Deuterium retention and isotope exchange studies in self-ion damaged tungsten exposed to neutral atoms

Project: Hydrogen retention in self-damaged and He-irradiated tungsten and alloys for PFC

Sabina Markelj, Anže Založnik, Primož Vavpetič, Mitja Kelemen, Primož Pelicon, Iztok Čadež

Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia

Thomas Schwarz-Selinger

Max-Planck-Institut für Plasmaphysik, Garching, Germany

Olga Ogorodnikova

National Research Nuclear University- MEPhI, Moscow, Russia

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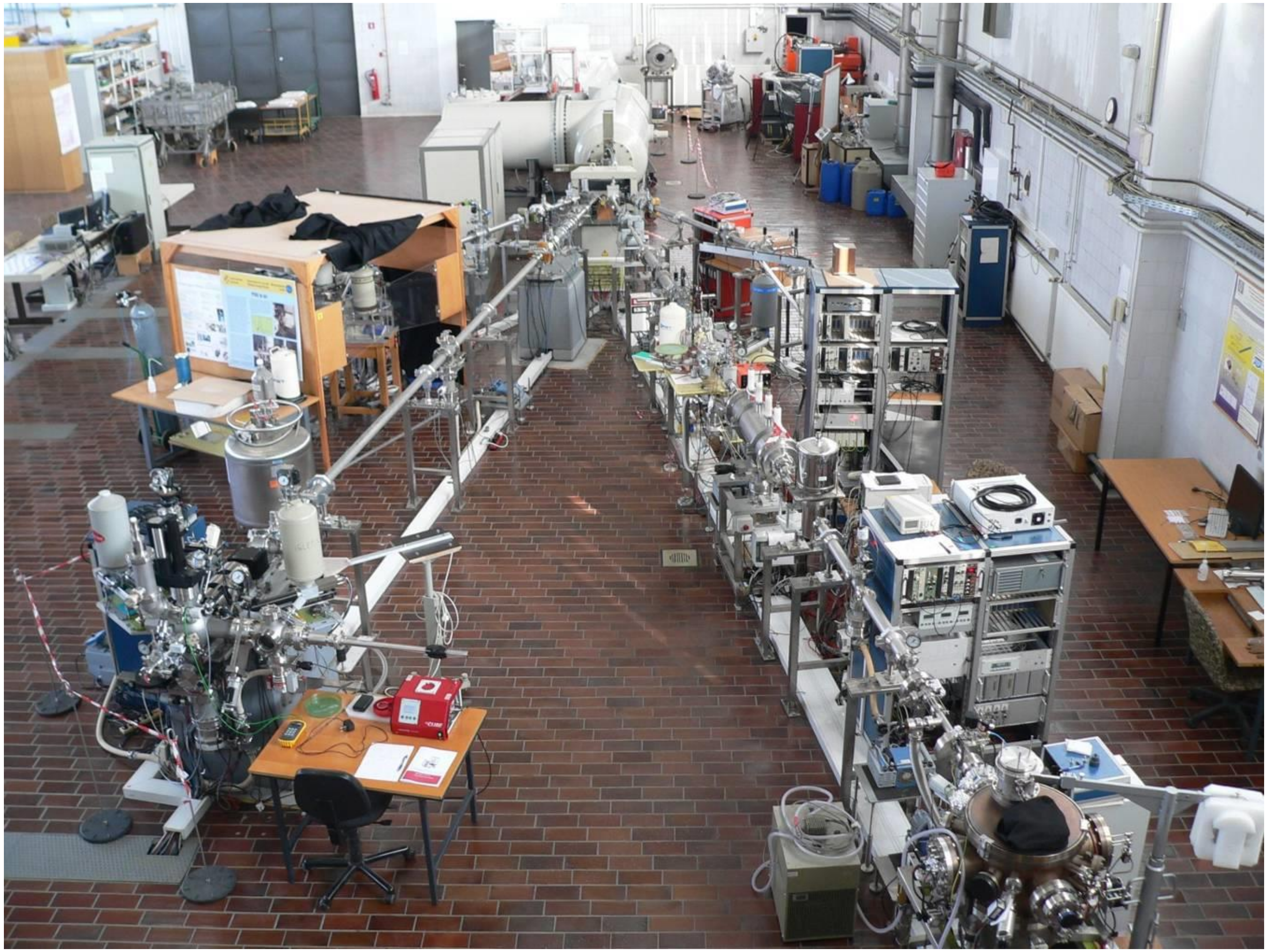
Outline

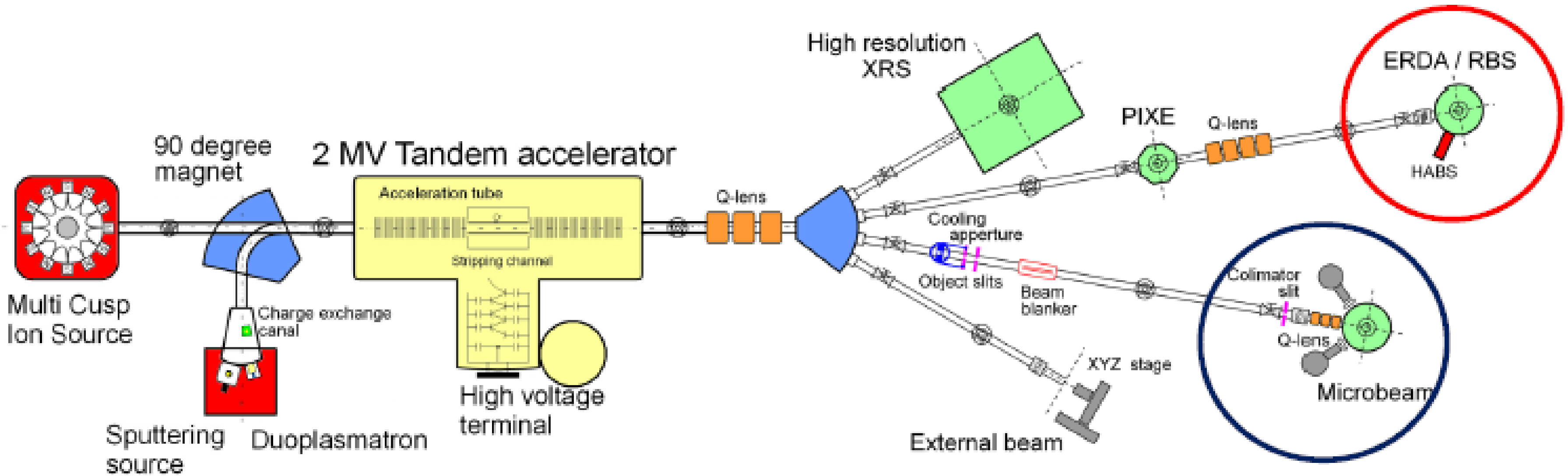
- The accelerator facility
- Motivation
- Study of D retention in self-ion damaged tungsten
  - D atom loading at different sample temperatures
  - Study of defect annealing + D atom loading
- Experimental set-up for in situ NRA and ERDA measurements
- Isotope exchange in bulk in self-ion damaged tungsten
- Preliminary results on simultaneous W ion irradiation and D atom loading
- Conclusion

Introduction - The accelerator

2 MV HVEE Tandem accelerator ”Tandetron”, Jozef Stefan Institute, Ljubljana



Ion beam studies at JSI - The accelerator



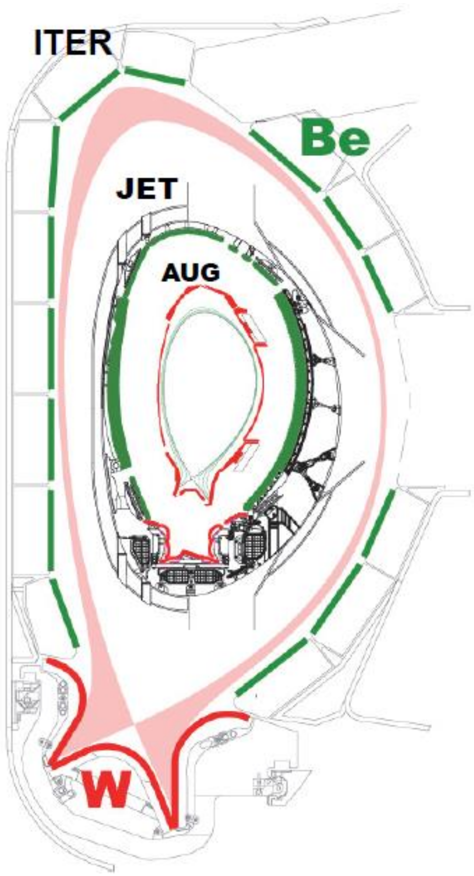
Multicusp ion source enabled duoplasmatron source to be permanently configured for He beam analysis by ^{4}He or ^{3}He for NRA. ^{3}He consumption optimized by construction of $^{3}He/^{4}He$ gas mixing set-up.

Broad beam NRA set for static and in situ D depth profile measurements and experiments and micro beam NRA for startic measurements.

Separate smaller experiment for fusion research:

- **Vibrational spectrometer for hydrogen molecules – atom recombination studies**

Motivation



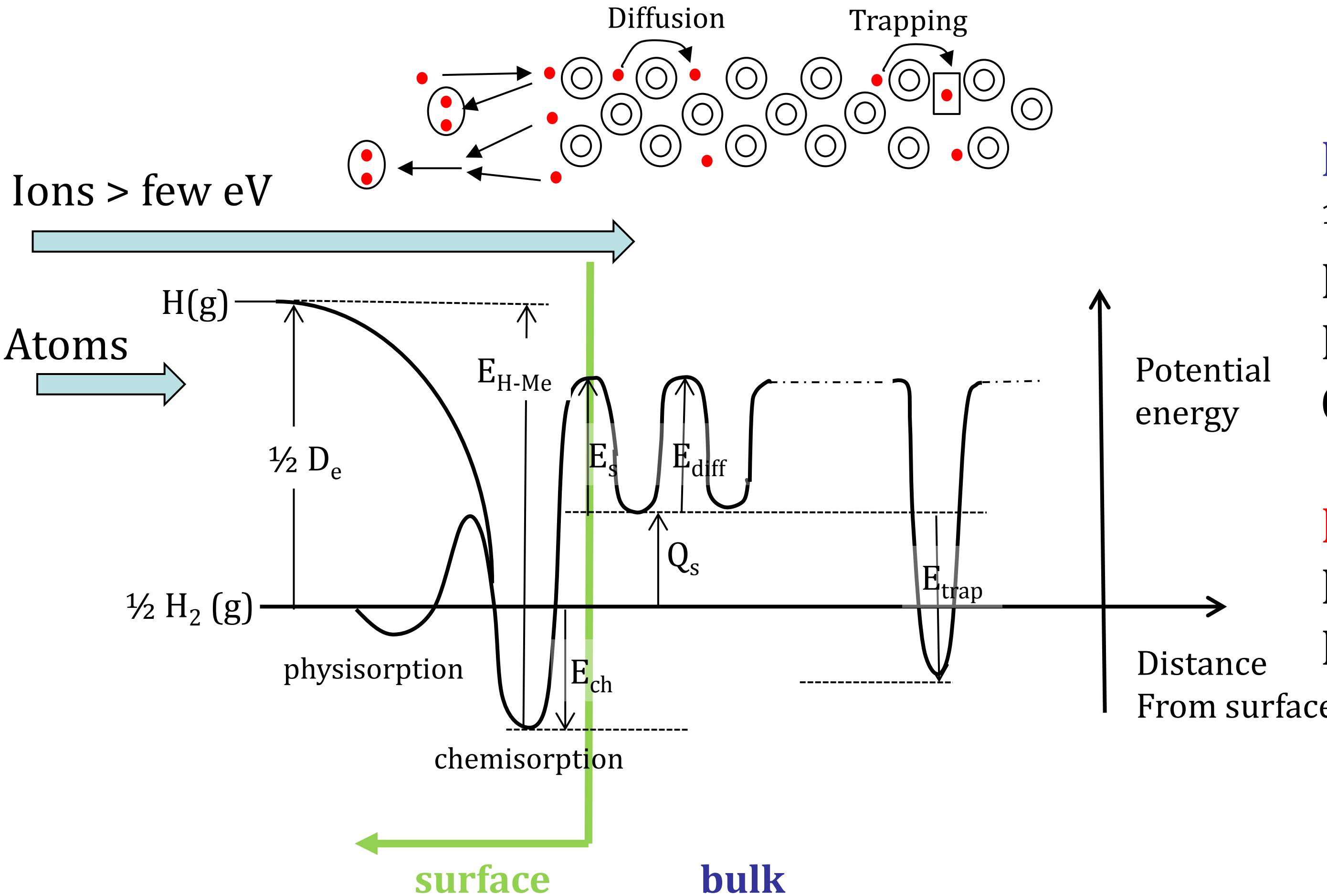
GF Matthews, PSI 2013

Study of deuterium retention in self-ion damaged tungsten

- Tungsten is the material of choice for divertor target plates
- Retention studies in damaged tungsten – simulate neutron damage by W ion irradiation
- D retention - a way to determine the trap concentrations
- Gentle exposure to damaged W
- Study processes with hydrogen/deuterium atoms (0.2 eV) – no additional defect production as in the case of plasma/ion exposure

Processes: atoms versus ions

- Proceses: neutral atom exposure versus ion/plasma exposure
- Effect of neutrals in plasma experiments – don't play major role?



Parameters for W

½ D_e= 2.25 eV

E_{ch}=0.5 – 0.8 eV

E_{des}=2E_{ch}

Q_s=1 eV

$E_{barr} \approx Q_s + E_{ch} + E_s$

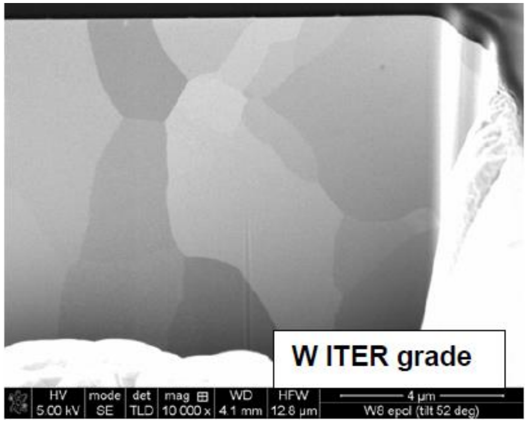
E_{diff}=0.39 eV

E_{trap} = 0.8 – 1.4 eV

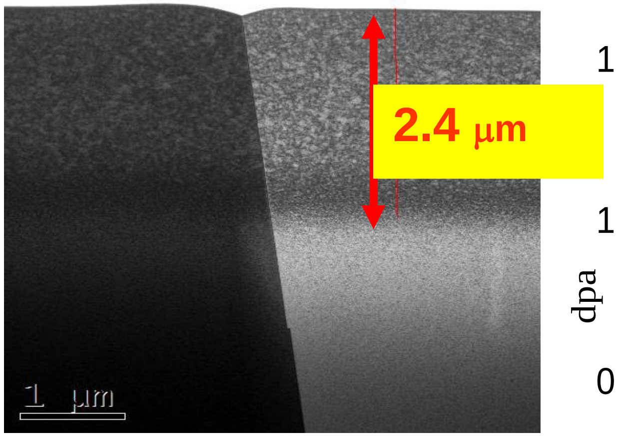
Damaged W + D atom loading @ different exposure temperatures

Neutron-like damage - W ion irradiation

- W samples - mirror polished polycrystalline tungsten (at IPP), manufactured by Plansee GA - large grains perpendicular to sample surface (ITER grade)
- Damaging at room temperature at IPP, 20 MeV W ions, fluence 1.4×10^{18} $W/m^2 \rightarrow 0.89$ dpa

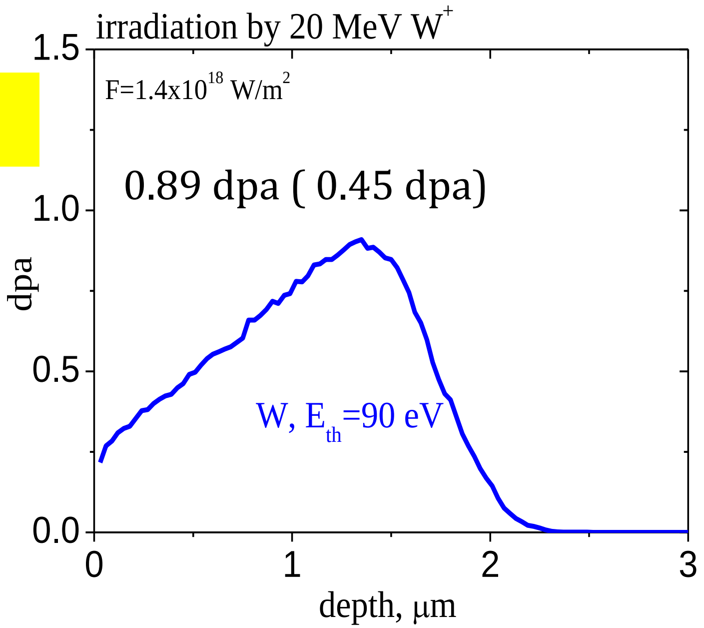


O.V. Ogorodnikova, H workshop (2012)



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

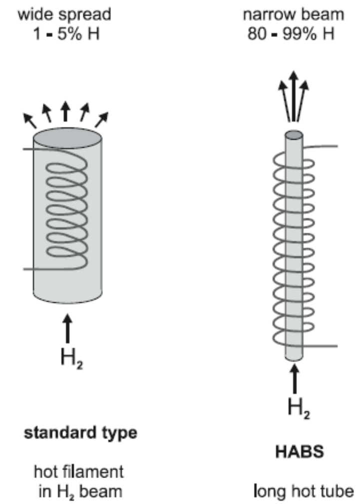
Calculation by SRIM



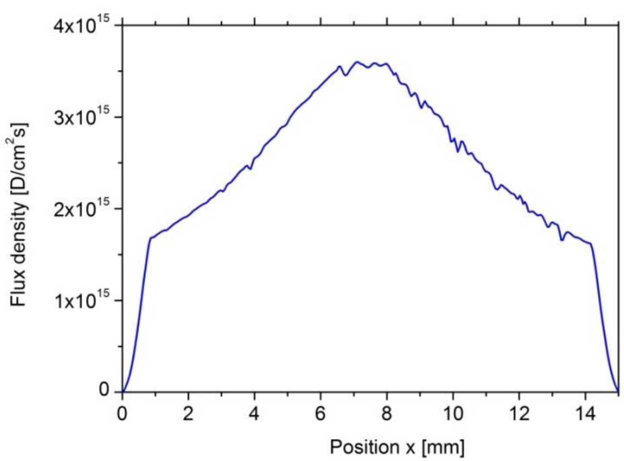
Calculation of damage profile by SRIM is in very good agreement with TEM observation

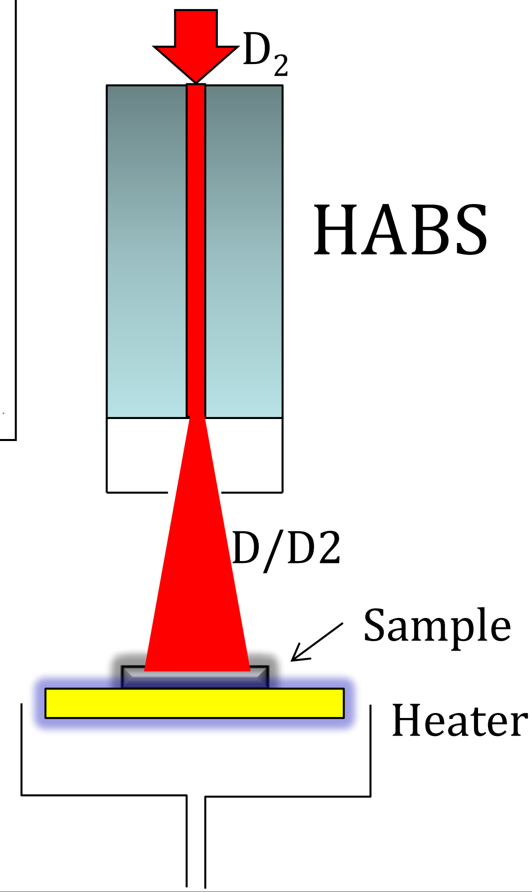
Hydrogen atom beam source

K.G. Tschersich, J.P. Fleischhauer and H. Schuler, *J. Appl. Phys.* 104, 034908 (2008); http://www.mbe-components.com/products/gas/habs.html



