



SP B.4 – Be Reference Layers Production in Support of PWI Studies / Coating Facility Update: B Containing Layers and Dust Production Capabilities

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ELEMENTARY PROCESSES IN PLASMA AND APPLICATIONS GROUP



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Be-based coatings with pre-defined properties

Set-ups development and tuning

Production of Be reference coatings Nov 2021-June 2023

Sample analysis – XRD TDS and SEM at IAP
- IBA at RBI, XRD at NCSR, TDS at JSI, etc..

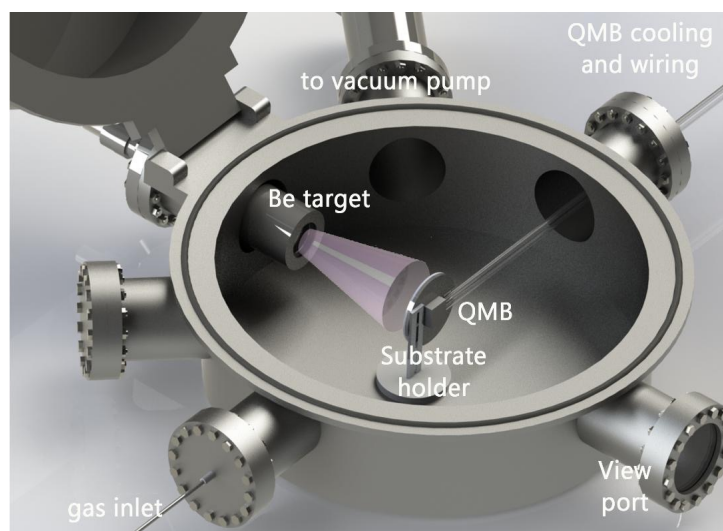
From Be/D to B/D and T experiments - BeHF upgrade to T facility

Boron coatings capabilities – with some preliminary results

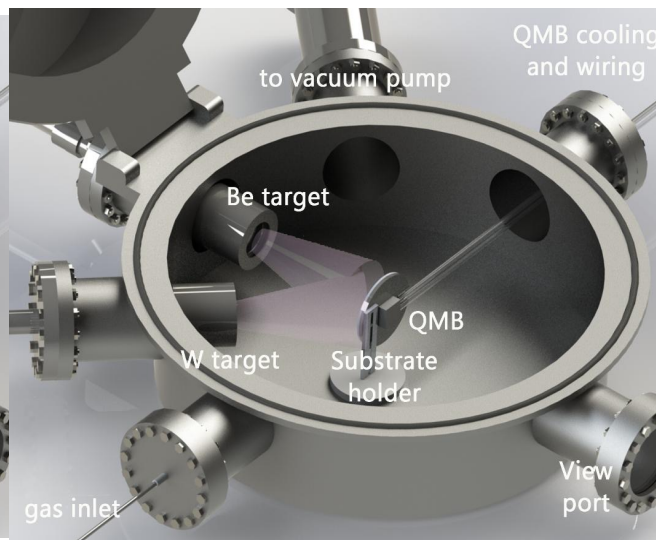
Other experimental capabilities

Future collaborations and plans

Be-based coatings with pre-defined properties



Schematic description of the coating system used for Be-D (Ne, N, He) layer deposition

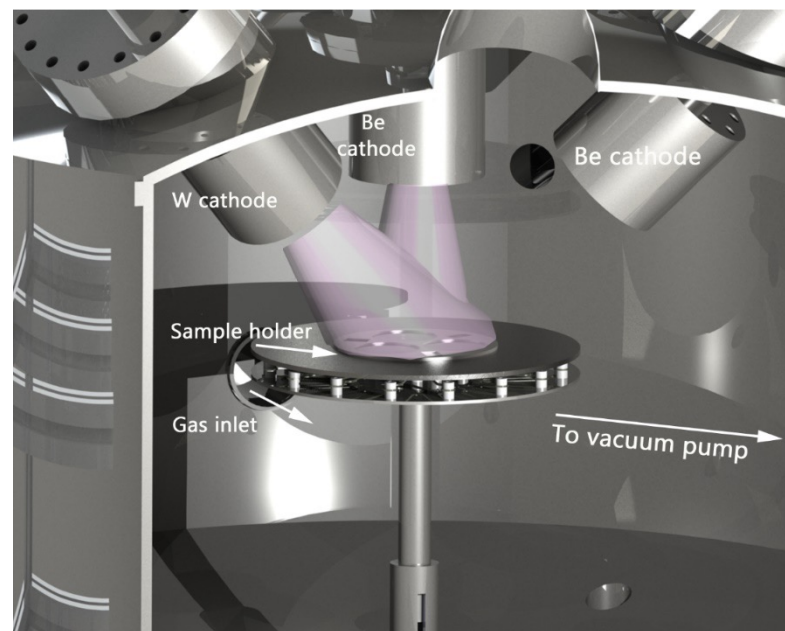
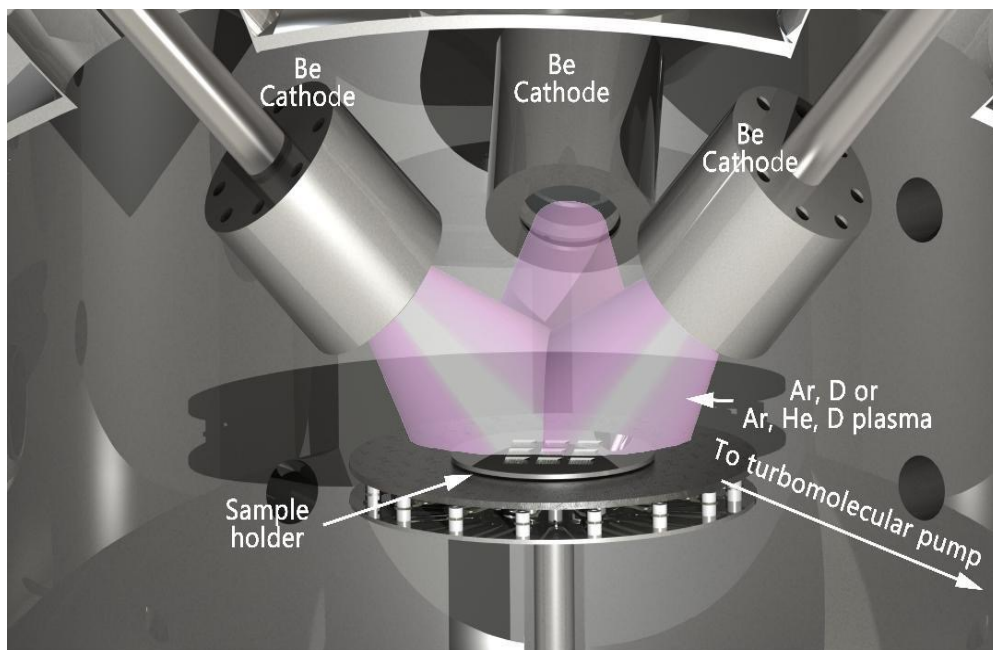


