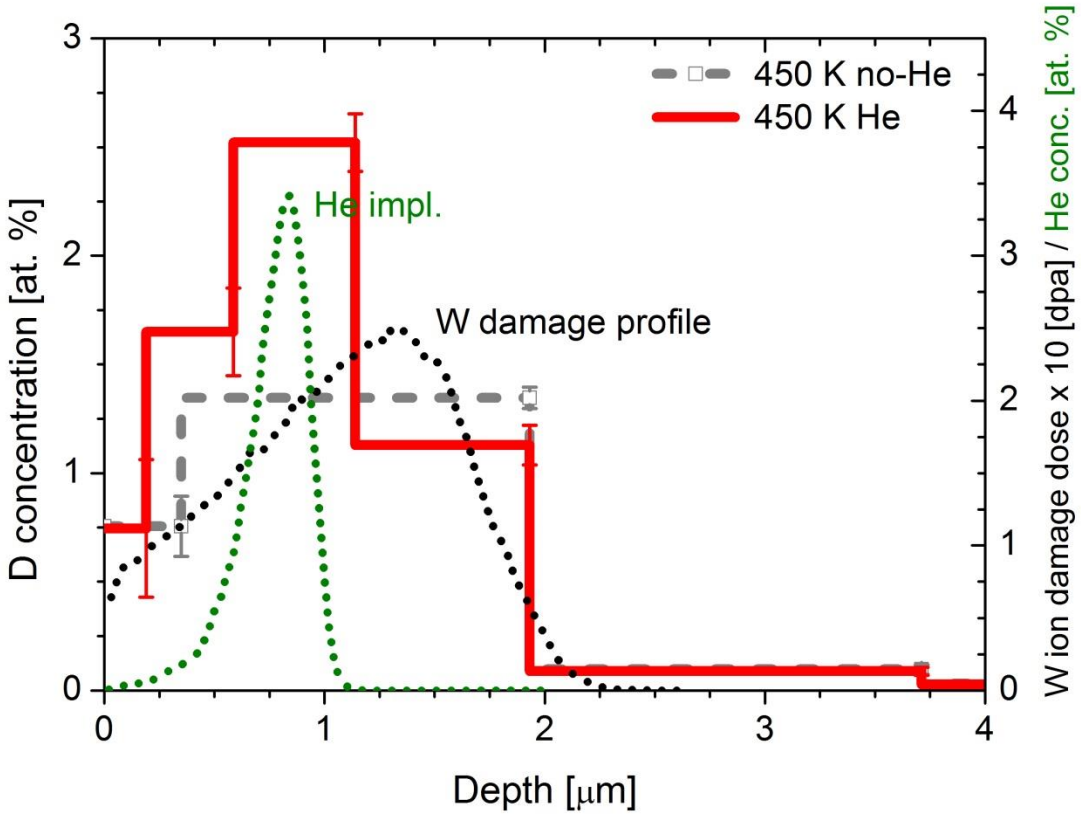


The experiment: Isochronal annealing

Comparison at 450 K

Observations:

- ✓ **D increases in the He zone!!!**
- ✓ **2 times higher D concentration in He zone**

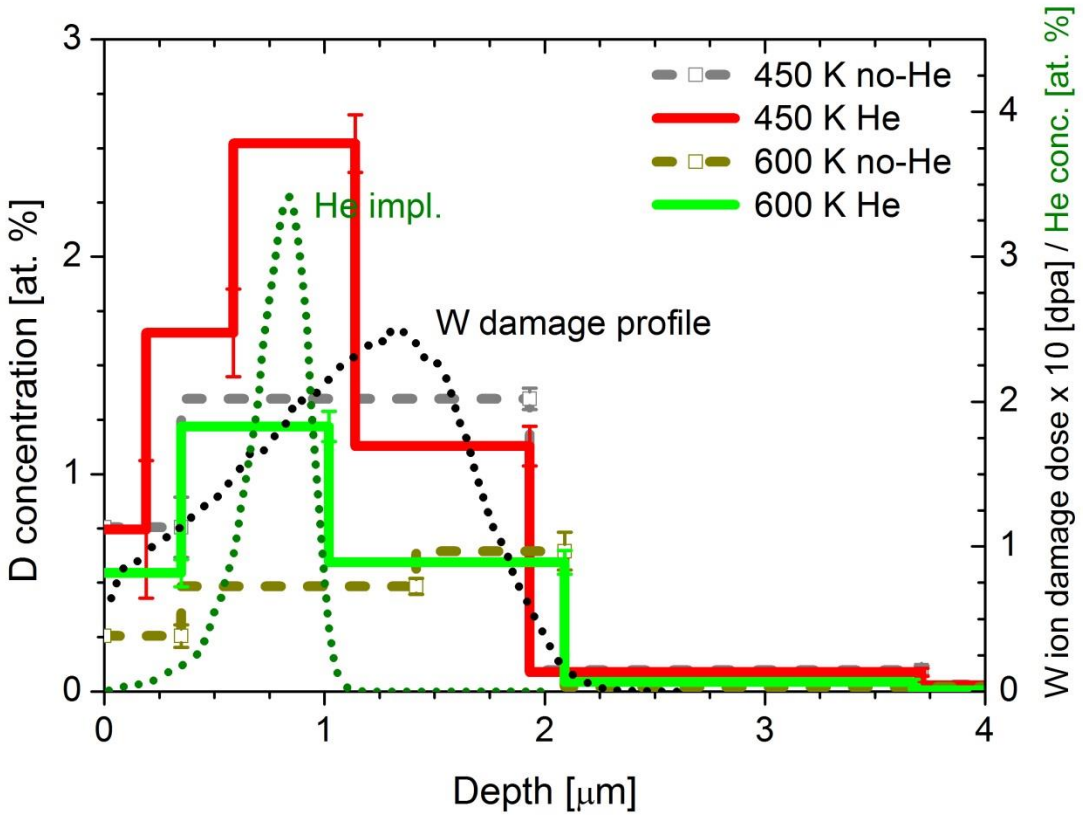


The experiment: Isochronal annealing

Comparison at 450 K

Observations:

- ✓ **D increases in the He zone!!!**
- ✓ **2 times higher D concentration in He zone**
- ✓ D content beyond the He layer drops in the same way as in the non-He-exposed part!

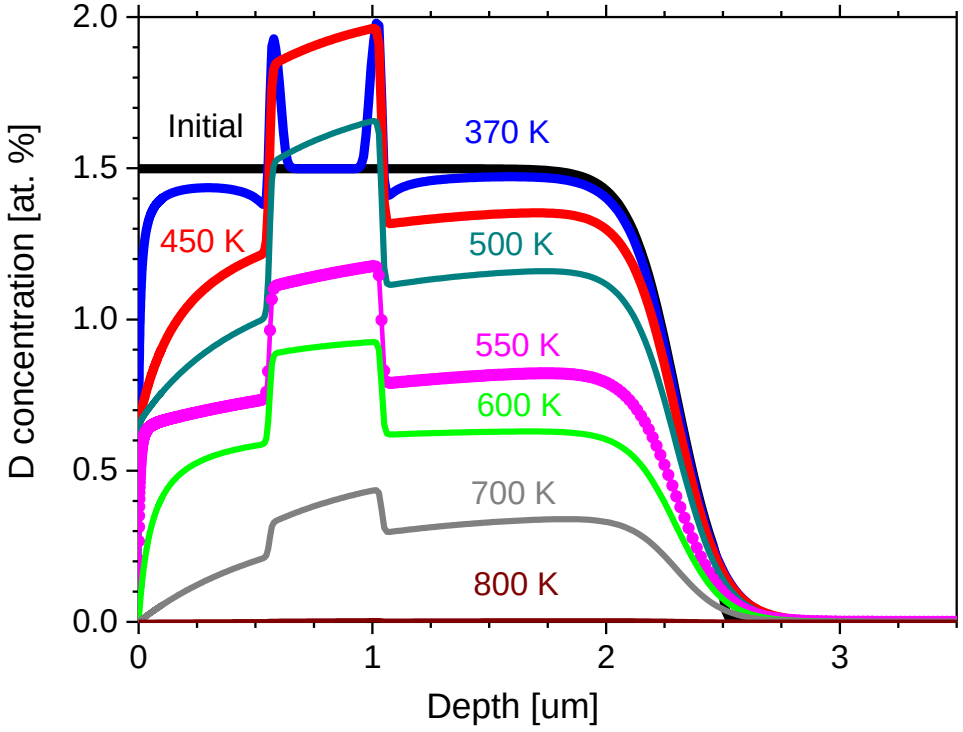


➢ **No diffusion barrier!!**

Diffusion trapping modelling with TESSIM code

- He is trapped in a vacancy there are a **factor of two more 'optimal charge density sites' for H** (12 sites) as compared to a He-free vacancy (6 sites) due to the volume expansion.
  [H-B. Zhou et al. *Nuclear Fusion* 50, no. 11 (2010)]

- Doubling locally trap density in the implantation zone



Result:

- **Local D increase not only**
  - qualitatively but
  - quantitatively matches the experiment!

Influence of He on D transport and retention in W

See also S. Markelj et al. Nucl. Fusion 57 (2017) 064002 (5pp)

- **He (nano-bubbles) does not act as diffusion barrier**
- Presence of **He increases D trap densities** above values known from displacement damage
- D concentration exceed “no He” values by up to a factor of three for isochronal annealing, isothermal loading and re-loading after TDS
- Diffusion trapping modelling can explain observation with an increased trap density only with unchanged detrapping energy quantitatively

Summary

- ✓ Part 1 - *in situ* benchmark experiments on self damaged
- ✓ Part 2 – first simultaneous W ion damaging and D loading – step toward the fusion conditions
- ✓ Part 3 – Influence of He irradiation on D retention – strong influence of He which confirms the current MD/DFT calculations

Thank you for your attention!