D atom – flux density profile



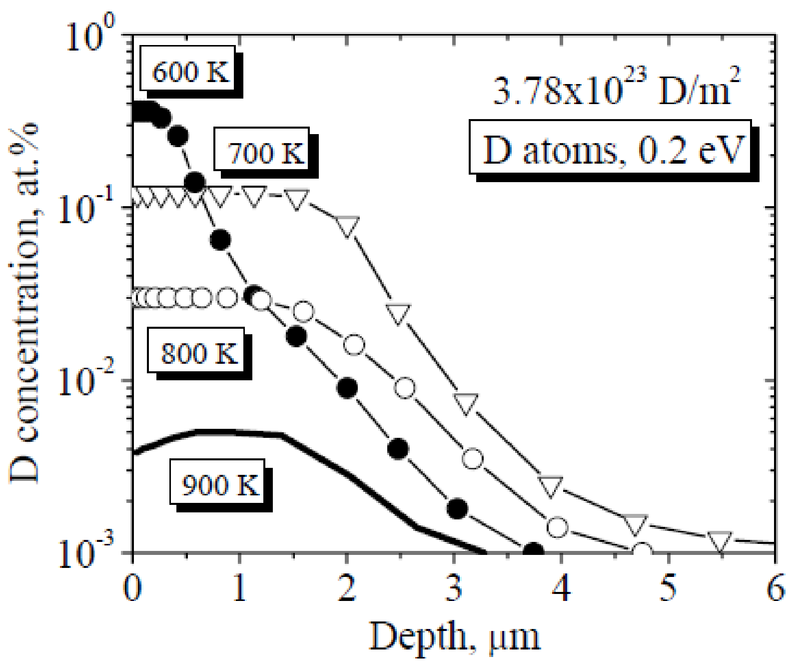


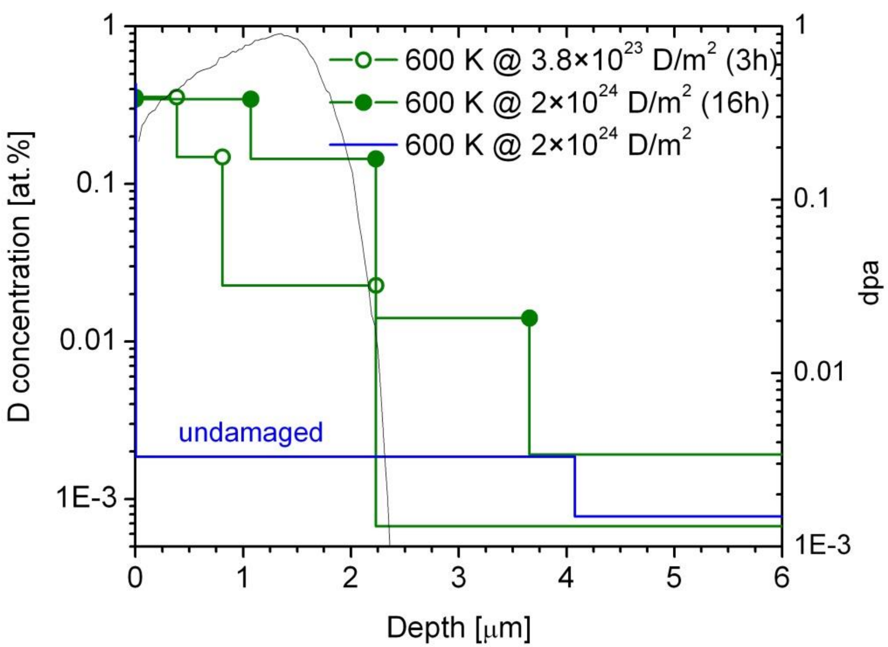
Different exposure temperatures

Maximum atom flux = 3.5×10^{19} D/m^2s

Damaged W + D atom loading @ different exposure temperatures

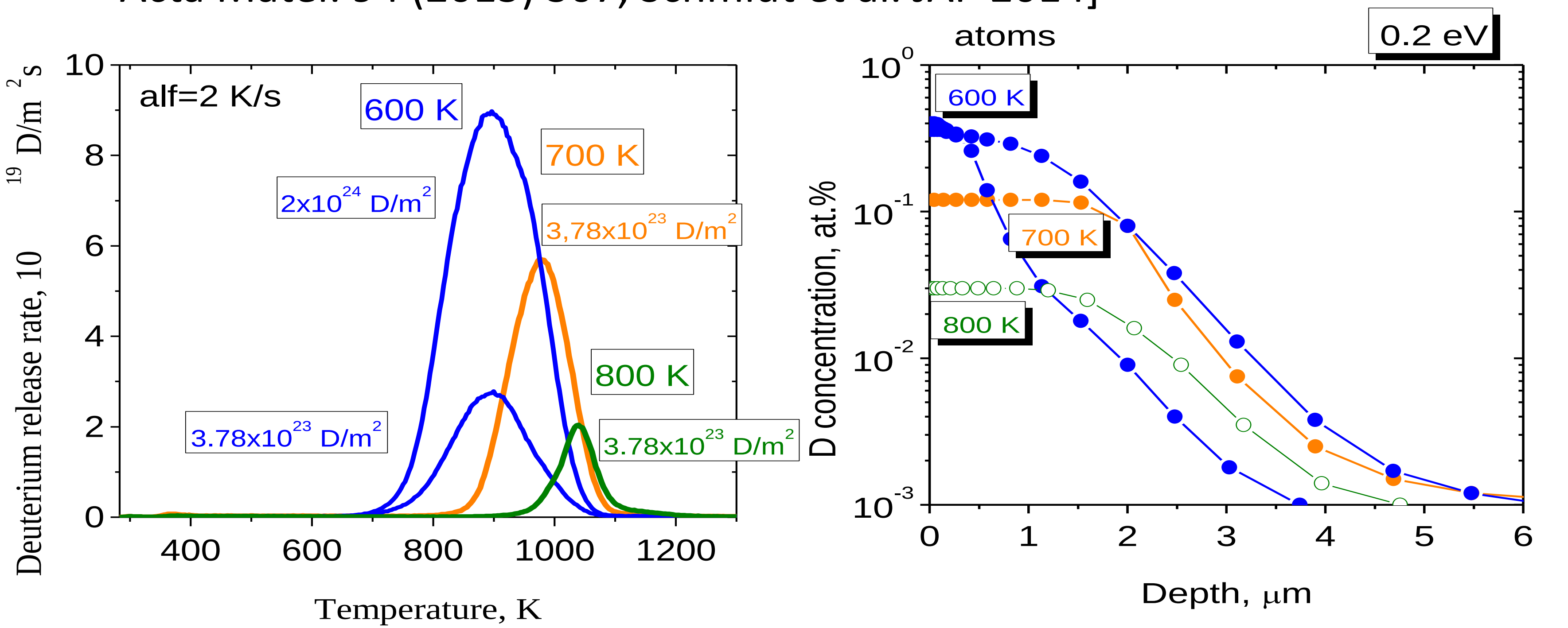
- Deuterium depth profiles measured by Nuclear Reaction Analysis - NRA
  Analyzing protons (≈12 MeV) from nuclear reaction D(^{3}He,p)^{4}He at different 3He energies from 650 (500) keV up to 4.5 MeV
- Different exposure temperatures – different saturation levels
- At lower temperatures higher fluence needed to saturate traps





Damaged W + D atom loading @ different exposure temperatures

- TDS spectra (heating rate 2K/s) [Yu. Gasparyan et al. JNM 463 (2015) 1013] – higher temperature less D inside
- Small peak shift – Fill level dependent de-trapping energies [Fernandes et al. Acta Mater. 94 (2015) 307, Schmidt et al. JAP 2014]

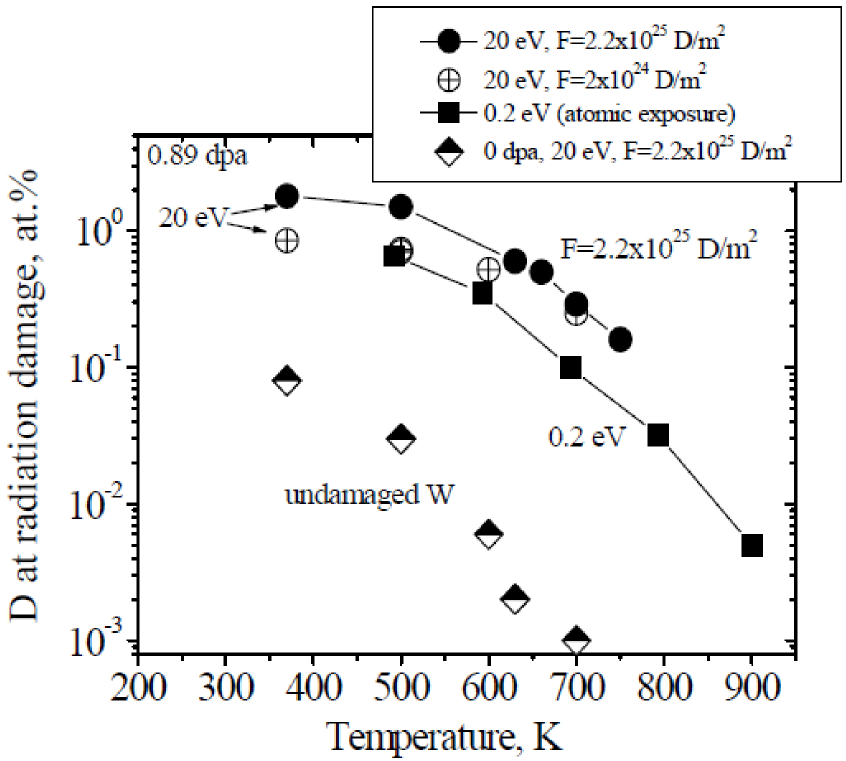


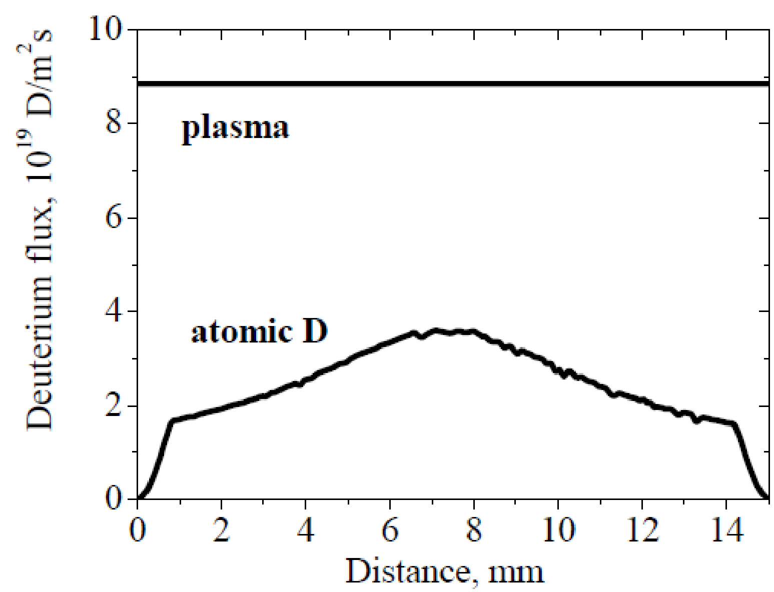
Yu. Gasparyan et al. JNM 463 (2015) 1013

O.V. Ogorodnikova, H workshop (2012)

Damaged W + D atom loading @ different exposure temperatures - comparison

- Comparison to with plasma loading PlaQ - 20 eV ion energy (IPP)
- Exposure at different sample temperatures



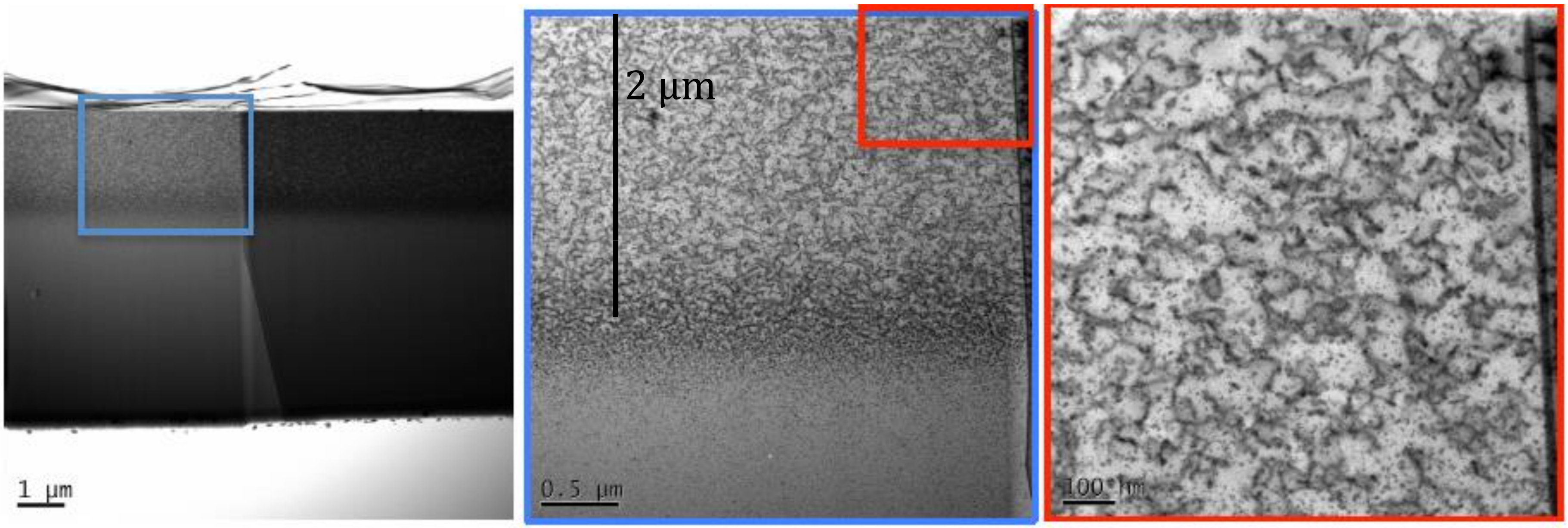


O. Ogorodnikova et al. in preparation

Annealing of damaged W
+ D atom loading @ the same
temperature

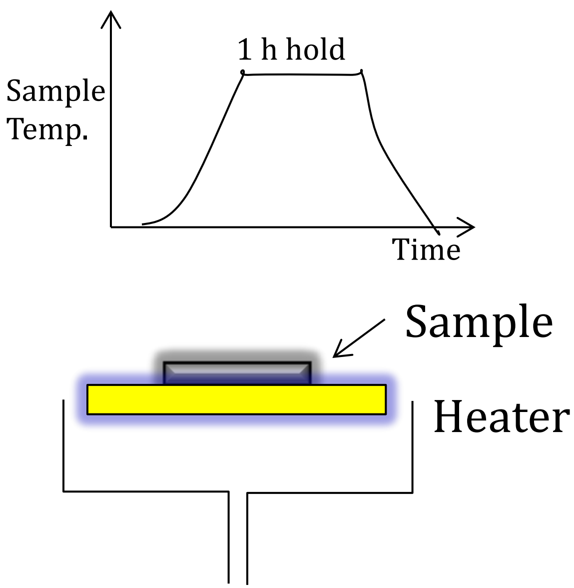
Damaged W material – the annealing study

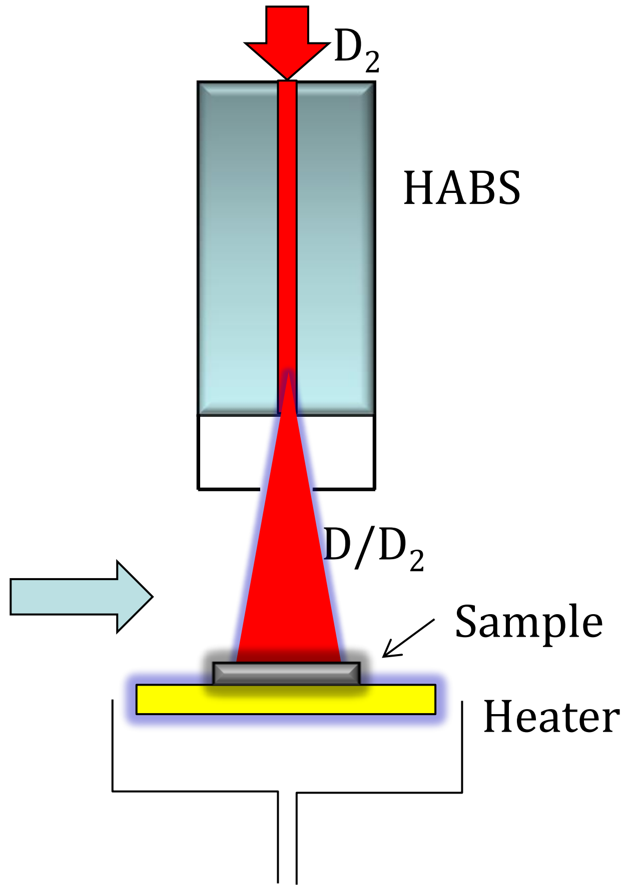
- W samples prepared at IPP - mirror polished polycrystalline tungsten, manufactured by Plansee GA – grains parallel to surface (MF reference material)
- Recrystallization – 2 min @2000 K
- Damaging at room temperature, 20 MeV W ions, fluence 7.8×10^{17} W/m^2 → 0.5 dpa



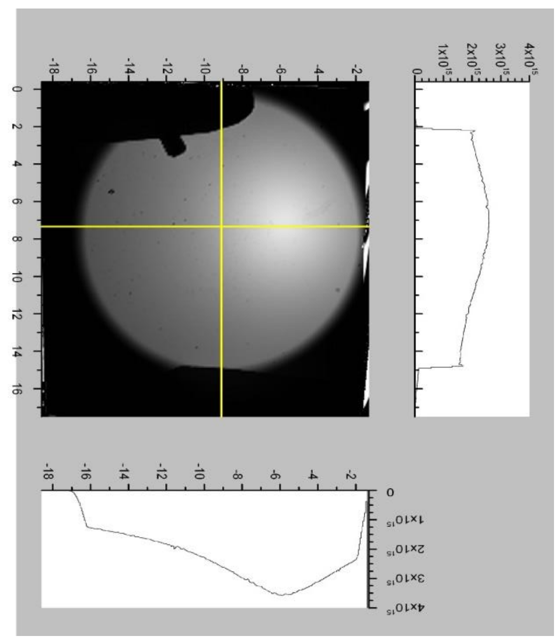
STEM analysis by L. Ciupinski – collaboration within EUROfusion
A. Založnik et al., PFMC 2015, submitted to Phys. Scripta

Damaged W material – the annealing study





Exposure @ 500 K
for 144 h

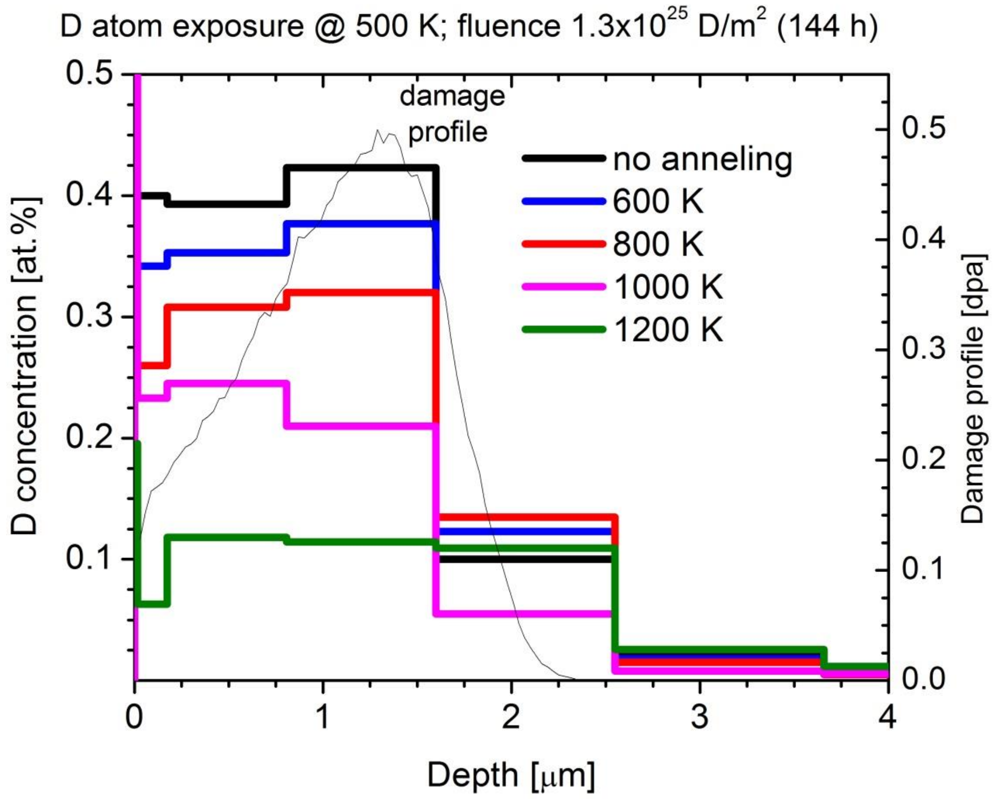


D central flux density
$2.6 \times 10^{19}\ Ds^{-1}m^{-2}$

Study of defect annealing – Depth profiles

- Long exposure time/fluence (6 days-144 h) needed to saturate traps – intermediate NRA measurement after 72 h of D atom exposure (final depth profiles shown).

- Observed effect of the annealing of damaged samples on the trap concentration – reduction of traps at higher annealing temperatures



A. Založnik et al., PFMC 2015, submitted to Phys. Scripta

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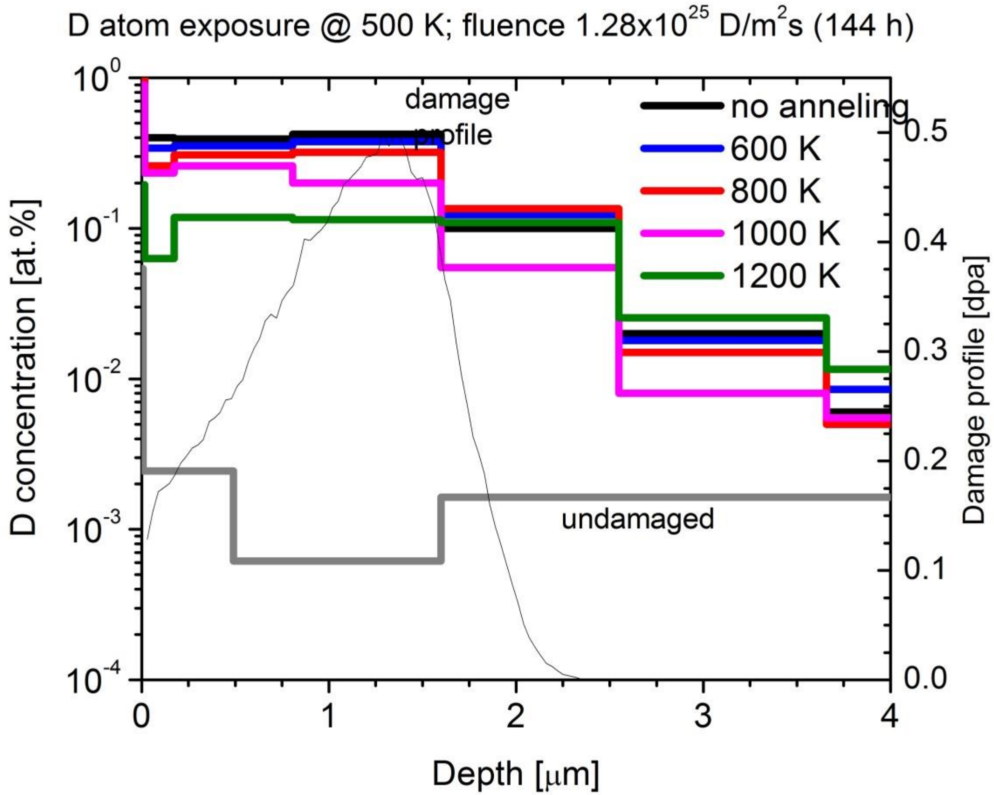
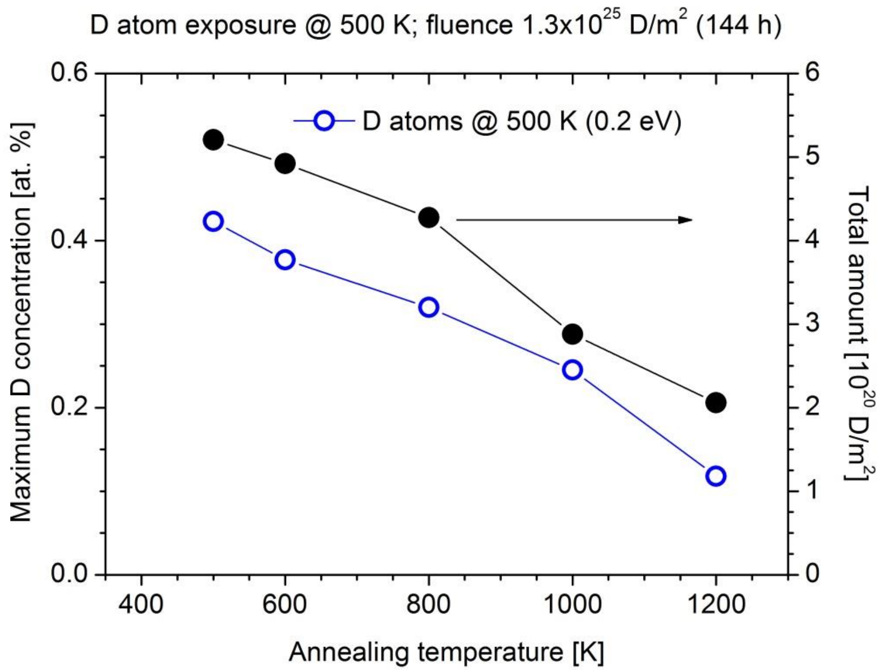
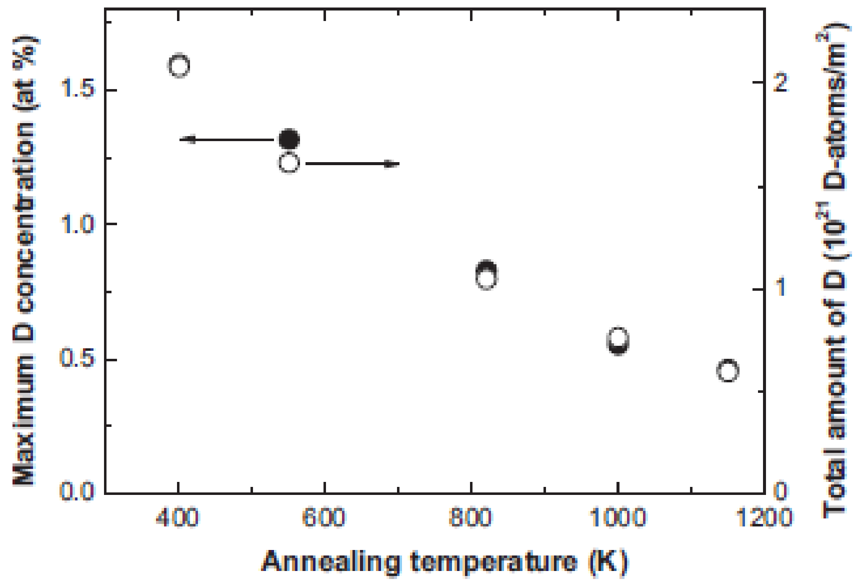


