Oxygen atoms on tungsten versus (native) tungsten oxides: contrasting effects onto deuterium retention and release

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The effect of oxygen in the bulk of tungsten on deuterium retention: a fundamental approach

1. D implantation in W samples (IB)

⇩

2a. D retention (TPD, NRA coll. JSI)
2b. W characterization (FIB-SEM, AES, LEED, XPS)

} experiments

UHV: 10^{-10} mbar
ion gun: 10^{16}-10^{18} ion.m^{-2}.s^{-1}
TPD: 1 – 10 K.s^{-1}

The effect of oxygen in the bulk of tungsten on deuterium retention: a fundamental approach

1. D implantation in W samples (IB)

2a. D retention (TPD, NRA coll. JSI)
2b. W characterization (FIB-SEM, AES, LEED, XPS)

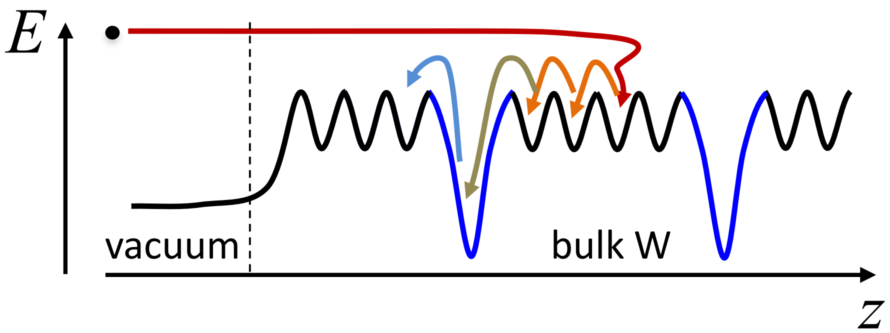
→ experiments

3. Macroscopic Rate Equations model (MRE)
(predict ^3H retention in fusion reactor)
initialized by Density Functional Theory (DFT)

→ modeling

4. Understand fundamental
D-W interaction

UHV: 10^{-10} mbar
ion gun: 10^{16}-10^{18} ion.m^{-2}.s^{-1}
TPD: 1 – 10 K.s^{-1}



ion implantation — bulk diffusion (Fick)

$$\partial c_m/\partial t = \varphi \cdot (1 - r) \cdot f(z) + \nu_{diff} \cdot \partial^2 c_m/\partial z^2 - \partial c_t/\partial t \quad (1)$$

$$\partial c_t/\partial t = \nu_{trap} \cdot (c_m/n_m) \cdot (n_t - c_t) - \nu_{detrap} \cdot c_t \quad (2)$$

trapping and detrapping at a defect

$$\nu_{process} = \nu_0 \times e^{\left(-\frac{E_a}{k_b T}\right)}$$

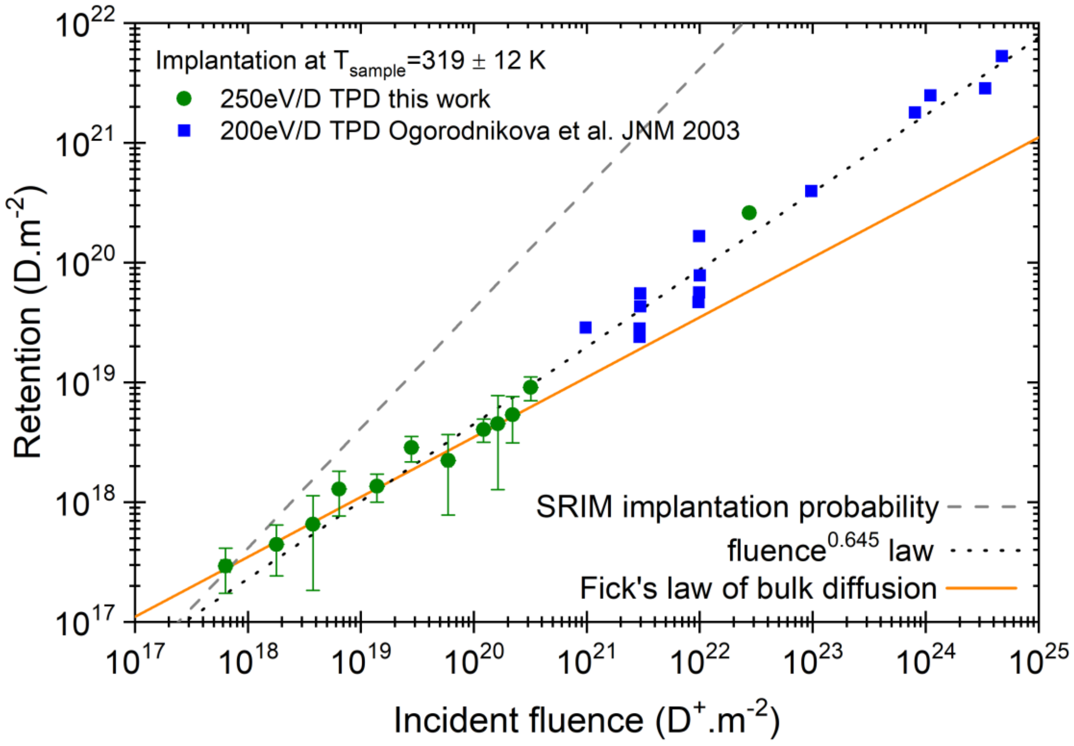
Deuterium retention in tungsten in polycrystalline W
experimental dataset to guide a DFT-MRE model

1. D implantation (IB)

2a. D retention (TPD, NRA)
2b. W characterization (FIB-SEM, AES, XPS)

3. DFT-MRE modeling

4. D – W interaction



- D retention in polycrystalline W does not follow Fick's law of bulk diffusion
- Higher D retention implies defect(s) trapping (bulk and/or near-surface)

Bisson *et al.*, J. Nucl. Mater. **467** (2015) 432

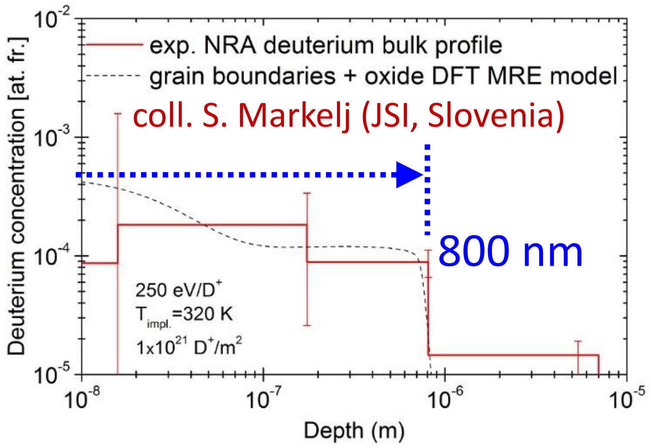
Deuterium retention in tungsten in polycrystalline W
experimental dataset reproduced by a DFT-MRE model

