ENABLING RESEARCH PROJECT ENR-MAT.02.VR

In-situ ion beam analysis of deuterium retention in W-B layers: effects of composition and incorporation pathway

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WP PWIE Meeting 2025, 27th of March

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Objectives and strategy

Effect of boron incorporation in re-deposited Plasma Facing Components.

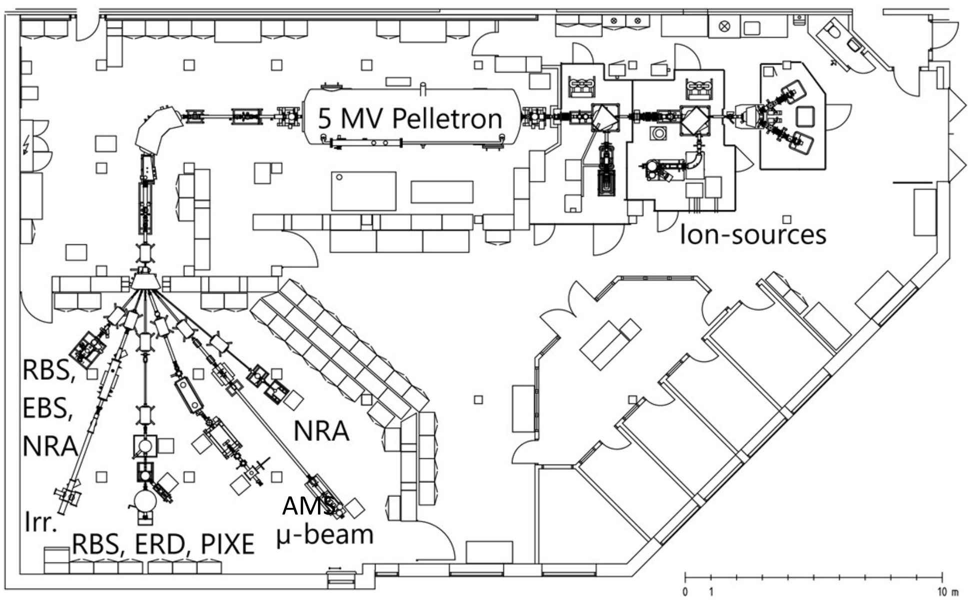
- Explore the use of **in-situ ion beam analysis** in the investigation of the real-time modifications:
- Analyze atomic composition and distribution in samples before/during/after ion irradiation and/or annealing.
- Identify surface enrichment, material segregation and H/D retention.
- Investigate the effect of deuterium incorporation route (implantation & co-deposition) during annealing.
- Assess the predictability of these properties for mixed B-PFC in different compositions.

Synthesis and analysis in-house (Tandem Laboratory at Uppsala University) of sputter-deposited layers.

Tandem Laboratory @ Uppsala University

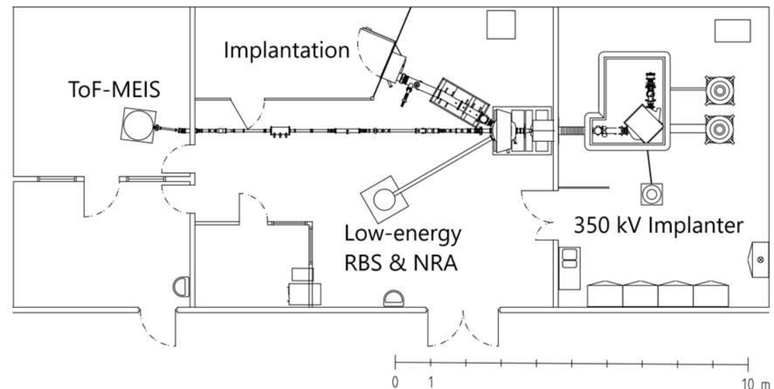
Equipment for IBA & IBMM – accessible for external users

5 MV 15-SDH2 pelletron accelerator ('01)

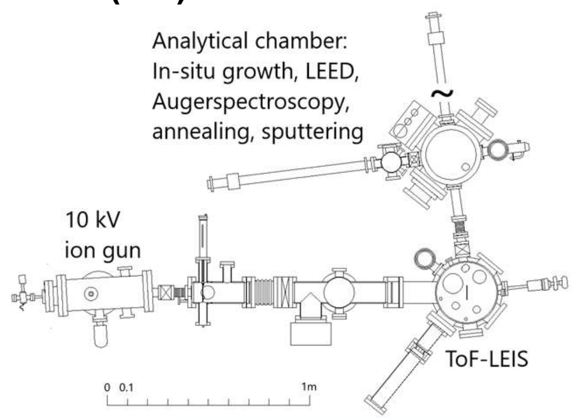


2 gas & 2 sputter ion sources – beams of H, D, ^{3}He, ^{4}He, C, N, O, Cu, Br, I, Au, …

350 kV Danfysik implanter, ToF-MEIS and Low-energy IBA ('03 &'15)



ToF-LEIS system ('18)



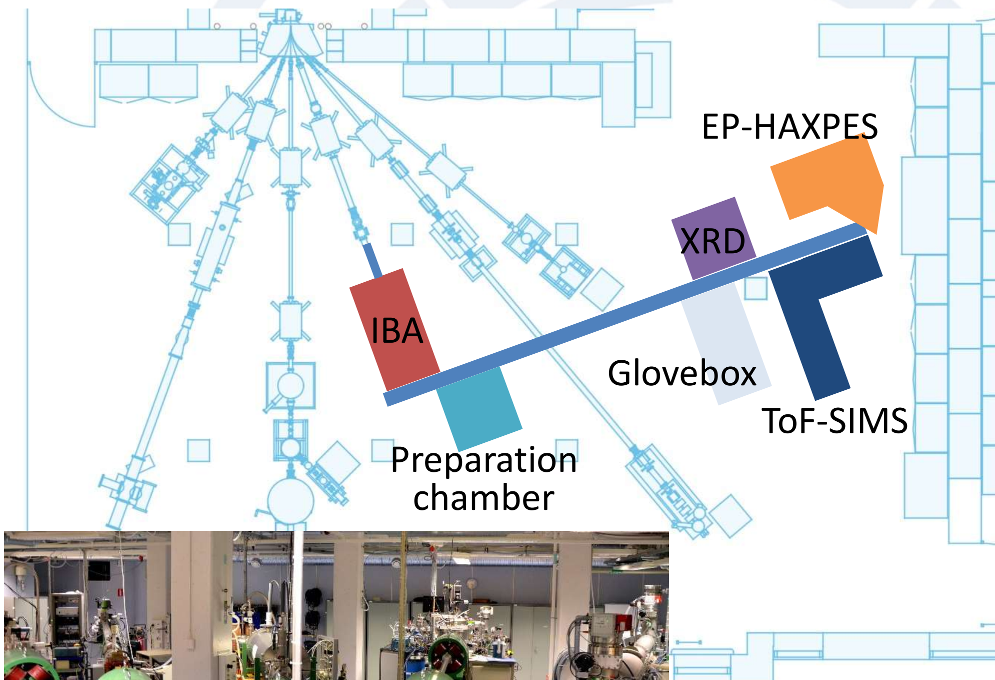
Tandem Laboratory @ Uppsala University

New infrastructure for multiscale characterization of (energy) materials

The light element characterisation platform (LigHt)

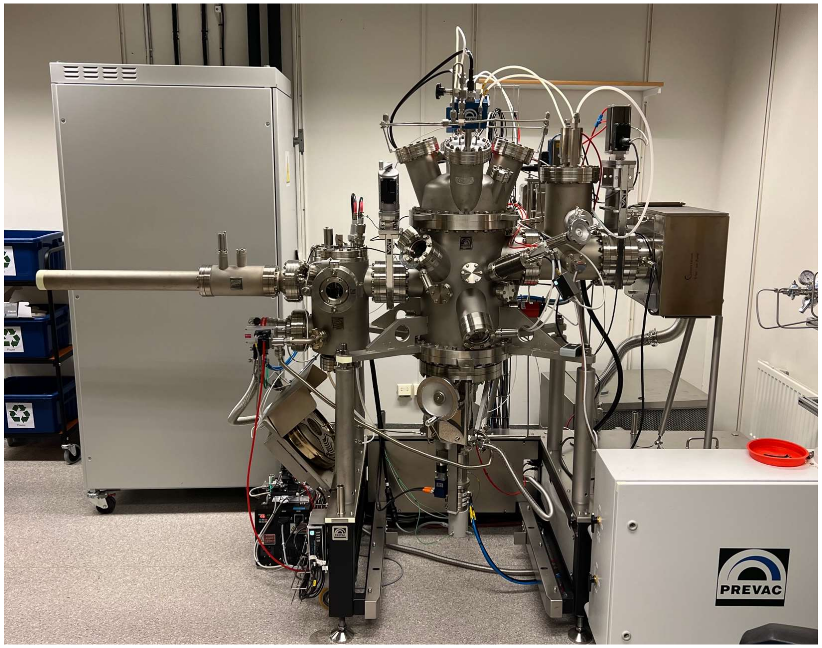
- Interdisciplinary user platform for materials science with specific focus on energy materials and sustainability
- Funded by the Wallenberg Initiative Materials Science for Sustainability (WISE)
- Will be accessible for internal and external researchers
- Located at the Tandem Laboratory, scientifically led by Material Physics and Condensed Matter Physics of Energy Materials research programs at Uppsala University
- Multimethod *in-situ* and *in-operando* characterisation on the atomic scale
- Optimised for light-element characterisation targeting among others hydrogen and lithium related aspects of corrosion, catalysis, storage, and recyclability
- **Highly relevant for fusion research.**

5 MeV Tandem accelerator



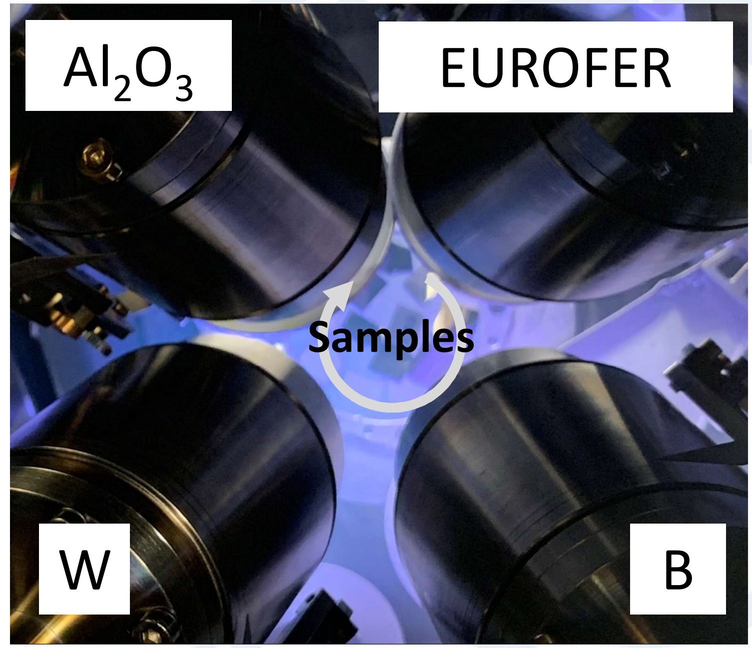
Tandem Laboratory @ Uppsala University

Sputtering machine for film deposition



Prevac sputtering machine:
4 Magnetrons (2 DC and 2 RF).
Deposition in Ar and Ar/D_2 mixed plasmas.
Base pressure < 10^{-7} mbar.
Possibility of annealing during deposition (up to 1000°C).
E. Pitthan et al. Nucl. Mater. Energy. 34 (2023).

Top-view:



Simultaneous deposition of W and B under different conditions to obtain different ratios of W and B.

Tandem Laboratory @ Uppsala University

W-B Film depositions:

Simultaneous deposition of W and B in
Ar atmosphere:

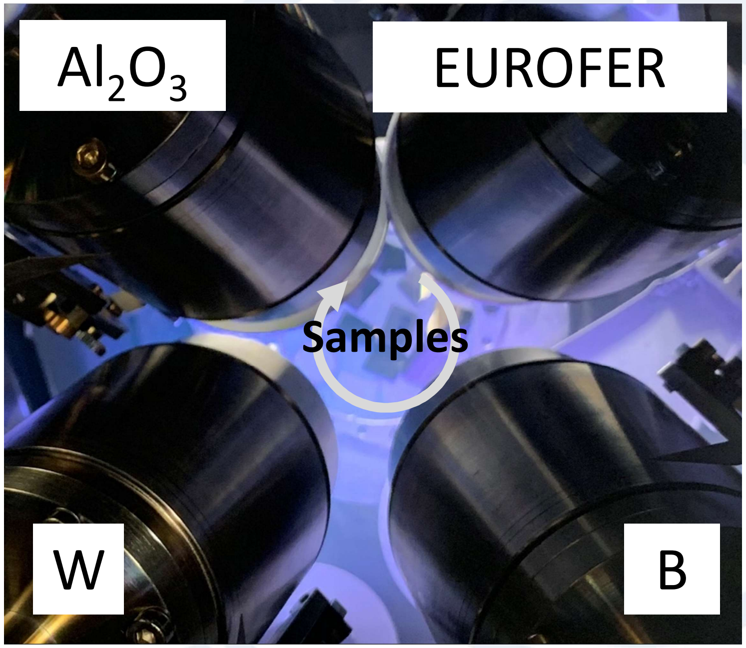
Mixed W-B layers (rich B, rich W, and ~1:1).
Unmixed W and B.