Discussion slides

Recent publications

IOP Publishing | International Atomic Energy Agency
Nucl. Fusion 57 (2017) 064002 (5pp)
Nuclear Fusion
https://doi.org/10.1088/1741-4326/aa6b27

Letter

Hydrogen isotope accumulation in the helium implantation zone in tungsten

S. Markelj[1], T. Schwarz-Selinger[2] and A. Založnik[1]

[1] Jožef Stefan Institute (JSI), Jamova cesta 39, 1000 Ljubljana, Slovenia
[2] Max-Planck-Institut für Plasmaphysik (IPP), Boltzmannstrasse 2, D-85748 Garching, Germany

E-mail: sabina.markelj@ijs.si

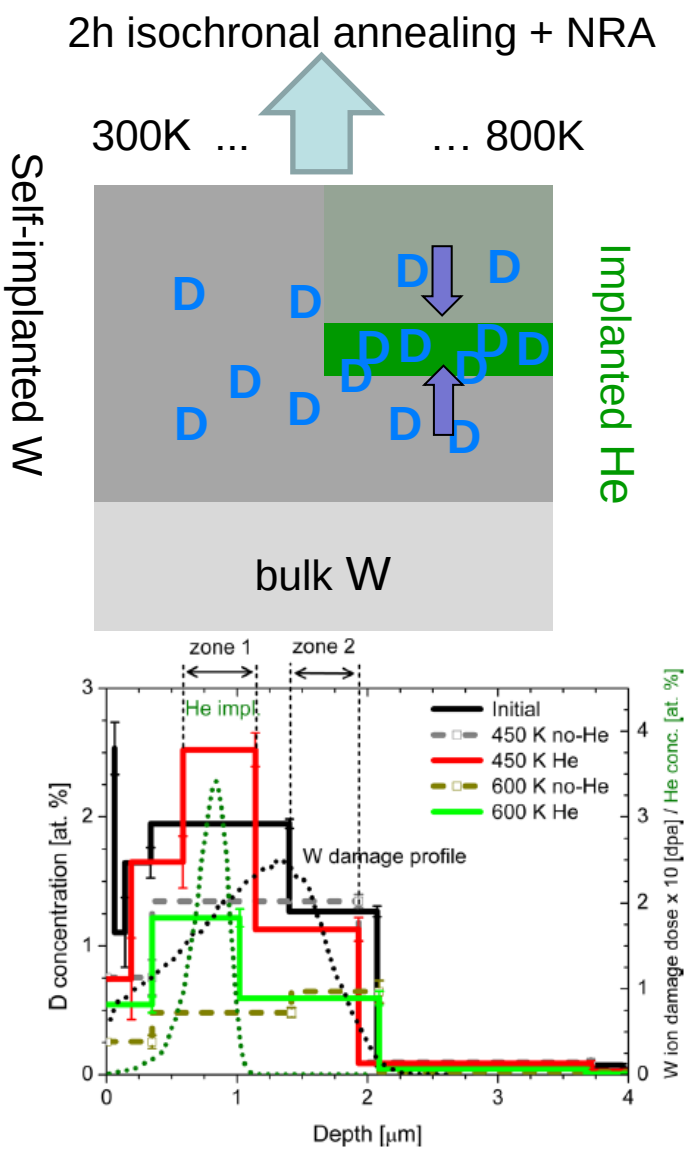
Received 5 December 2016, revised 8 March 2017
Accepted for publication 4 April 2017
Published 28 April 2017

Abstract

The influence of helium (He) on deuterium (D) transport and retention was studied experimentally in tungsten (W). Helium was implanted 1 μm deep into W to a maximum calculated concentration of 3.4 at.%. To minimize the influence of displacement damage created during the He implantation on D retention, so-called self-damaged W was used. W was damaged by 20 MeV W ion bombardment and defects were populated by low-temperature D plasma at room temperature before He implantation. Deuterium depth profiling was performed *in situ* during isochronal annealing in the temperature range from 300 K to 800 K. It is shown for the first time unambiguously that He attracts D and locally increases D trapping. Deuterium retention increased by a factor of two as compared to a non-He implanted W reference after sample annealing at 450 K. Rate equation modelling can explain the measured D depth profiles quantitatively when keeping the de-trapping parameters unchanged but only increasing the number of traps in the He zone. This bolsters the confidence in the theoretical calculations predicting that more hydrogen isotopes can be stored around a He cluster zone.

Keywords: tungsten, helium, deuterium retention, displacement damage, NRA

(Some figures may appear in colour only in the online journal)



Recent publications

IOP Publishing | International Atomic Energy Agency
Nuclear Fusion
Nucl. Fusion 57 (2017) 056002 (15pp)
https://doi.org/10.1088/1741-4326/aa5aa5

Simulations of atomic deuterium exposure in self-damaged tungsten

E.A. Hodille[1], A. Založnik[2], S. Markelj[2], T. Schwarz-Selinger[3], C.S. Becquart[4], R. Bisson[5] and C. Grisolia[1]

[1] CEA, IRFM, F-13108 Saint-Paul-lez-Durance, France
[2] Jožef Stefan Institute, Jamova cesta 39, 1000, Ljubljana, Slovenia
[3] Max-Planck-Institut für Plasmaphysik, Boltzmannstrasse 2, D-85748 Garching, Germany
[4] Université Lille I, UMET, UMR 8207, ENSCL, 59655 Villeneuve d'Ascq Cedex, France
[5] Aix-Marseille Université, CNRS, PIIM, Marseille, France

E-mail: christian.grisolia@cea.fr

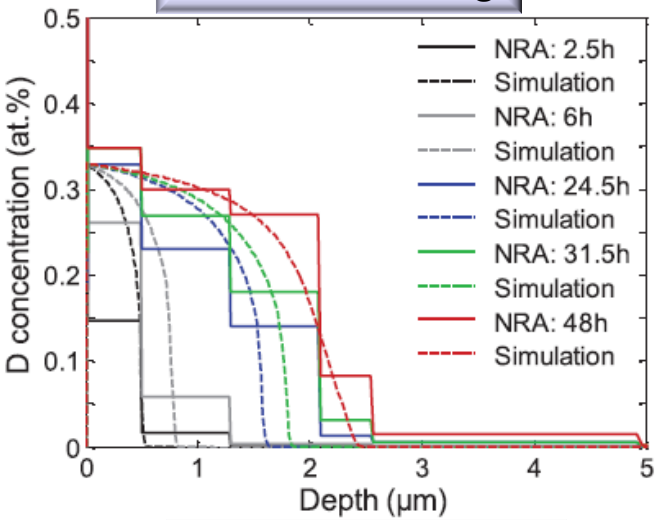
Received 1 September 2016, revised 12 December 2016
Accepted for publication 4 January 2017
Published 14 March 2017

Abstract

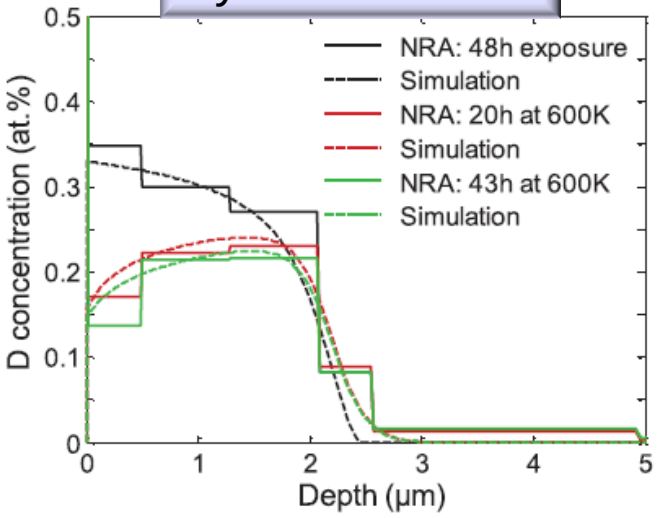
Simulations of deuterium (D) atom exposure in self-damaged polycrystalline tungsten at 500 K and 600 K are performed using an evolution of the MHIMS (migration of hydrogen isotopes in materials) code in which a model to describe the interaction of D with the surface is implemented. The surface-energy barriers for both temperatures are determined analytically with a steady-state analysis. The desorption energy per D atom from the surface is 0.69 ± 0.02 eV at 500 K and 0.87 ± 0.03 eV at 600 K. These values are in good agreement with *ab initio* calculations as well as experimental determination of desorption energies. The absorption energy (from the surface to the bulk) is 1.33 ± 0.04 eV at 500 K, 1.55 ± 0.02 eV at 600 K when assuming that the resurfacing energy (from the bulk to the surface) is 0.2 eV. Thermal-desorption spectrometry data after D atom exposure at 500 K and isothermal desorption at 600 K after D atom exposure at 600 K can be reproduced quantitatively with three bulk-detrapping energies, namely 1.65 ± 0.01 eV, 1.85 ± 0.03 eV and 2.06 ± 0.04 eV, in addition to the intrinsic detrapping energies known for undamaged tungsten (0.85 eV and 1.00 eV). Thanks to analyses of the amount of traps during annealing at different temperatures and *ab initio* calculations, the 1.65 eV detrapping energy is attributed to jogged dislocations and the 1.85 eV detrapping energy is attributed to dislocation loops. Finally, the 2.06 eV detrapping energy is attributed to D trapping in cavities based on literature reporting observations on the growth of cavities, even though this could also be understood as D desorbing from the C-D bond in the case of hydrocarbon contamination in the experimental sample.