1. D implantation (IB)

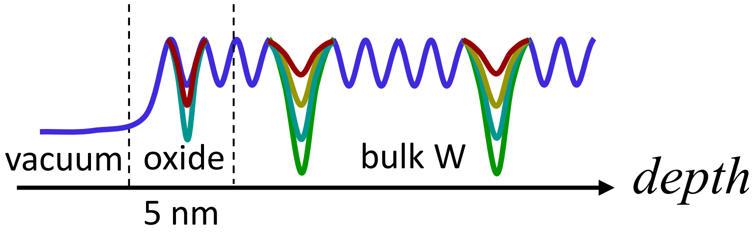
2a. D retention (TPD, NRA)
2b. W characterization (FIB-SEM, AES, XPS)

3. DFT-MRE modeling (oxide + GB)

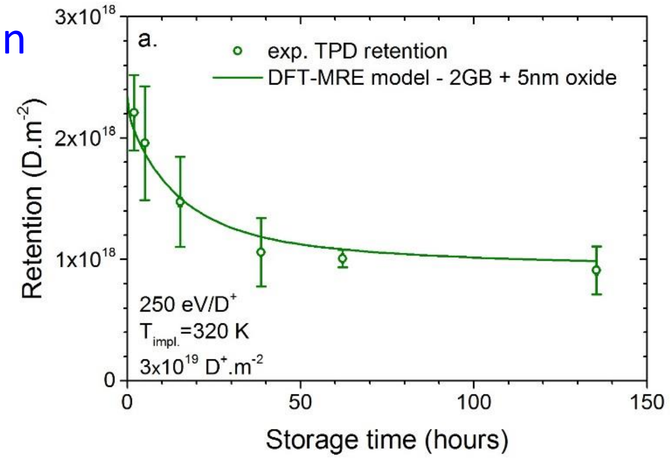
4. D – W interaction



NRA deuterium depth profile in poly-W
→ near surface trapping + bulk trapping
« native oxide » (AES) + grain boundaries (FIB-SEM)



- DFT detrapping energies → drive isothermal desorption
  - Oxygen – W vacancy cluster (native oxide)
    Kong *et al.* J. Nucl. Mater. 433 (2013) 357
  - Grain boundaries (GB)
    Xiao *et al.* J. Nucl. Mater. 430 (2012) 132
- 3 free parameters → quantitative agreement
  2 densities: native oxide + GB
  native oxide thickness (guided by AR-XPS)



Hodille *et al.*, Nuclear Fusion **57** (2017) 076019

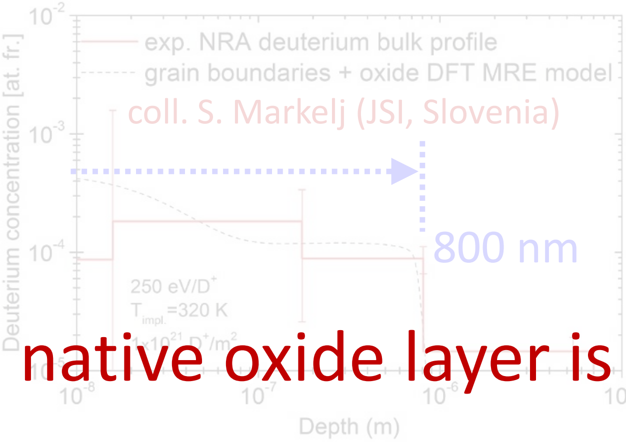
Deuterium retention in tungsten in polycrystalline W
experimental dataset reproduced by a DFT-MRE model

1. D implantation (IB)

2a. D retention (TPD, NRA)
2b. W characterization (FIB-SEM, AES, XPS)

3. DFT-MRE modeling (oxide + GB)

4. D – W interaction



NRA deuterium depth profile in W
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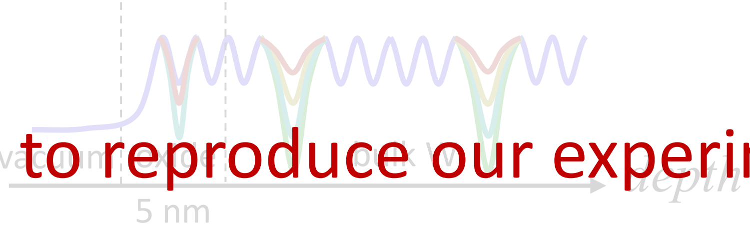

- native oxide layer is essential to reproduce our experiments
- is W native oxide really a trapping layer for deuterium ?

➢ looking for a direct evidence on W single crystal

- DFT detrapping energies → drive isothermal desorption
  - Oxygen – W vacancy cluster (native oxide)
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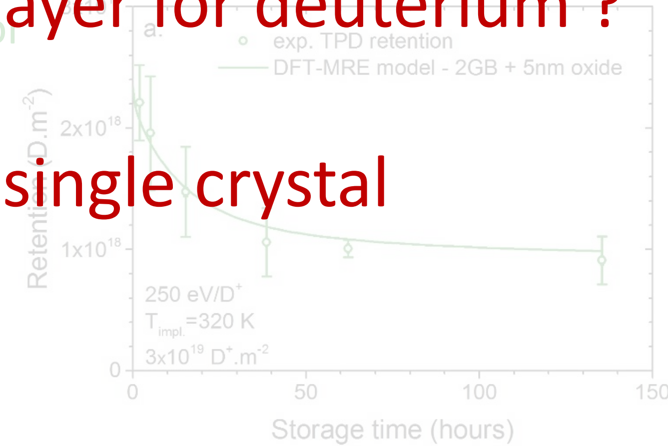