Simultaneous deposition of W and B in
mixed Ar and D_2 atmosphere:

Mixed W-B layers (rich B, rich W, and ~1:1).
Unmixed W and B.

Substrates: W, Si, MgO, C, and quartz crystals.

Top-view:

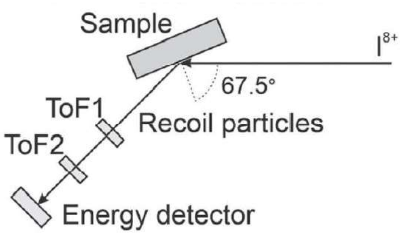


Simultaneous deposition of W and B under different conditions to obtain different ratios of W and B.

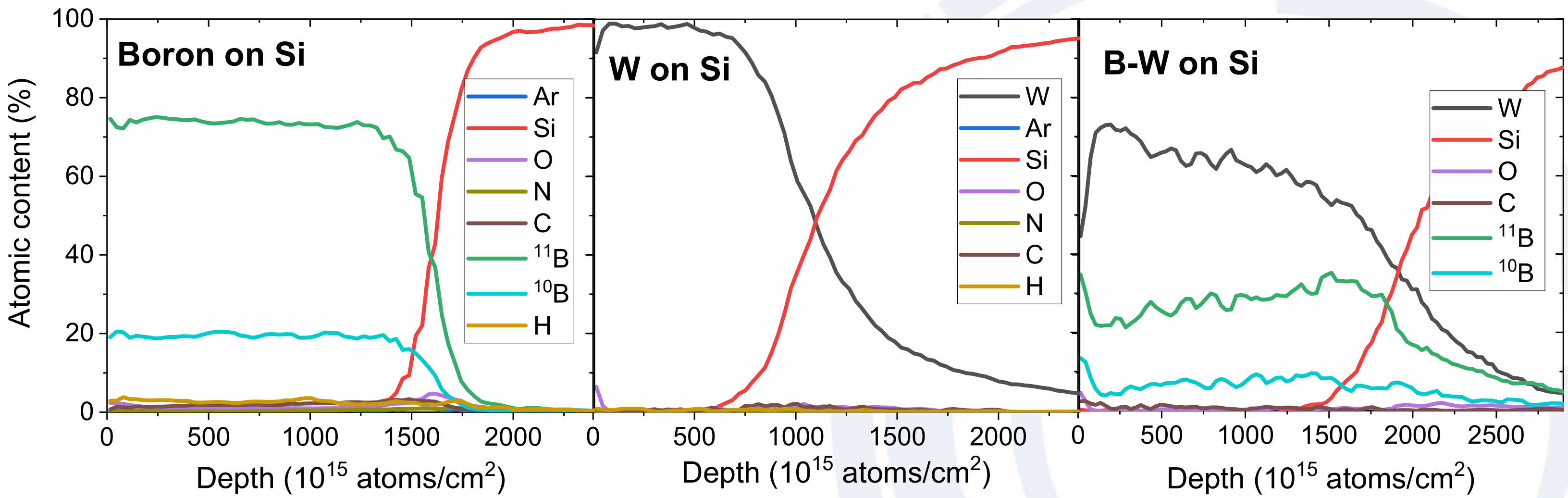
W-B film characterization

Sputter depositions in argon atmospheres

Atomic concentration depth profiles by ToF-ERDA:



Average film composition calculated from 150-500×10^{15} atoms/cm^2



W-B film characterization

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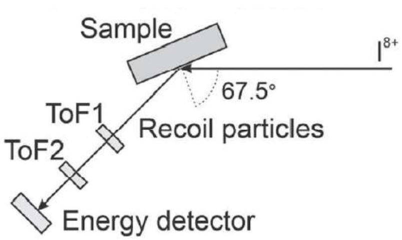

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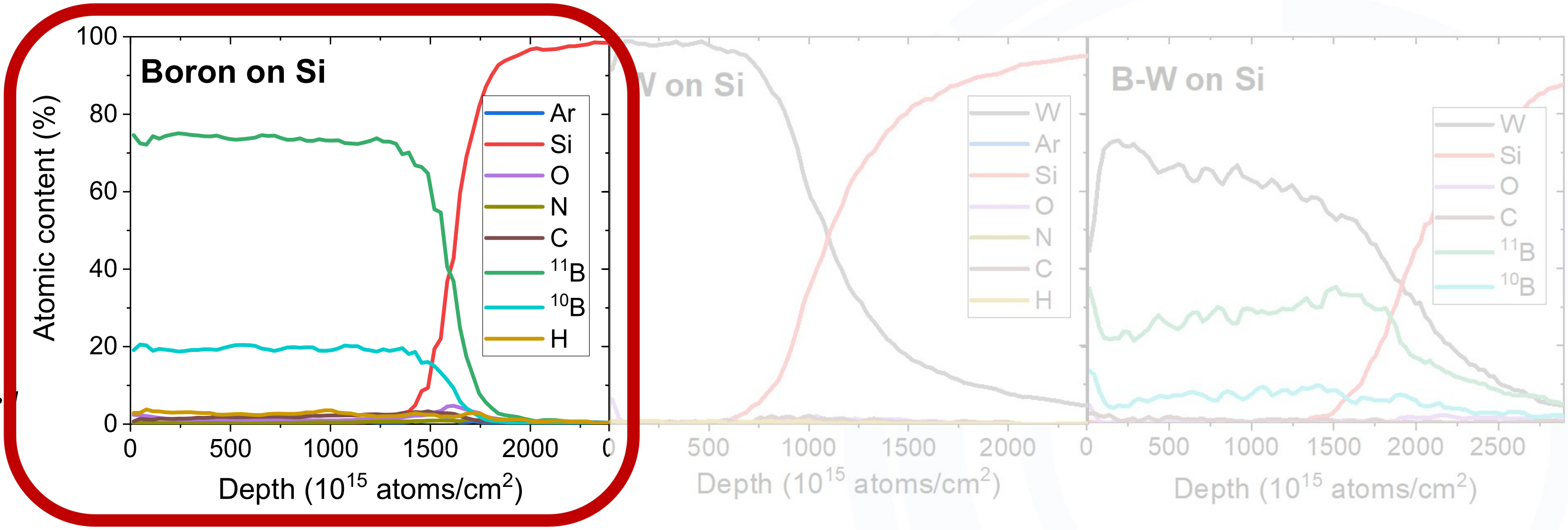
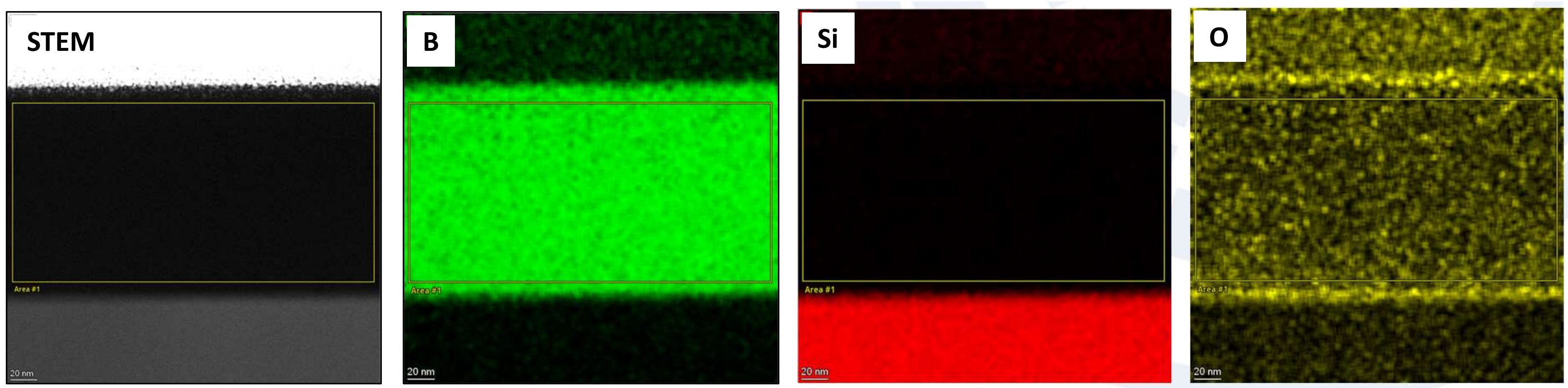


Boron on Si:

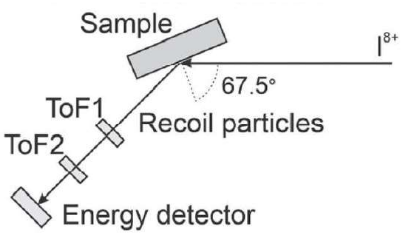
- B at. % >95;
- 96% of bulk density; (RBS+TEM);
- EDX → $O_{surf/interf}$



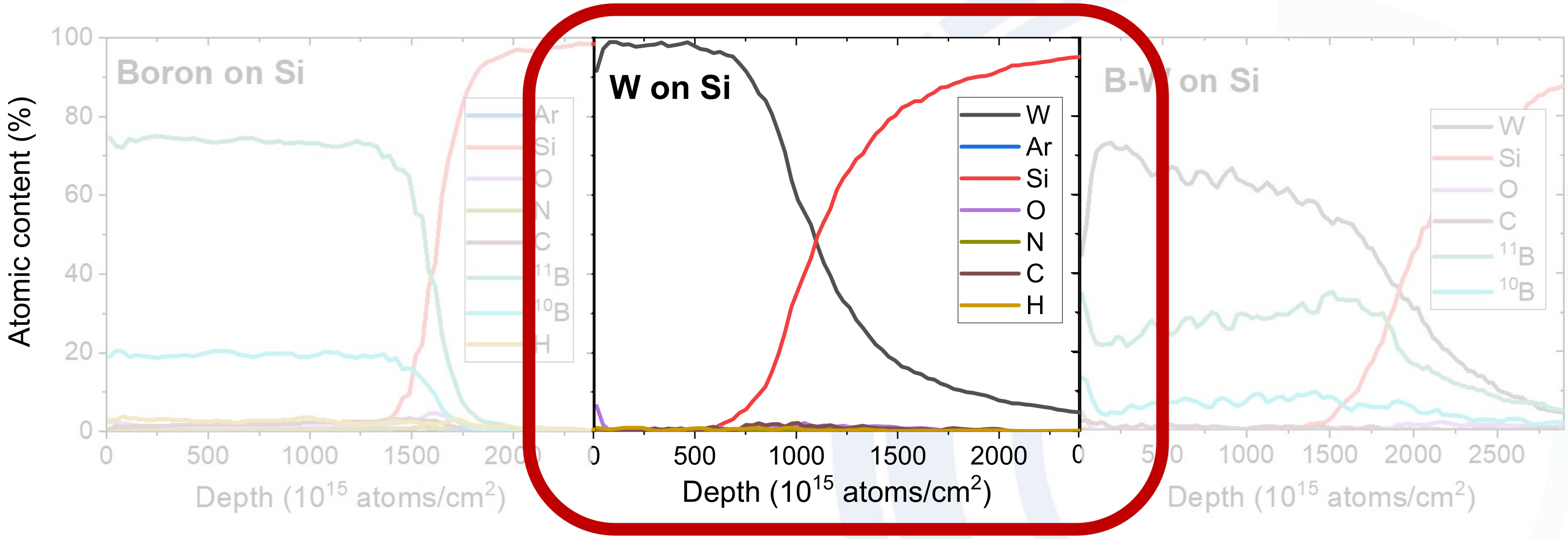
W-B film characterization

Sputter depositions in argon atmospheres

Atomic concentration depth profiles by ToF-ERDA:

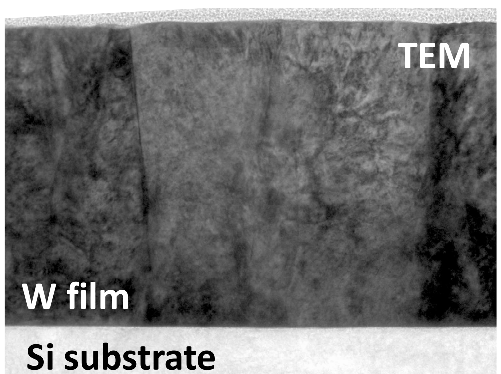


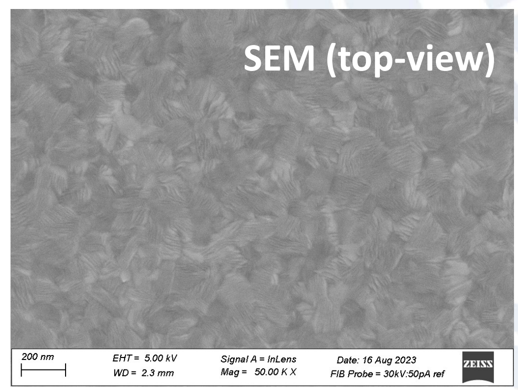
Average film composition calculated from 150-500×10^{15} atoms/cm^2