Keywords: tungsten, damaged material, rate-equation modeling, deuterium atoms, fuel retention

D atom loading



Dynamic release



Recent publications

Nuclear Materials and Energy 000 (2016) 1–6

Contents lists available at ScienceDirect

Nuclear Materials and Energy

journal homepage: www.elsevier.com/locate/nme

Deuterium retention in tungsten simultaneously damaged by high energy W ions and loaded by D atoms

S. Markelj[a,*], T. Schwarz-Selinger[b], A. Založnik[a], M. Kelemen[a,d], P. Vavpetič[a], P. Pelicon[a], E. Hodille[c], C. Grisolia[c]

[a] Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia
[b] Max-Planck-Institut für Plasmaphysik, Boltzmannstrasse 2, D-85748 Garching, Germany
[c] CEA, IRFM, F-13108 Saint Paul Lez Durance, France
[d] Jožef Stefan International Postgraduate School, Jamova cesta 39, 1000 Ljubljana, Slovenia

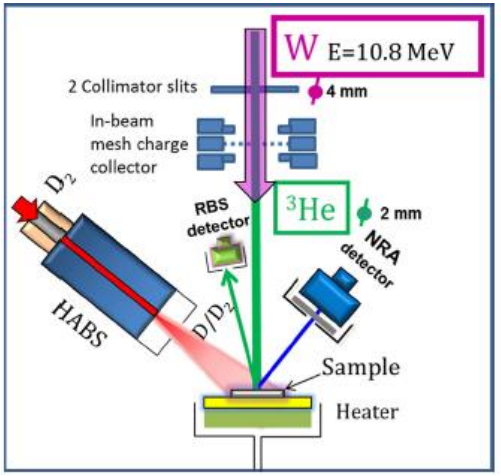
ARTICLE INFO

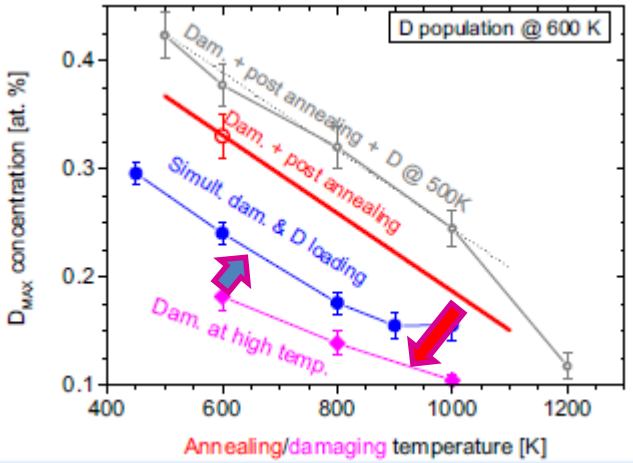
Article history:
Received 8 July 2016
Revised 27 September 2016
Accepted 15 November 2016
Available online xxx

Keywords:
Tungsten
Deuterium retention
Displacement damage
Neutral atoms
NRA

ABSTRACT

Deuterium retention was for the first time measured in tungsten samples simultaneously irradiated by ions and exposed to D atoms at five different temperatures from 450 K to 1000 K. In order to obtain formation on the defect concentration, samples were afterwards exposed to D atoms at 600 K to popul the created defects. The results were compared to different sequential damaging/exposure experimen Synergistic effects were observed, namely, higher D concentrations were found in the case of simul neous damaging and D-atom loading as compared to sequential damaging at elevated temperatures a populating the defects afterwards. However, the deuterium retention is still lower as compared to quential damaging at room temperature and post-damaging annealing. The observations are explained stabilization of defects by the presence of solute hydrogen in the bulk that would annihilate at high te peratures without the presence of hydrogen. Results of simultaneous W-ion damaging and D exposure elevated temperatures were also compared to a sequential experiment of W-ion damaging at room te perature and then D-atom loading at high temperatures showing that thermal D de-trapping domina deuterium retention at high temperatures.

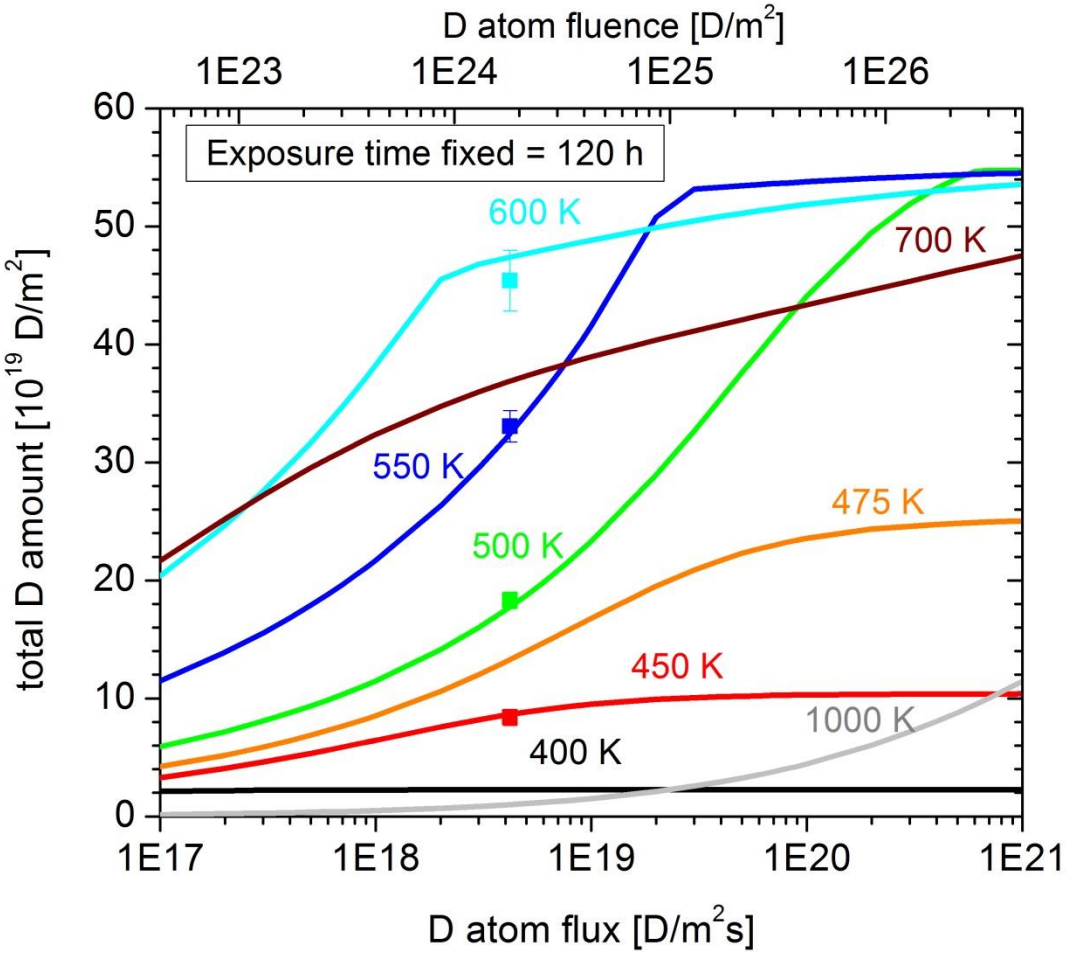




- ***Simultaneous damaging and D exposure*** - increased D retention compared to sequential damaging and exposure ⇒ competition: defect annihilation at elevated temperatures and defect stabilization by D

D atom loading of self-damaged W at different temperatures – comparison to plasma

Hydrogen Atom beam source
Energy: 0.3 eV - thermal energy
Fixed time of exposure 120h



Small penetration depth = reason why low energy neutrals can be ignored at plasma exposures at temperatures ≤ 450 K

In situ studies by ion beam methods in fusion

- *In situ* = Hydrogen/Deuterium concentration measured during the exposure, annealing,..

- Meyers et al. J. Appl. Phys. 56 (1984) 1561: Trapping and surface recombination of ion-implanted deuterium in stainless steel
- Morita et al. JNM 162 (1989) 990: *Dynamic measurements of depth profiles of hydrogen implanted into graphite at elevated temperatures*
- Scherzer JNM 168 (1989) 121: *On the dynamic inventory of deuterium implanted in graphite*
- Langhoff and Scherzer JNM 245 (1997) 60: *The hydrogen inventory in plasma exposed graphite surfaces*
- *Markelj et al. NIM B 259 (2007) 989: Studying processes of hydrogen interaction with metallic surfaces in situ and in real time by ERDA*

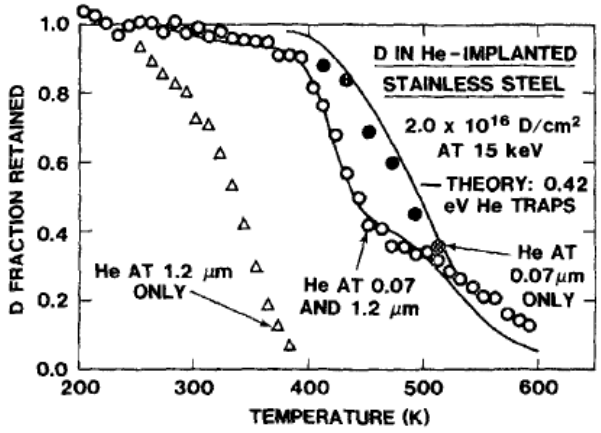


FIG. 2. Deuterium retention vs temperature in He-implanted Type 304 stainless steel for a D fluence of 2×10^{16} atom/cm^2

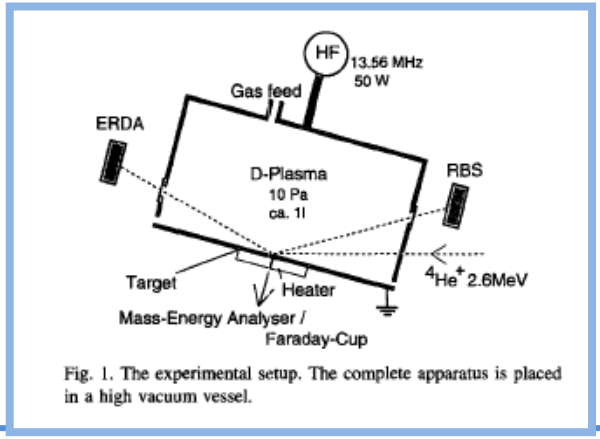


Fig. 1. The experimental setup. The complete apparatus is placed in a high vacuum vessel.