Study of defect annealing – total amounts

- Reduction of total D amount by 60% from 52×10^{19} D/m^2 at 500 K to 21×10^{19} D/m^2 at 1200 K
- Comparison with plasma loading PlaQ – floating potential (3-5 eV/D) @ 400 K , fluence 1×10^{25} D/m^2 - 70% reduction of total amount
- Difference in maximum concentration – D thermal detrapping – different fluxes





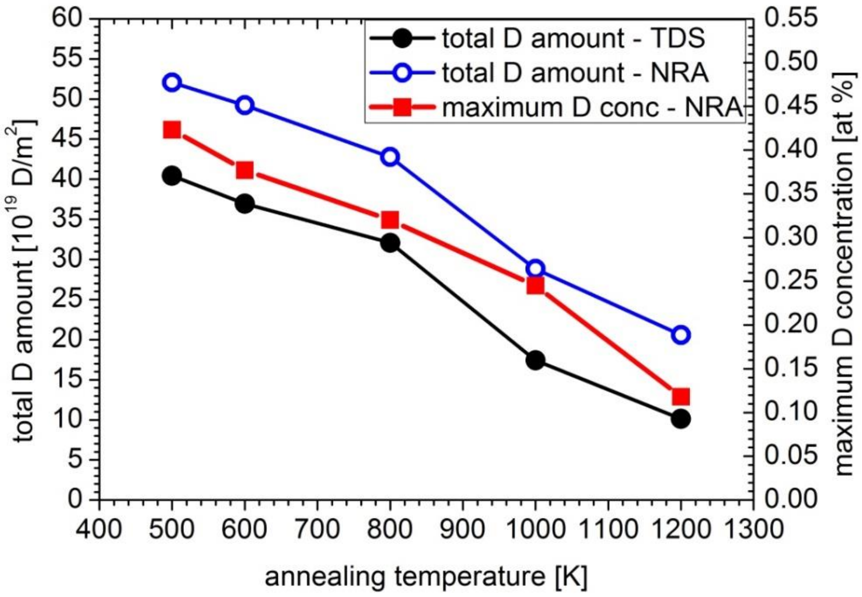
[E. Markina et al. JNM 463 (2015) 329]

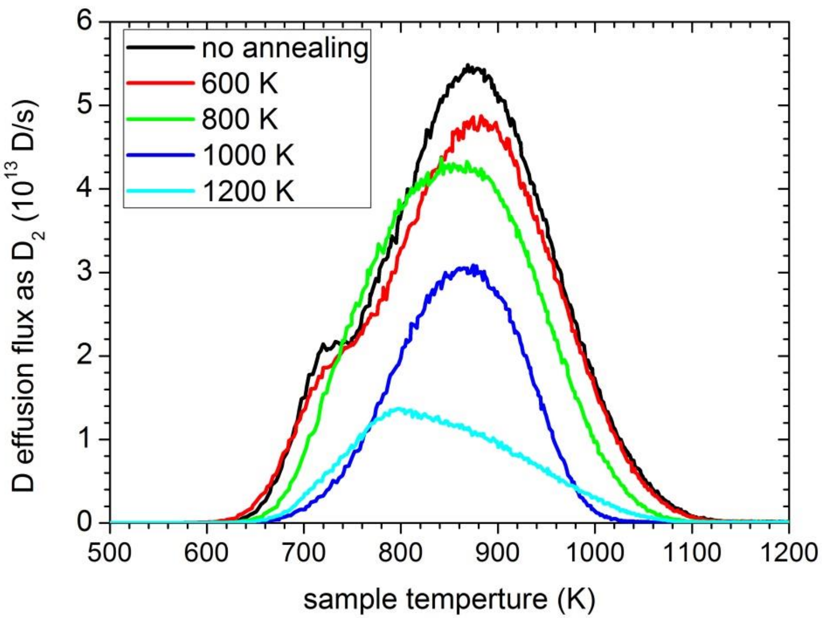
Study of defect annealing – total amounts TDS

- TDS performed at IPP – heating rate 15 K/min
- Comparison of reduction of total amount NRA vs. TDS in good agreement

- Between 400-720 K single vacancies become mobile and form larger defects or annihilate – stage III
- Annealing between 800 K and 1000 K – intermediate recovery region
- Between 920 and 1220 K large vacancy recovery – stage IV

  [L.K. Keys and J. Moteff , JNM 34 (1970) 260]
  [H. Schultz Mater. Sci. Eng. A141 (1991) 149]



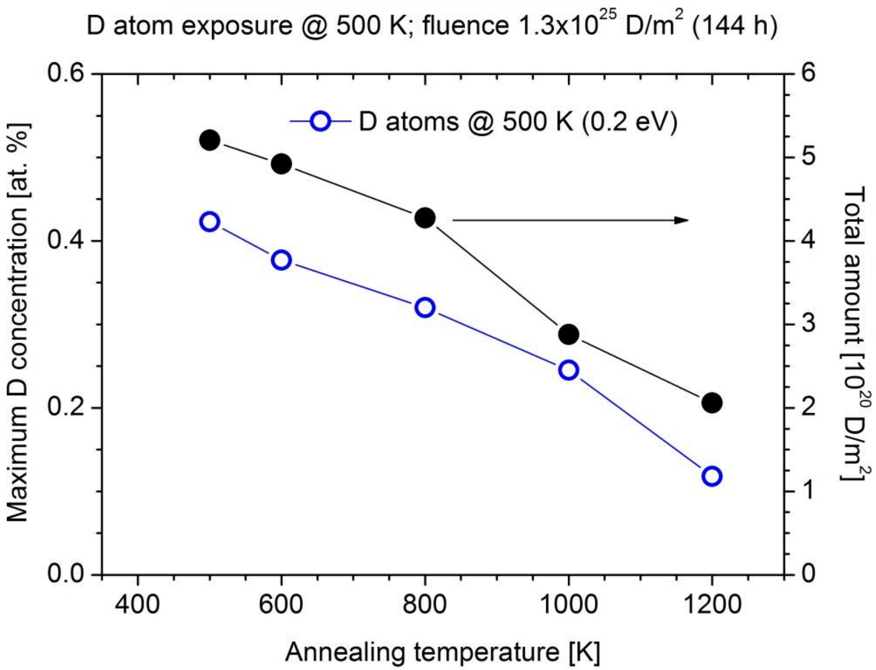


A. Založnik et al., PFMC 2015, submitted to Phys. Scripta

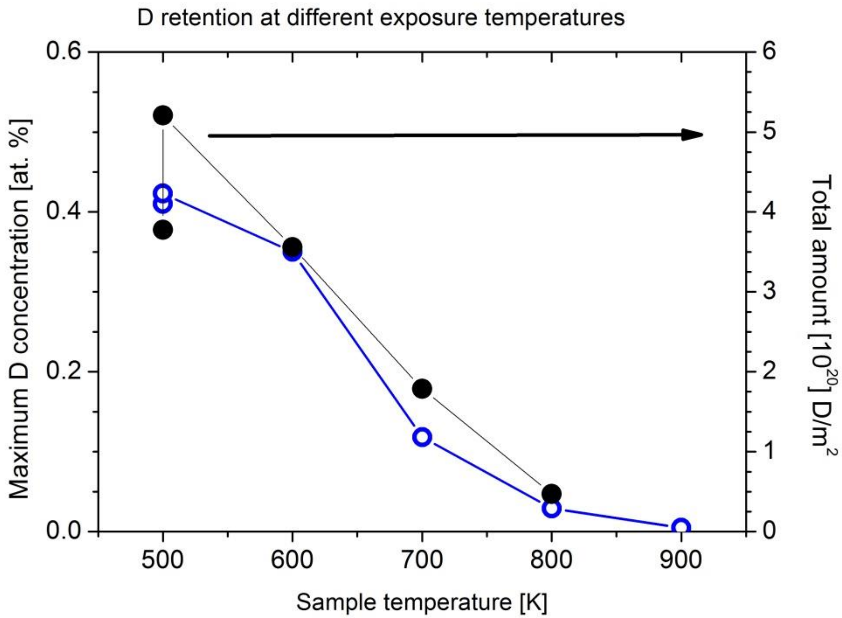
Defect annealing versus D exposure at high temperatures

- Significant decrease of D retention when exposure at higher temperatures – 90% decrease (500 – 800 K)
- Thermal D desorption is the dominant process at elevated temperatures

Defect annealing



Exposure at higher temperatures



In situ studies by ERDA/NRA
The isotope exchange

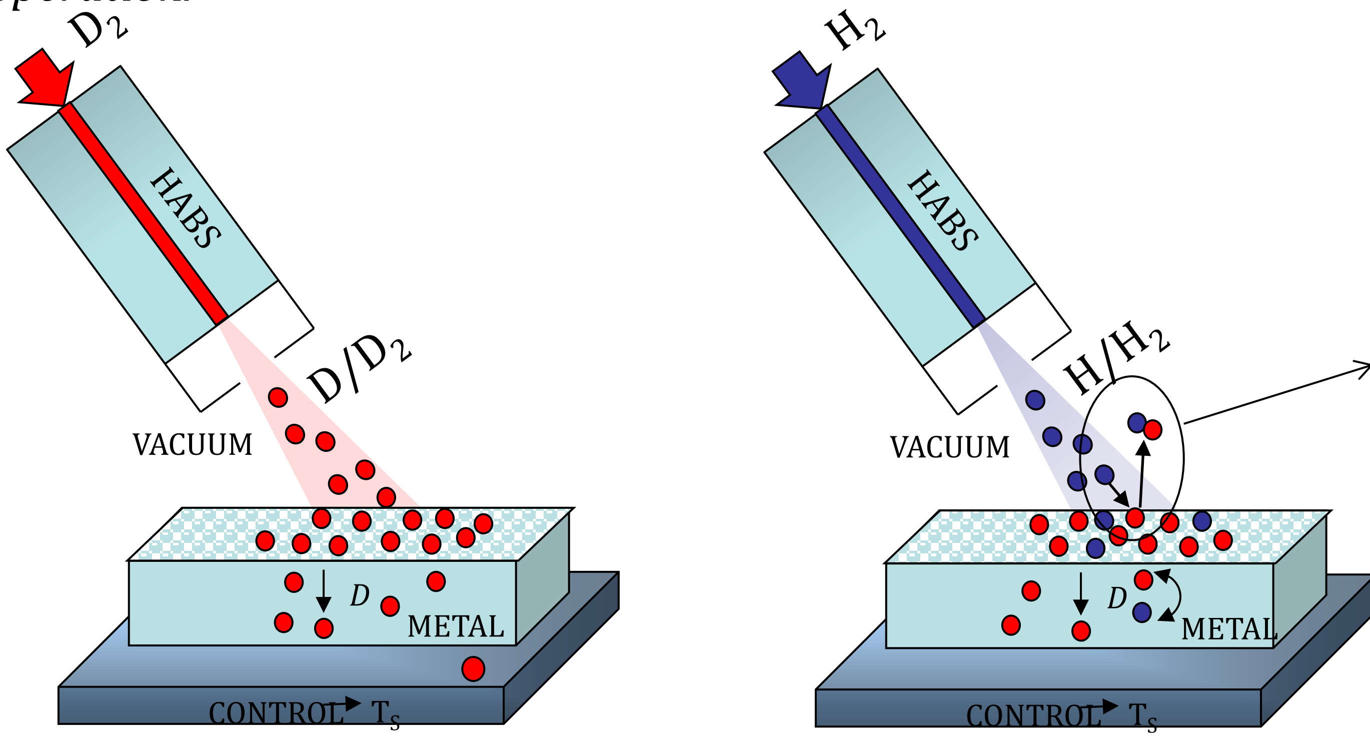
Wikipedia: IN SITU is a Latin phrase that translates literally to “on site” or “in position”.

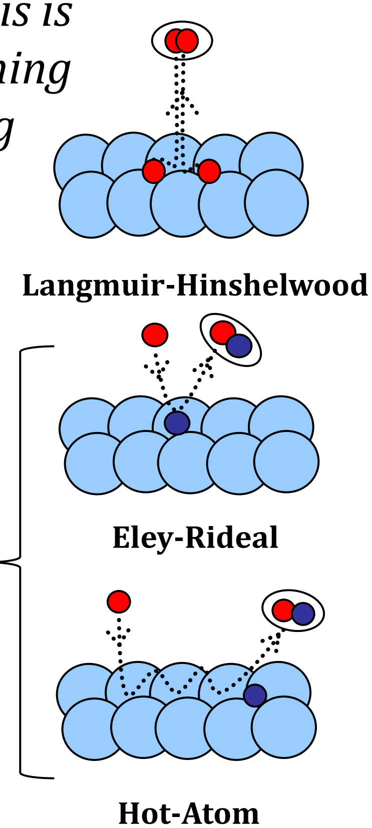
In situ studies by Ion Beam Methods

- *In situ* = Hydrogen/Deuterium concentration measured during the exposure, annealing,..
- No transport trough air between sample exposure and analysis
- Possibility to study the dynamics of processes on the surface and in the bulk
- Measurements of all parameters - computer control of the system
- Possible beam effect on retention

The isotope exchange process

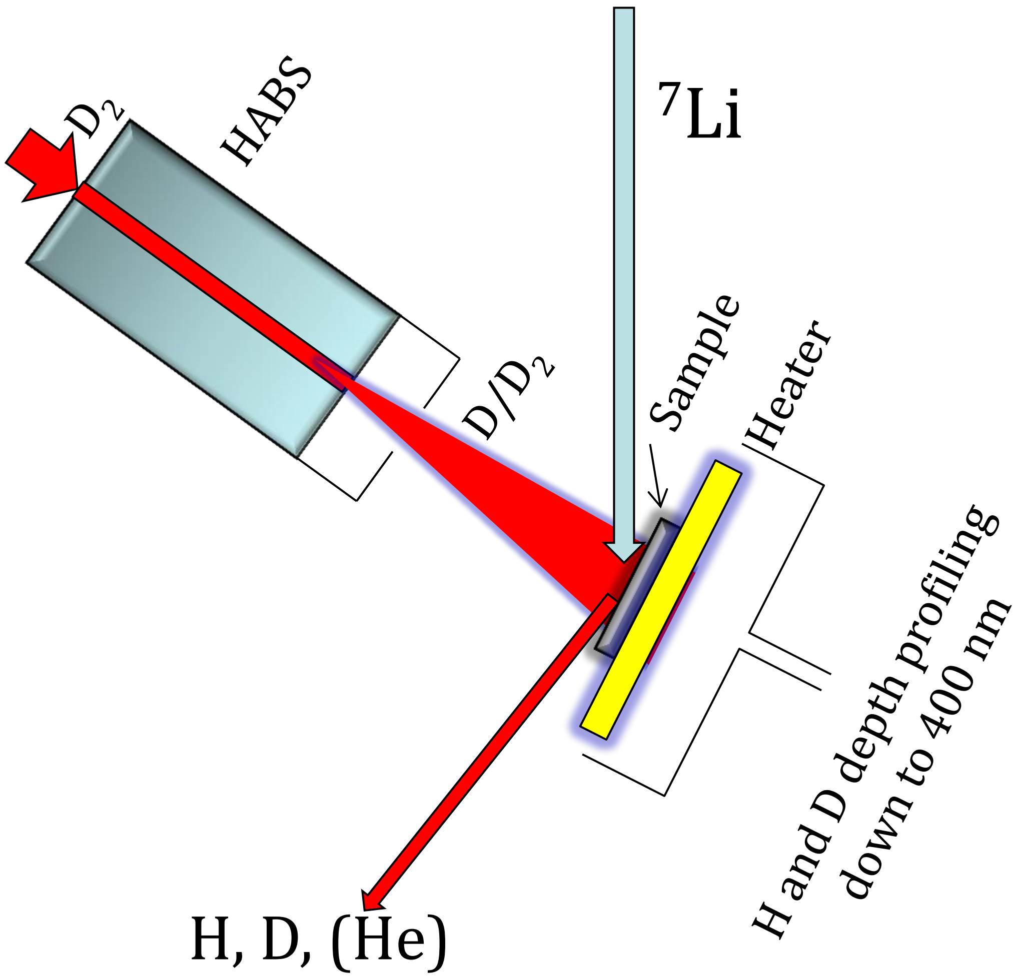
Process where one isotope is exchanged by the other. The purpose of this is to study the efficiency of the process on the surface and in bulk as cleaning method to reduce amount of tritium in the walls in fusion device during operation.



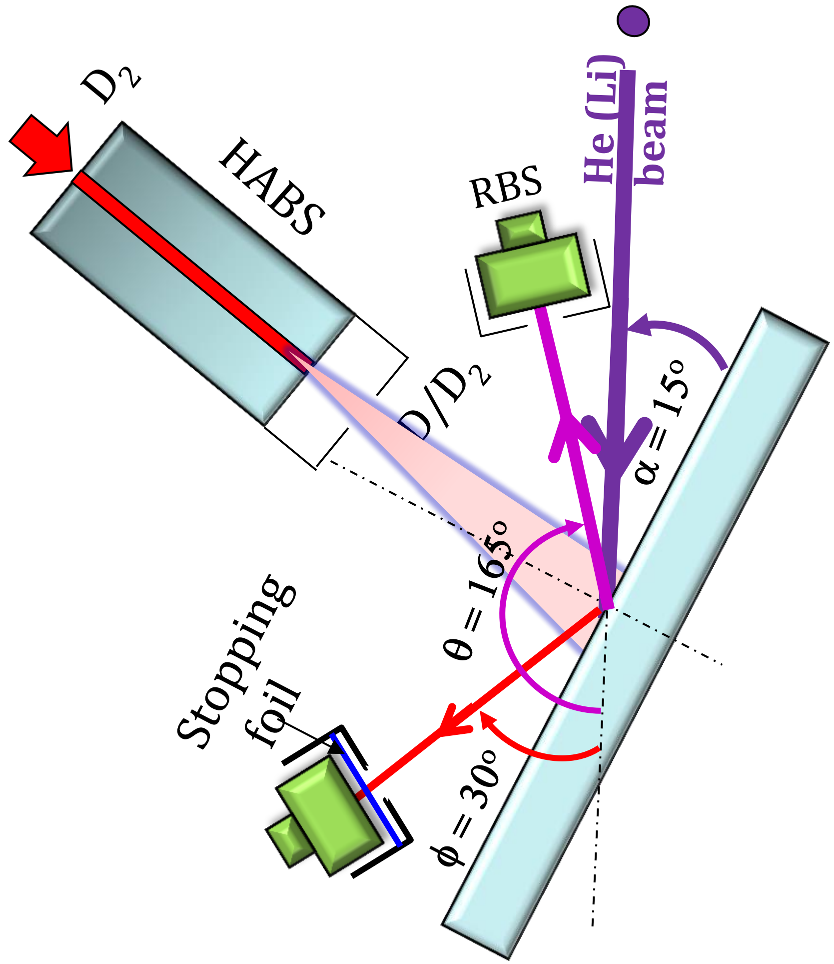


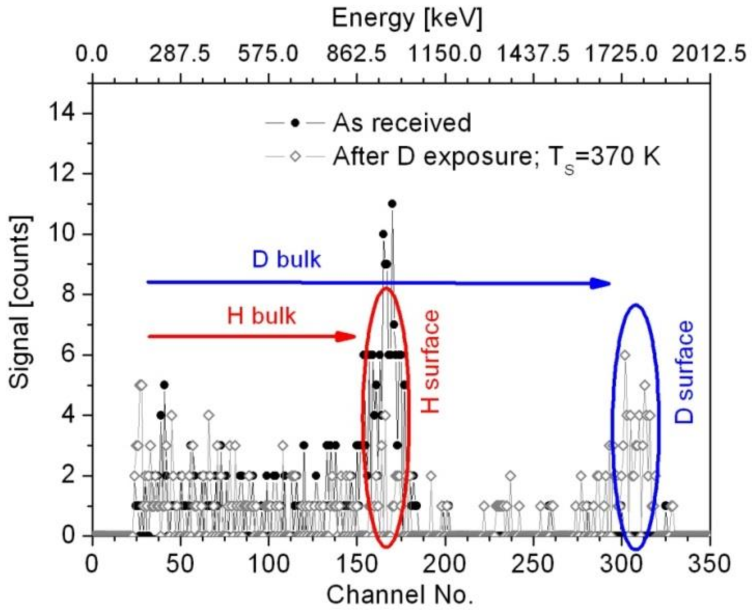
Isotope exchange is a well studies surface science process, where adsorbed atoms on the surface are abstracted by incoming free atoms, the so called Eiley-Rideal or Hot-Atom recombination mechanisms.