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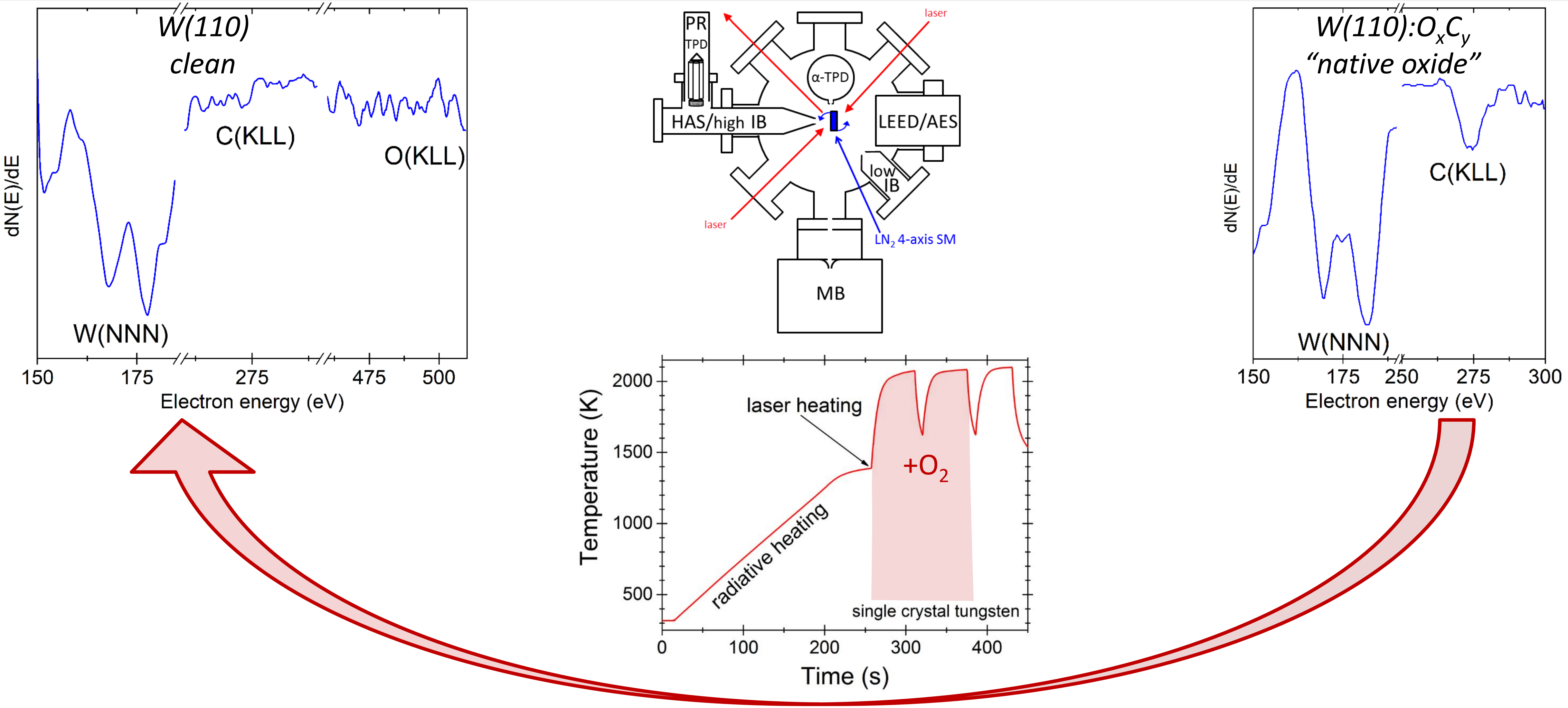
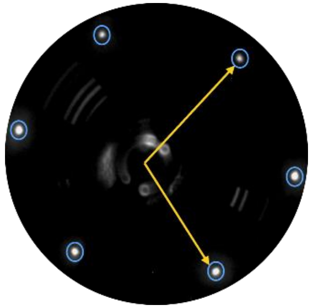
Deuterium retention in single crystal tungsten
W(110) – is the native oxide a trapping layer ?



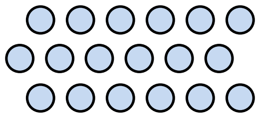
Deuterium retention in single crystal tungsten

W(110) – is the native oxide a trapping layer ?

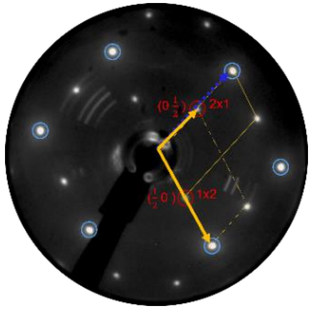
W(110)
clean



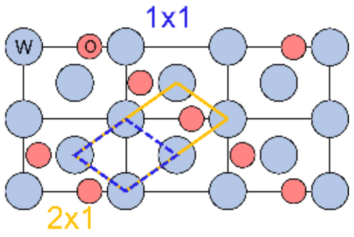
- LEED: 1x1
- structure of clean W(110)
- AES: only W

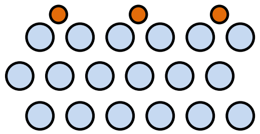


W(110):$O_{0.50ML}$
(2x1)

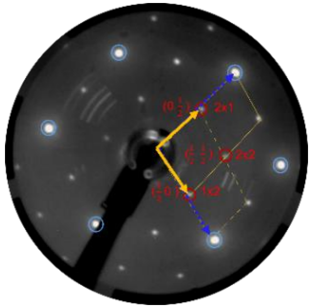


- LEED: 2x1
- ~0.50 ML

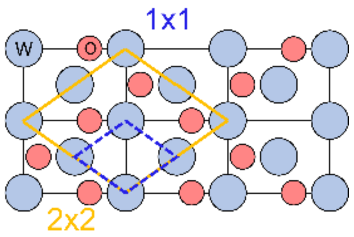


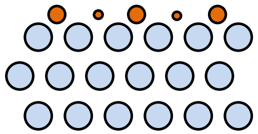


W(110):$O_{0.75ML}$
(2x2)

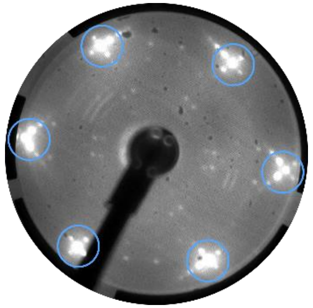


- LEED: 2x2
- ~0.75 ML

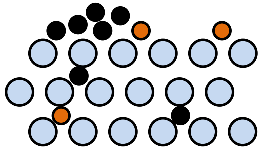




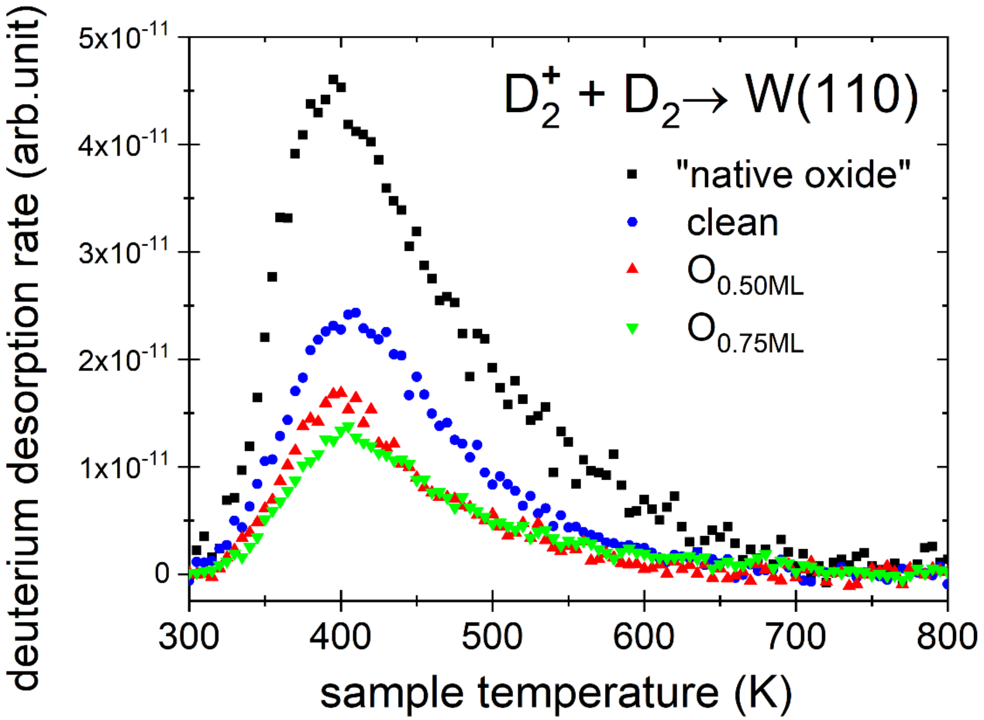
W(110):O_xC_y
“native oxide”



- LEED: crystalline structures + amorphous background
- AES: presence of C and O in the “native oxide”



Deuterium retention in single crystal tungsten
W(110) – is the native oxide a trapping layer ?