W on Si:

- W at. % >98;
- Polycrystalline;
- Columnar µ-structure;
- 95% of bulk density; (RBS+TEM);

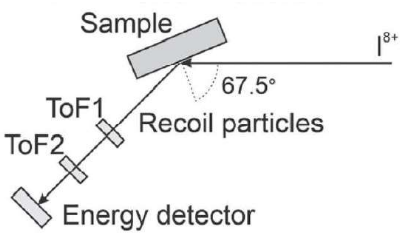




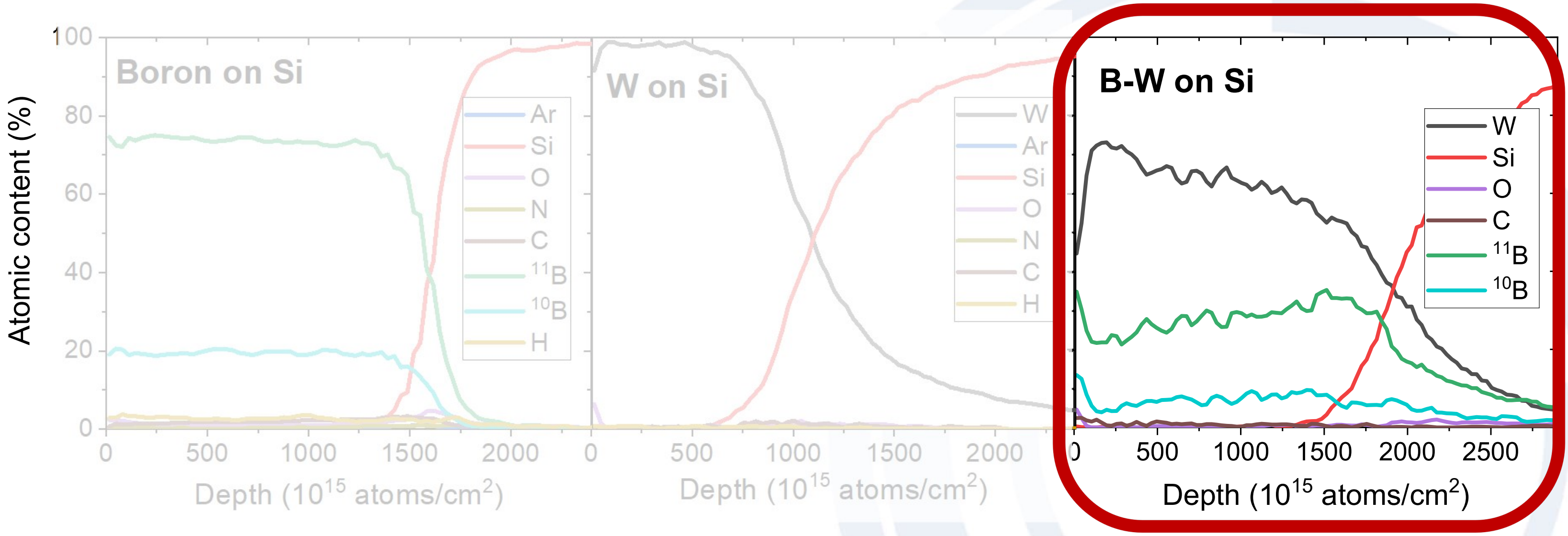
W-B film characterization

Sputter depositions in argon atmospheres

Atomic concentration depth profiles by ToF-ERDA:



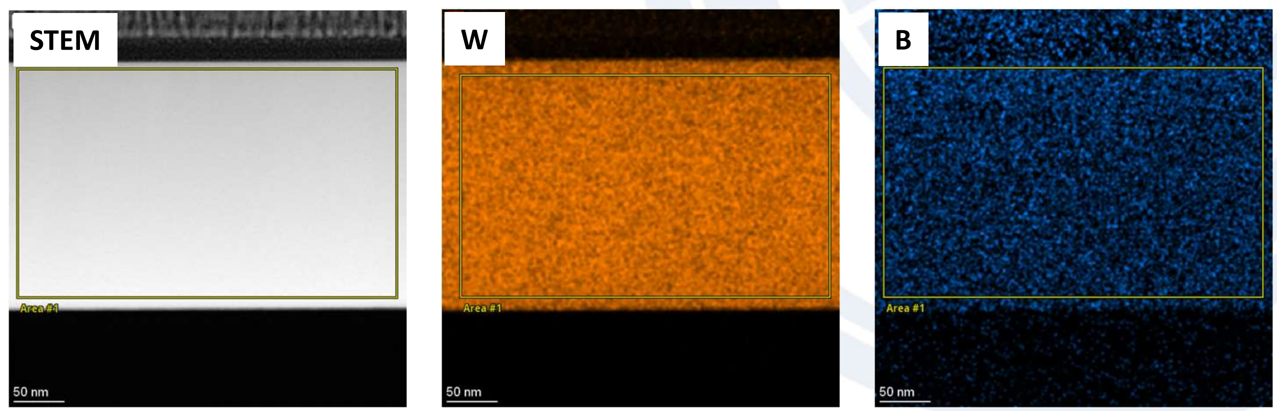
Average film composition calculated from 150-500×10^15 atoms/cm²



W-B on Si (example):

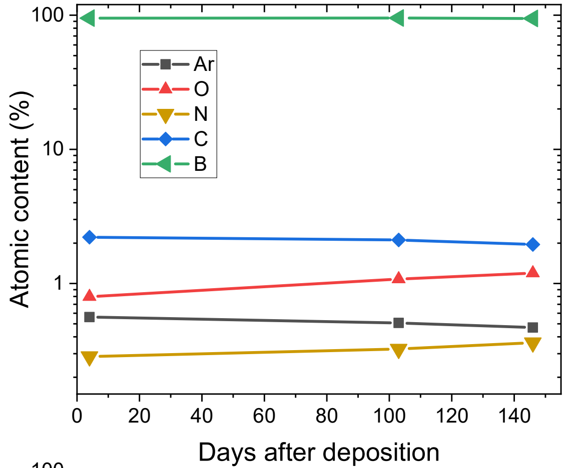
- W:B (2:1);
- Low contamination (<1%);
- EDX: no clear signal of B.
- Clear B on ToF-ERDA signal (multiple scattering effect from W).

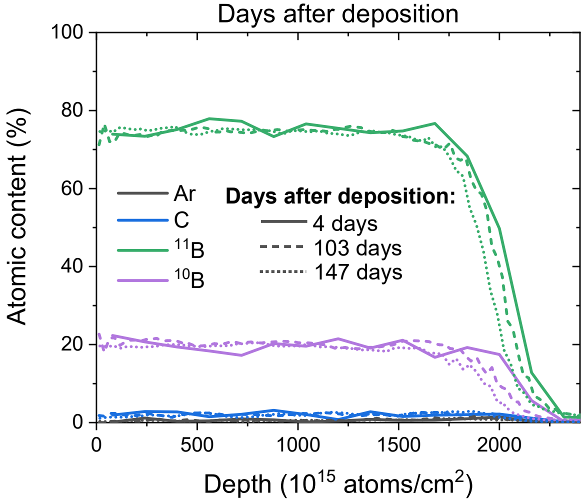
E. Pitthan et al. Surf. Coat. Tech. 417 (2021)



W-B film characterization: aging effect

Stability of boron layers over time (deposited in argon).





No significant change in composition in the bulk of layers over time.
Average film composition calculated from 150-500×10^{15} atoms/cm^2

Agreement with L.B. Bayu Aji et al.:
"thicknesses of ≥55 nm have expected excellent corrosion resistance during storage in laboratory air at room temperature over several months".
L.B. Bayu Aji et al. Appl. Surf. Sci. 448 (2018) 498.

Boron loss over time (thickness reduction) not accompanied by significant change of film composition.

L.B. Bayu Aji et al.: Boron loss from surface oxidation → formation of boric acid (evaporation).

W-B mixed layers presented good stability overtime: no change of composition and thickness.

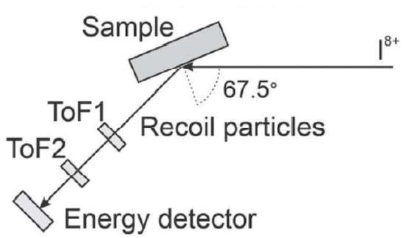
Sample characterization immediately before/during each experiment.

W-B film characterization

Sputtering depositions under argon and deuterium atmospheres:

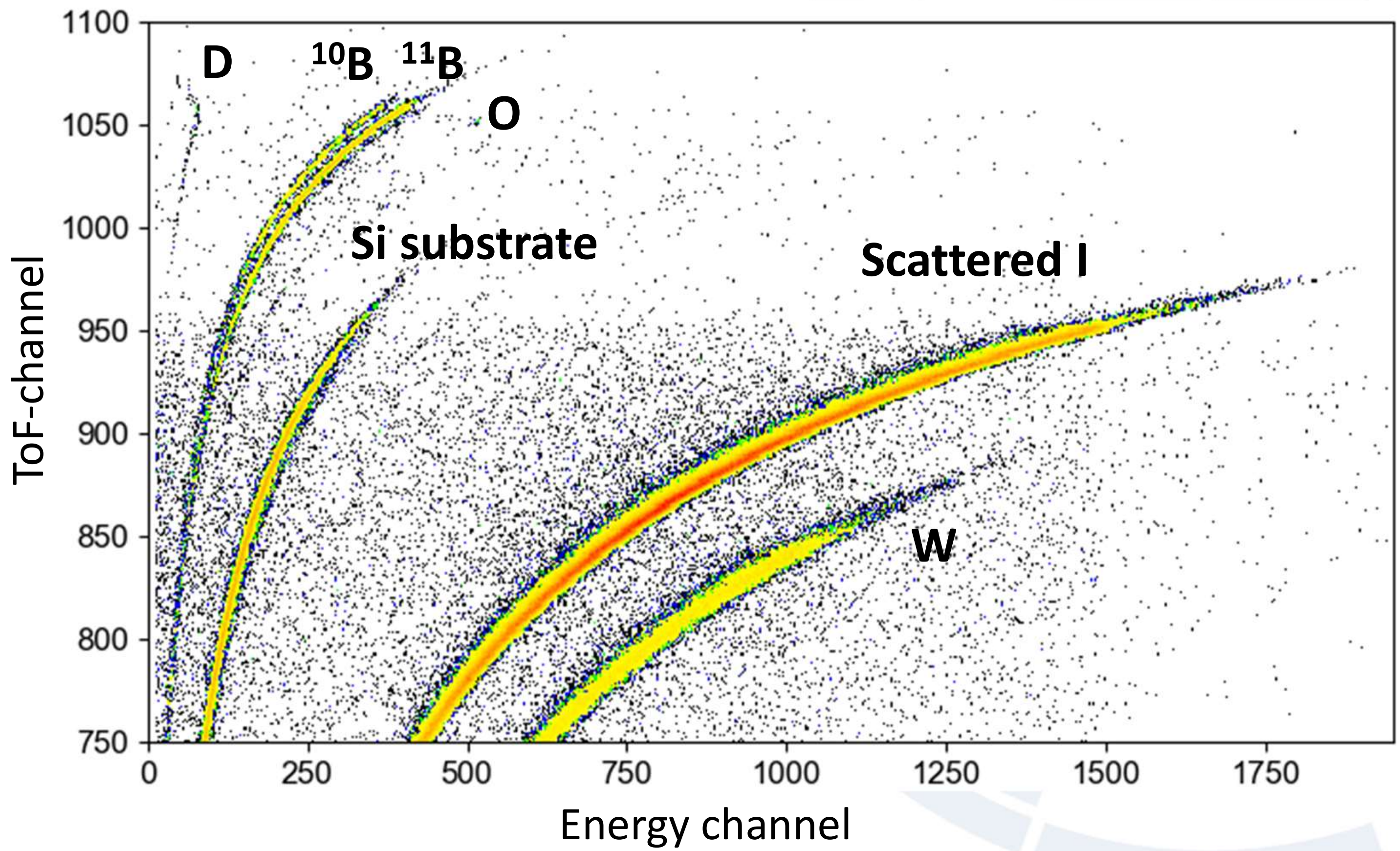
f_{Ar} = 10 sccm; f_{D2} = 18 sccm; P_{Ar+D2} = 7×10^{-3} mbar.