In situ ERDA measurements



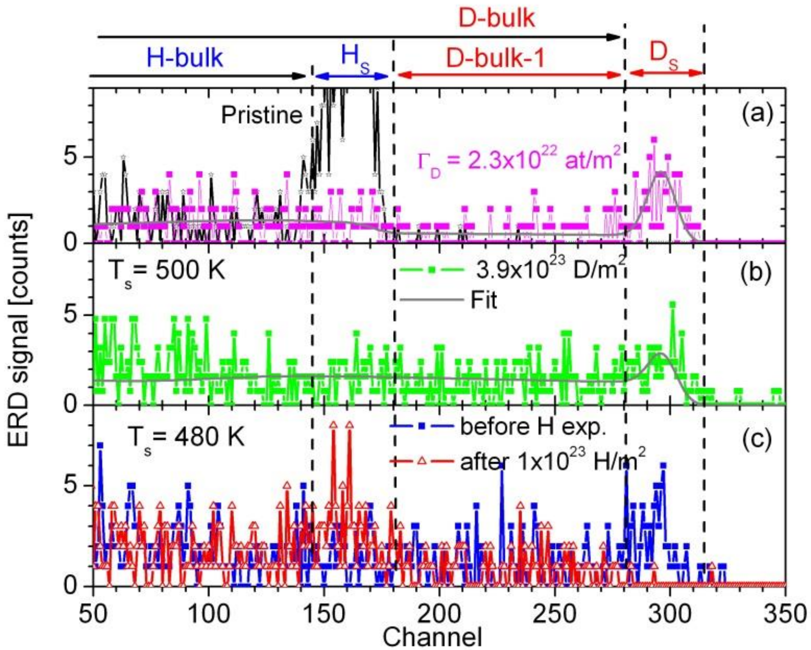
In situ ERDA measurements

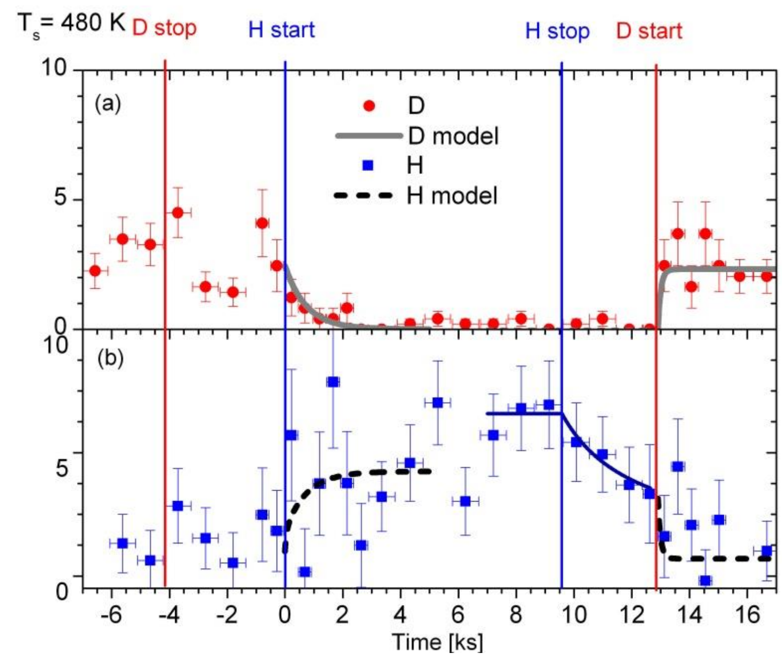




Typical mean atom flux density at the beam position was for D 6.4×10^{18} at.$m^{-2}s^{-1}$ and for H 1.0×10^{19} at.$m^{-2}s^{-1}$.

Isotope exchange on surface - ERDA





Isotope exchange study

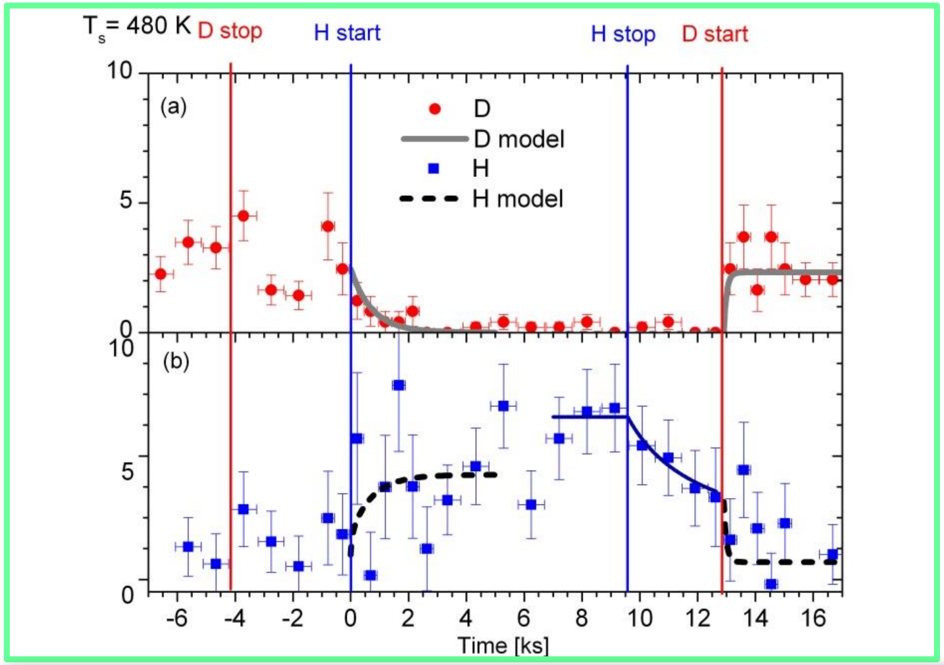
- Measurement of both H and D
- One can study surface processes
- ERDA method not sensitive enough for bulk
- D signal in undamaged W exposed to D atoms – close to detection sensitivity

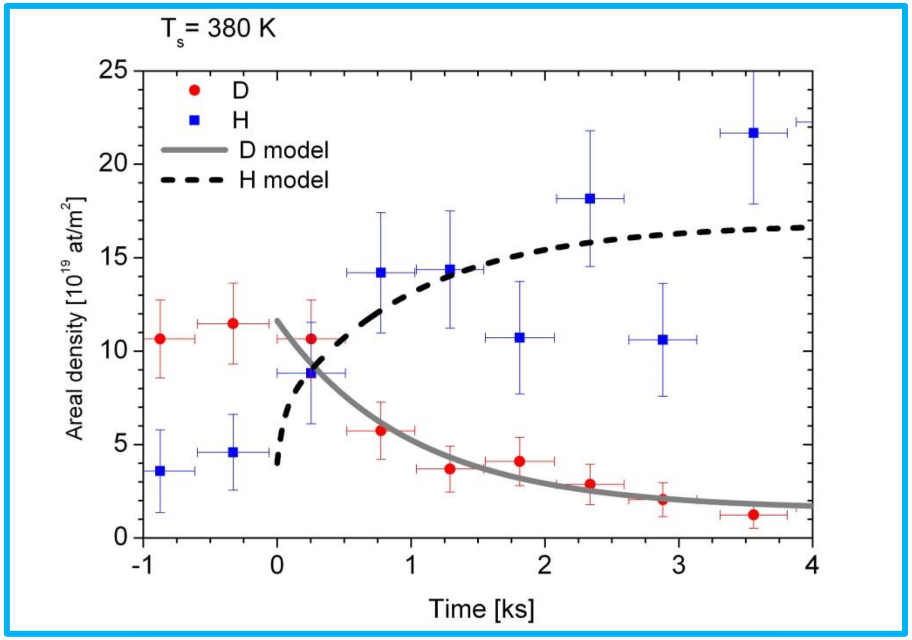
Markelj et al. JNM 438 (2013) S1027

Isotope exchange on surface - modelling

$$\frac{d[c_{S-D}]}{dt} = -\phi_H \sigma_{exc}[c_{s-D}] - 2k_d[c_{s-D}]^2 - k_d[c_{s-D}][c_{s-H}]$$

$$\frac{d[c_{s-H}]}{dt} = \phi_H(1-P_r)(1-[c_{s-H}]/N_o - [c_{s-D}]/N_o) - \phi_H \sigma_{exc}[c_{s-H}] - 2k_d[c_{s-H}]^2 - k_d[c_{s-D}][c_{s-H}]$$





σ_{480}(H→D)=1.2±0.6×10^{-22} m^2, P_{r480}(H→D)=0.94±0.2
σ_{480}(D→H)=1.7±0.7×10^{-21} m^2, P_{r480}(D→H)=0.88±0.05

σ_{380}(H→D)=0.9±0.15×10^{-22} m^2,
P_{r380}(H→D)=0.74±0.15

Isotope effect also observed on W in theory– R. Petuya et al. J Phys. Chem. C 2015

Markelj et al. Submitted to JNM - under review

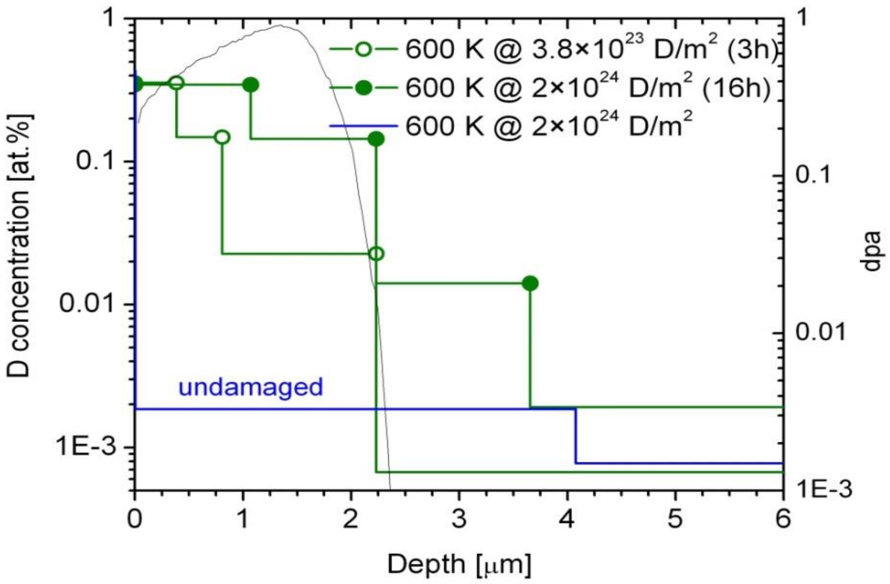
ERDA vs. NRA studies in self-damaged W

ERDA – undamaged/self-damaged W

- Measurement of both H and D
- One can study surface processes
- ERDA method not sensitive enough for bulk

NRA – self-damaged W

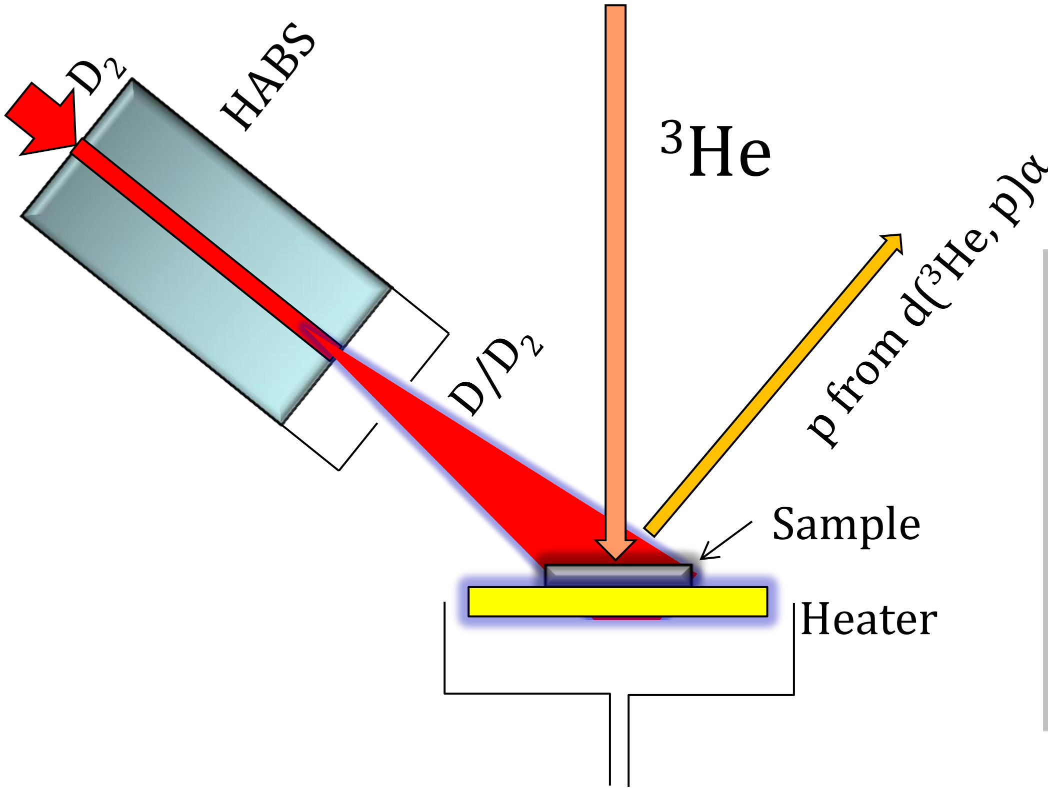
- D atoms can penetrate onto bulk and saturate the traps induced by heavy ion irradiation
- Damage profile dominates the D retention – large NRA signal



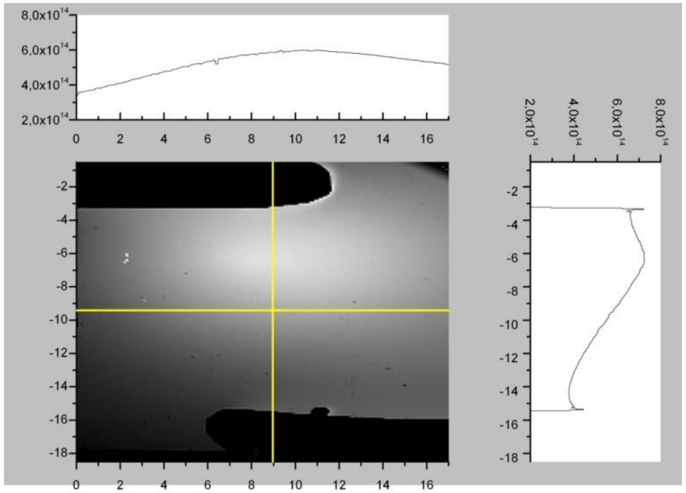
Perfect case for studying dynamics of D atom diffusion and isotope exchange in bulk

Isotope exchange - Possible tritium removal technique

In situ NRA measurements

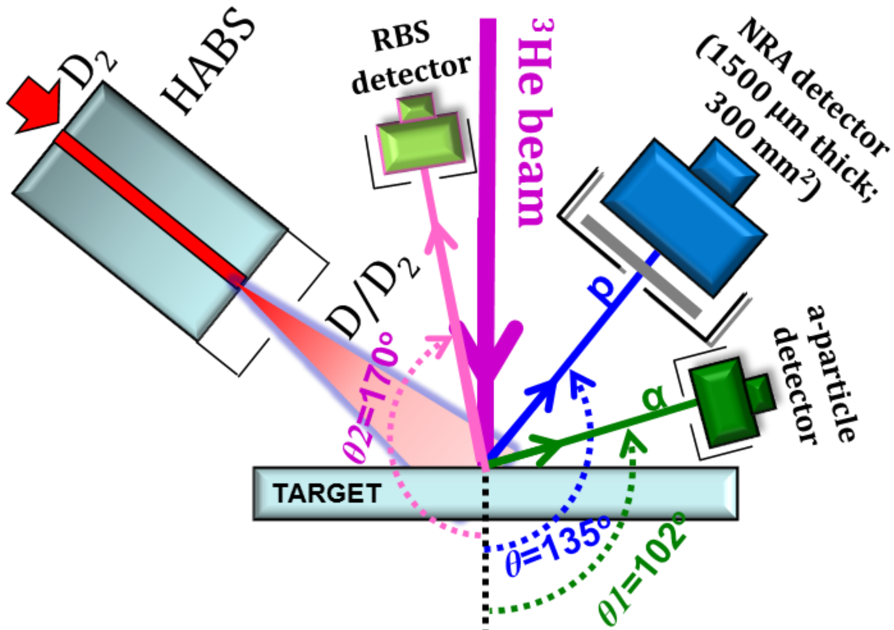


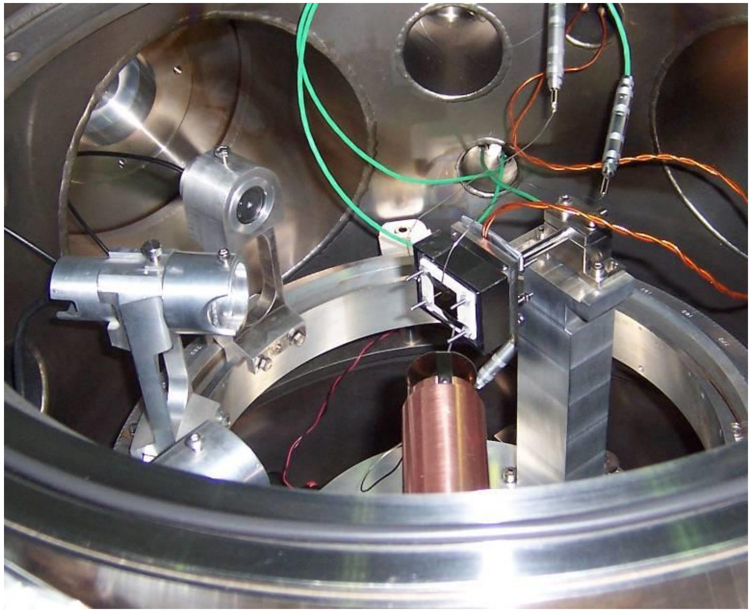
D depth profiling during atom exposure – down to 7 μ*m*



Mean flux density @ ion beam position 5.8×10^{18} D/m^2s

In situ NRA measurements





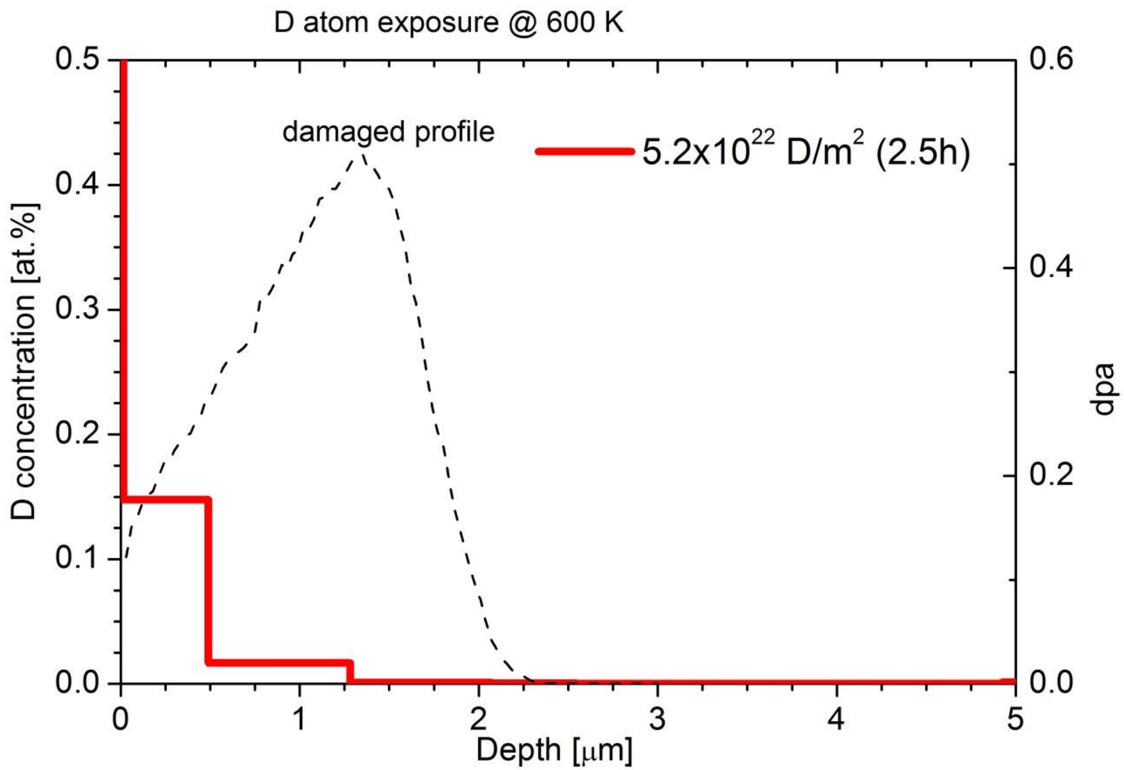
- Nuclear Reaction Analysis (NRA) - detecting proton signal from nuclear reaction $D(^3He,p)^4He$
- Depth profile - 5 different energies: 776, 1550, 2580, 3400 and 4300 keV
- Calibration measurements at on standard: a-C:D layer (60 nm)

- Takes about 1.5 h to go through the whole cycle, avoid too much current due to temperature increase.
- Time of studied processes - hours/days

Markelj et al. Phys. Scr. T159 (2014) 014047

In situ NRA measurements – D atom exposure

- Exposure to D atom beam @ 600 K for 48 h.
- D atom beam flux density: 5.8×10^{18} D/m^2 s.
- Filling of damaged area by D atoms.