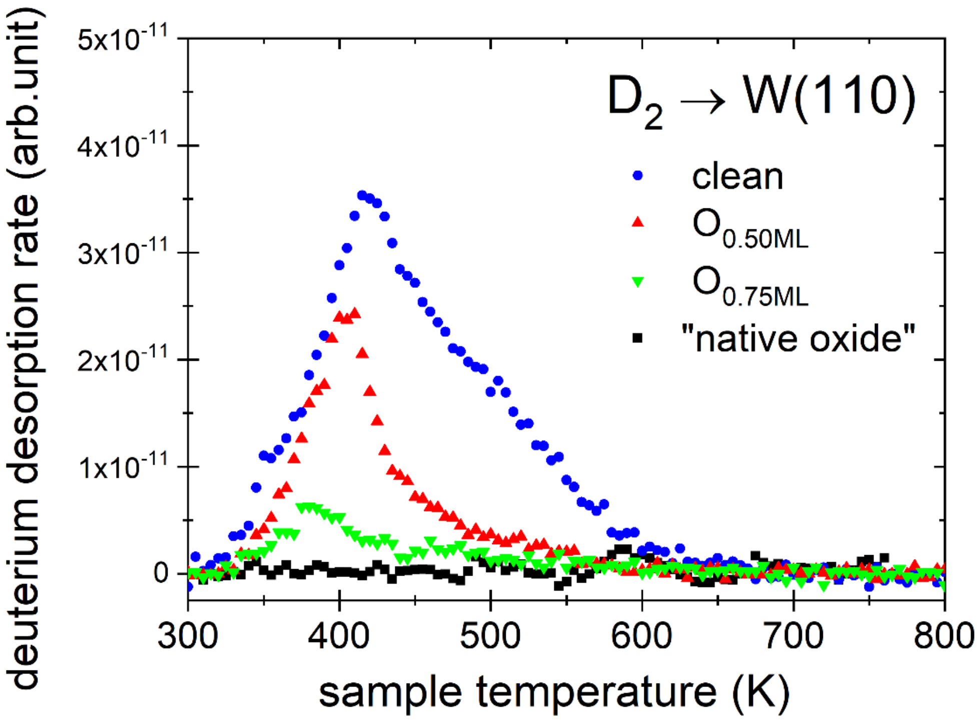


- ✓ removing the "native oxide" reduces D retention
- ! adding a sub-monolayer "oxide" reduces D retention !?!

- ✓ here, we have both D_2^+ implantation and residual D_2
- ➢ D retention can originate from both <u>bulk & surface</u>

Dunand *et al.*, Nuclear Fusion **65** (2022) 054002

Deuterium retention in single crystal tungsten
W(110) – is the native oxide a trapping layer ?



- ✓ the "native oxide" forbids D retention on the W surface
- ✓ the clean W surface and sub-monolayers of O exhibit D surface retention

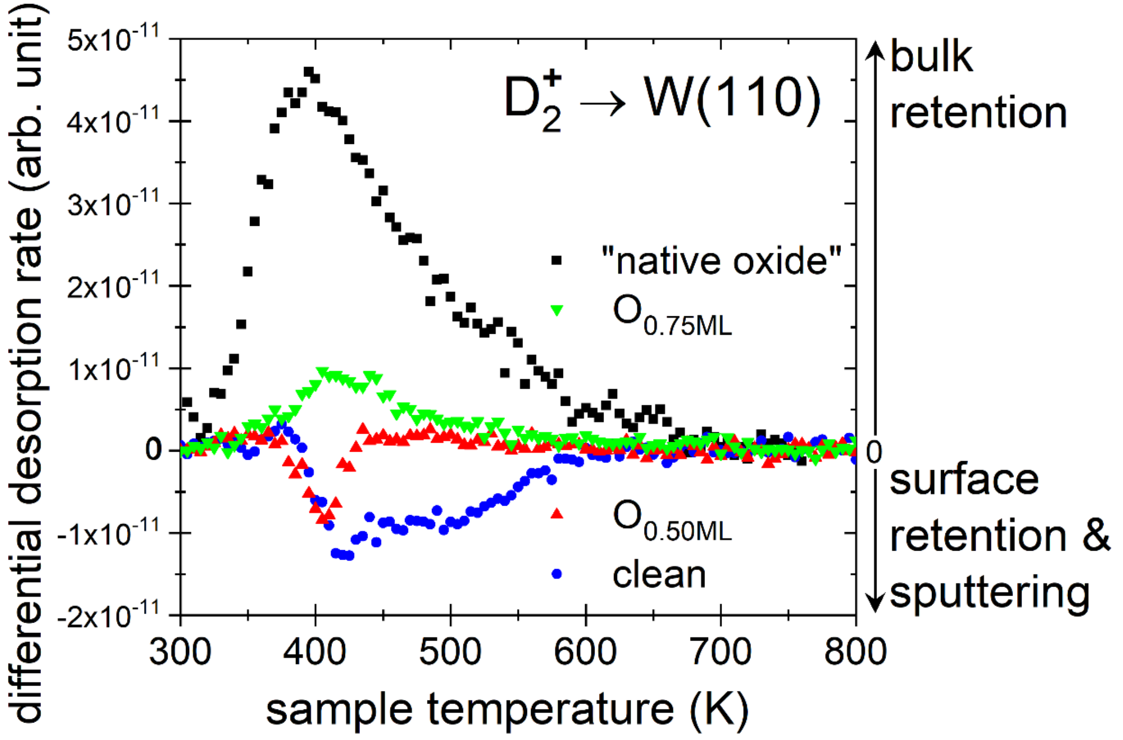
consistent with Whitten & Gomer Surf. Sci. **409** (1998) 16

- ➢ subtract this D adsorption from TPD of D_2^+ implantation to estimate roughly the bulk retention significance

Dunand *et al.*, Nuclear Fusion **65** (2022) 054002

Deuterium retention in single crystal tungsten

W(110) – is the native oxide a trapping layer ?