Atomic concentration depth profiles by ToF-ERDA:



→ **H and D detected.**

→ **D amounts verified by NRA using D(^{3}He,p)^{4}He at 2 MeV.**



W-B film characterization

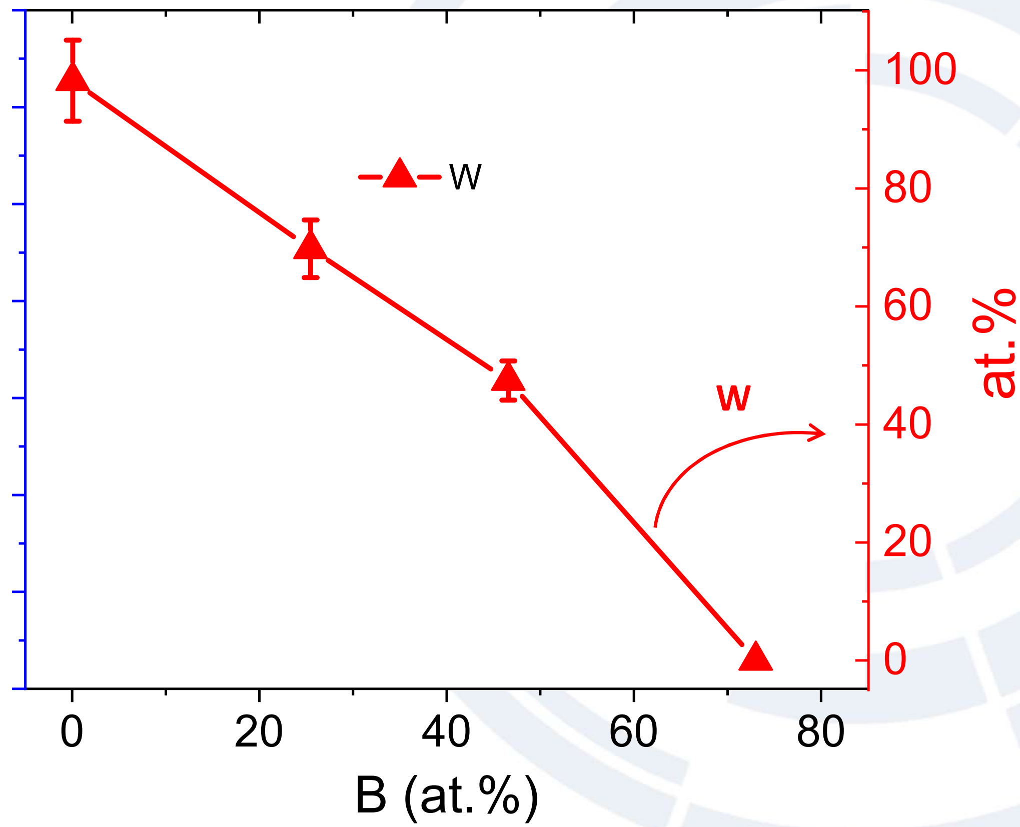
Sputter depositions in argon and deuterium atmospheres:

f_{Ar} = 10 sccm; f_{D2} = 18 sccm; P_{Ar+D2} = 7×10^{-3} mbar.

→ **f_{Ar} and f_{D2} fixed;**

→ **W and B magnetron power varied to obtain different B/W ratios.**

→ **Average composition from bulk of films.**



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- → **f_{Ar} and f_{D2} fixed;**
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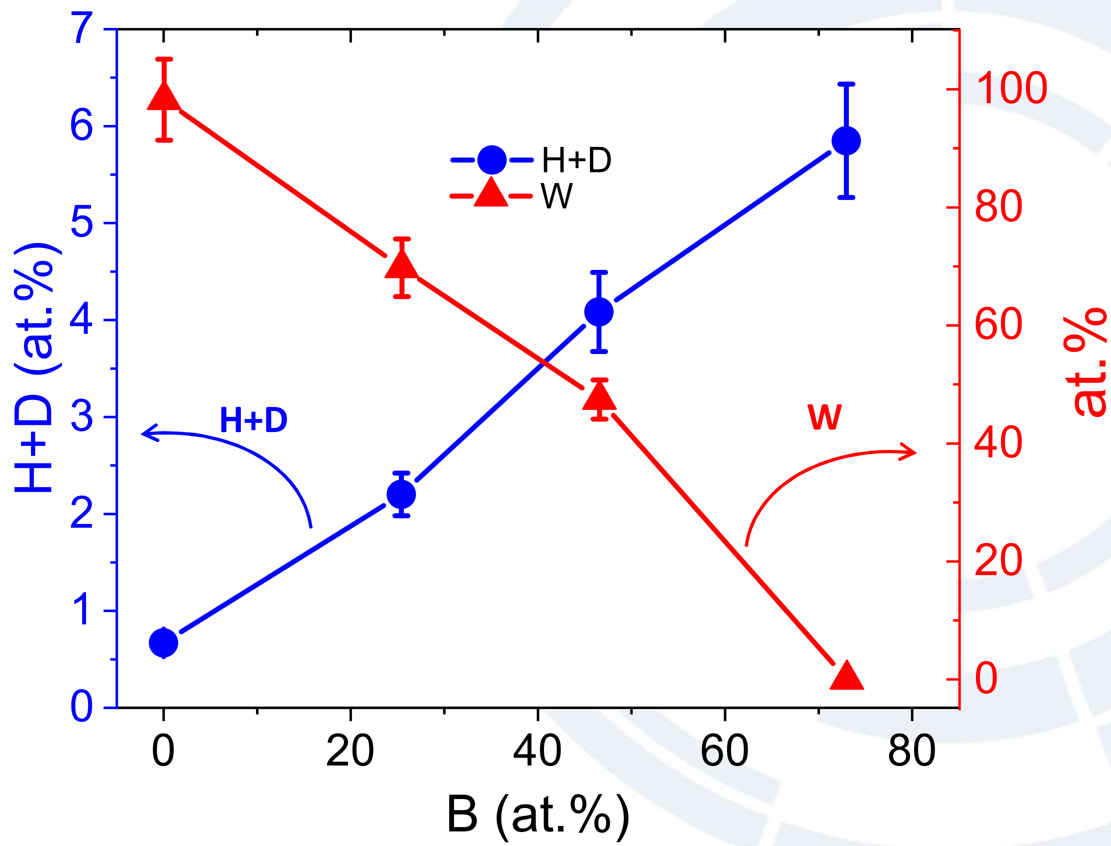
- → **Average composition from bulk of films.**
- → **Detection of hydrogen attributed to isotopic exchange from air exposure and different aging of samples.**
- → **Hydrogen and deuterium atomic content scales with boron in B+W mixed layers.**



W-B film characterization

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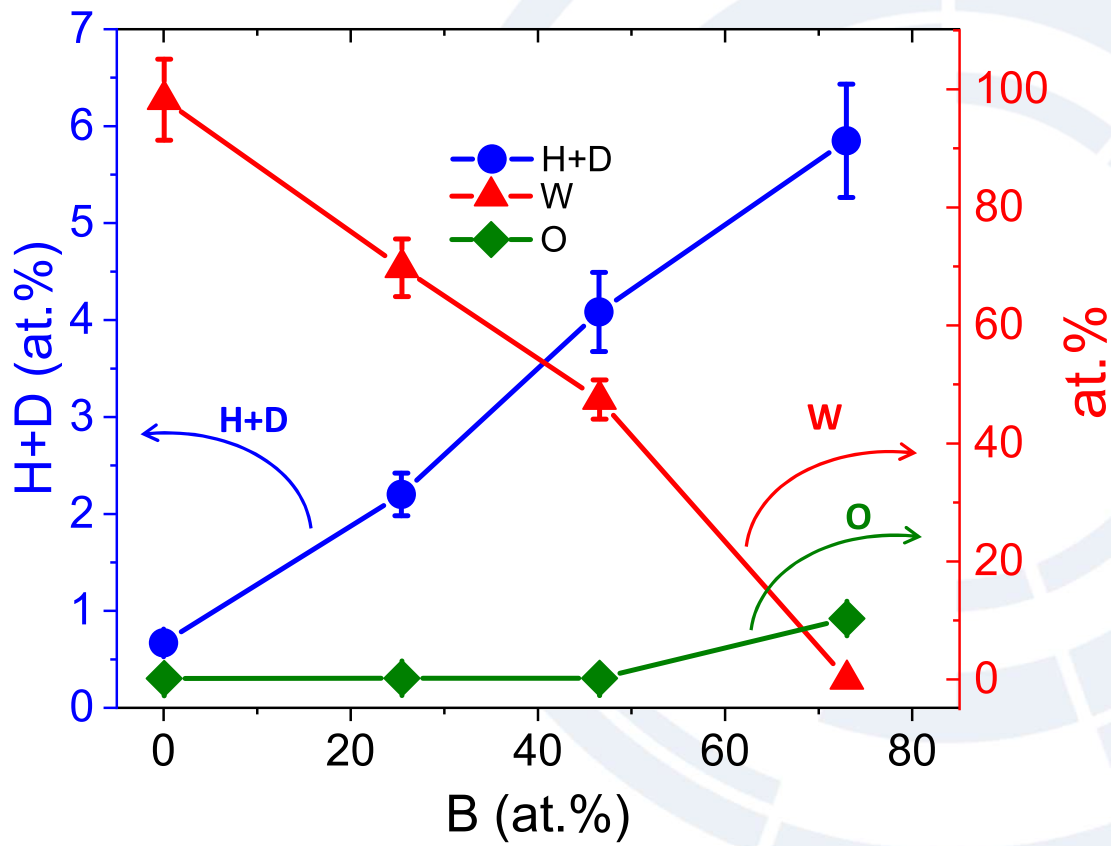
- → **f_{Ar} and f_{D2} fixed;**
- → **W and B magnetron power varied to obtain different B/W ratios.**
- → **Average composition from bulk of films.**
- → **Detection of hydrogen attributed to isotopic exchange from air exposure and different aging of samples.**
- → **Hydrogen and deuterium atomic content scales with boron in B+W mixed layers.**
- → **Oxygen around 10 at.% only at high B/W:**

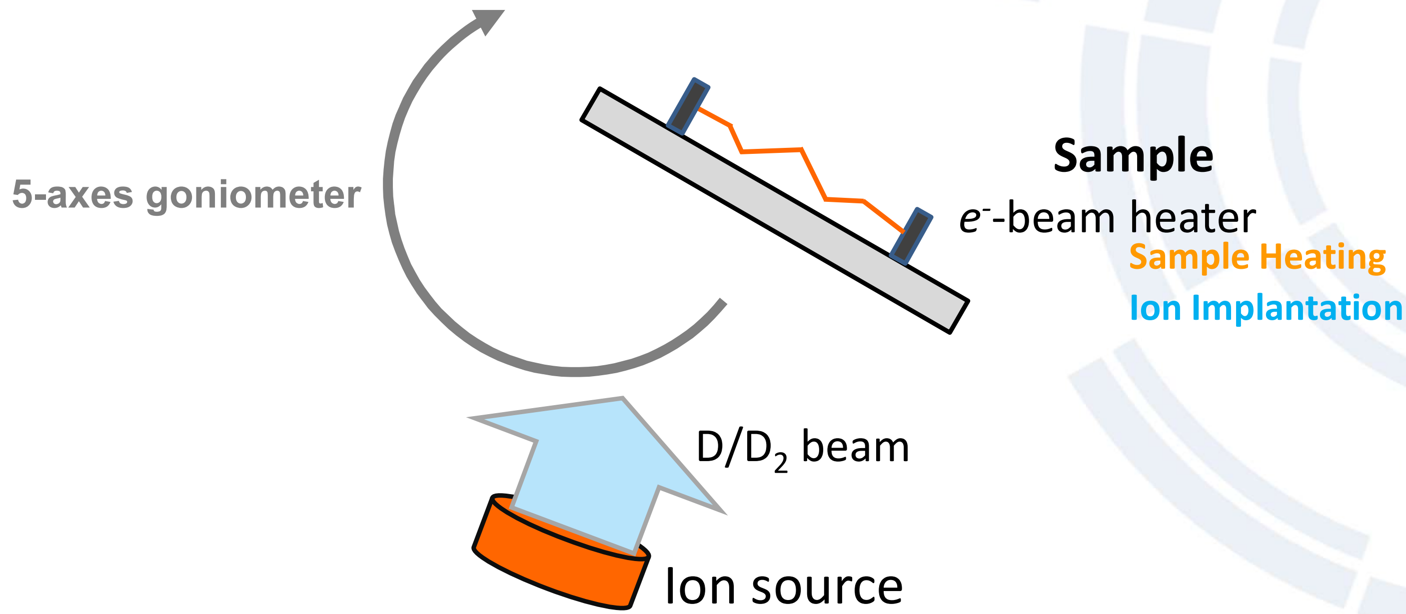
Presence of W might suppress oxygen incorporation.