Markelj et al. Submitted to JNM - under review

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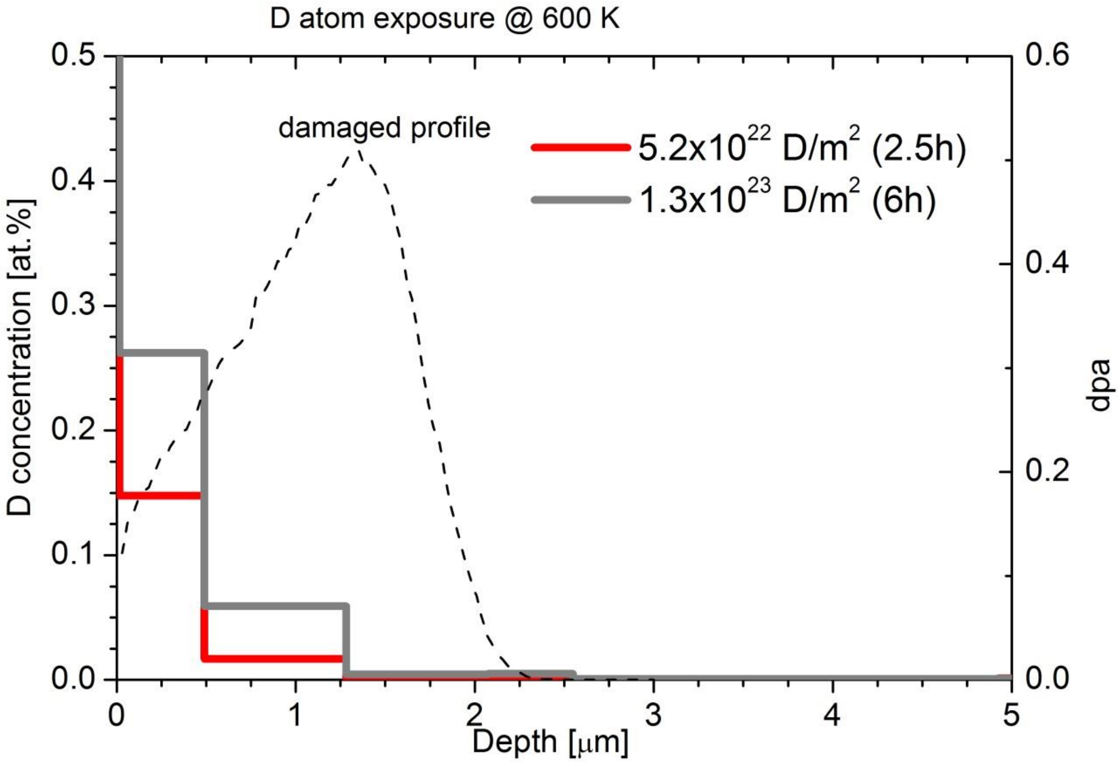

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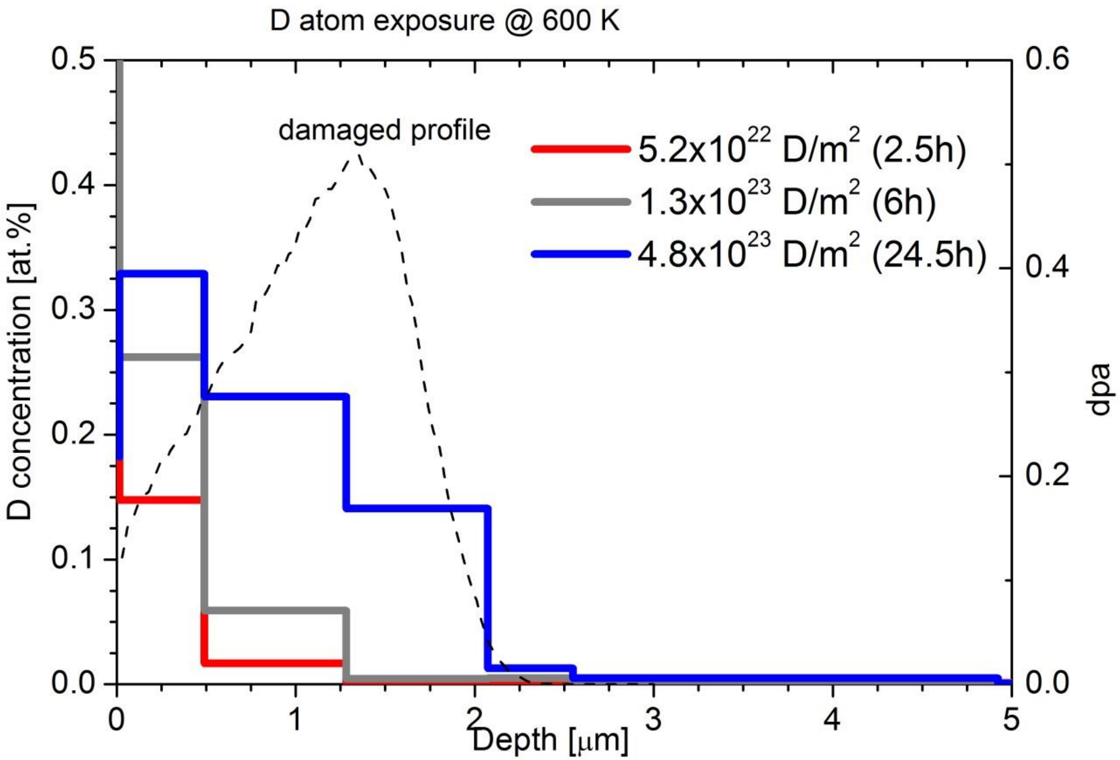

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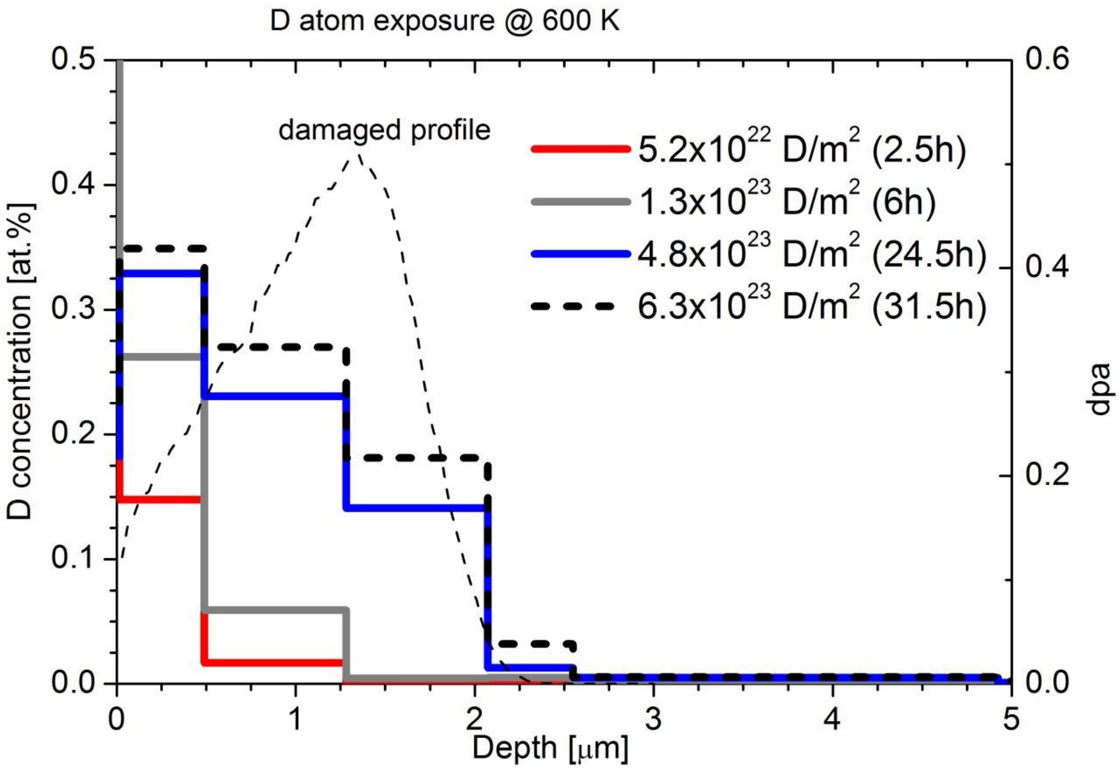

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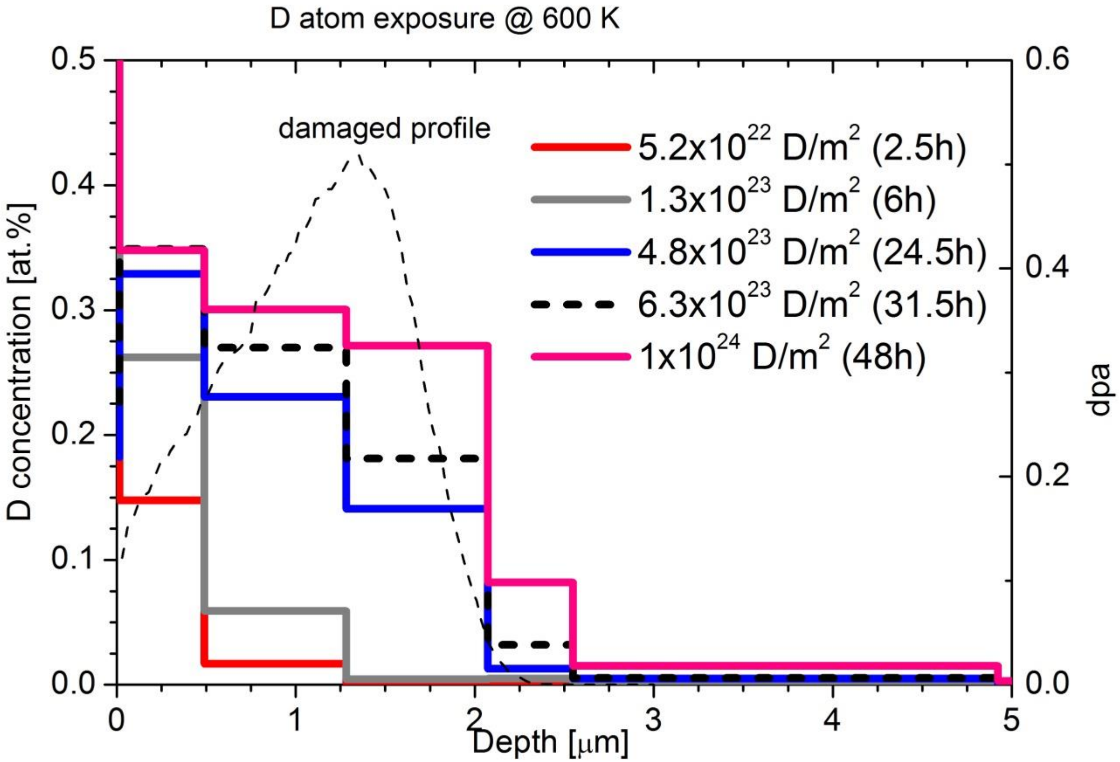
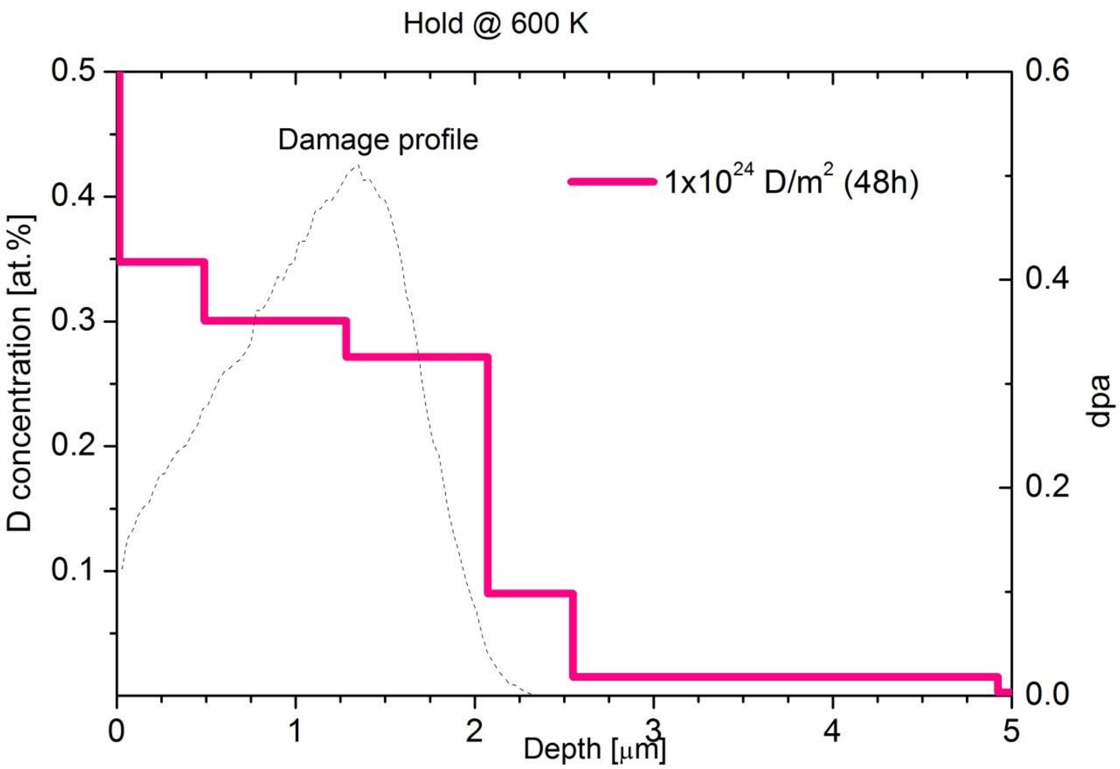


In situ NRA measurements – thermal desorption @ 600 K

- Exposure to D atom beam @ 600 K for 48 h, fluence 1x10^{24} D/m^2.
- Atomic beam switch off; 43 h at 600 K – D self desorption



In situ NRA measurements – thermal desorption @ 600 K

- Exposure to D atom beam @ 600 K for 48 h, fluence $1x10^{24}$ D/m^2.
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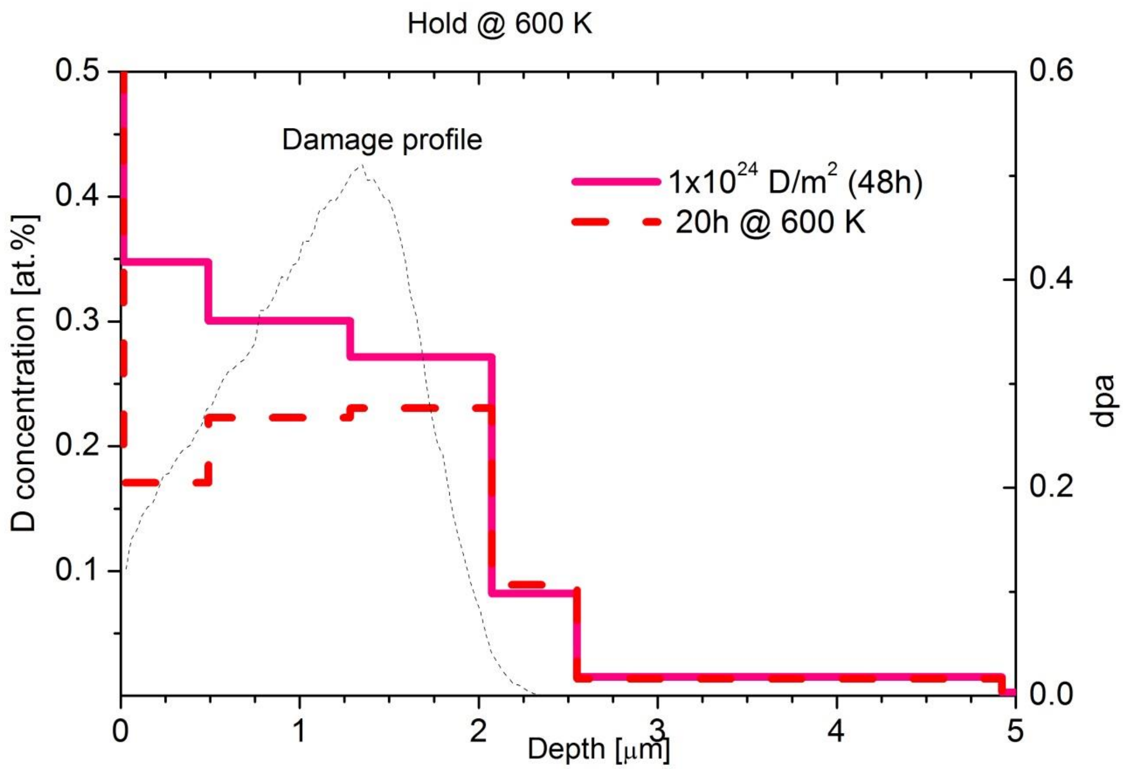

In situ NRA measurements – thermal desorption @ 600 K

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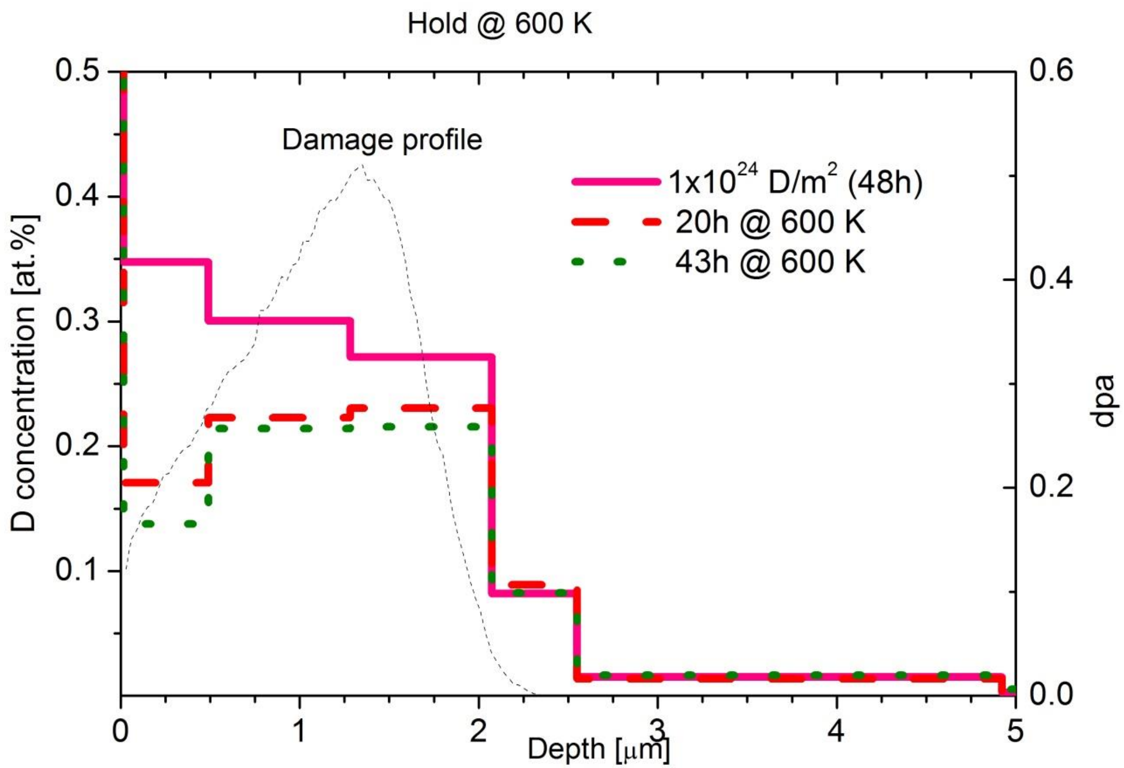
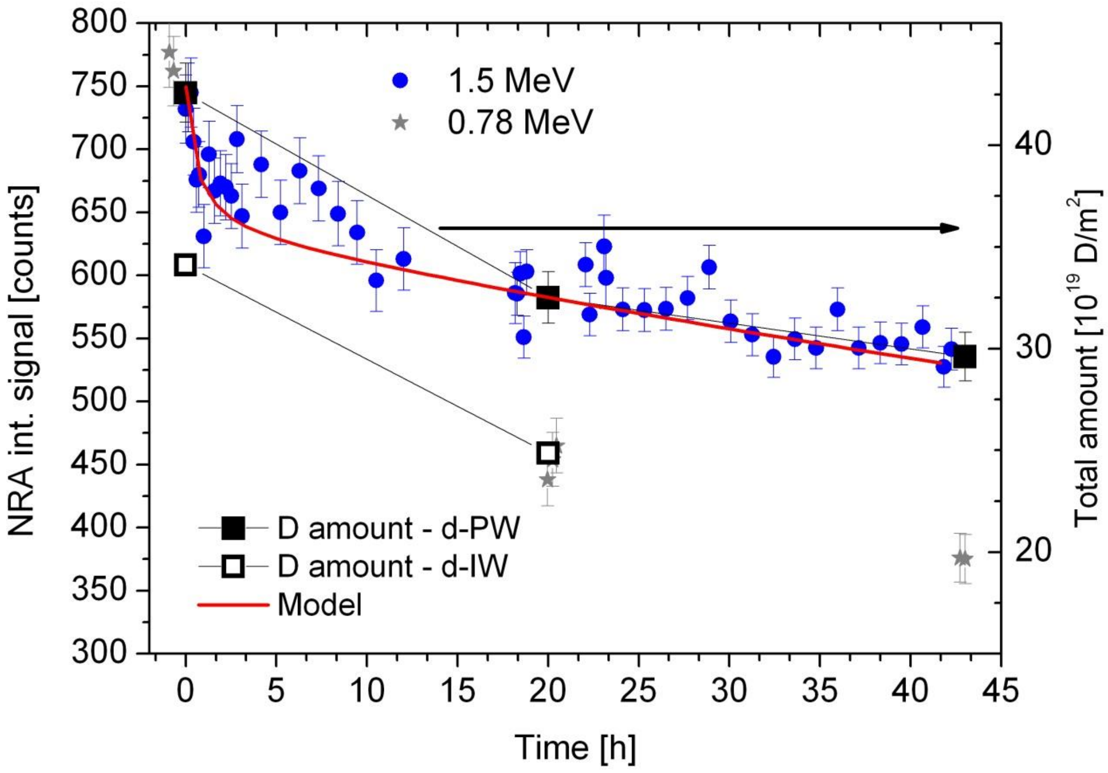


In situ NRA measurements – thermal desorption @ 600 K

- Atomic beam switch off; 43 h at 600 K – D self desorption – 30 % decrease in total concentration in damaged layer
- Previous study on IW– only hold @ 590 K for 20 h -> 27% decrease



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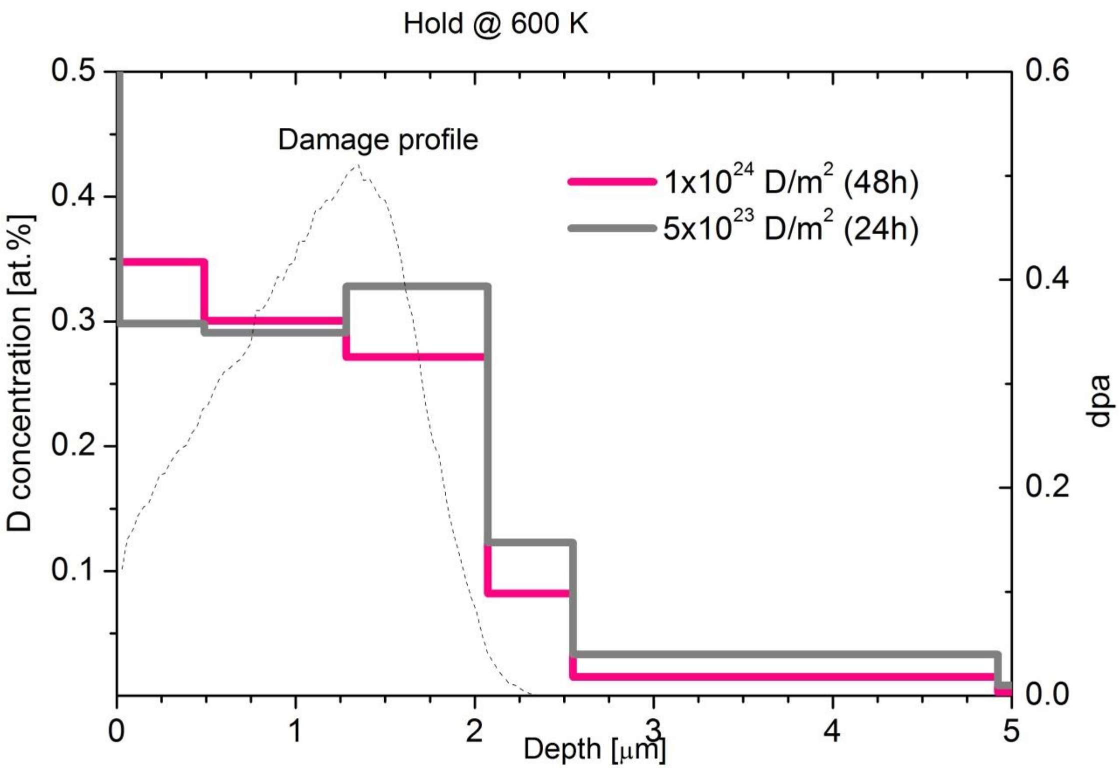
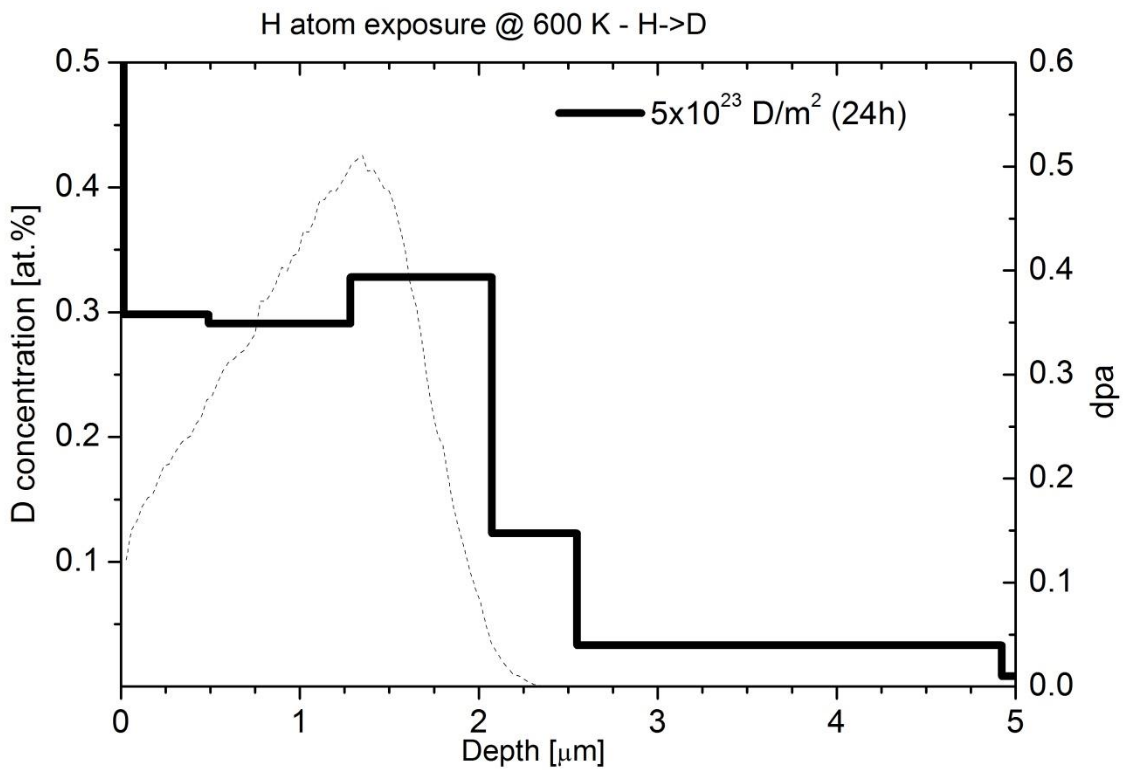
In situ NRA measurements – bulk isotope exchange