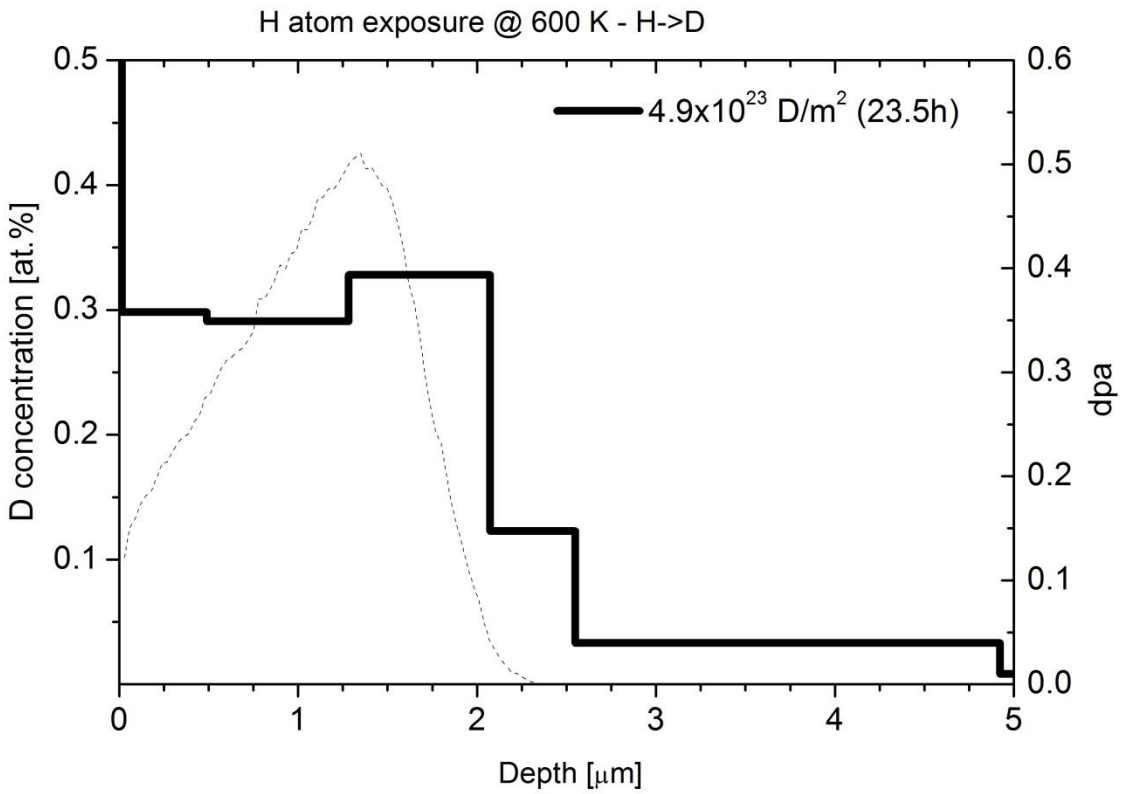
Langhoff and Scherzer JNM 245 (1997) 600

New: *in situ* study on **self-damaged tungsten** and exposure to deuterium **atoms**

Bulk isotope exchange H → D in self-damaged W

Study of bulk isotope exchange at 600 K

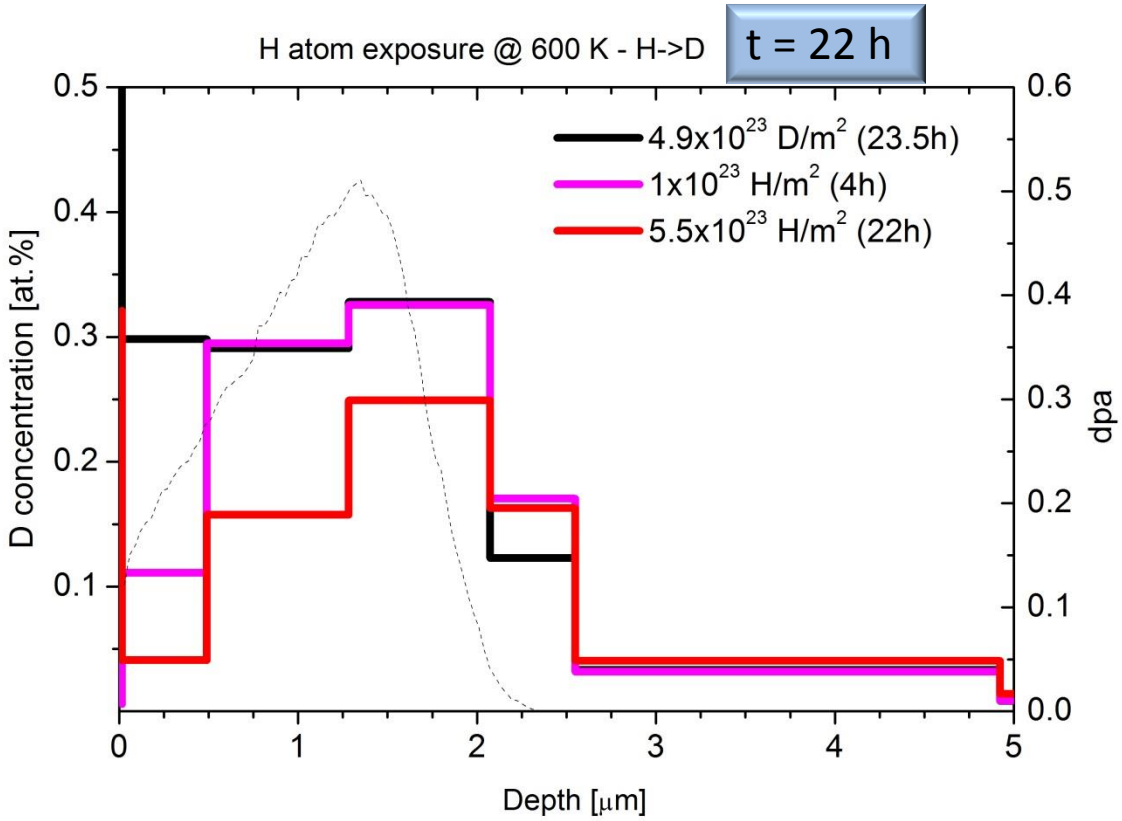
- Exposure to H atoms
- H atom beam flux density: 6.9×10^{18} H/m^{2}s
- **D depth profile before start of H exposure**



Bulk isotope exchange H → D in self-damaged W

Study of bulk isotope exchange at 600 K

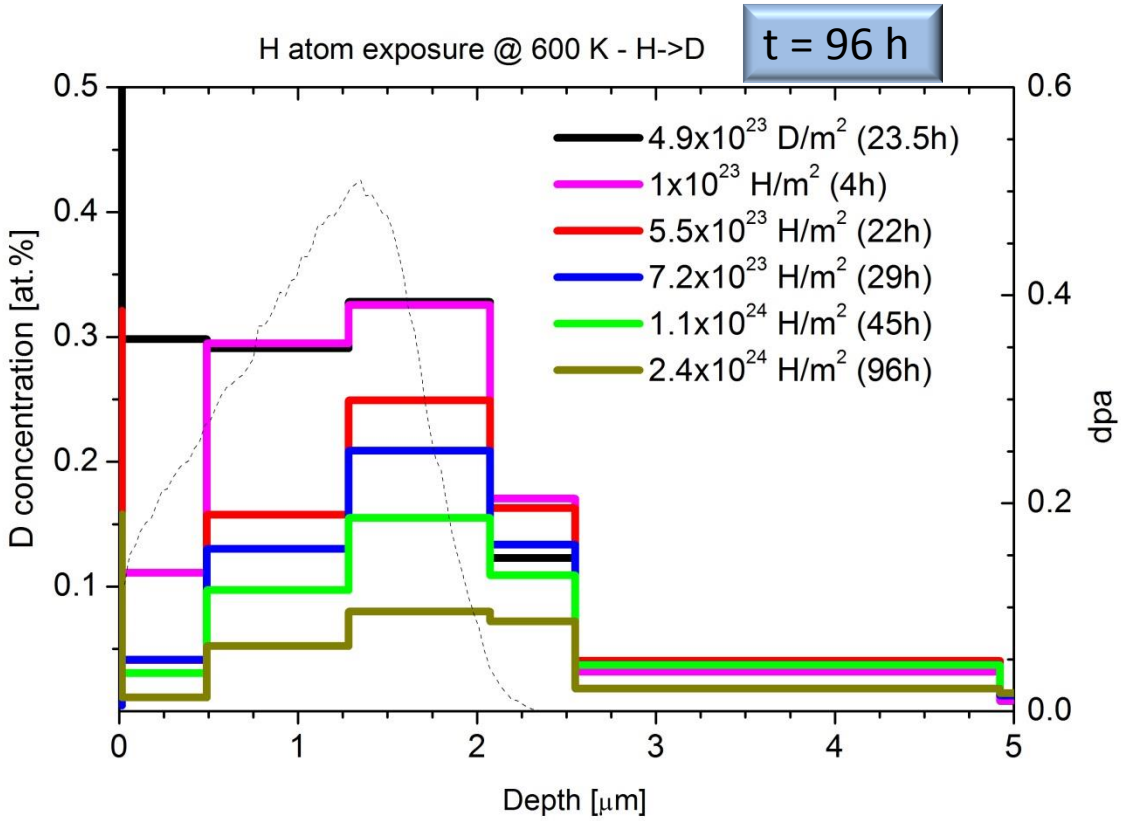
- Exposure to H atoms
- H atom beam flux density: 6.9×10^{18} H/m^{2}s
- **Decrease of D in the bulk – faster near surface**



Bulk isotope exchange H → D in self-damaged W

Study of bulk isotope exchange at 600 K

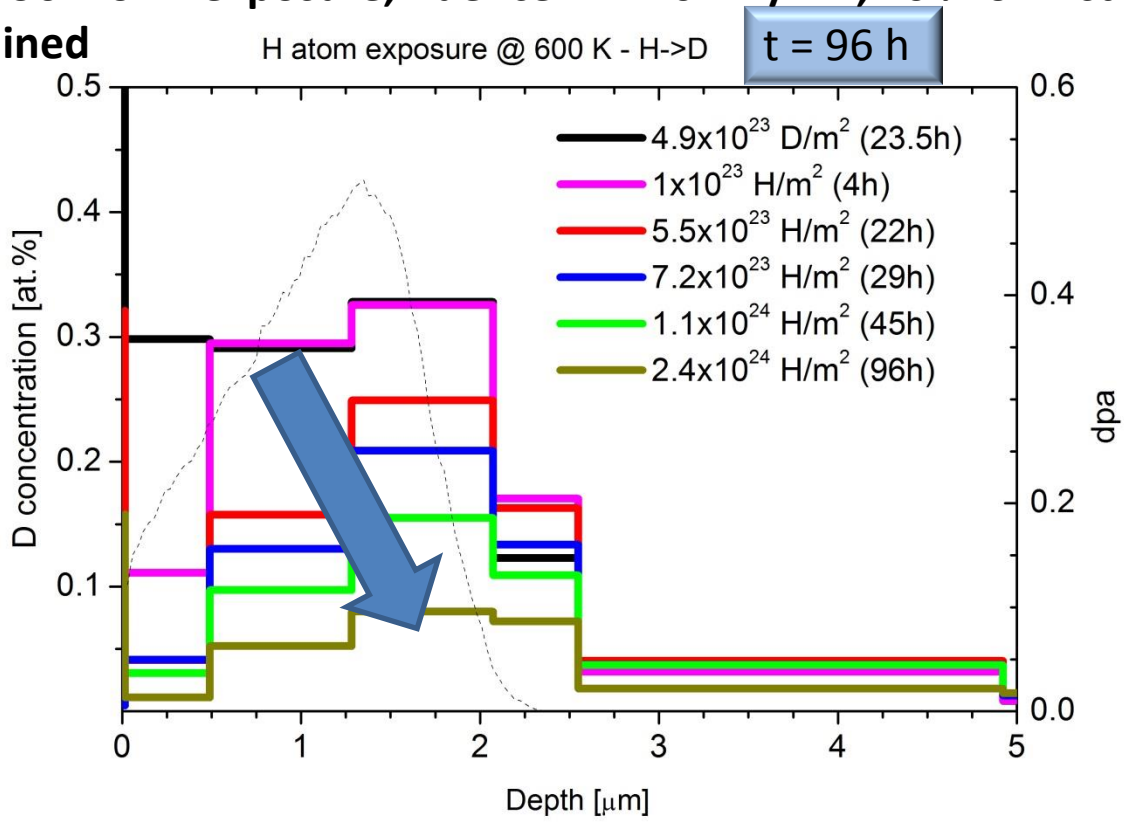
- Exposure to H atoms
- H atom beam flux density: 6.9×10^{18} H/m^{2}s
- **After 96 h of H exposure, fluence $2.4\text{x}10^{24}$ H/m^2 , 20 % of D still remained**