In-situ experiments of hydrogen and deuterium desorption

SIGMA: Set-up for In-Situ Growth, Material modification and Analysis

K. Kantre et al. Nuclear Inst. and Methods in Physics Research B 463 (2020) 96–100



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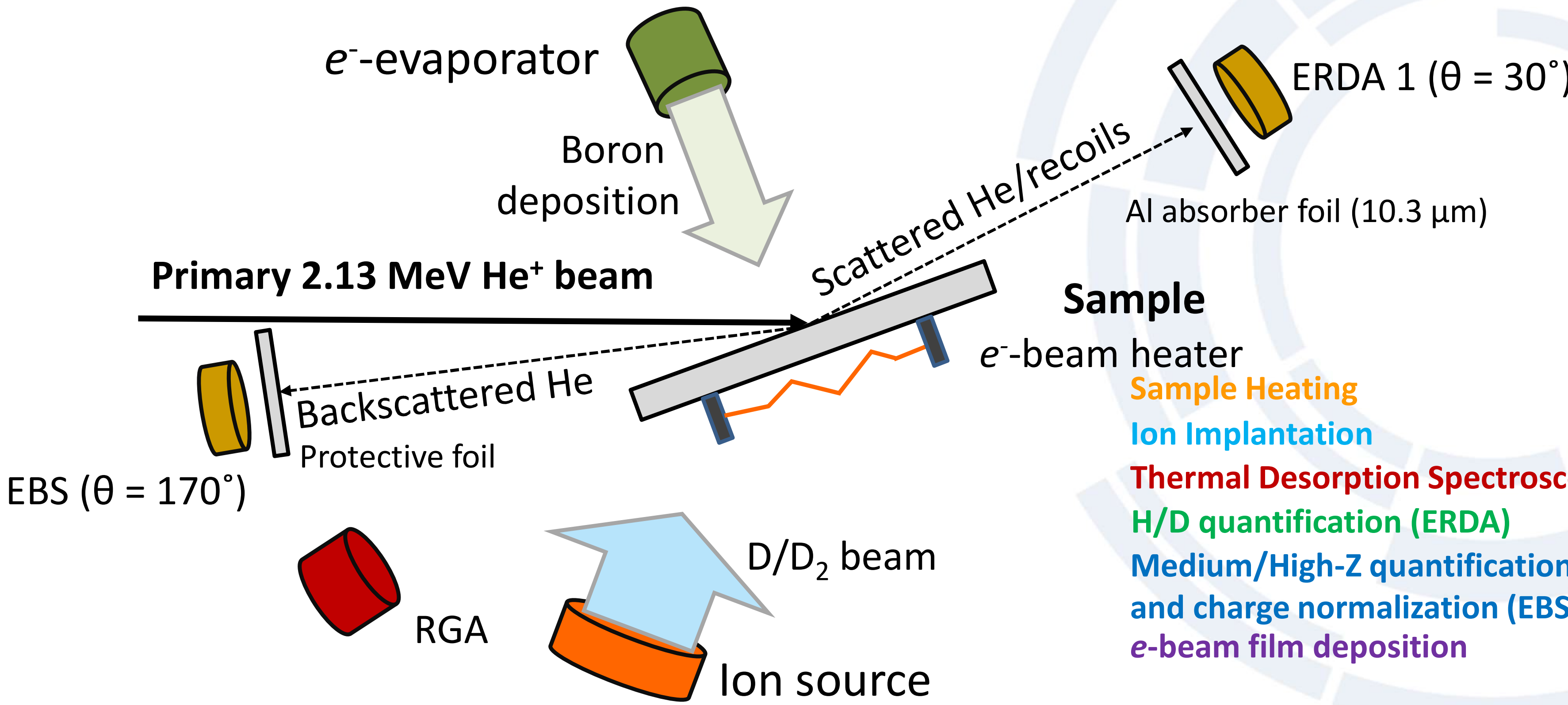


Sample Heating

Ion Implantation

Thermal Desorption Spectroscopy (TDS)

H/D quantification (ERDA)

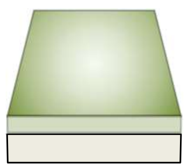
Medium/High-Z quantification and charge normalization (EBS/RBS)

e-beam film deposition

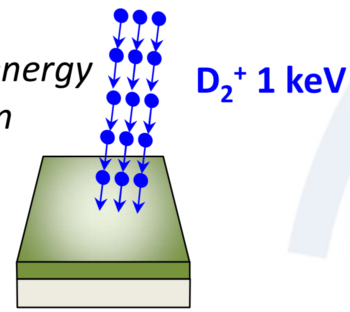
In-situ experiments of hydrogen and deuterium desorption

1st experimental campaign (implantation):

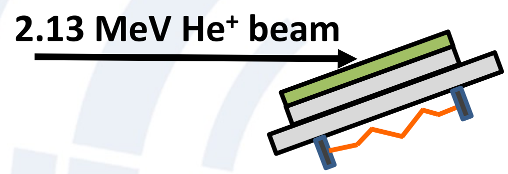
W-B film deposition in Ar:
Mixed W-B and unmixed W and B layers.



In-situ low energy implantation



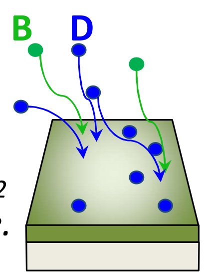
IBA (RBS & ERDA during annealing)



Effect of boron in deuterium retention.

2nd experimental campaign (co-deposition):

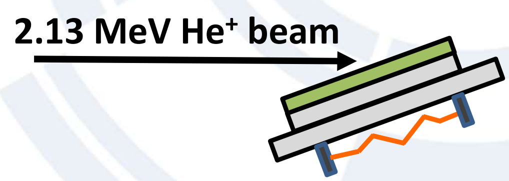
B layers deposited in D_2 containing atmosphere.



Co-deposition of B and D_2 by sputtering (ex-situ).

Co-deposition of B and D_2 by e-beam evaporator (in-situ). (in progress).

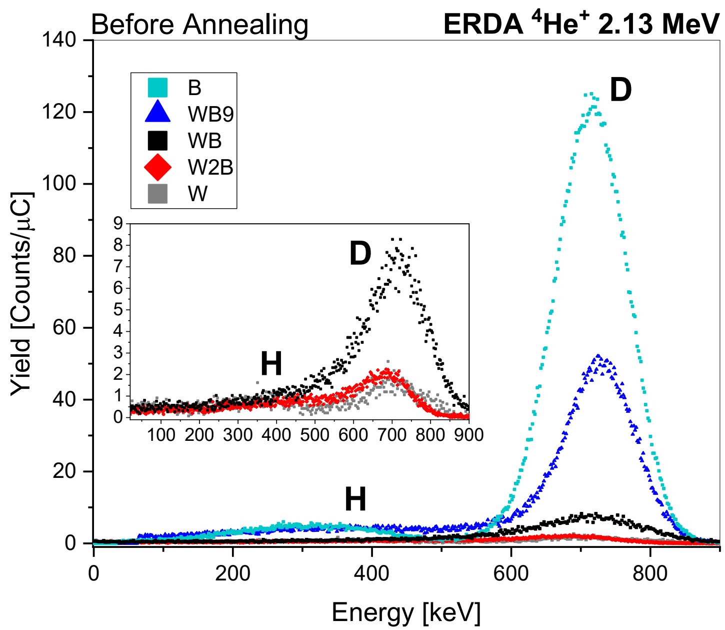
IBA (RBS & ERDA during annealing)

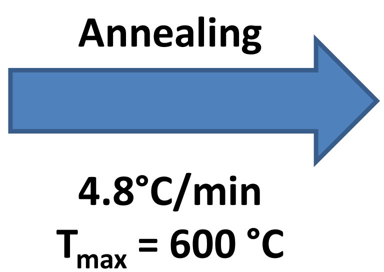


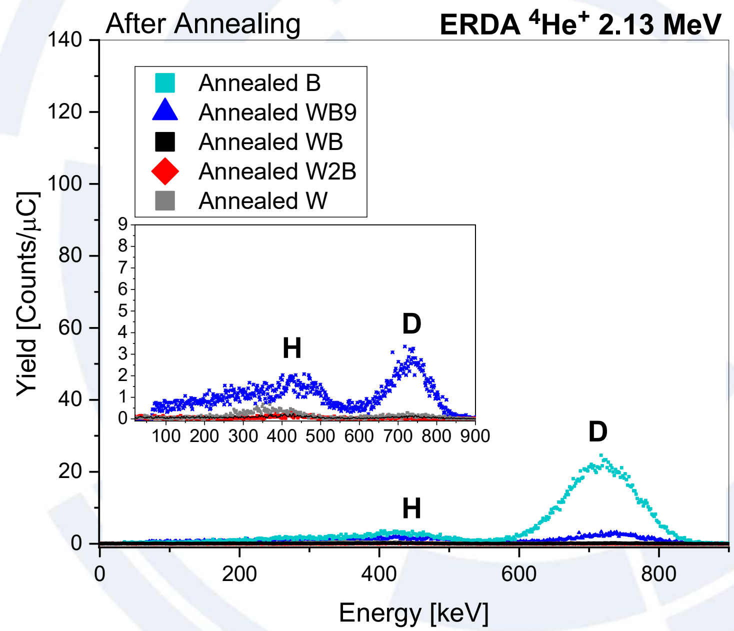
Effect of incorporation pathway (implantation vs. co-deposition).

In-situ experiments of hydrogen and deuterium desorption

Deuterium implantations in W-B layers on Si:
1 keV D_2^+ implantation fluence ≈ 6×10^{17} at/cm^2.
TRIM: Implantation range within 40 nm.
Film thicknesses: 150-200 nm.





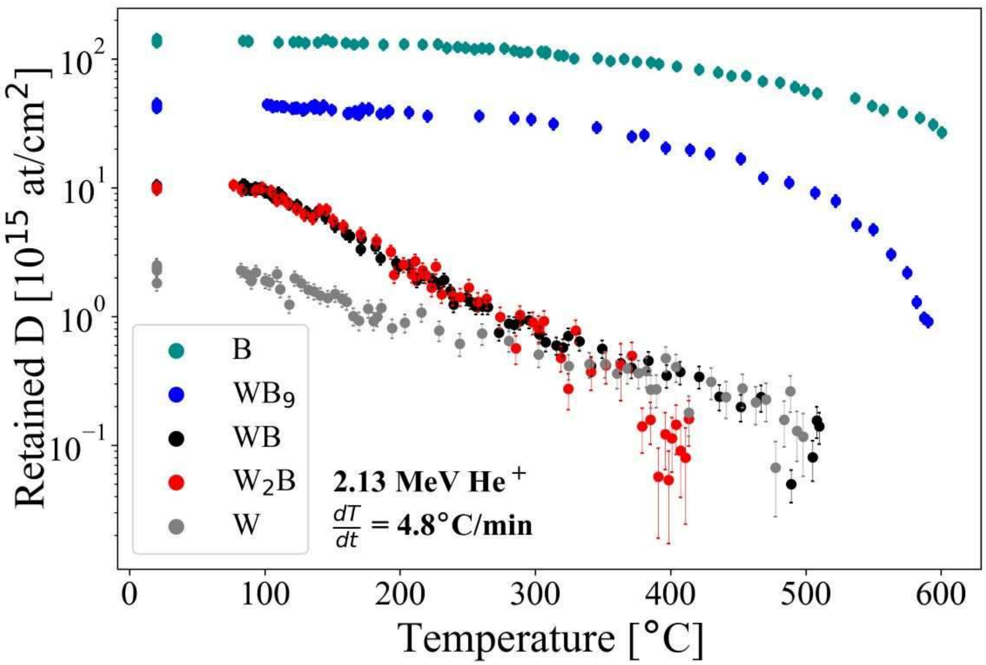


Low amounts of hydrogen.
Deuterium areal density scales with boron concentration.

Significant amount of deuterium in boron layer after annealing.

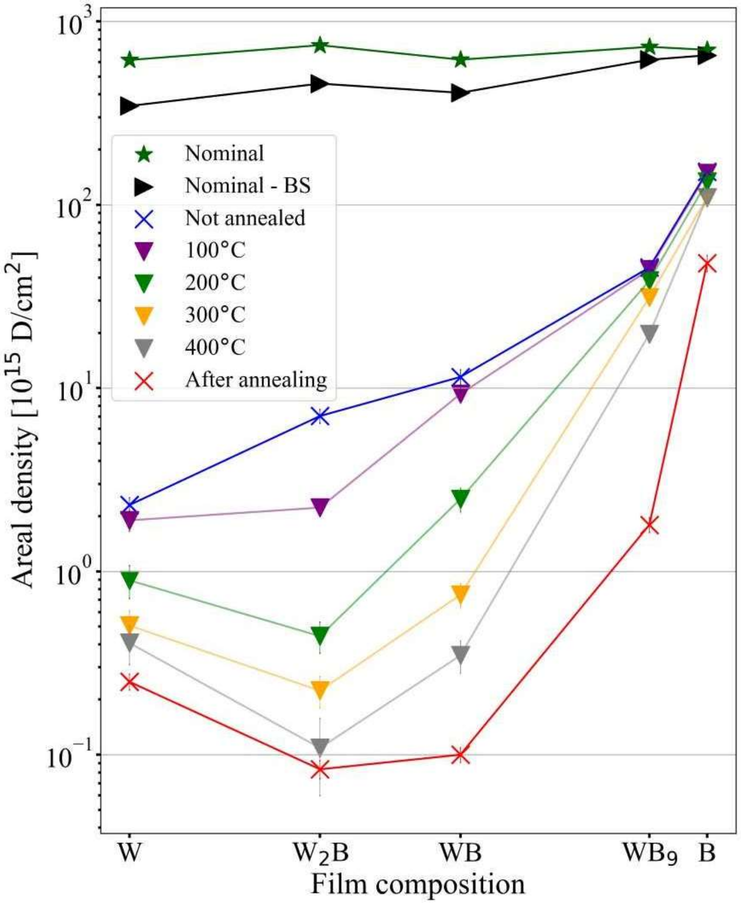
In-situ experiments of hydrogen and deuterium desorption

Deuterium quantification (ERDA)
before and during annealing.