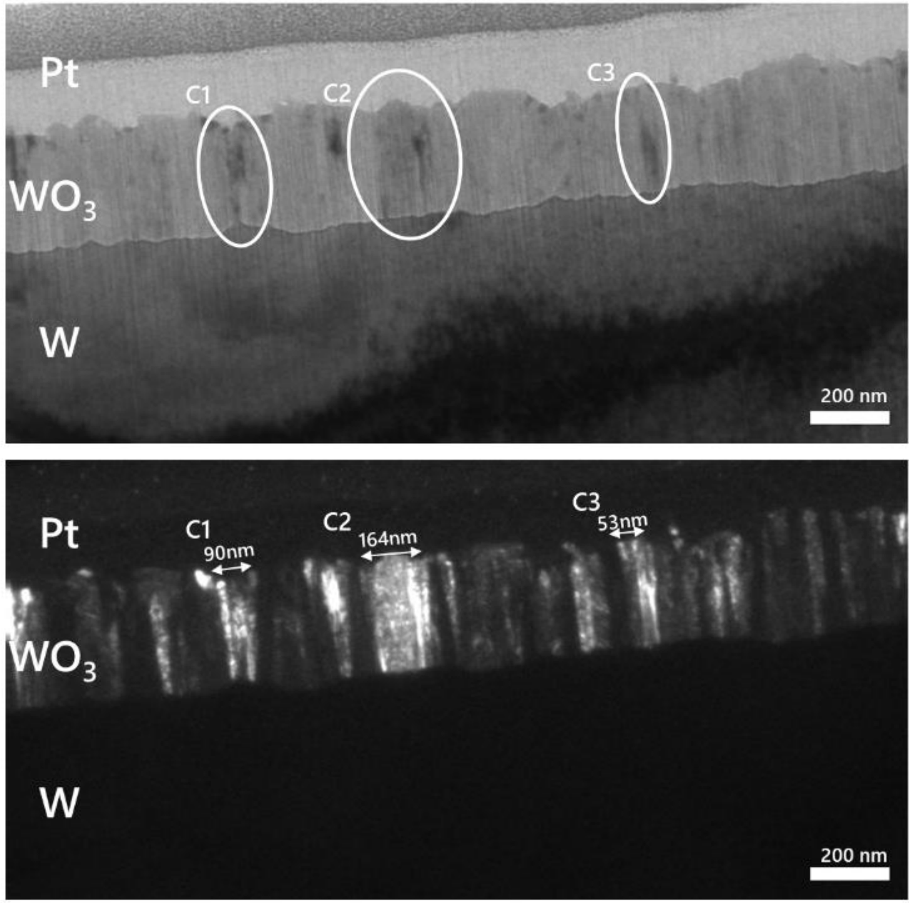
- ✓ for O ≤ 0.50 ML: D surface retention is significant and D sputtering plays a role
- ✓ for O ≥ 0.75 ML bulk trapping is preponderant
- ➢ Native oxide a "bulk (near-surface)" trapping layer… but it contains carbon impurities

→ grow pure thick oxide to probe the effect of oxygen only

Dunand *et al.*, Nuclear Fusion **65** (2022) 054002

Deuterium retention in bulk polycrystalline tungsten oxide

WO_3 – is pure bulk oxide also a trapping layer ?



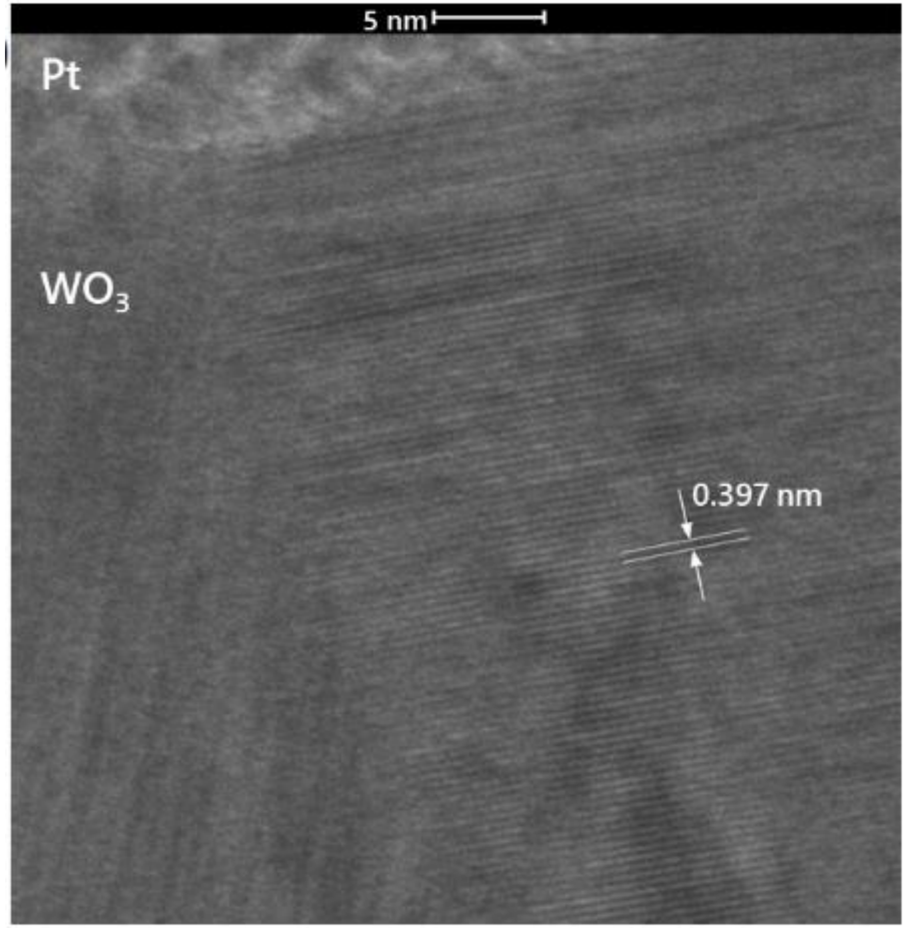
TEM
top/bottom: bright/dark field

200 nm thick WO_3 with columnar structure

SRIM D_2^+ implantation range of about 20 nm

Repeated D_2^+ implantation/TPD on a single sample possible since this WO_3 is thermally stable up to ~800 K

Ialovega *et al.*, in preparation



HRTEM

Deuterium retention in bulk polycrystalline tungsten oxide

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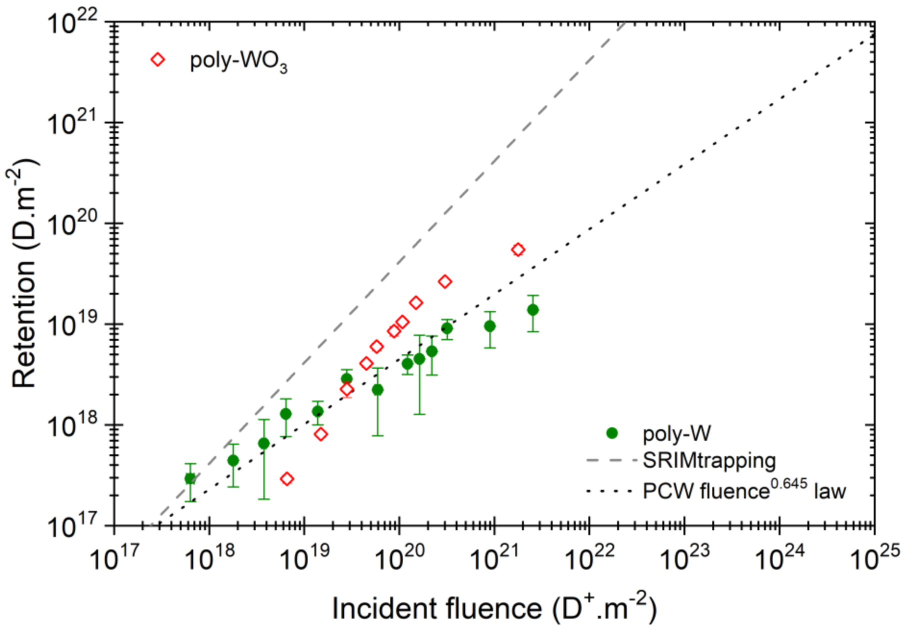