Bulk isotope exchange H → D in self-damaged W

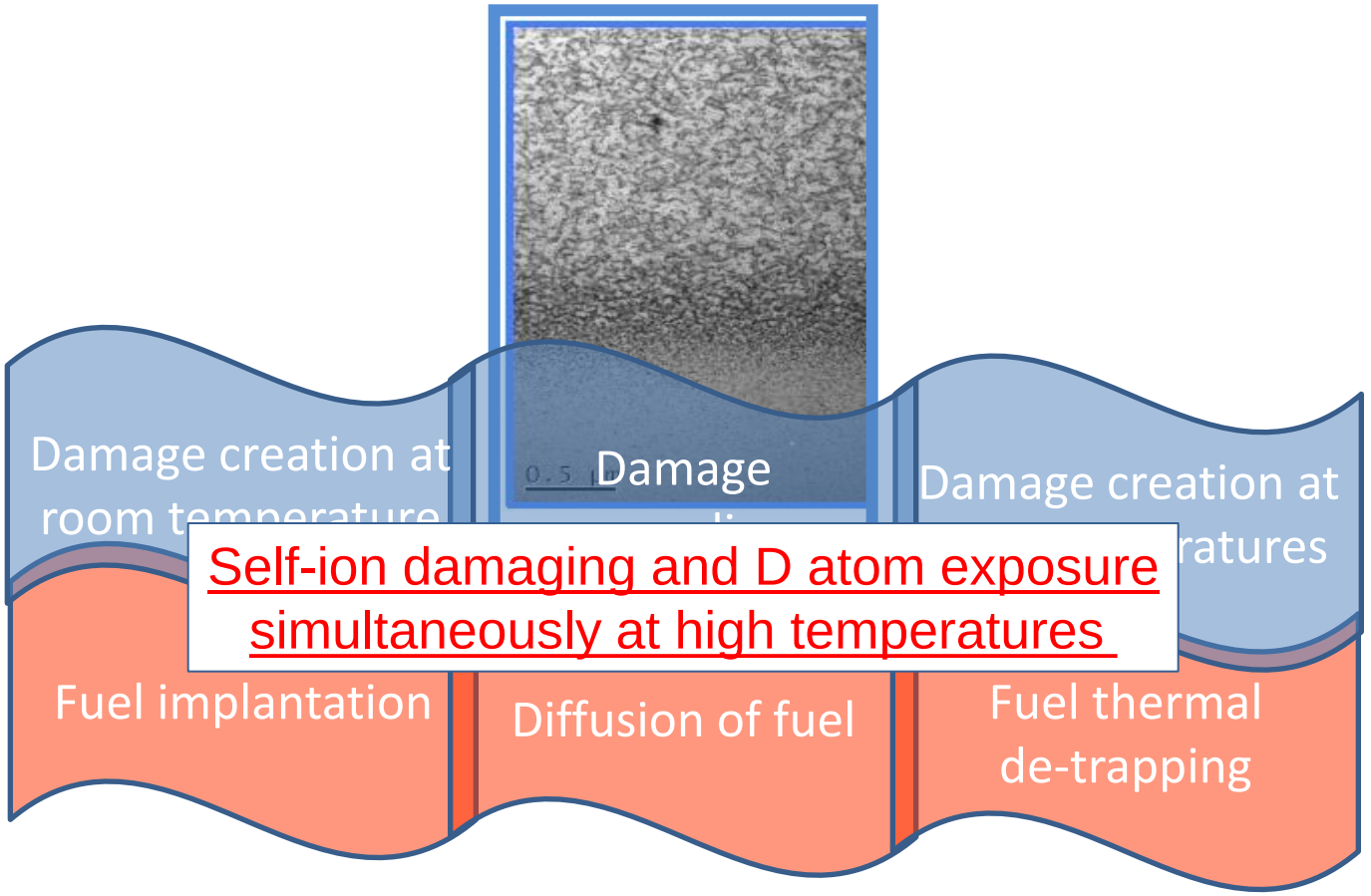
Study of bulk isotope exchange at 600 K

- Exposure to H atoms
- H atom beam flux density: 6.9×10^{18} H/m^{2}s
- **After 96 h of H exposure, fluence $2.4\text{x}10^{24}$ H/m^2 , 20 % of D still remained**



D removal in bulk of damaged layer by H atoms = isotope exchange!!!
No kinetic energy for exchange

First simultaneous W irradiation and D loading



- Comparison to post annealing/exposure experiments – look at the individual building blocks to sort out the effects.

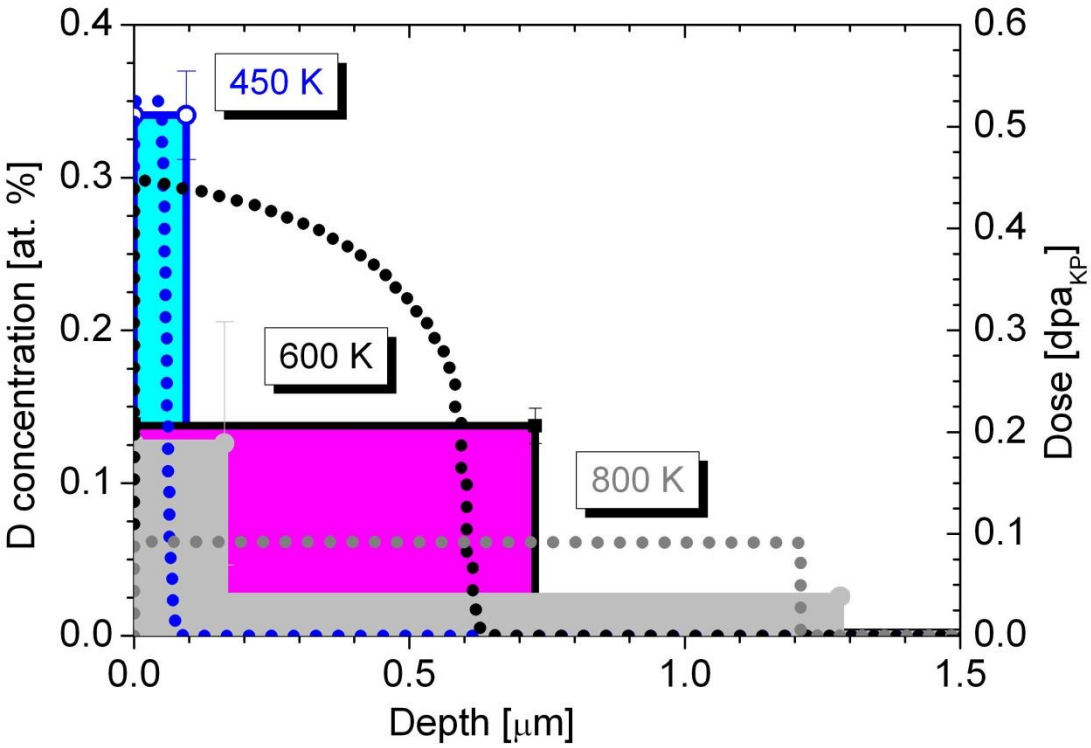
Modeling of simultaneous W irradiation and D loading

- Modelling D depth profiles by rate equation model – the MHIMS code

- Surface processes included [Hodille et al. NF 57 (2017) 056002]

- Simulation of trap density increasing over time.

- Trap concentration taken from reference sample: sequential RT damaging and D exposure

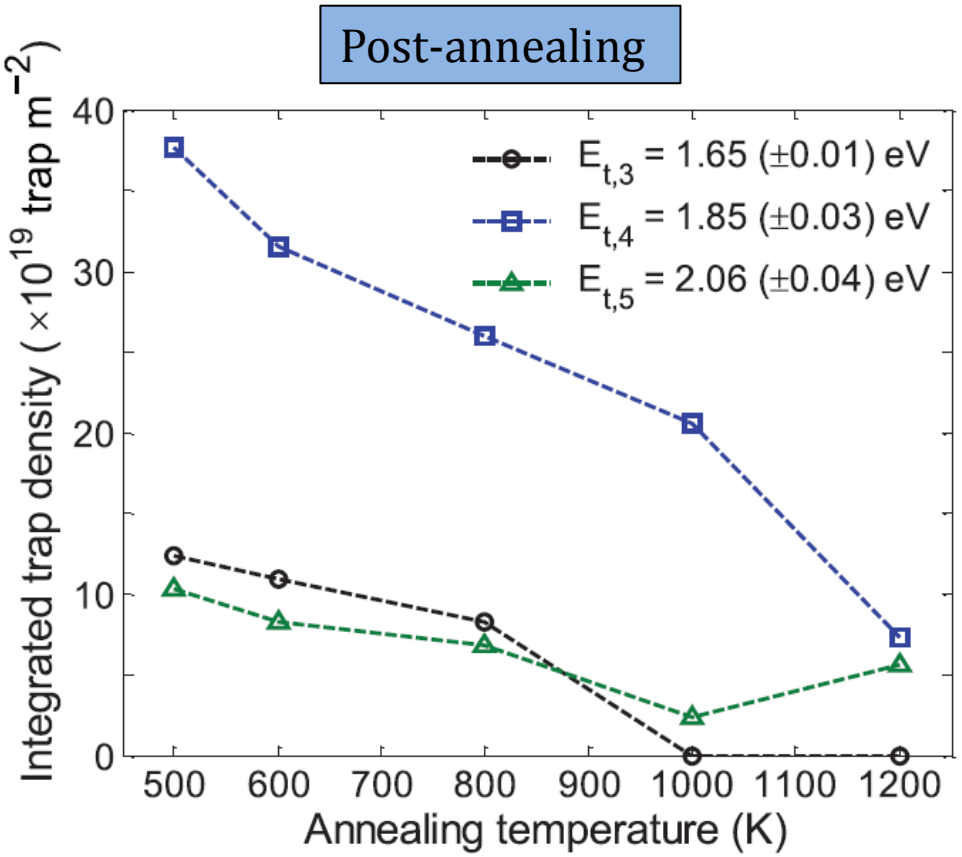


Calculated deuterium depth ranges in agreement with the experiment

MHIMS code [E. A. Hodille, X. Bonnin, R. Bisson et al., *J. Nucl. Mater.467,* pp. 424-431, 2015.]