In-situ experiments of hydrogen and deuterium desorption

Simulations (TRIM) and experimental results:



- Lower deuterium content than nominal values (beyond saturation).
- Deuterium saturation scales with B content but not linearly.
- W-B mixed layers present deuterium outgassing at lower temperatures.
- After annealing, unmixed W tungsten present higher deuterium content than W-B mixed layers.
- Ex-situ characterization was performed.

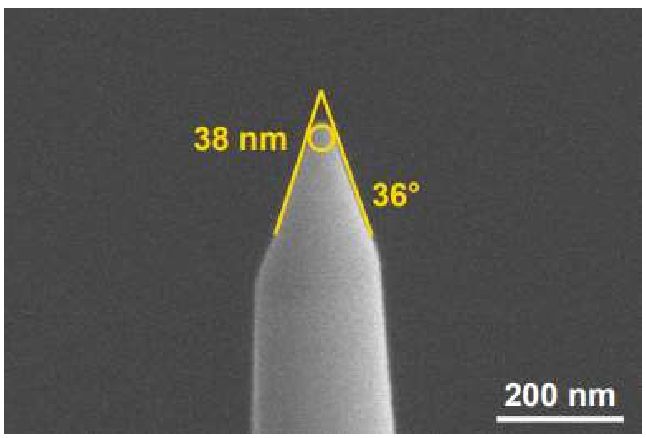
Ex-situ characterization after implantation/annealing

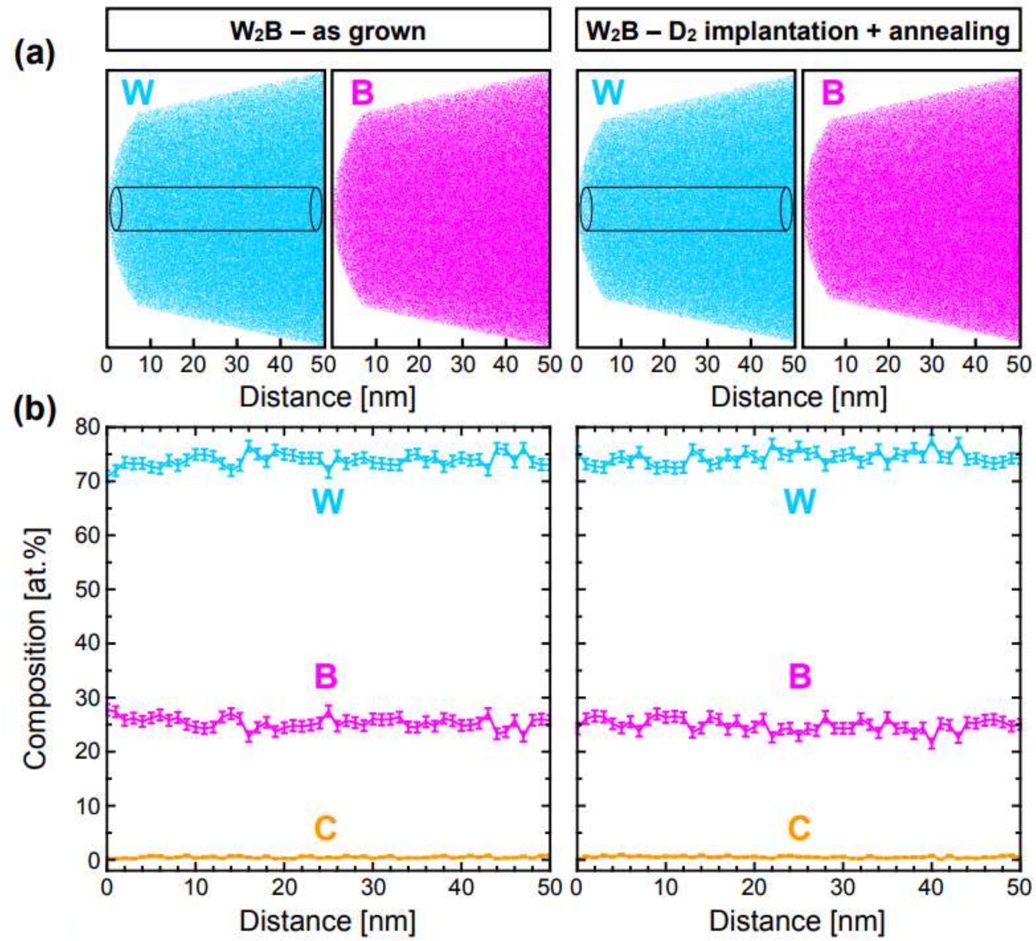
Measurement and analysis: Marcus Hans, RWTH Aachen University

Atom probe tomography (APT):
Verification of residual deuterium, and possible change in composition/phase after deuterium implantation followed by annealing.

No detection of residual deuterium.

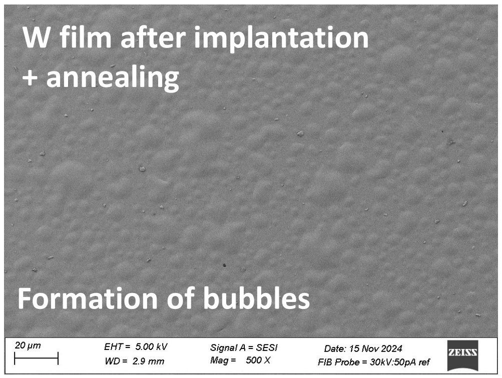
No significant modification between samples: agreement with RBS results.

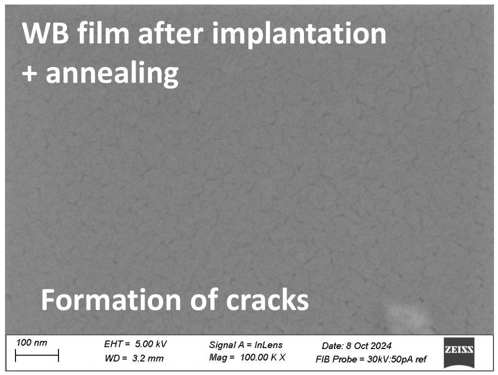


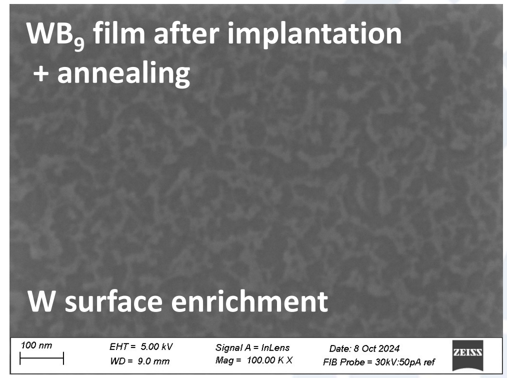


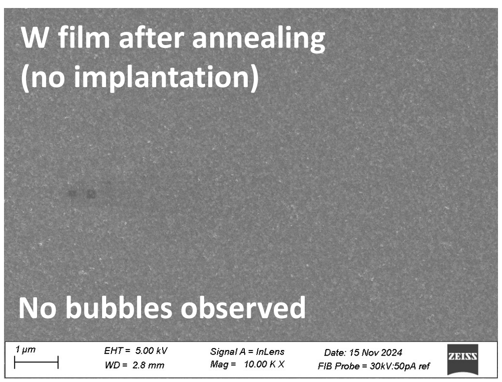
Ex-situ characterization after implantation/annealing

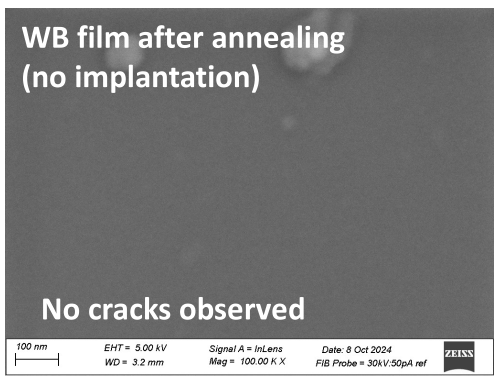
SEM:

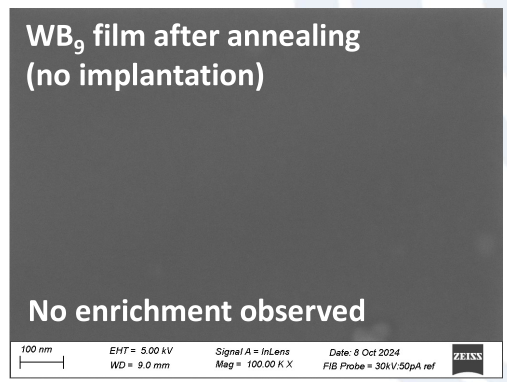




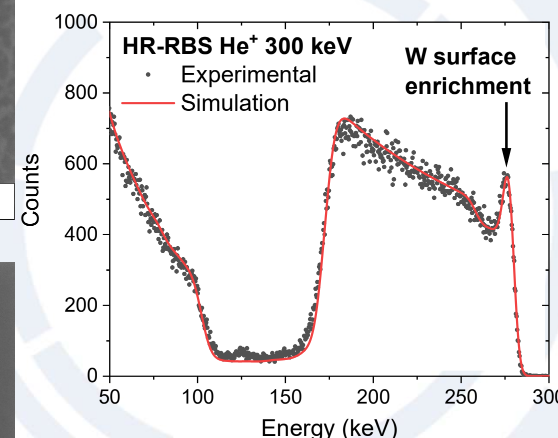








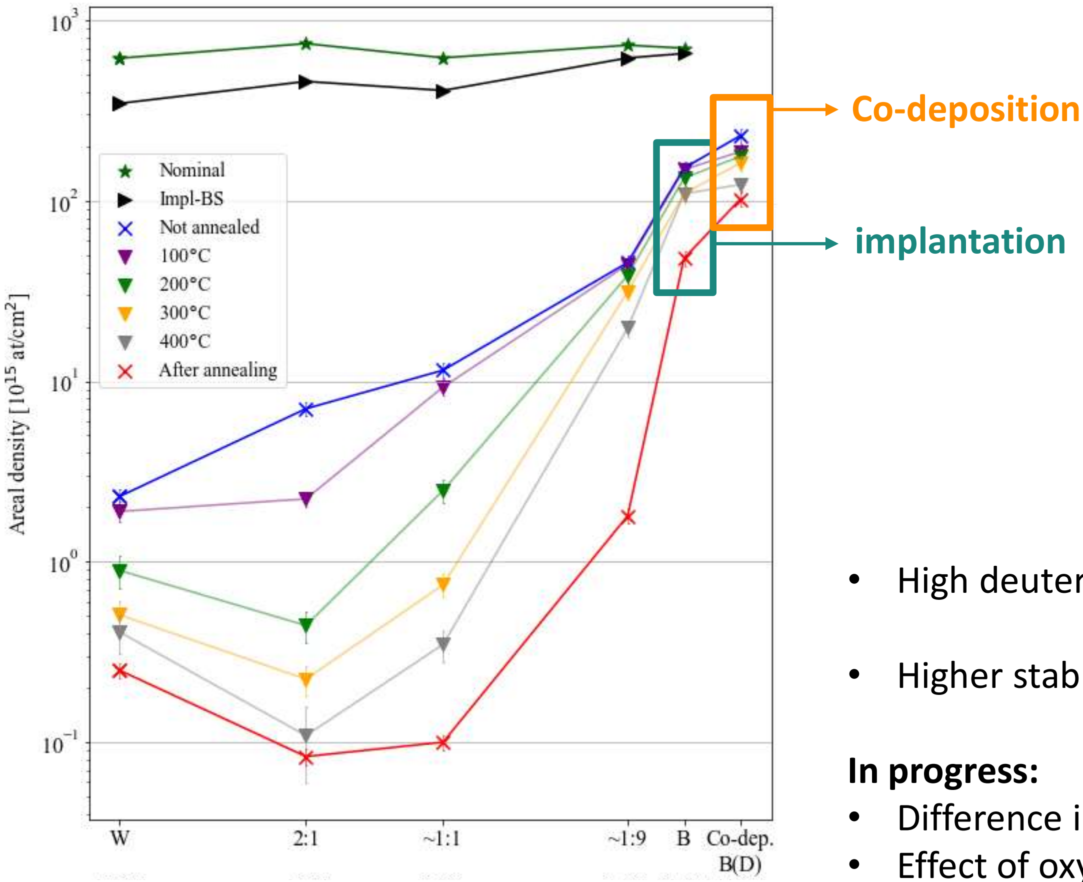
Confirmation using high-resolution RBS:

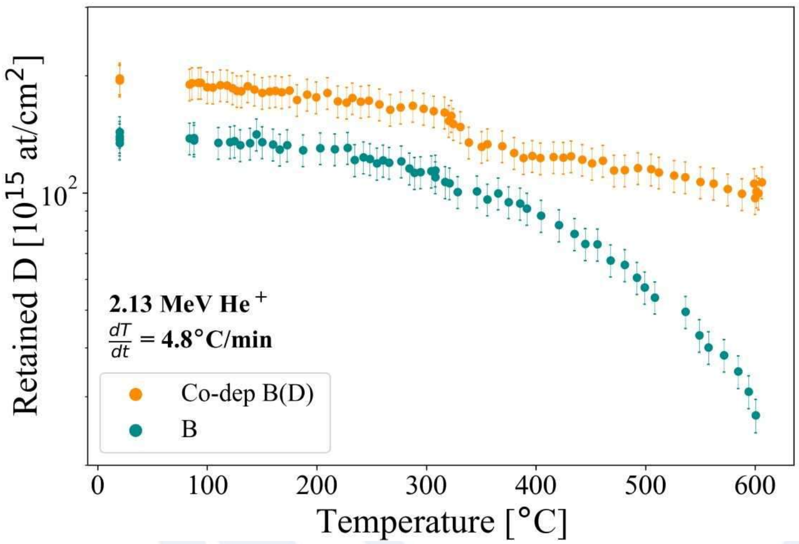


Overall observation:
Significantly different behavior after implantation for each composition.

Influence of incorporation pathway

Deuterium retention in boron layers: implantation & co-deposition





- High deuterium retention in both boron layers (unmixed with W).
- Higher stability of deuterium in co-deposited layer even up to 600°C.

In progress:

- Difference in chemistry of layers.
- Effect of oxygen in deuterium retention.

Overview and Conclusions

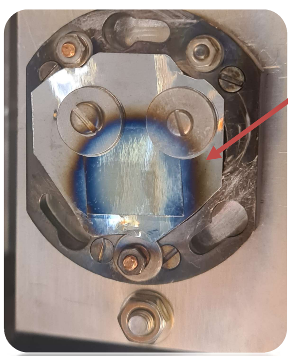
Combined RBS/ERDA in-situ analysis can be used to obtain H&D distribution during annealing:

- Deuterium saturation scales with B content.
- Highest D content and stability in boron co-deposited in D_2 atmosphere (different incorporation than implanted).
- W-B mixed layers present deuterium outgassing at lower temperatures (synergistic effect): Under investigation.

- Ex-situ analysis: no bubbles observed when boron is mixed in W→ cracks and surface enrichment instead.

In progress:

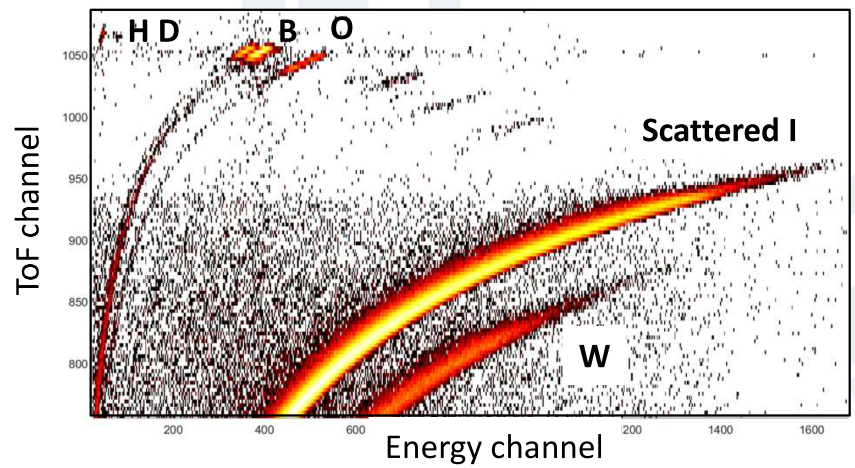
- *e*⁻-beam evaporator also available in the SIGMA beamline: possibility to grow B films in different atmospheres in-situ.



In-situ e^--beam boron deposition in W in D_2 atmosphere.

Stable after air exposure.

Ex-situ ToF-ERDA:



- Investigation of oxidation (oxygen getter) in W-B layers using $^{18}O_2$: oxidation and/or low energy implantation.

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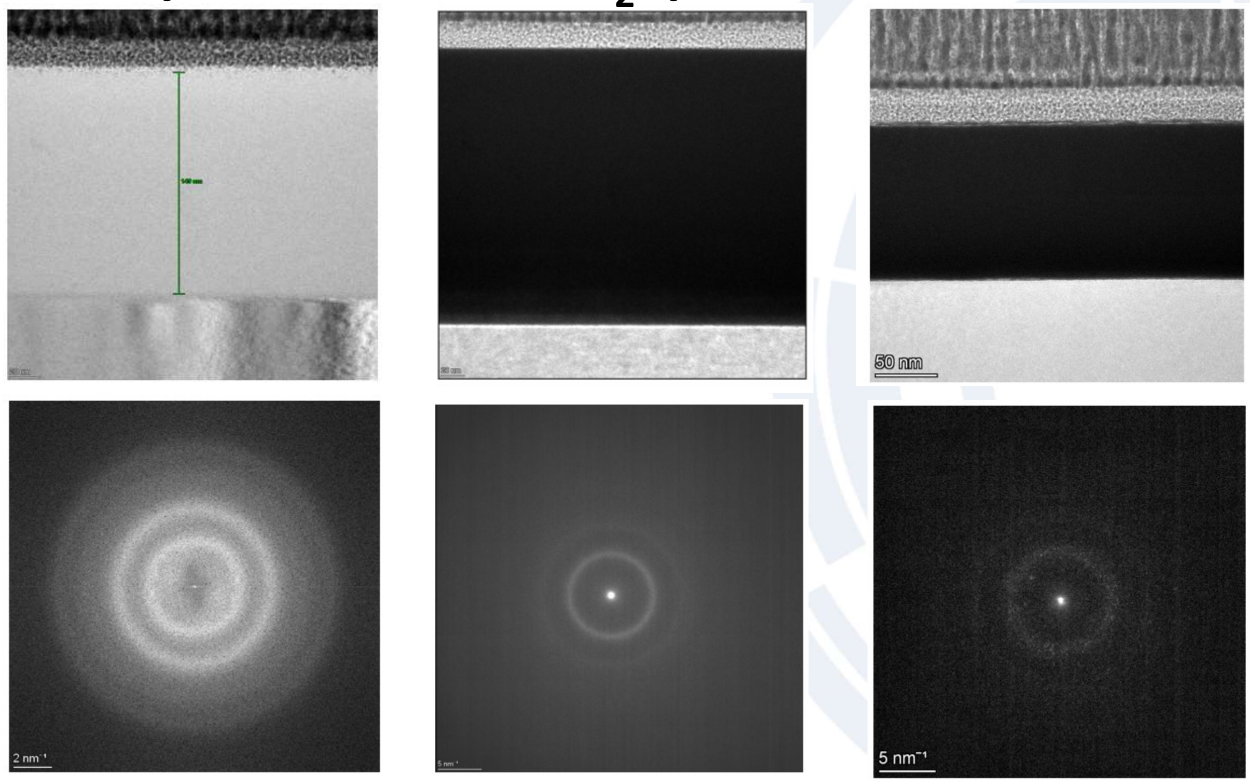
W-B film characterization (100-150 nm films)

TEM for W-B layers

B/Si | W_2B/Si | WB/Si

TEM

Electron-diffraction of selected regions



Amorphous B and W-B layers

W-B film characterization (100-150 nm films)

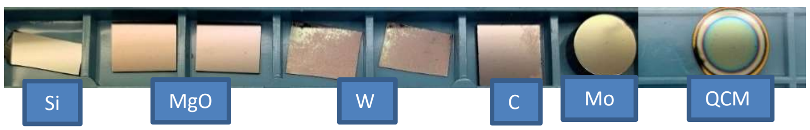
Sputtering depositions under argon atmospheres:

B target (RF-150 W):

0.5 nm/min; 5 hours deposition.

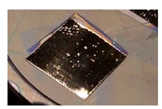
Substrate effect:

- <u>Layers are stable in vacuum.</u>
- After air exposure (within minutes): roughness on W substrates.



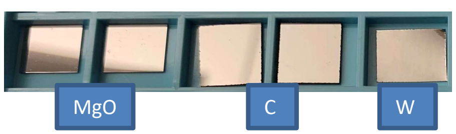
Improved on W substrates by:

- W layer deposition (20 nm) before B deposition (no air exposure).
- Optimization still needed (including annealing before air exposure).



B target (RF-150 W) + W target (RF-50 W):

- Layers are stable in vacuum and in air for all substrates.



Sputtering depositions under argon Ar+D_2:

B target (RF-150 W):

f_{Ar} = 10 sccm; f_{D2} = 18 sccm; P_{Ar+D2} = 7×10^{-3} mbar.

As-grown

20 minutes in air

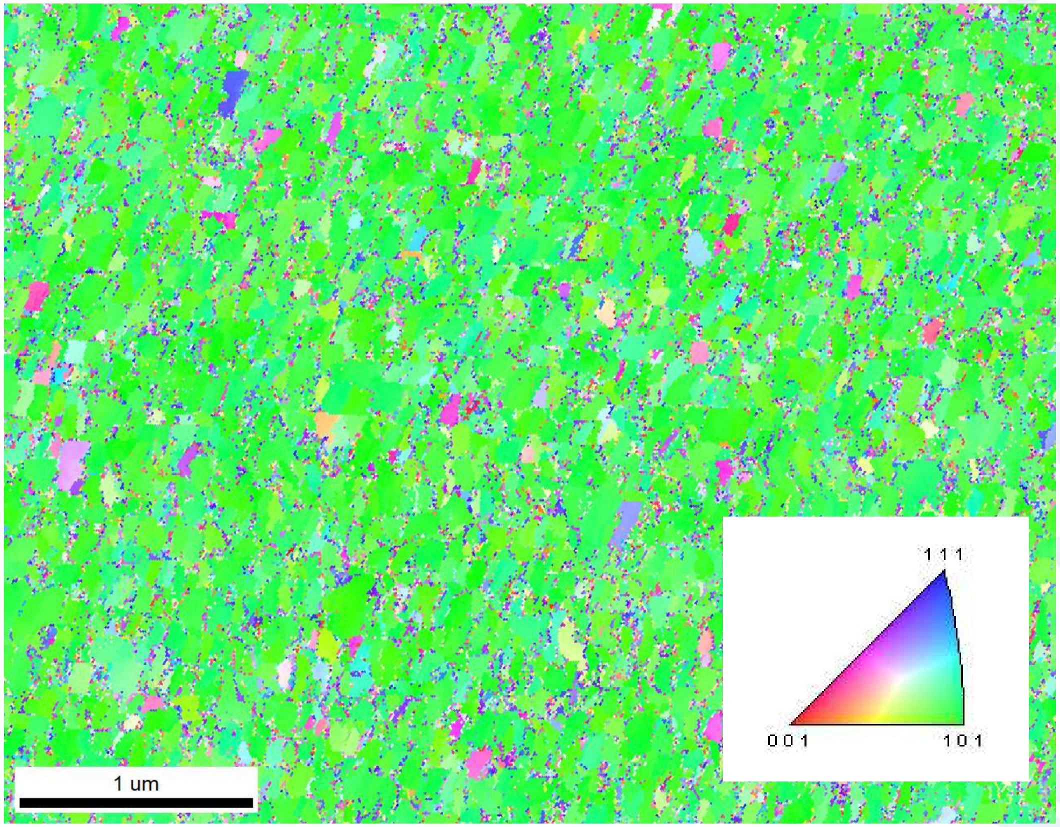
- Layers are stable in vacuum, flat and homogeneous.
- Change of color within minutes in all substrates.
- Layers remain flat on all substrates.

B target (RF-150 W) + W target (RF-50 W):

- Similar as in Ar depositions: flat, homogeneous, stable in air.