- Exposure to D atom beam @ 600 K for 48 h, fluence $1x10^{24}$ D/m^2.
- Atomic beam switch off; 43 h at 600 K – D self desorption
- Additional exposure to D beam for 24 h after hold



In situ NRA measurements – bulk isotope exchange H → D

- Exposure to H atoms for 96h - bulk isotope exchange at 600 K
- H atom beam flux density: 6.9×10^{18} H/m^{2}s
- D removal in damaged layer by isotope exchange



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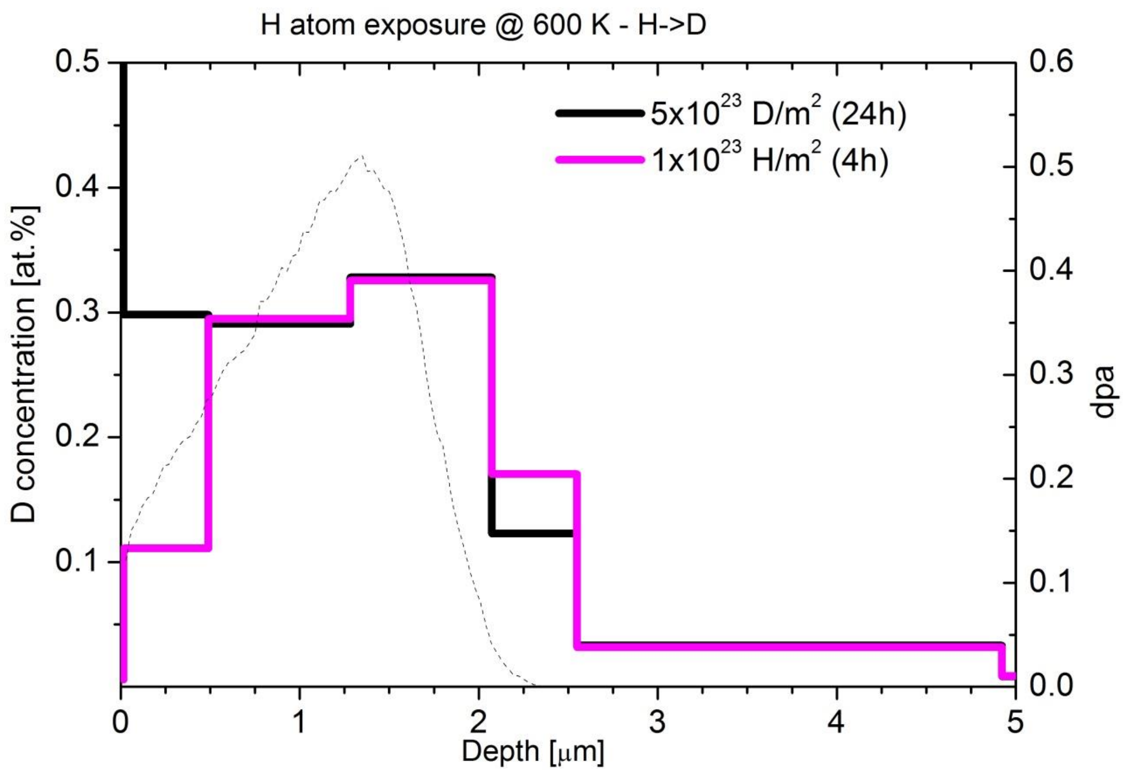

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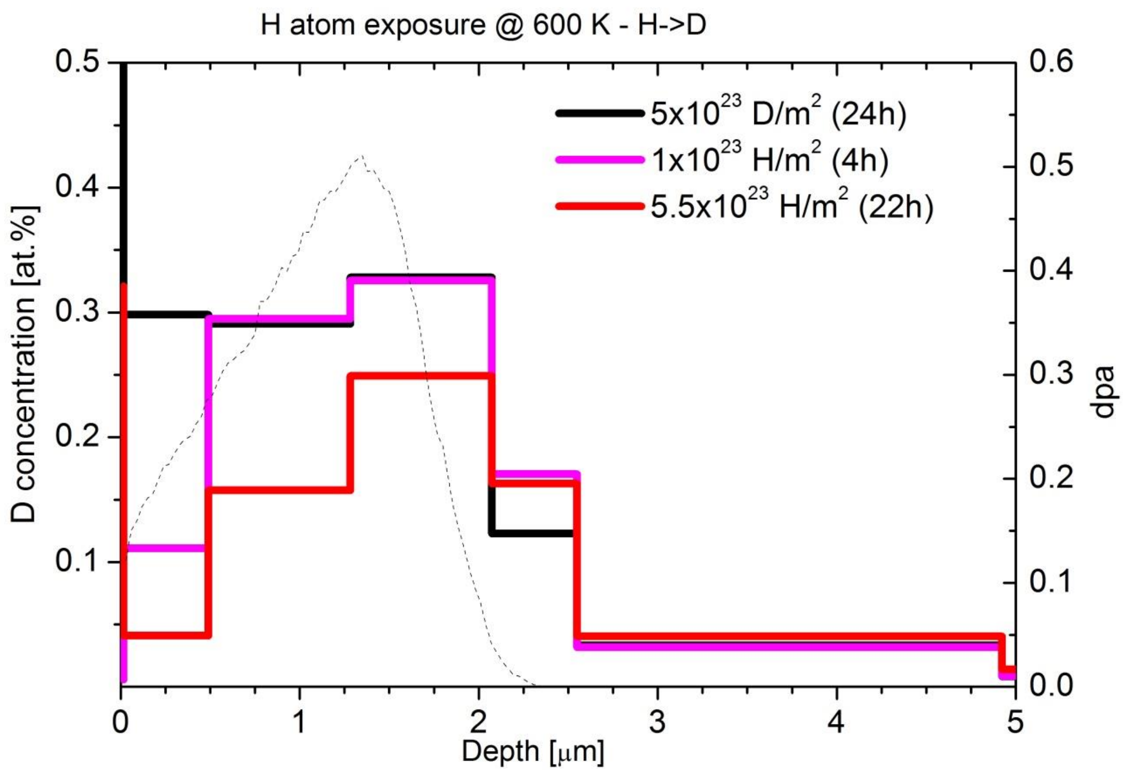

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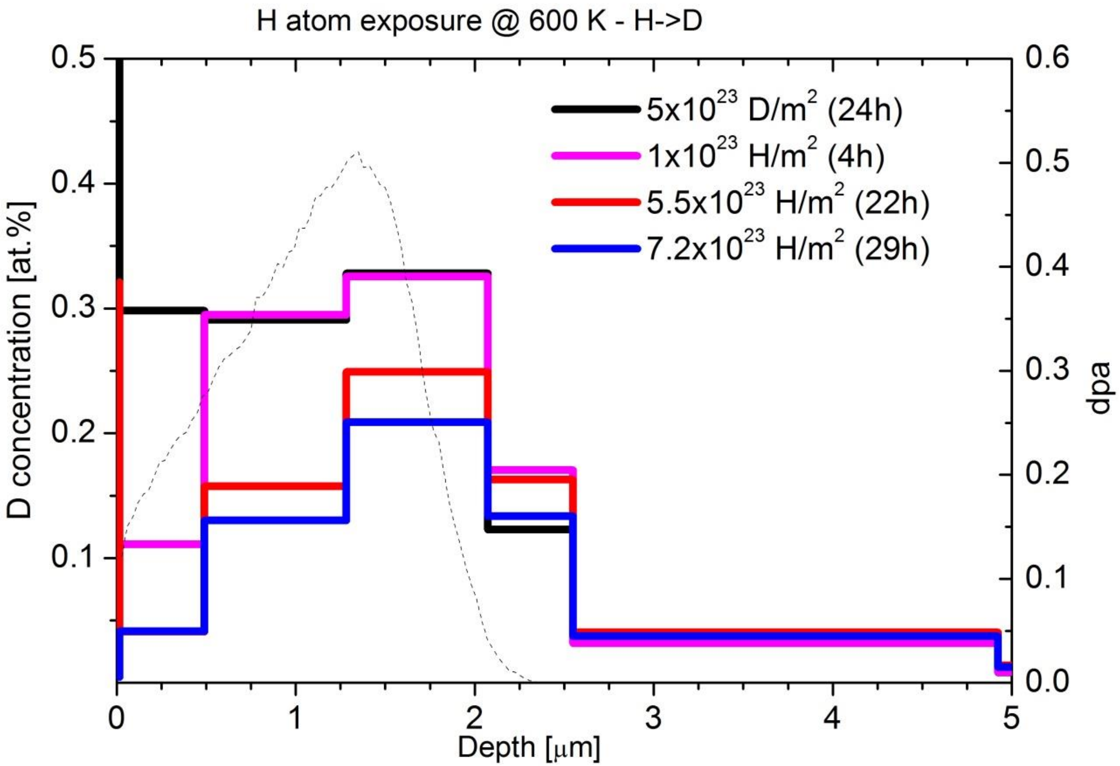

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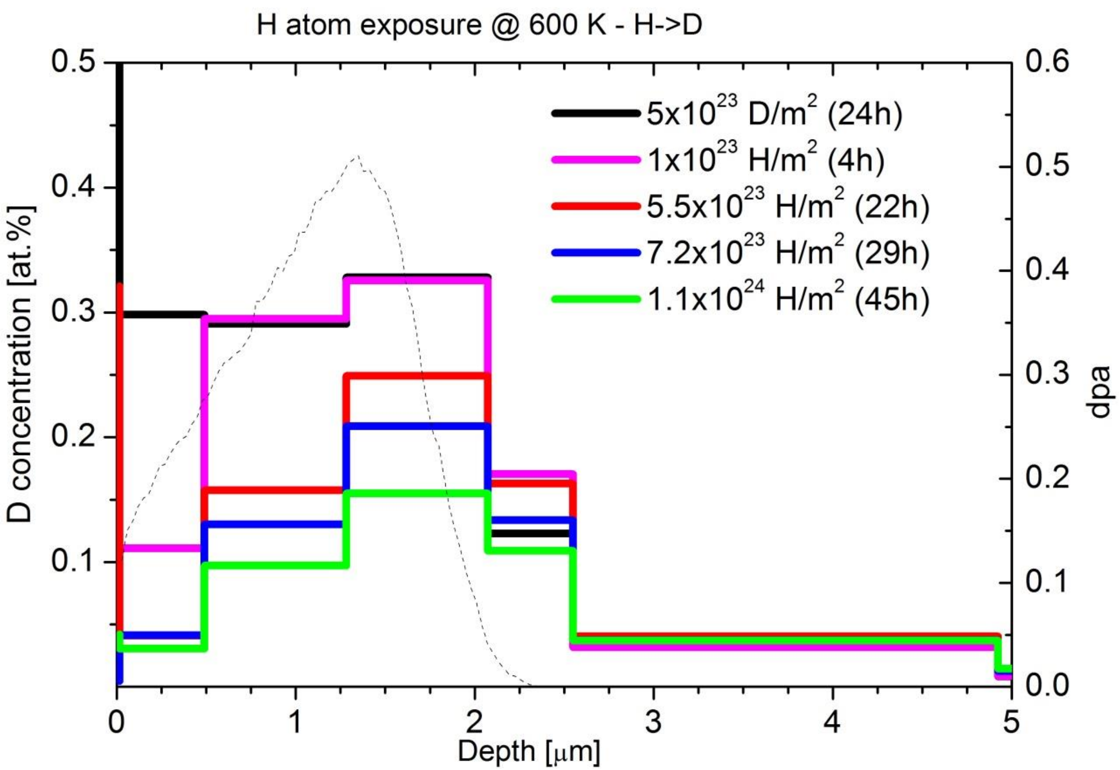

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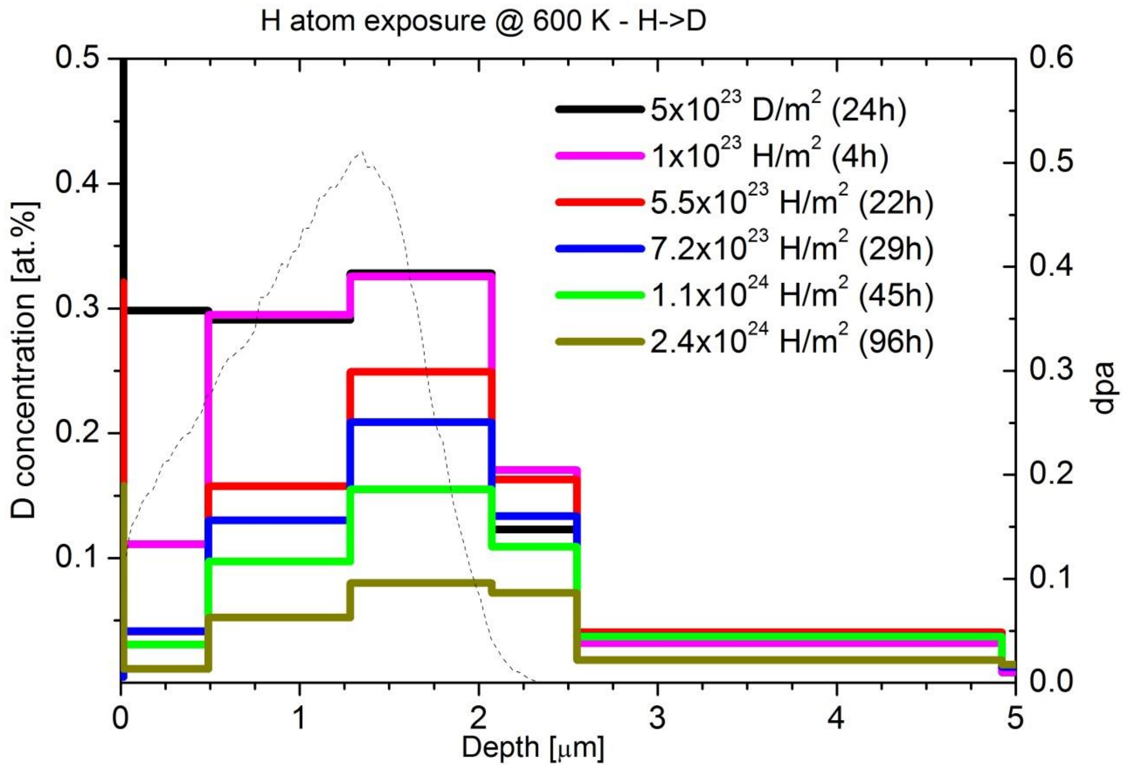

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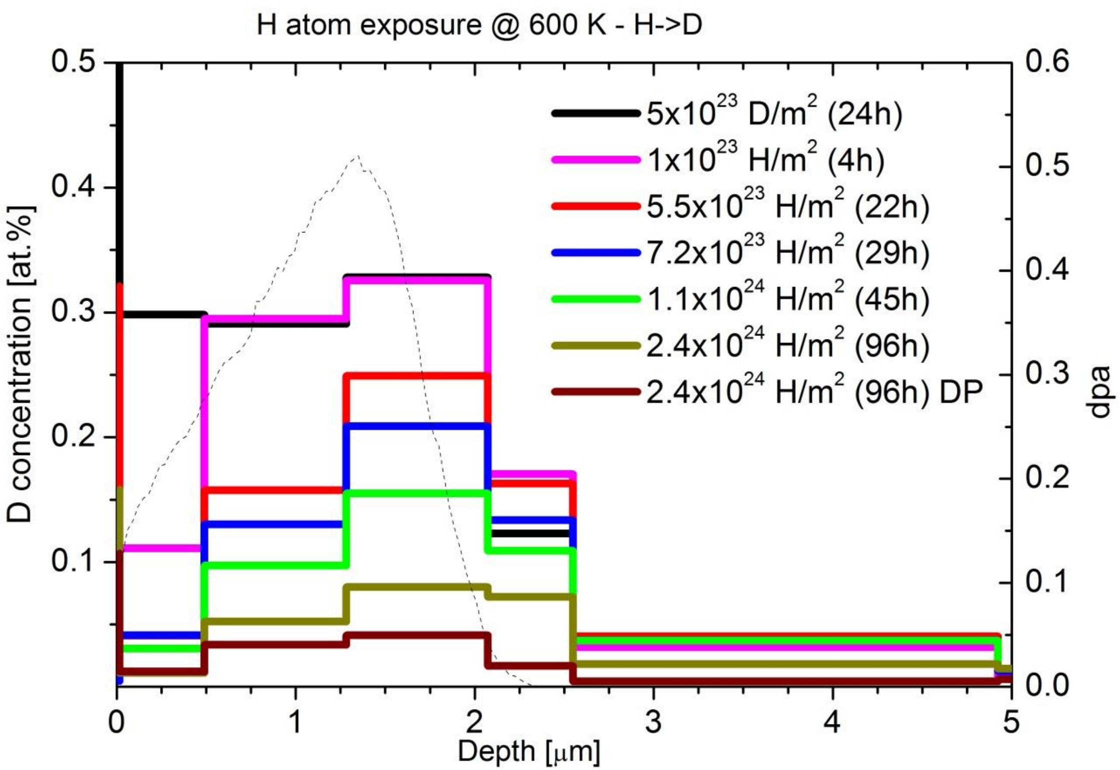
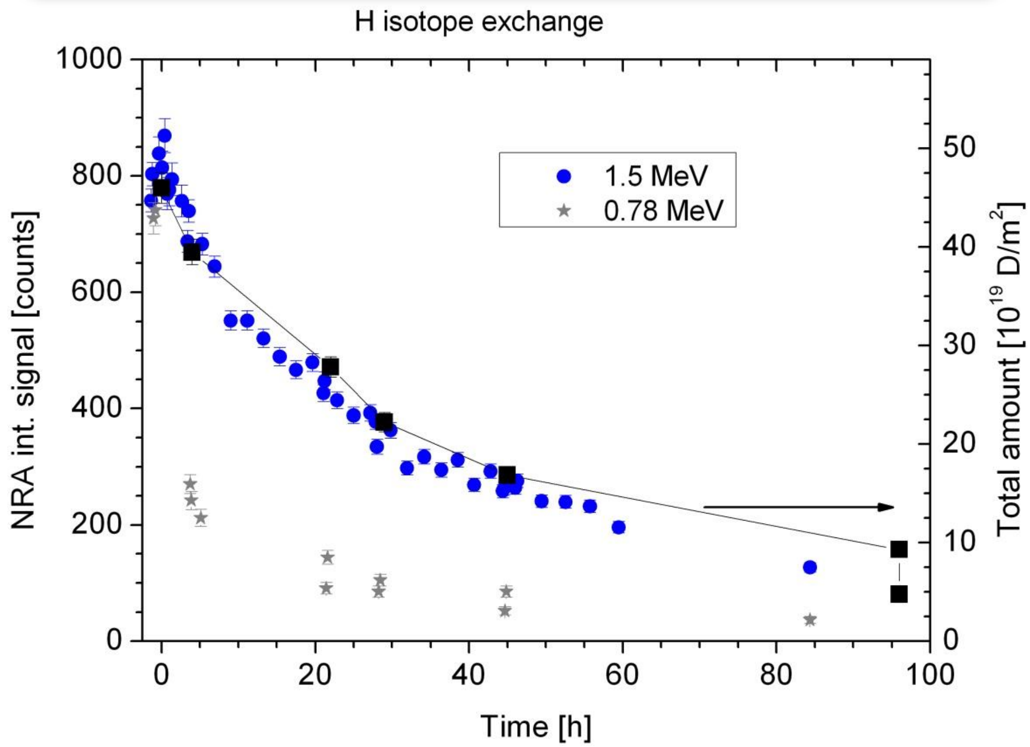
- Exposure to H atoms for 96h - bulk isotope exchange at 600 K
- H atom beam flux density: 6.9×10^{18} H/m^{2}s
- D removal in damaged layer by isotope exchange – after 96 h of H exposure, fluence 2.4×10^{24} H/m^2 , 20 % of D still remained, 10 % at DP



In situ NRA measurements – bulk isotope exchange H → D

- Exposure to H atoms for 96h - bulk isotope exchange at 600 K
- H atom beam flux density: 6.9×10^{18} H/m^2s
- Comparison to isothermal desorption - after 20 h the signal drops by 48% and after 43 h it has decreased by 68%.