The damage annealing study

Trap energies and density from modelling



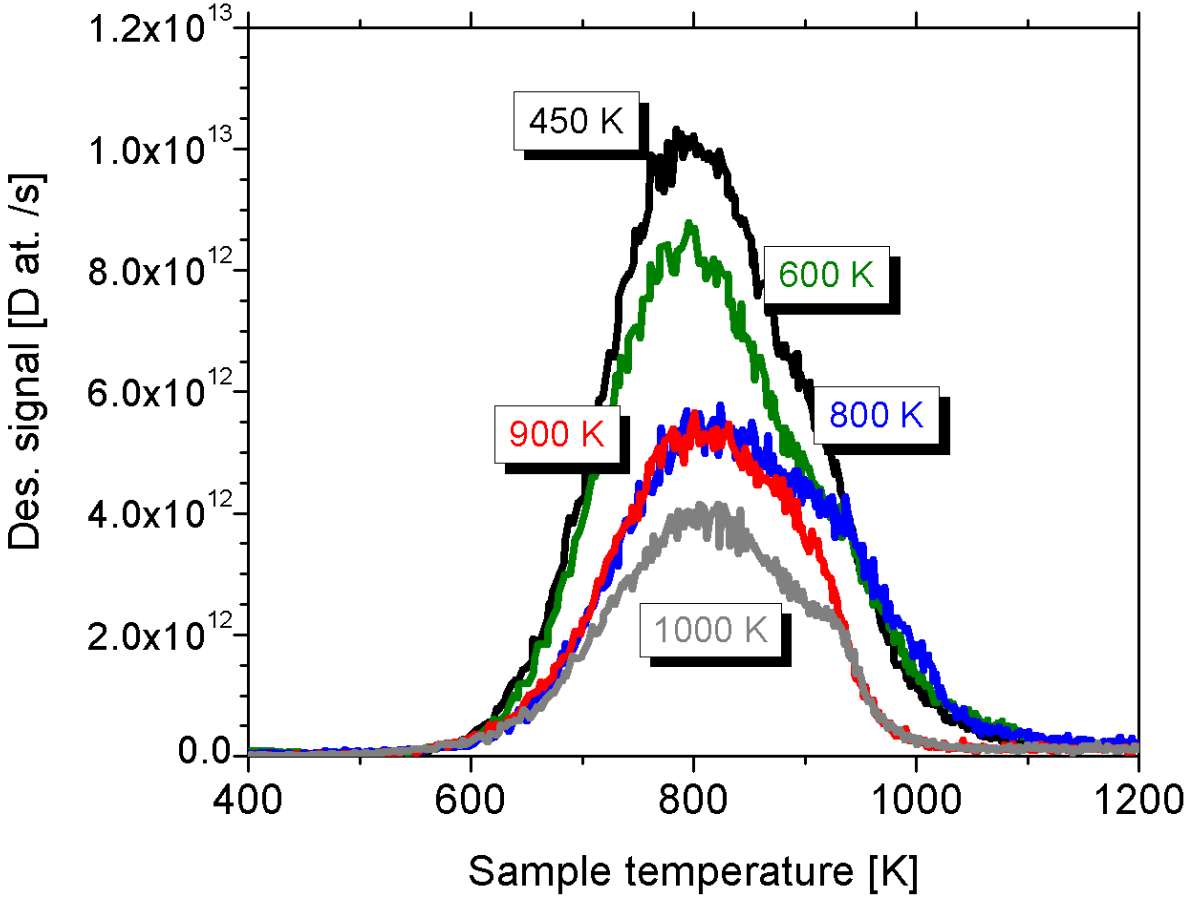
[Hodille et al. Nucl. Fus. 57 (2017) 056002]

- ***Decrease of trap @ 1.65 eV – jogged dislocation***
- ***Decrease of trap @ 1.85 eV– dislocation loop***

Simultaneous W irradiation and D loading

TDS spectra

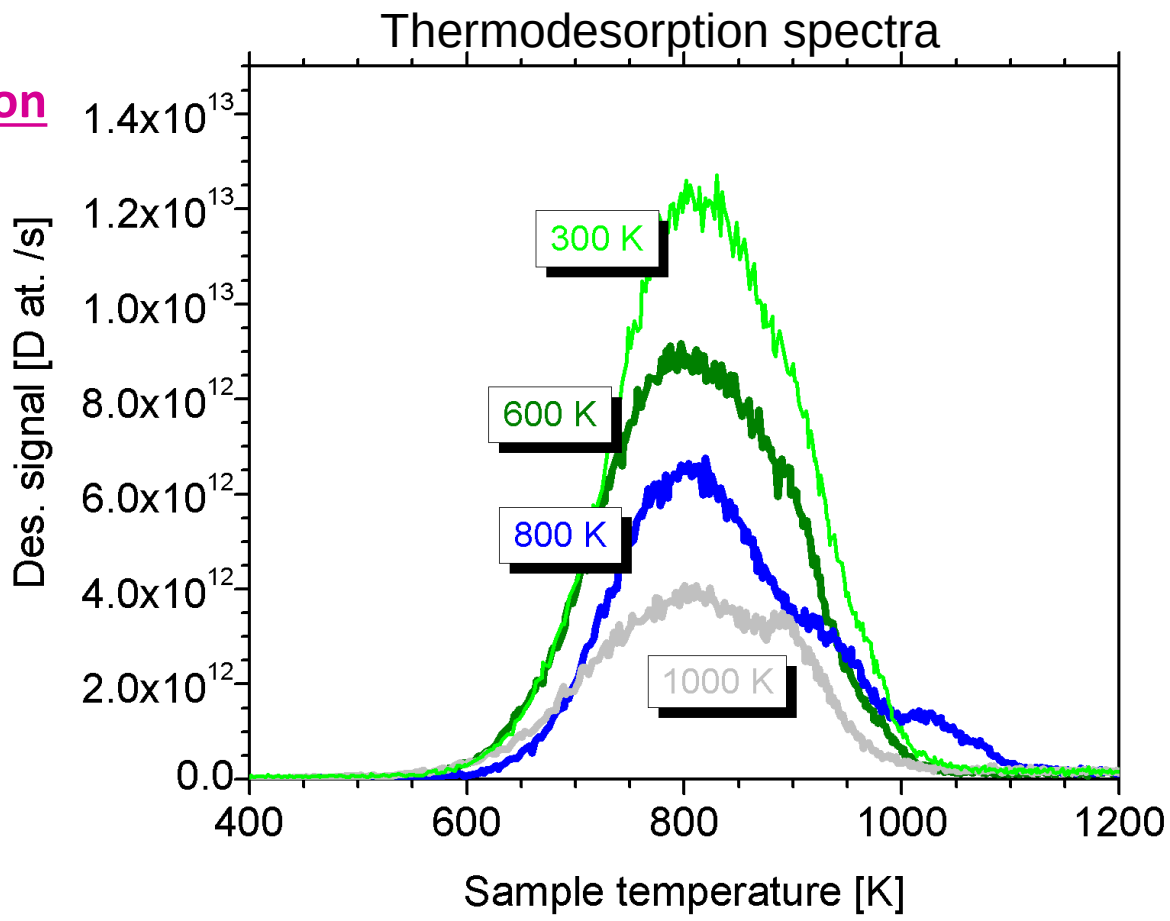
- D conc. depth profiles after additional D atom exposure at 600 K
- Indicated temperatures apply for damaging + D loading temperatures
- ✓ D concentration in the damaged zone decreases with temperature



Damaging at elevated temperatures
TDS spectra

The damaging procedure

- **Damage at T^{EXP}; D population at 600 K**
- Damaging at high temp. (10.8 MeV W ions, ~0.47 dpa_{KP})
- D atom loading at 600 K, $\Gamma_D = 4x10^{23} D/m^2$