200 nm thick
WO_3 stable up
to ~800 K

- Low fluence = lower D retention vs poly-W
- High fluence = higher D retention vs poly-W

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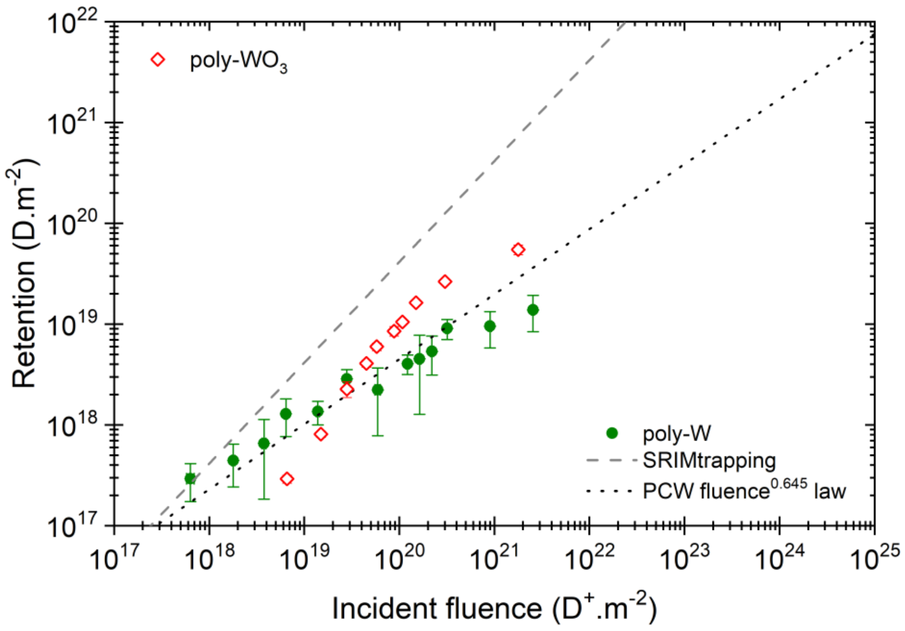

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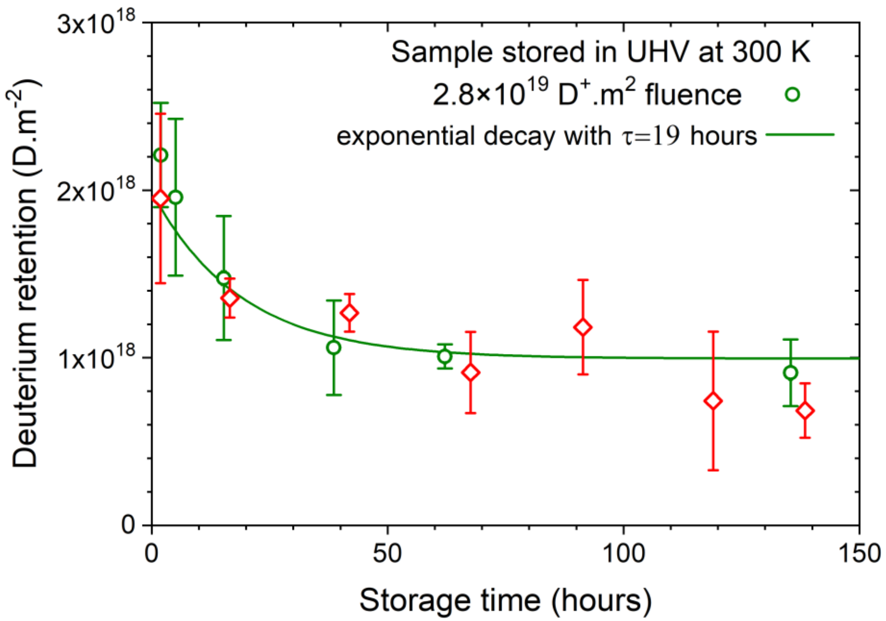

- Low fluence = lower D retention vs poly-W
- High fluence = higher D retention vs poly-W

- Isothermal desorption looks similar but…

Ialovega *et al.*, in preparation

Deuterium retention in bulk polycrystalline tungsten oxide
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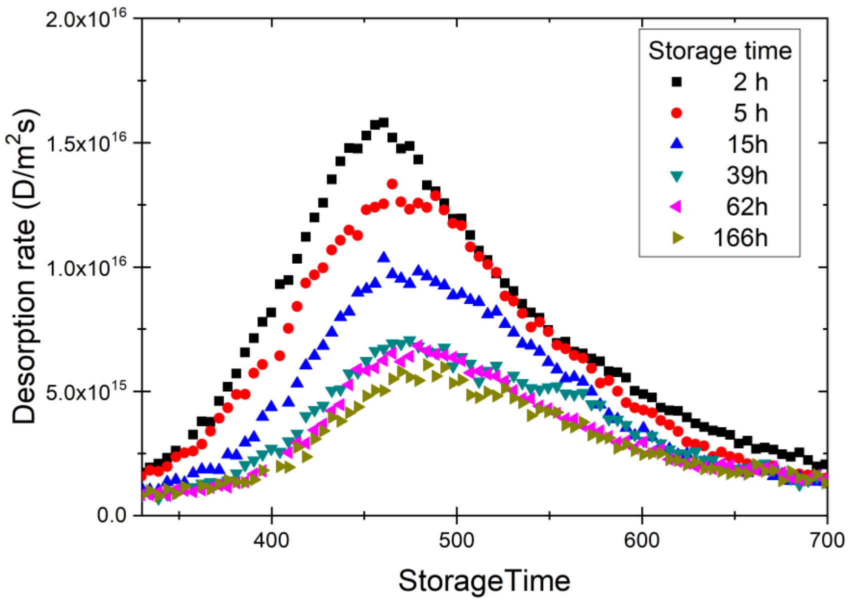