Signal decrease @1.5 MeV, 0.78 MeV



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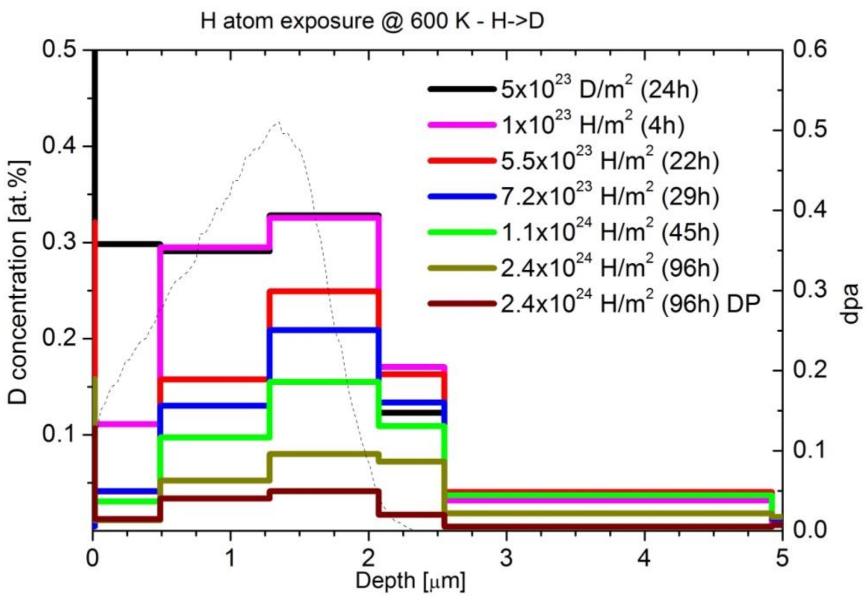
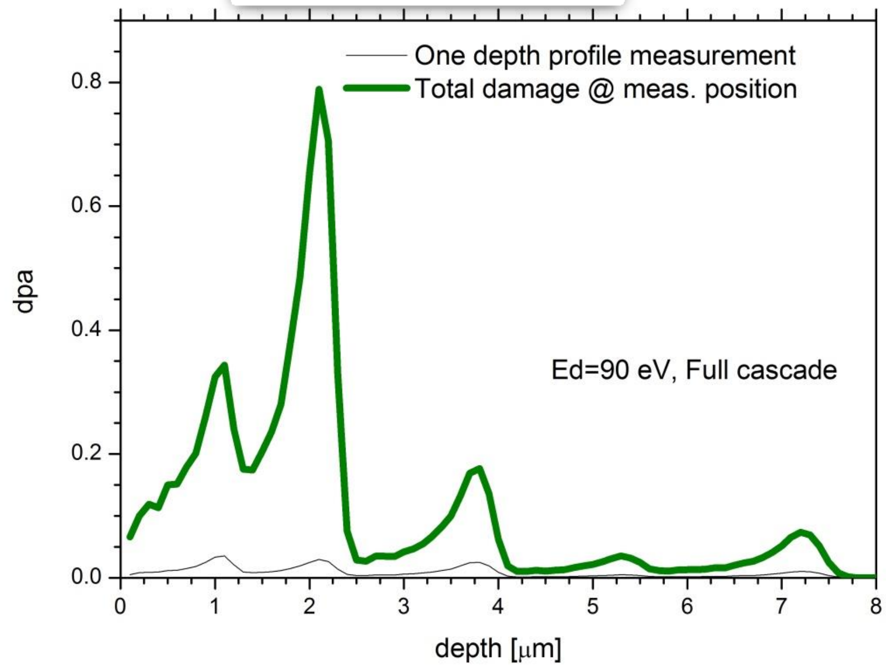
- Possible ^{3}He beam effect – stronger binding of D around He interstitials

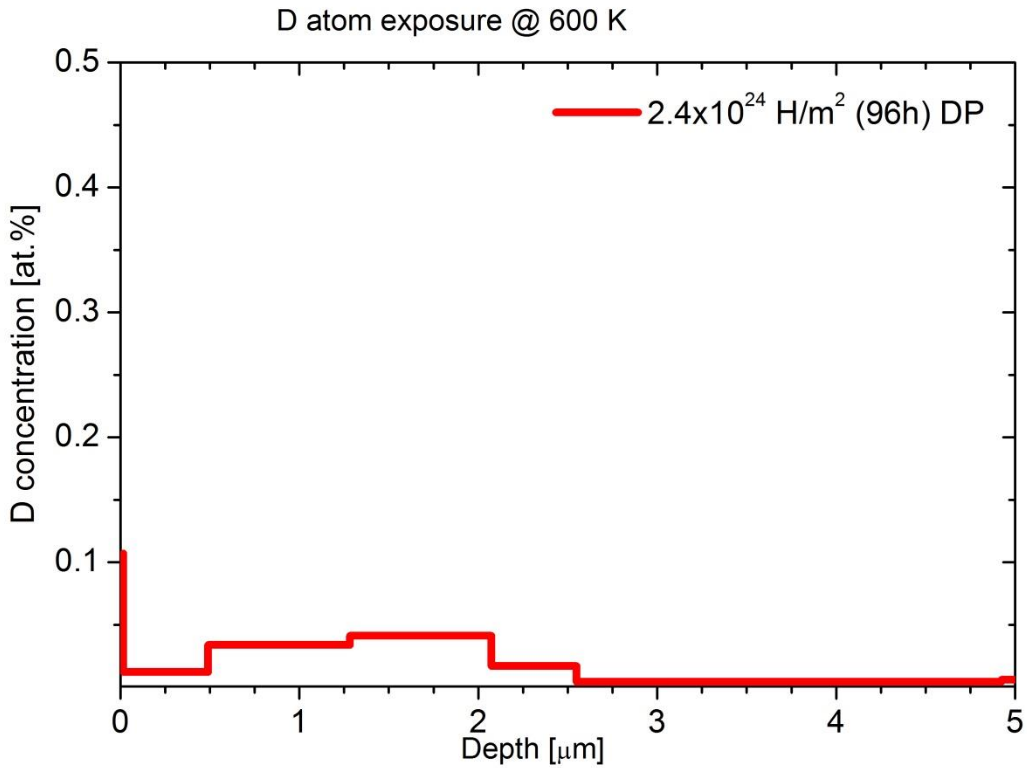


SRIM calculation



In situ NRA measurements – bulk isotope exchange D → H

- Exposure to D atoms for 71 h - bulk isotope exchange at 600 K
- D atom beam flux density: 5.8×10^{18} D/m^2 s.
- H removal in damaged layer by isotope exchange



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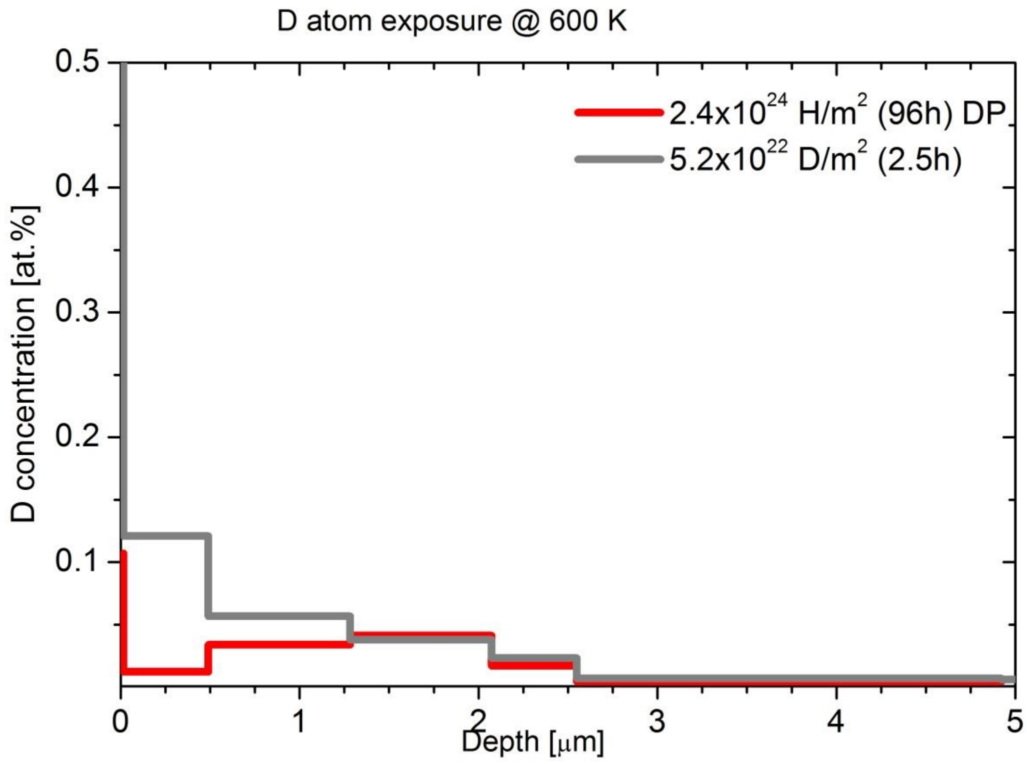

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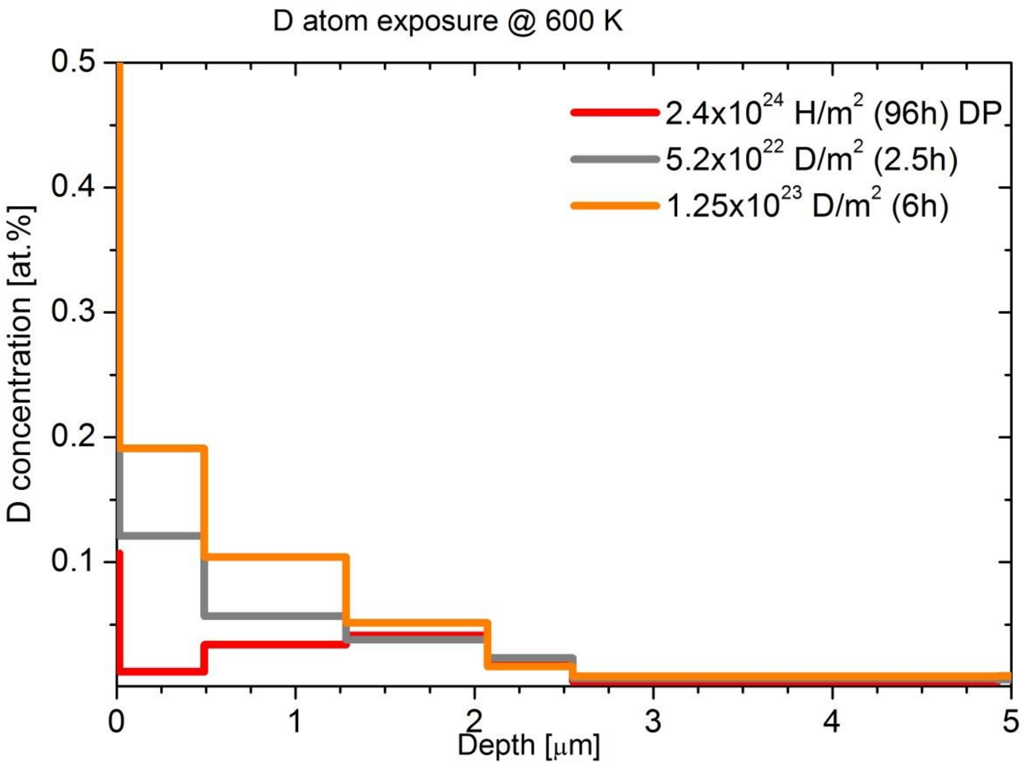

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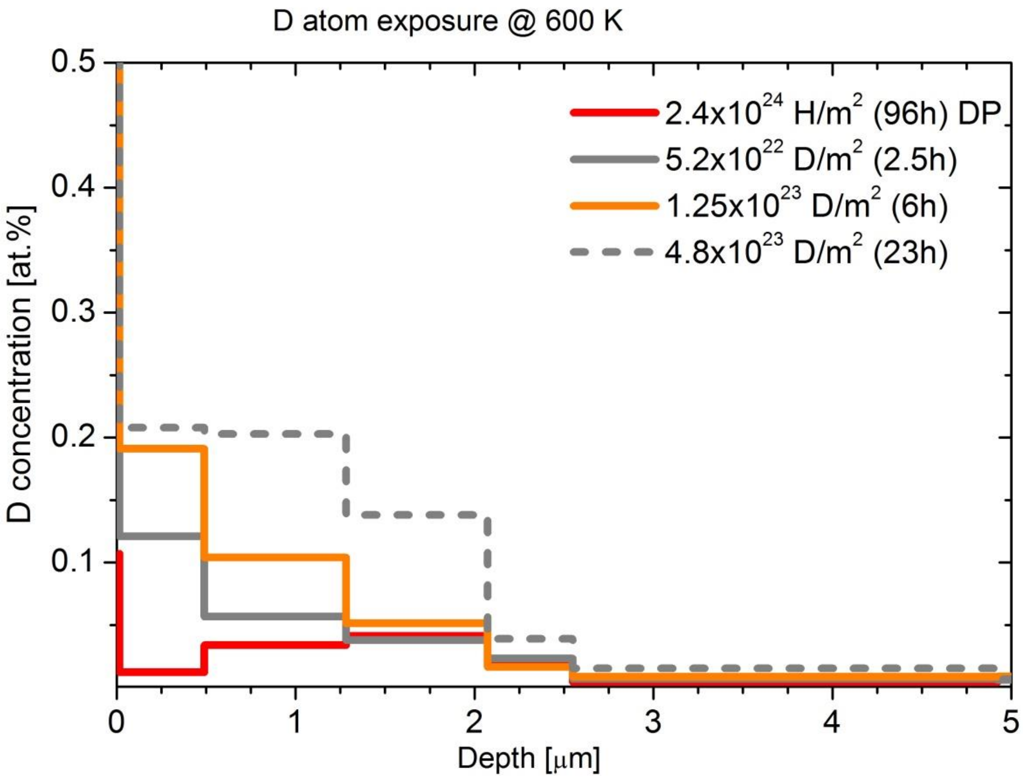

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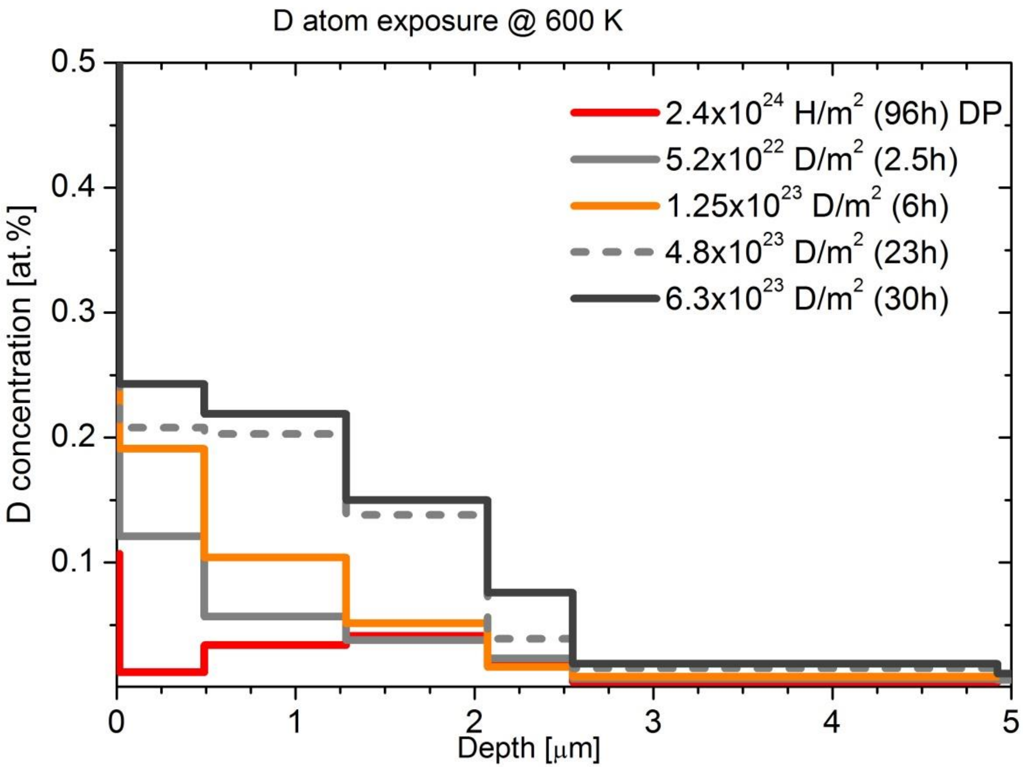

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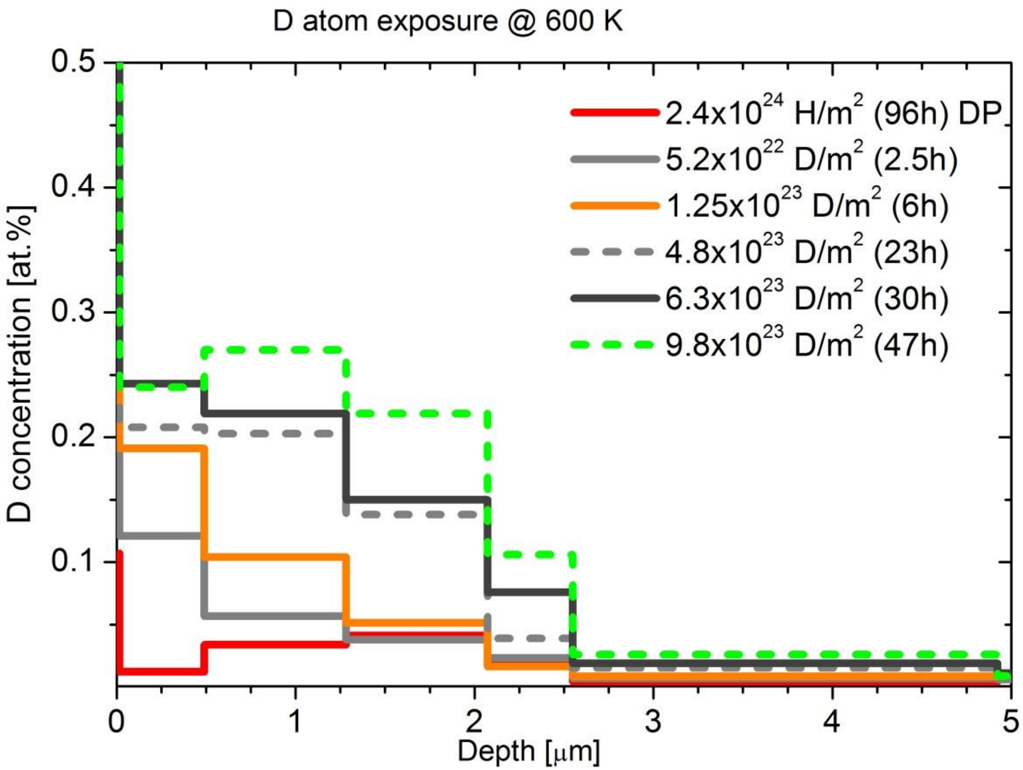

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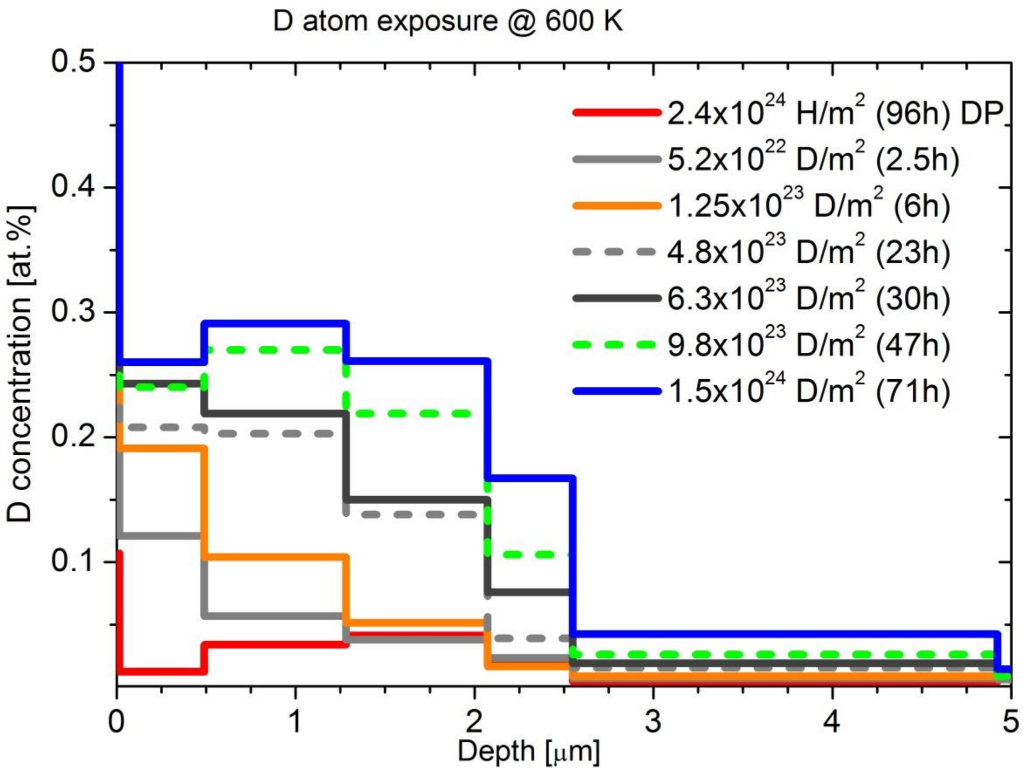
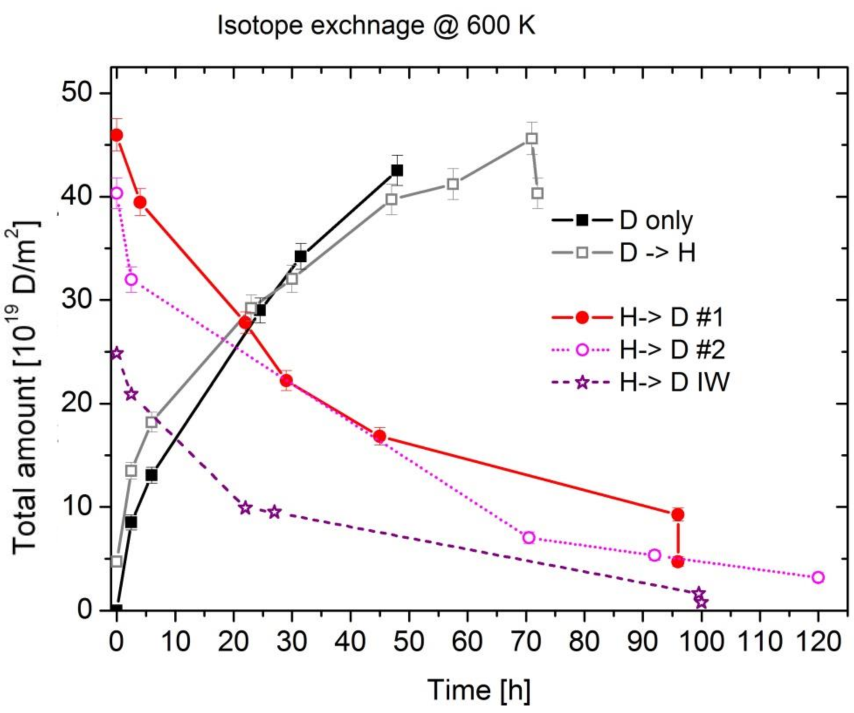
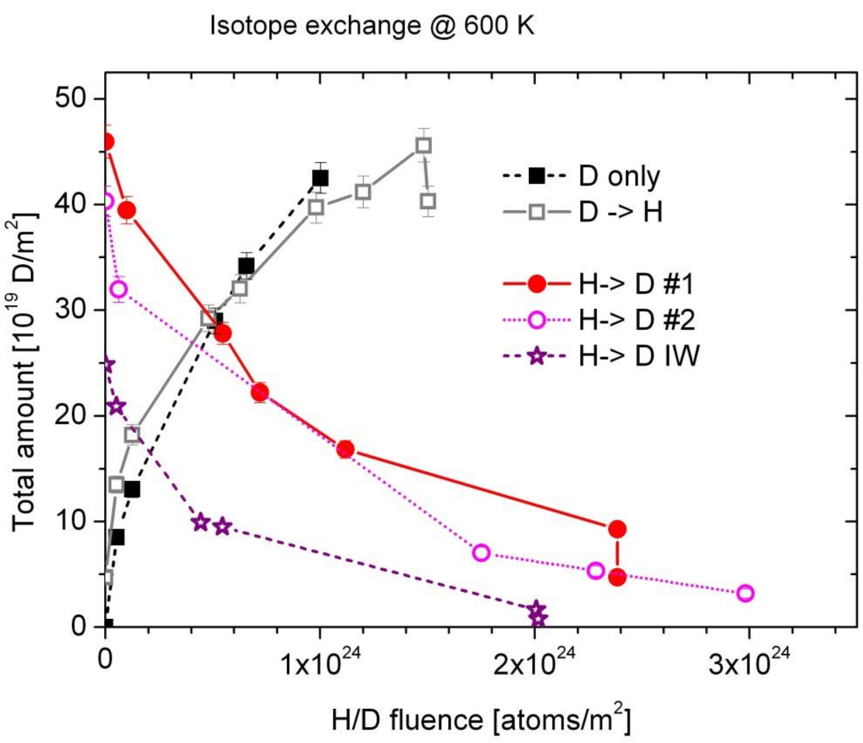