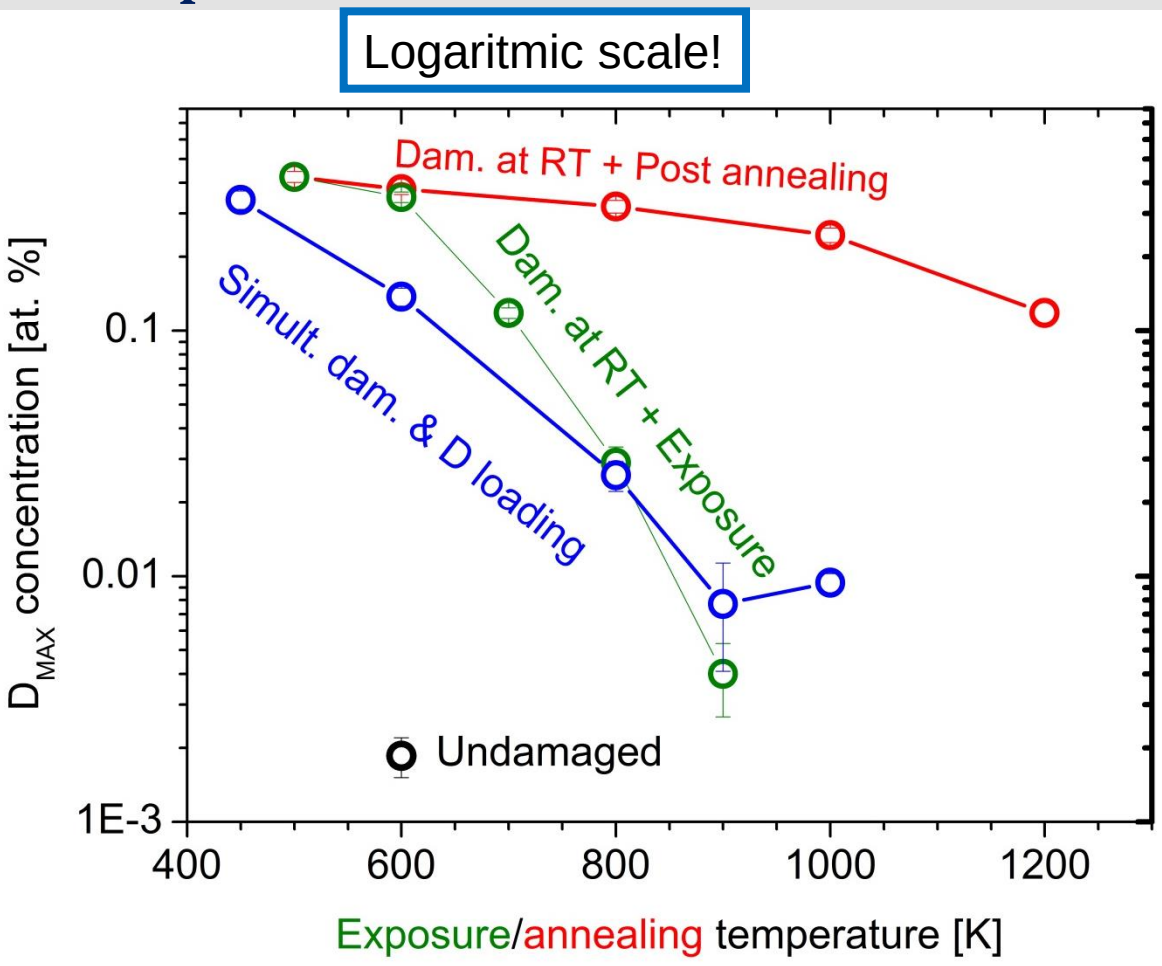
Comparison post annealing versus exposure at high temperatures

- Max. D concentration comparison - damaging at RT in both cases of sequential damaging and exposure

- ✓ Significant decrease of D retention when exposure at higher temperatures
- ✓ Damage annealing and thermal D de-trapping takes place at the same time

Thermal D de-trapping is the dominant process at high temperatures

- **Simultaneous exp. – D conc. stabilization at temp. > 900 K – dramatic ?**



[Ogorodnikova et al., Appl. Phys 119 (2016) 054901 & Markelj et al. NENE proceedings 2015]

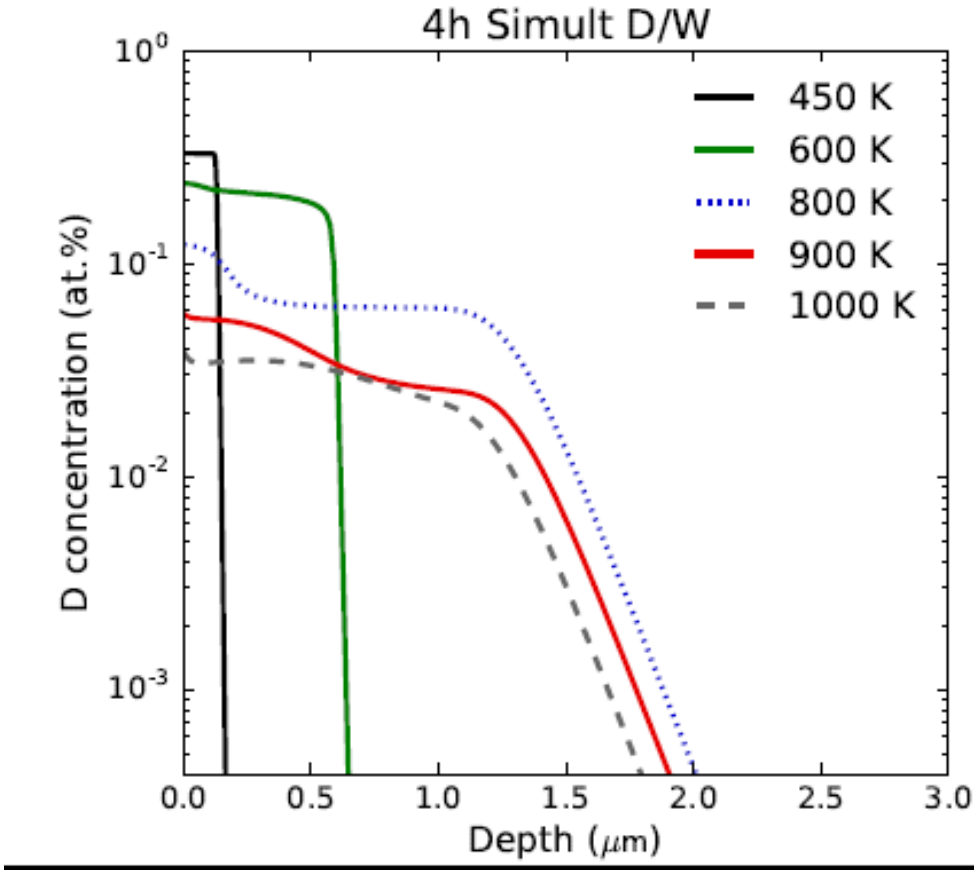
Simultaneous W irradiation and D loading

Modelling

- The MHIMS code – developed at CEA (C. Grisolia, E. Hodille) to model bulk H rapping/detrapping and diffusion [Hodille at al., JNM 467 (2015) 424]
- For our needs surface processes included [Hodille et al. Nucl. Fus. 57 (2017) 056002]

- Simulation of trap density increasing over time.

- Trap concentration taken from final D depth profiles and trap energies from TDS spectra



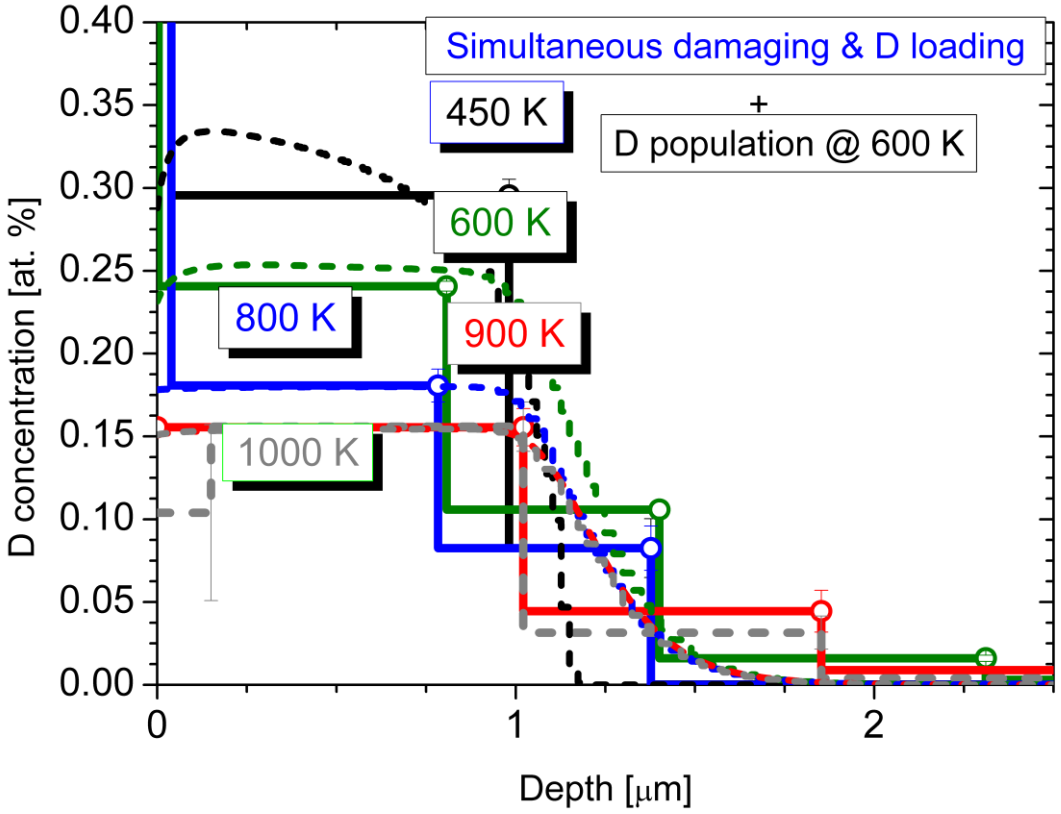
[Hodille et al. unpublished]

✓ Calculated deuterium depth ranges in very nice agreement with the experiment

Simultaneous W irradiation and D loading

Modeling D depth profiles

- Modelling D depth profiles by rate equation model – the MHIMS code
- D conc. depth profiles after additional D atom exposure at 600 K
- Indicated temperatures apply for damaging + D loading temperatures
- ✓ D concentration in the damaged zone decreases with temperature