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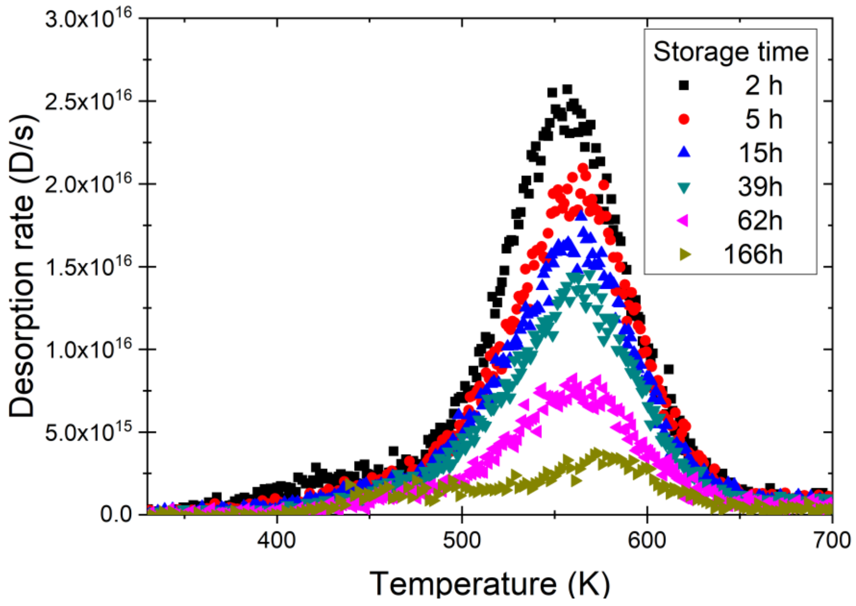

- Low fluence = lower D retention vs poly-W
- High fluence = higher D retention vs poly-W

- Isothermal desorption looks similar but…
- WO_3 decreases down to almost null retention and TPD is really different from poly-W !?

Ialovega *et al.*, in preparation

Deuterium retention in bulk polycrystalline tungsten oxide

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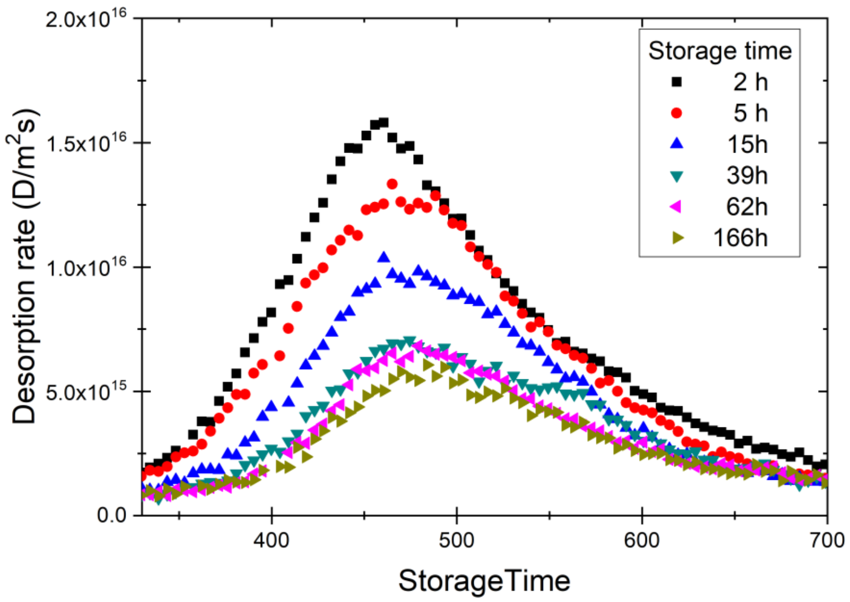

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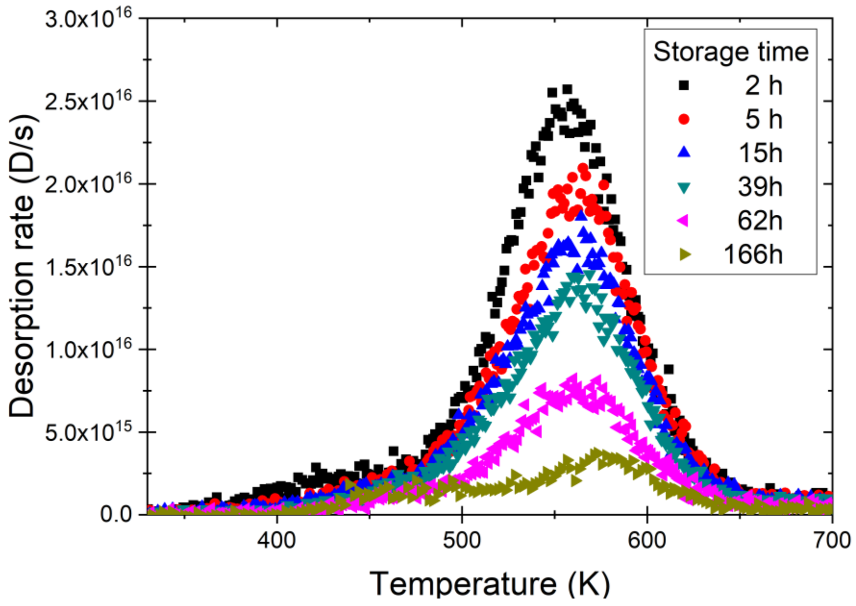

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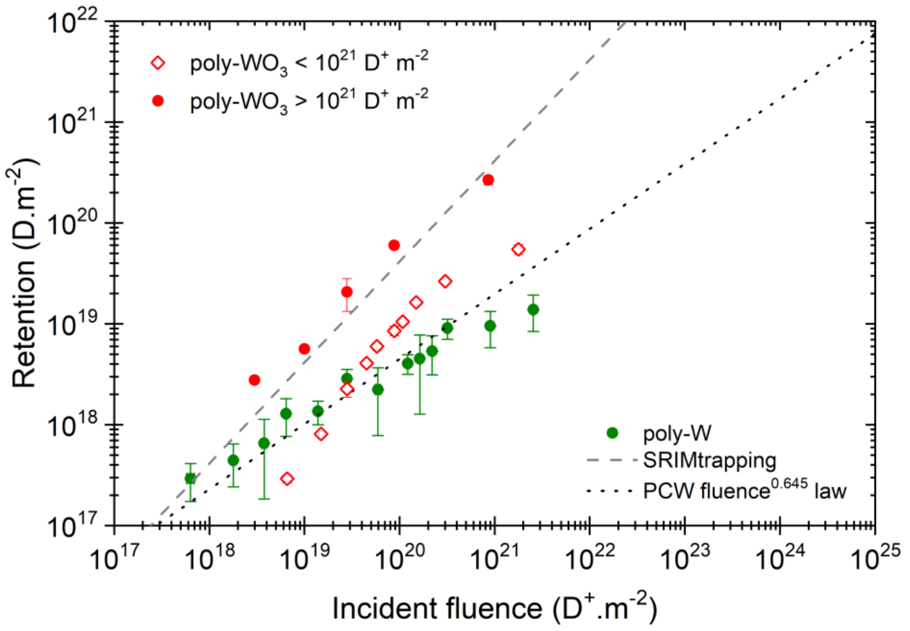
Ialovega *et al.*, in preparation

- Isothermal desorption looks similar but…
- WO_3 decreases down to almost null retention and TPD is really different from poly-W !?