Bulk isotope exchange

- Total amounts of D in damaged area
- Only D loading and exchange D → H – similar dynamics
- Approximately 2 times higher fluence needed for H → D isotope exchange
- Isotope exchange is efficient



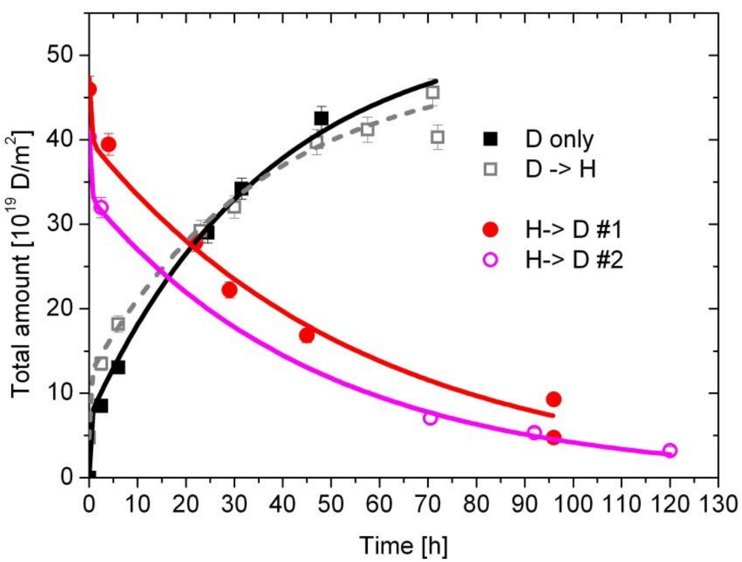


Bulk isotope exchange - modelling

$$\frac{d[c_{B-D}]}{dt} = -\phi_H \sigma_{excB} [c_{B-D}] - \upsilon^{(1)} [c_{B-D}] e^{-E_{d2}/kT}$$

$$\frac{d[c_{B-H}]}{dt} = \phi_H \sigma_{excB} [c_{B-D}] - \upsilon^{(1)} [c_{B-H}] e^{-E_{d2}/kT} + (1 - [c_{B-D}]/c_{B0} - [c_{B-H}]/c_{B0})\, \phi_H\, s$$

Isotope exchange @ 600 K



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Observed isotope effect

σ_{excB}(H→D;#1)=5.2±0.6×10^{-25} m^2
σ_{excB}(H→D;#2)=6.5±0.3×10^{-25} m^2
σ_{excB}(D→H)=1.1±0.5×10^{-24} m^2

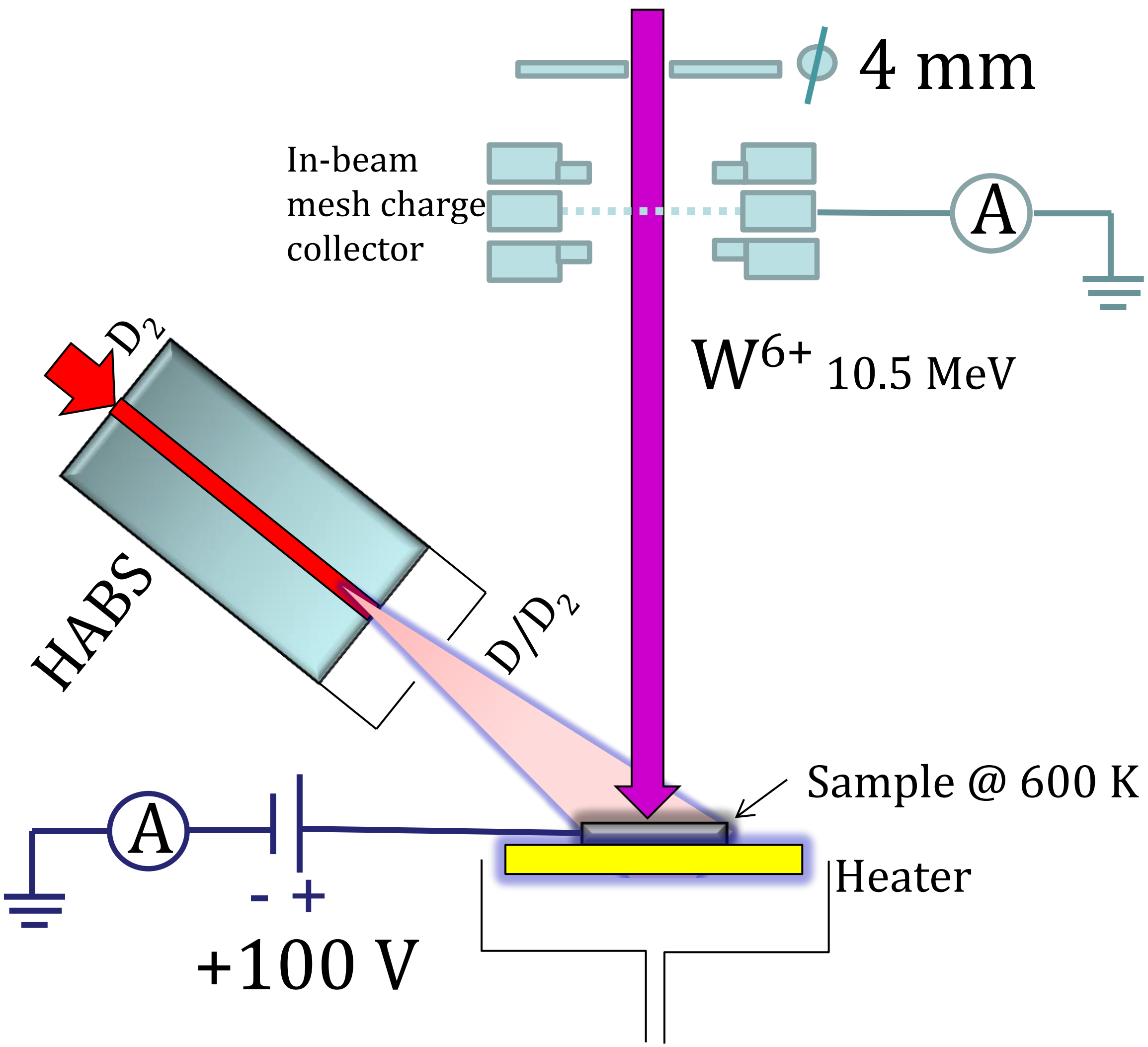
Uptake only

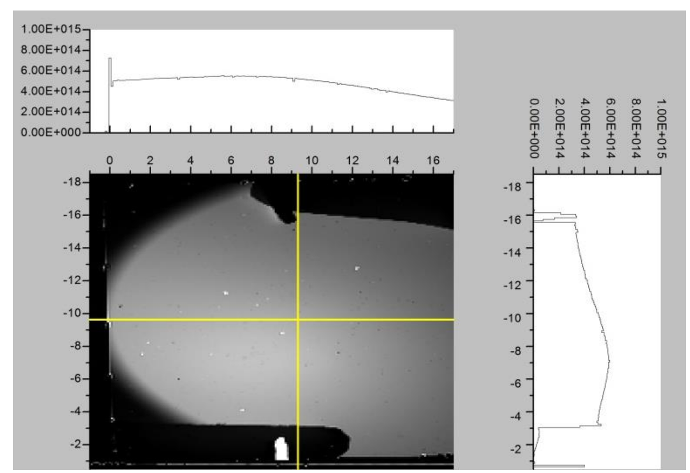
$$\frac{d[c_{B-D}]}{dt} = -\upsilon^{(1)} [c_{B-D}] e^{-E_{d2}/kT} + (1 - [c_{B-D}]/c_{B0})\ \phi_D(bulk)$$

$\phi_D(bulk)$=3.5±0.3×10^{15} D/m^{2}s
$R=\phi_D(bulk)/\phi_D$ = 7×10^{-4}

Preliminary results on Simultaneous high energy W ion irradiation and D atom loading

Simultaneous W irradiation and D loading
The set up





Mean flux density @ ion beam position 5.4×10^{18} D/m^2s

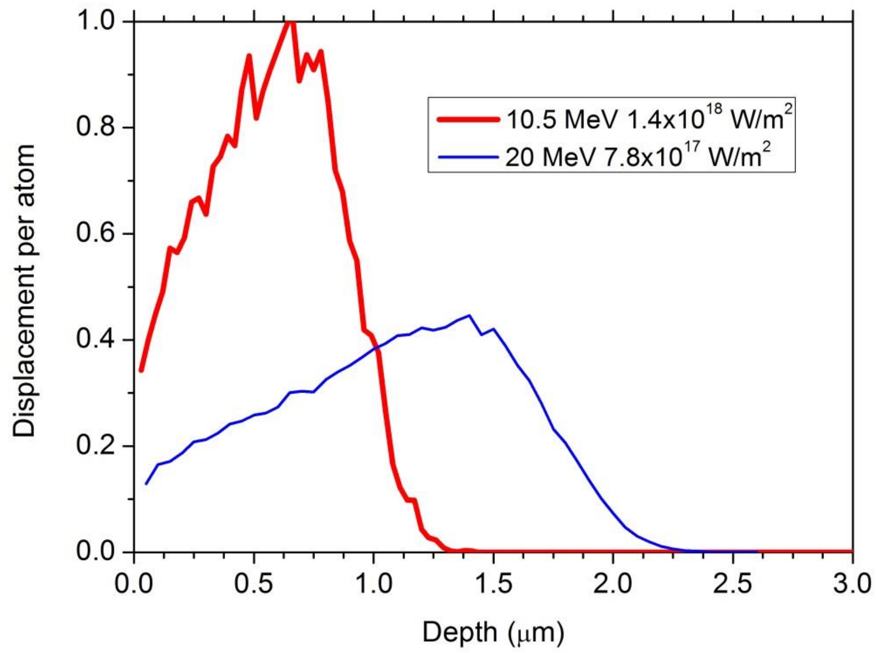
Simultaneous W irradiation and D loading

Damage W samples by MeV self-implantation at different temperatures + simultaneous loading by D atoms

Sample A0897-A
- Simultaneous W irradiation and D atom exposure @ 600 K
- Current-W^{6+} = 1.2 nA
- Irrad. Time = 14400 s
- W Fluence = 1.43×10^{18} W/m^2

Sample A0894-A
- Simultaneous W irradiation and D atom exposure @ 800 K
- Current-W^{6+} = 1.15 nA
- Irrad. Time = 14400 s
- W Fluence = 1.37×10^{18} W/m^2

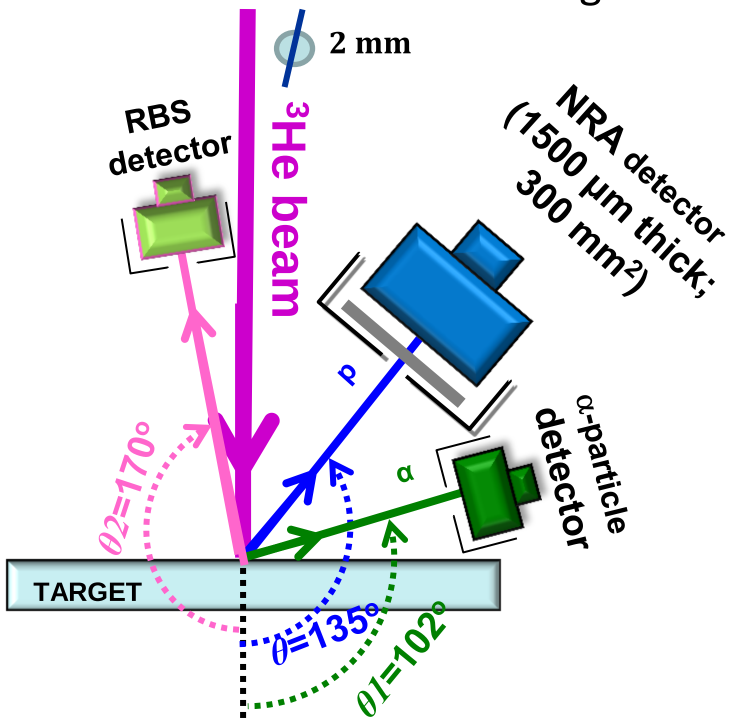
Sample A0896-A
- Simultaneous W irradiation and D atom exposure @ 450 K
- Current-W^{6+} = 1.15 nA
- Irrad. Time = 14400 s
- W Fluence = 1.37×10^{18} W/m^2

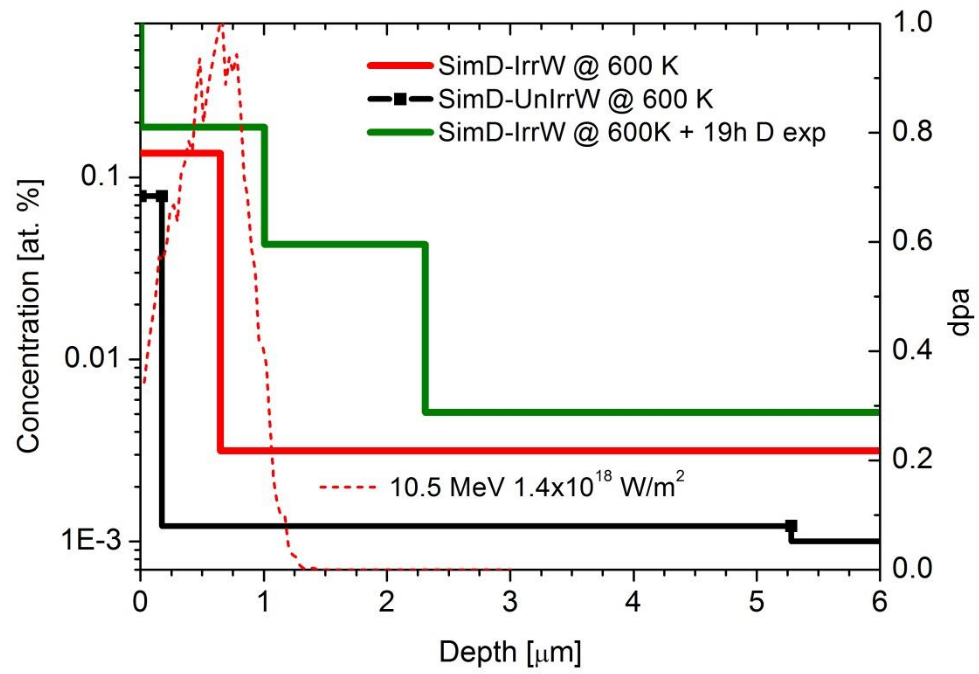


SRIM calculation

Simultaneous W irradiation and D loading

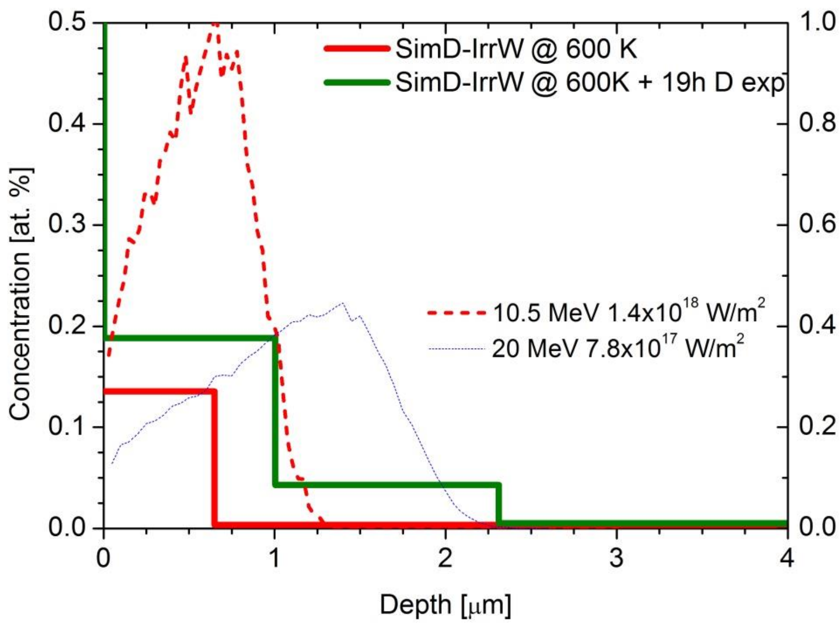
- Deuterium depth profiles measured by Nuclear Reaction Analysis - NRA Analyzing protons (≈12 MeV) from nuclear reaction $D(^3He,p)^4He$ at 5 different ^{3}He energies from 780 keV to 4.2 MeV
- Additional D atom loading for 19h

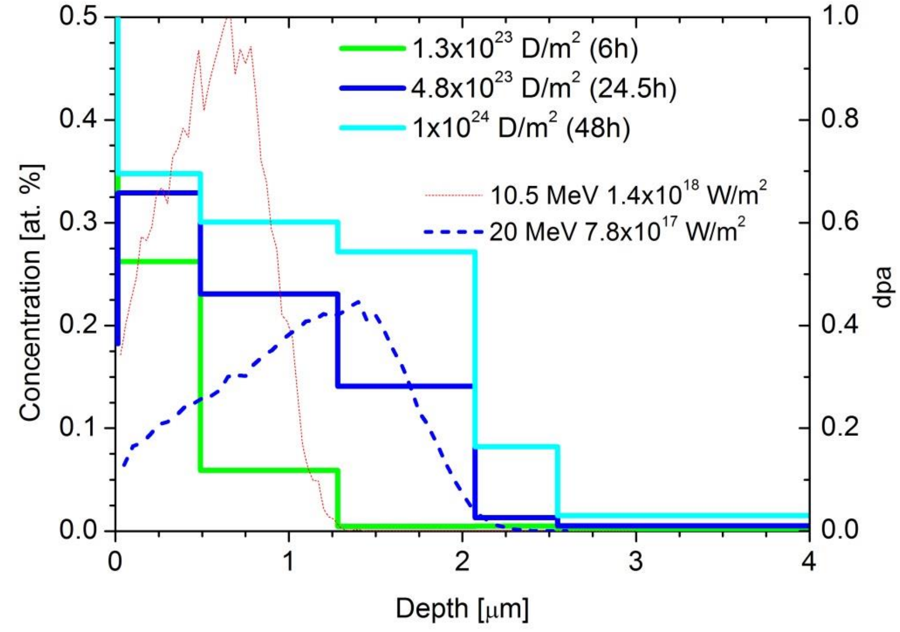




Simultaneous W irradiation and D loading

- Comparison of simultaneous W irradiation + D loading to sequential W irradiation and exposure at 600 K





Conclusions and Outlook for RCP

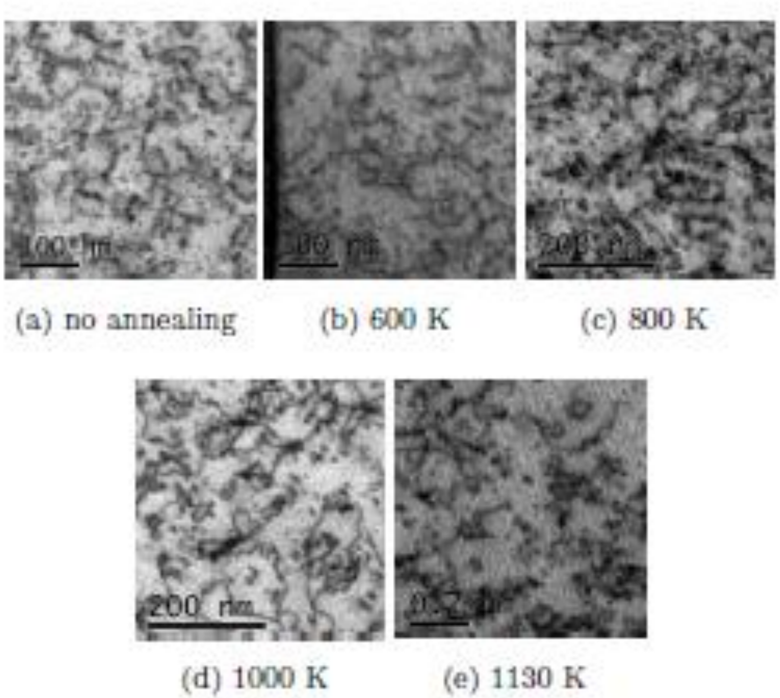
- Penetration of atomic D into bulk, saturation of the traps induced by W ion irradiation.
- D retention in self-ion damaged studied – different exposure temperatures versus damage annealing
  - Less retention at higher temperatures
- *In situ* measurements gave direct information about the dynamics of D migration and isotope exchange in radiation-induced defects in W.
- Efficient isotope exchange of D in bulk of damaged tungsten by H atoms at 600 K

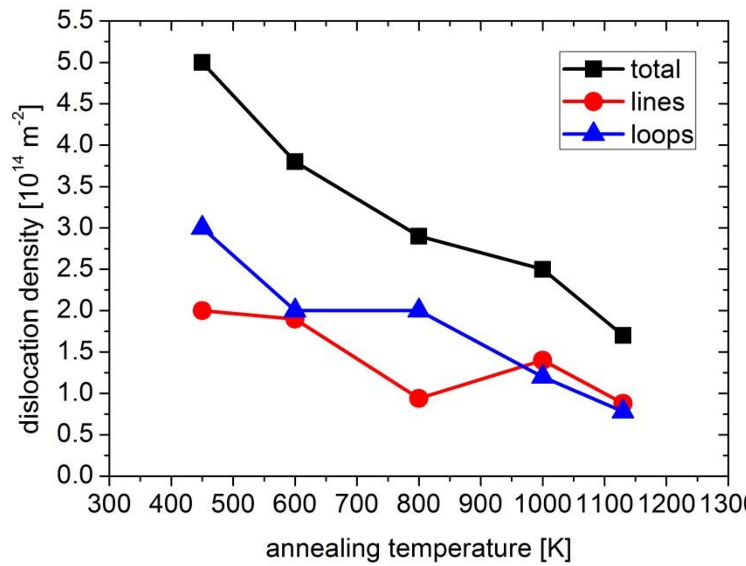
- Simultaneous W ion irradiation and D exposure – under evaluation
- Isotope exchange at lower temperatures (500 K)
- Detail study of the effect of He beam implantation on D retention: simultaneous irradiation with high-energy (200-4500 keV) ^{4}He beam and atomic D beam, followed by D NRA profiling
- Installation of ion gun for simultaneous irradiation with high-energy W ions and low energy D ions (500 eV – 5 keV)
- Effect of heavy ion irradiation on deuterium retention in W-based advanced materials

Thank you for your attention!

Study of defect annealing – total amounts

- STEM analysis by Ł. Ciupiński (Poland) of damaged W annealed at indicated temperatures
- Reduction od dislocation density by 66% - good agreement with NRA





A. Založnik et al., PFMC 2015, submitted to Phys. Scripta