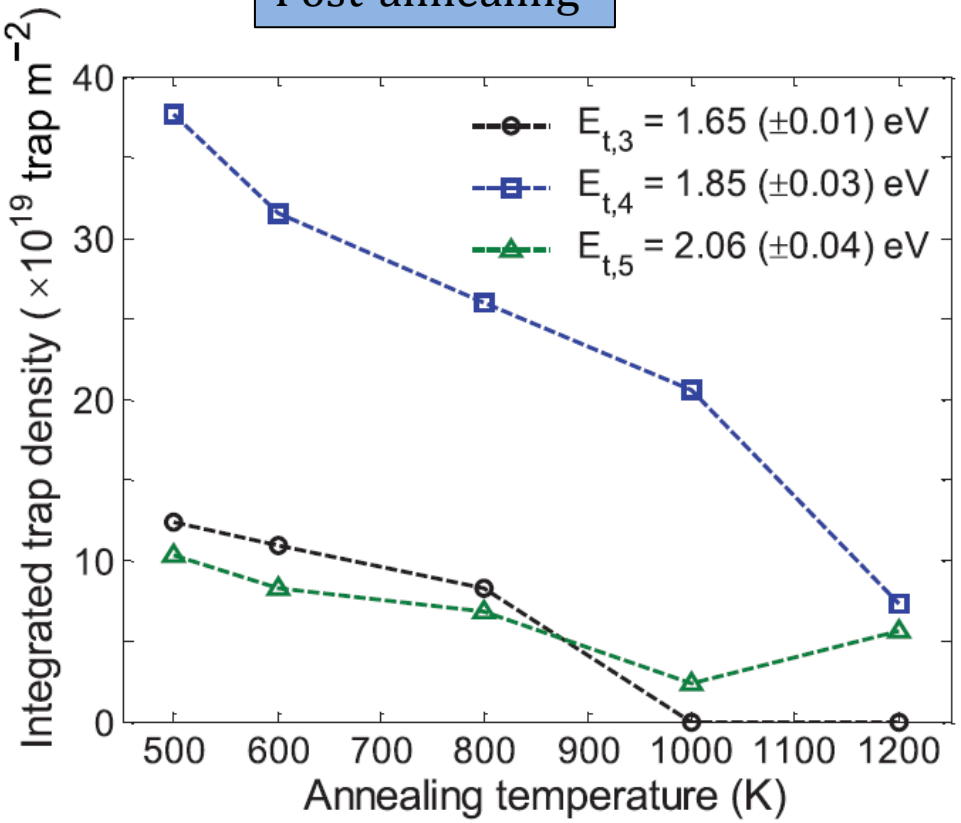


[Hodille et al. unpublished]

Comparison of different damaging procedures

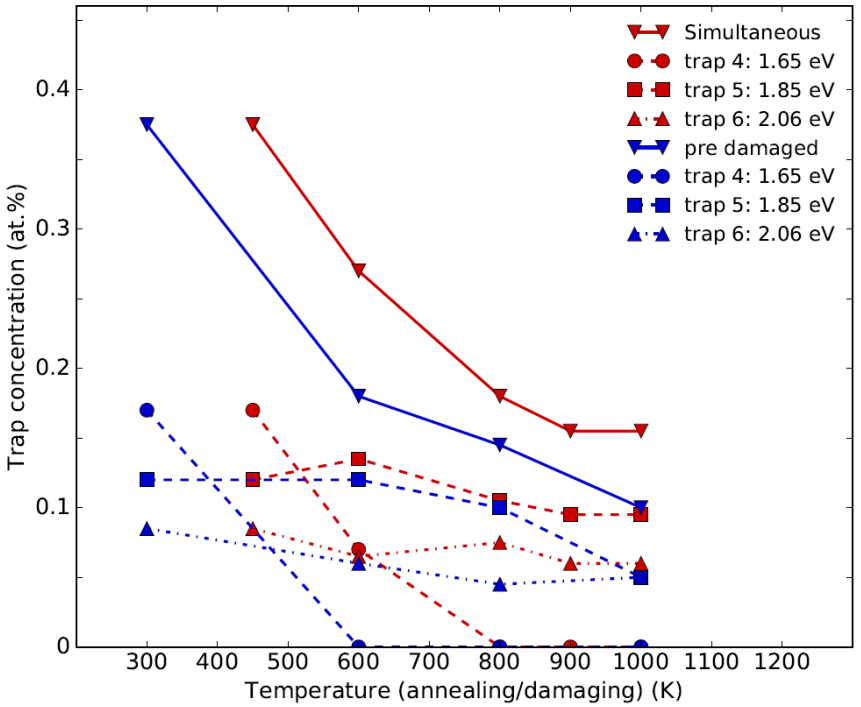
Comparison of trapping energies and concentrations

Post-annealing



[Hodille et al. Nucl. Fus. 57 (2017) 056002]

Simultaneous and damaging at elevated temperatures

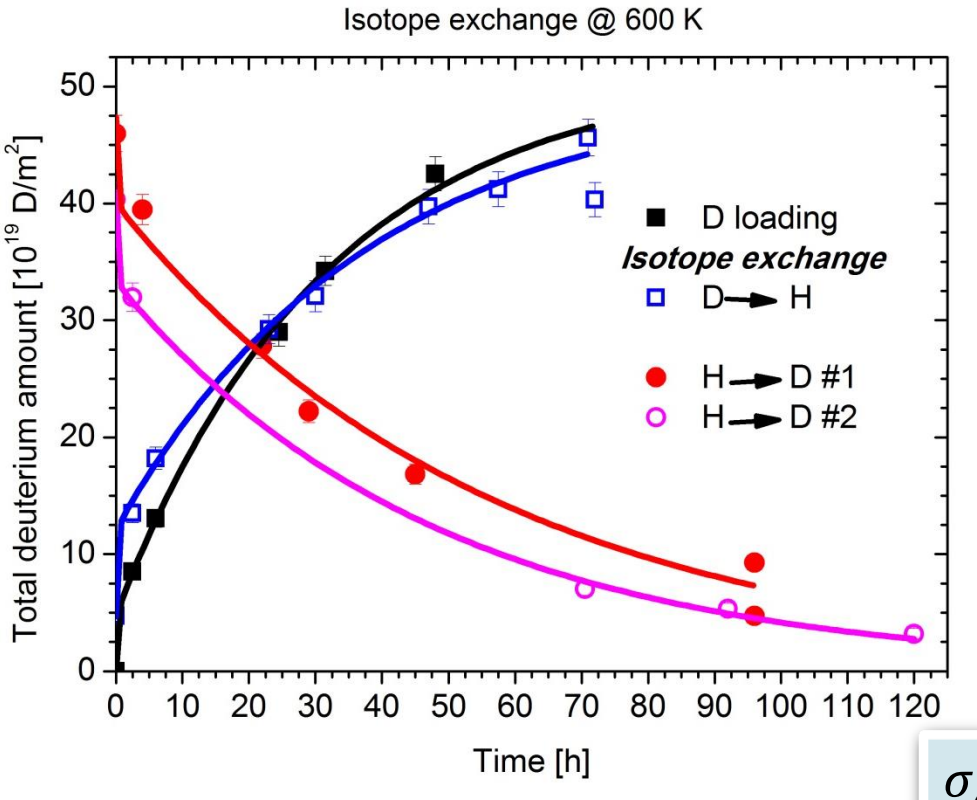


[Hodille et al. unpublished]

Simultaneous and damaging:

- ***Decrease of trap @ 1.65 eV – jogged dislocation***
- ***Small decrease of trap @ 1.85 eV– dislocation loop***

Bulk isotope exchange H → D in self-damaged W



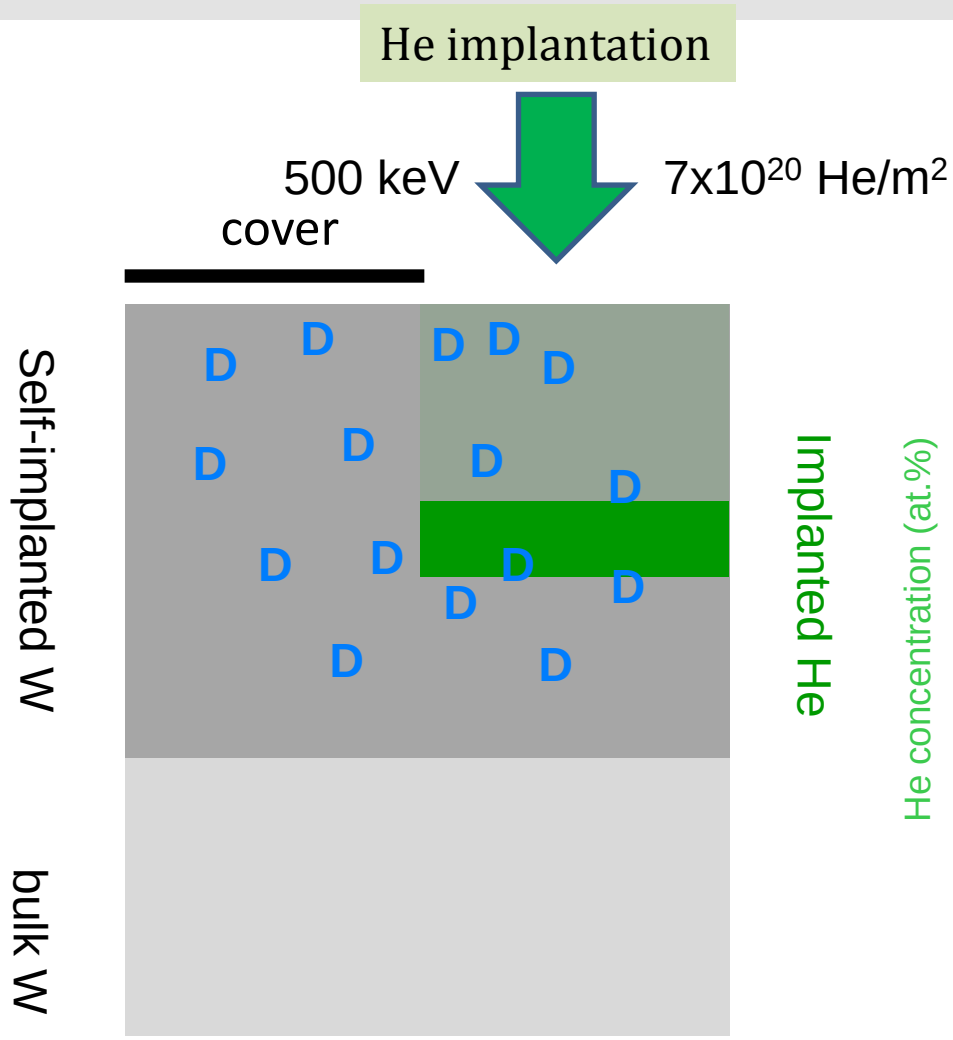
- The isotope exchange in bulk works in both directions:
  - H exchanging D
  - D exchanging H
- Using simple modelling gave us values for bulk exchange cross section

- Observed isotope effect

$\sigma_{excB}(H \rightarrow D;\#1) = 5.2 \pm 0.6 \times 10^{-25}\ m^2$
$\sigma_{excB}(H \rightarrow D;\#2) = 6.5 \pm 0.3 \times 10^{-25}\ m^2$
$\sigma_{excB}(D \rightarrow H) = 1.1 \pm 0.5 \times 10^{-24}\ m^2$

For more information see: Markelj et al. JNM 469 (2016) 133

Sample preparation



*SRIM
Kinchin Pease
E_d = 90eV