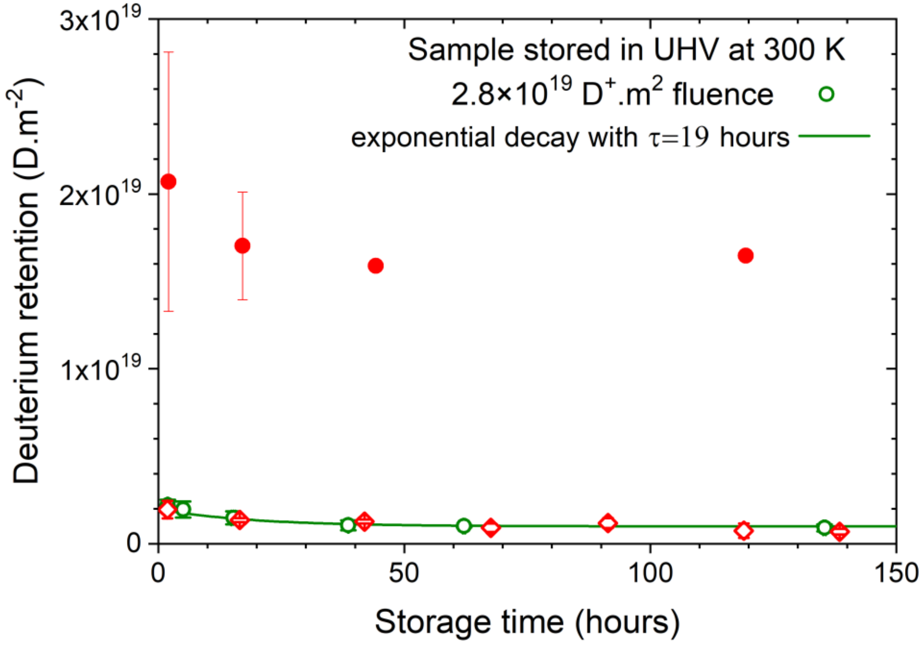
➢ MRE interpretation not straightfoward…

Deuterium retention in bulk polycrystalline tungsten oxide

WO_3 – is pure bulk oxide also a trapping layer ?



200 nm thick WO_3 stable up to ~800 K



- High cumulated fluence = higher D retention vs poly-W for all implantation fluence

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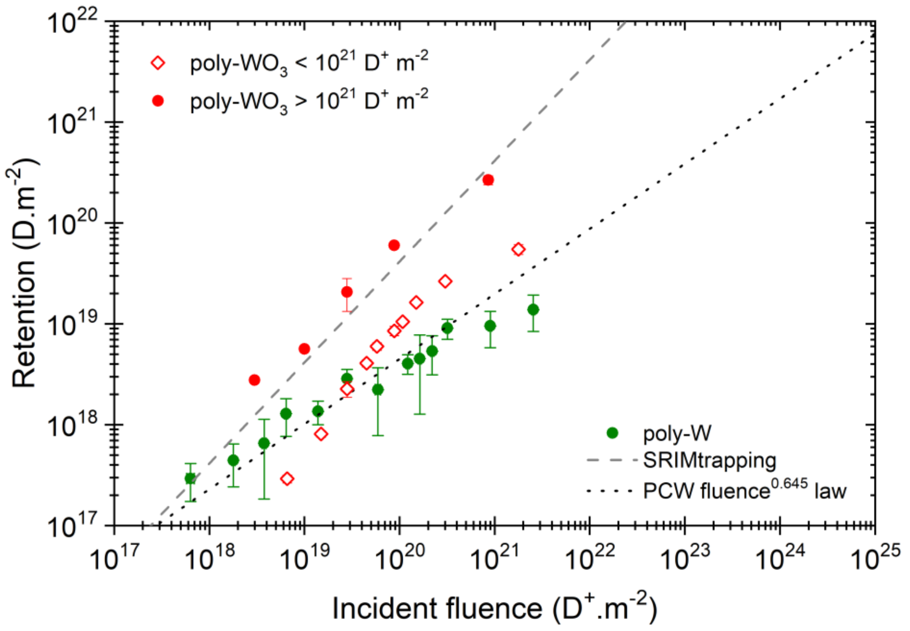
- Isothermal desorption now looks almost negligible…

➢ MRE interpretation will be complex…
➢ 3D effects ? columnar structure of WO_3
➢ Interface effect ? Next slide

Deuterium retention in bulk polycrystalline tungsten oxide
WO_3 – is pure bulk oxide also a trapping layer ?



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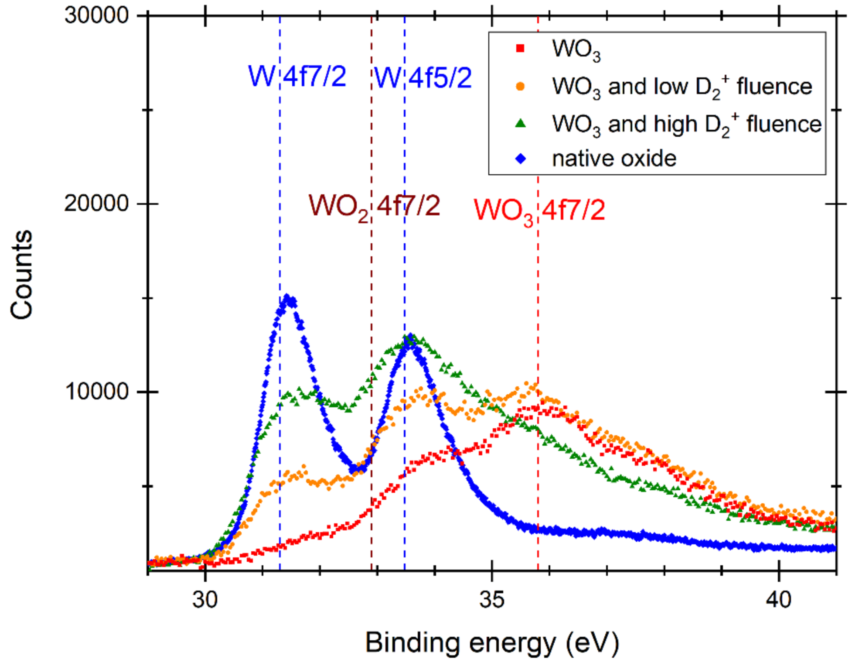

- High cumulated fluence = higher D retention vs poly-W for all implantation fluence

Ialovega *et al.*, in preparation

- Increasing cumulated fluence of D_2^+ results in an increasing signature of metallic tungsten at the surface → WO_{3-x}

➢ O vacancy in the near surface of WO_3 increases D retention

- WO_{3-x} XPS is still quite different to native oxide's one

Oxygen atoms on tungsten versus (native) tungsten oxides: effects onto deuterium retention - summary

- W native oxide (WO_xC_y) is responsible for some bulk D retention
- Surface oxygen (WO_x with $x<1$) reduces D retention in W (at the surface and in the bulk)
- Stoichiometric WO_3 reduces D retention at low D ion fluence
- WO_{3-x} with $1<x<2$ increases drastically D retention at high cumulated fluence

→ Isolated O atoms in the bulk of W should explain some of the trapping of hydrogen isotopes in technical tungsten

- Perspective: native oxide = thin WO_xC_y layer
  - Probing interfaces effect by varying (decreasing) WO_3 layer thickness
  - What about the effect of C on D retention in W ?