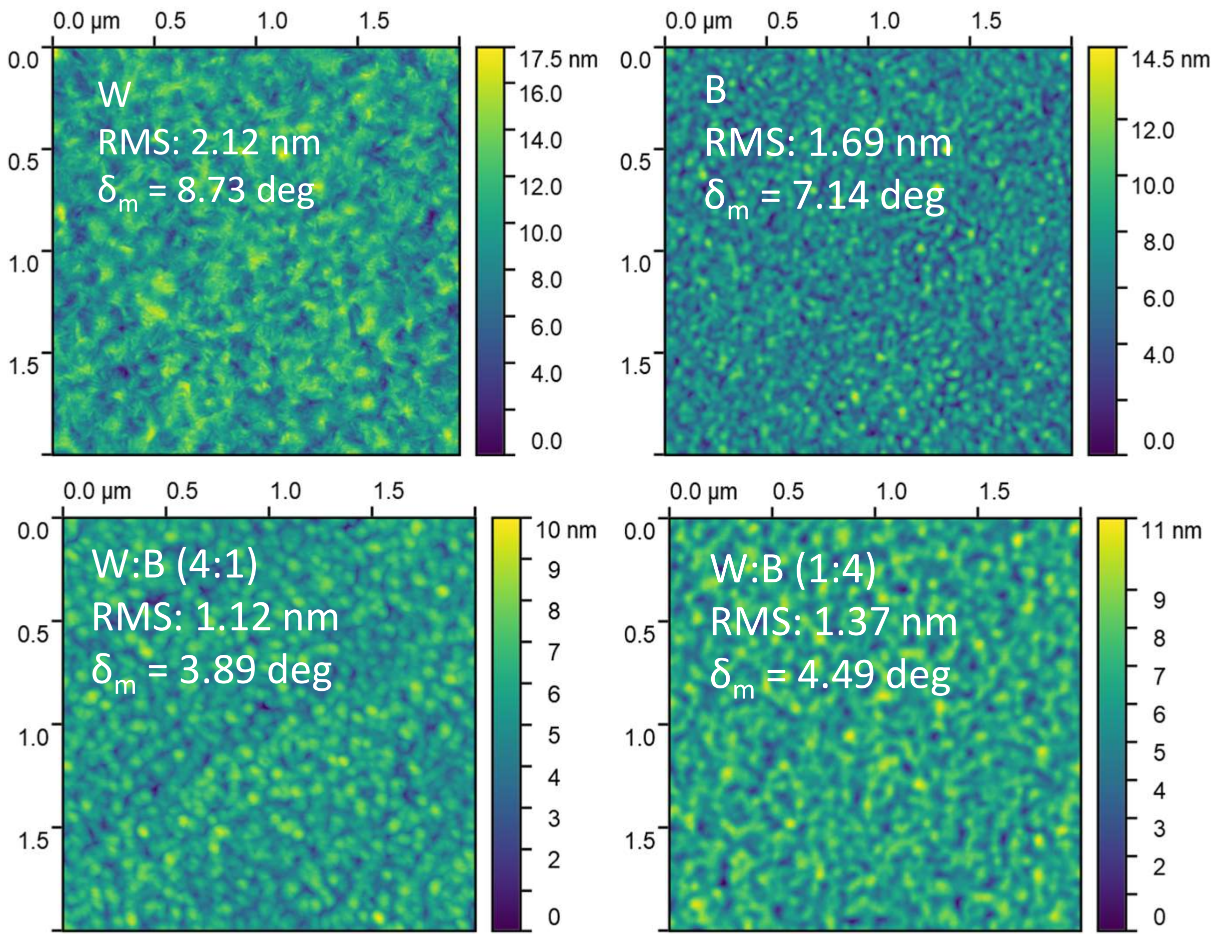
W-B film characterization (100-150 nm films)

EBSD for W layer on QCM (TU Wien)



Sputtering yields

Surface morphology of W-B films on QCM (pre-irradiation):

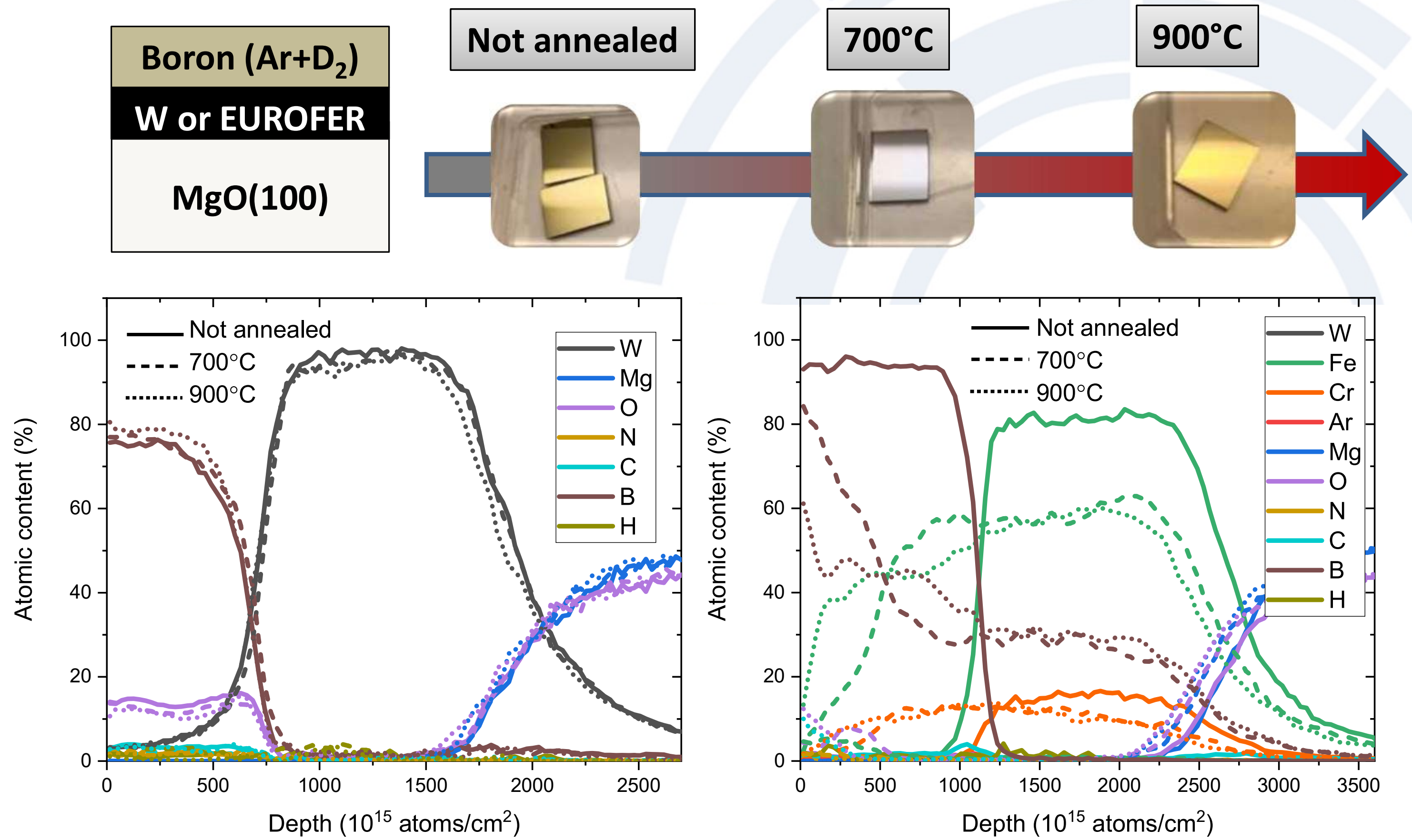


- Measured in different spots (center and edge);
- Typical RMS<2 nm for films (measured in different spots);
- New measurements are planned after SY analysis to verify if ion bombardment resulted and modified surface morphology;

Boron migration in re-deposited PFC

Effect of annealing in B/PFC stack layers

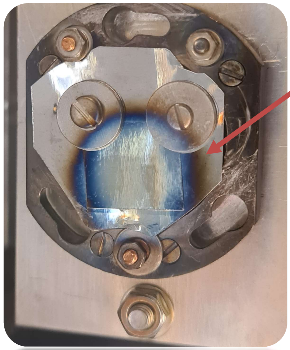
- Effect of annealing at higher temperatures was performed and analyzed ex-situ in different structures to evaluate atomic migration of boron on re-deposited PFC (W&EUROFER97).
- Significant temperature dependence in the intermixing of boron with sputter-deposited layers from EUROFER97.



Overview and Conclusions

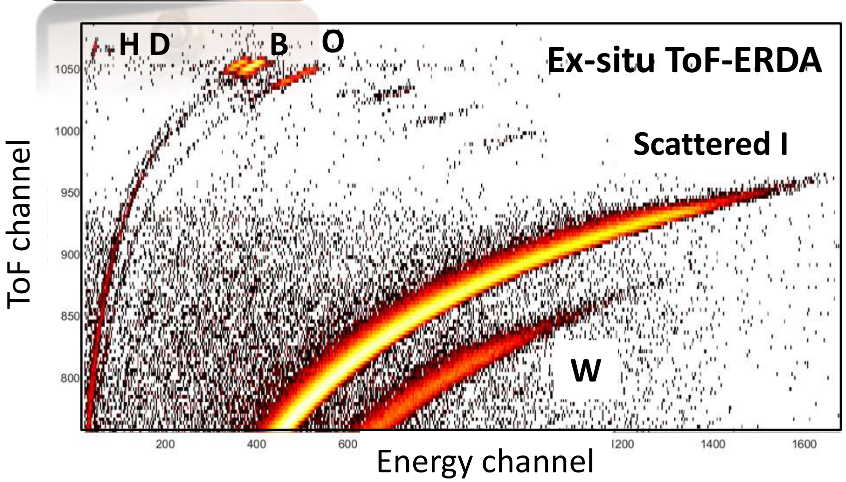
In progress:

- *e*$^{-}$-beam evaporator also available in the SIGMA beamline: possibility to grow B films in different atmospheres in-situ.

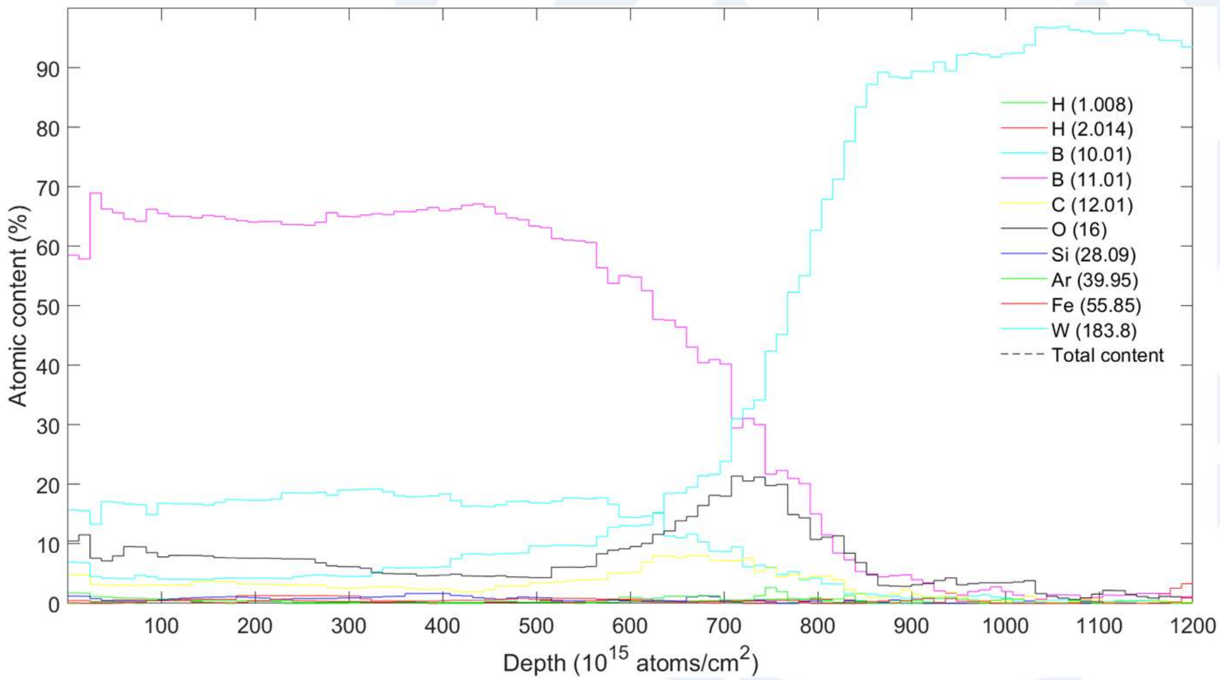


In-situ e^{-}-beam boron deposition in W in D_2 atmosphere.

Stable after air exposure.



Ex-situ ToF-ERDA depth profile



Round-Robin exercise (SP-B)

Samples prepared:

- *Around 100 nm of boron on W (polished disks) and Si(100) substrates*.
- 1000°C annealing before deposition.
- More layers can be deposited if needed.