Deposition system used for obtaining Be(-W)-D/H/etc.



Ignited W and Be MS plasmas under D/Ar atmosphere

Be-based coatings with pre-defined properties



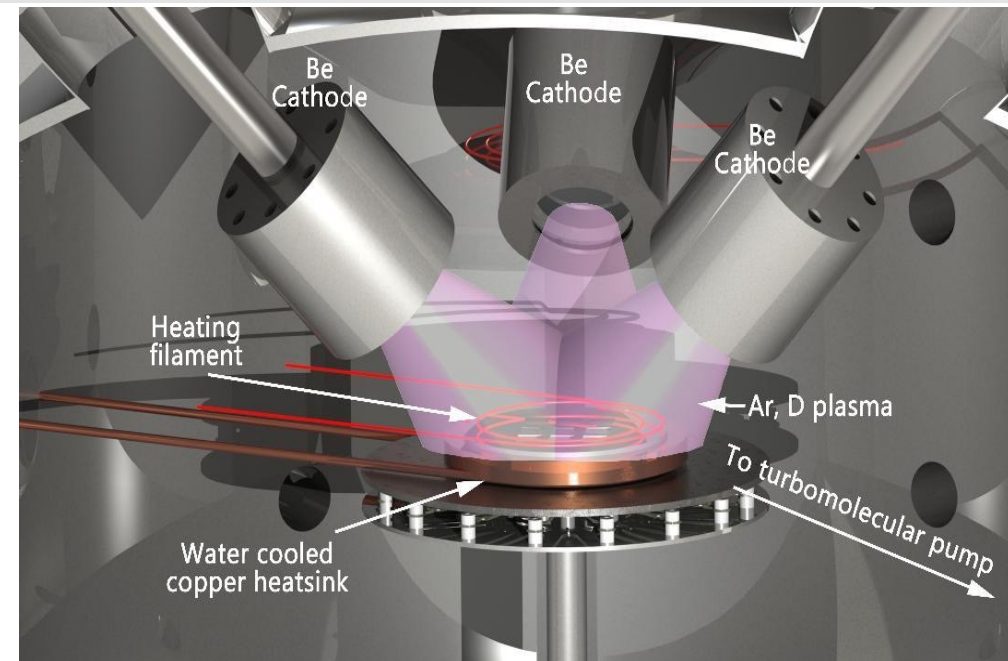
Schematic description of the coating system used for Be-D (H, O) layer deposition

Deposition system used for obtaining Be(-C, W, etc.)-D/H/O/etc layers

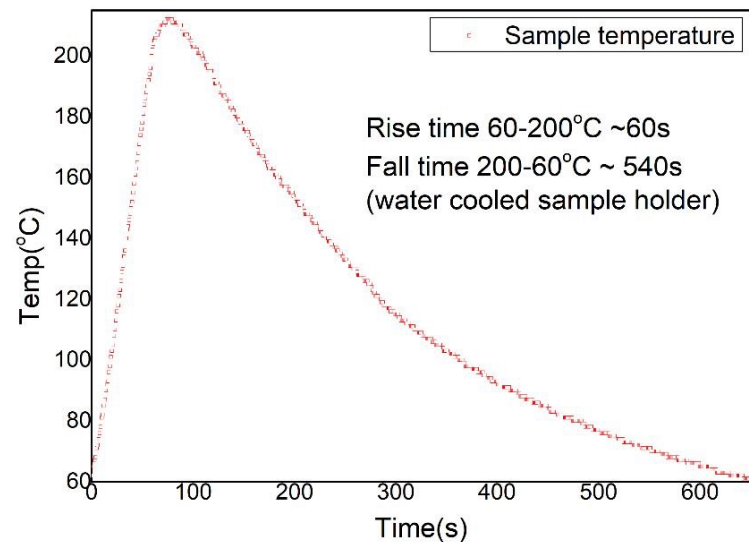
Upgraded Be coating set-up for JET-like Pulses



Be-D/Be-H sample production for the EUROfusion Project



Schematic description of the coating system used for Be-D/Be-H (4:1 at ratio) layer deposition

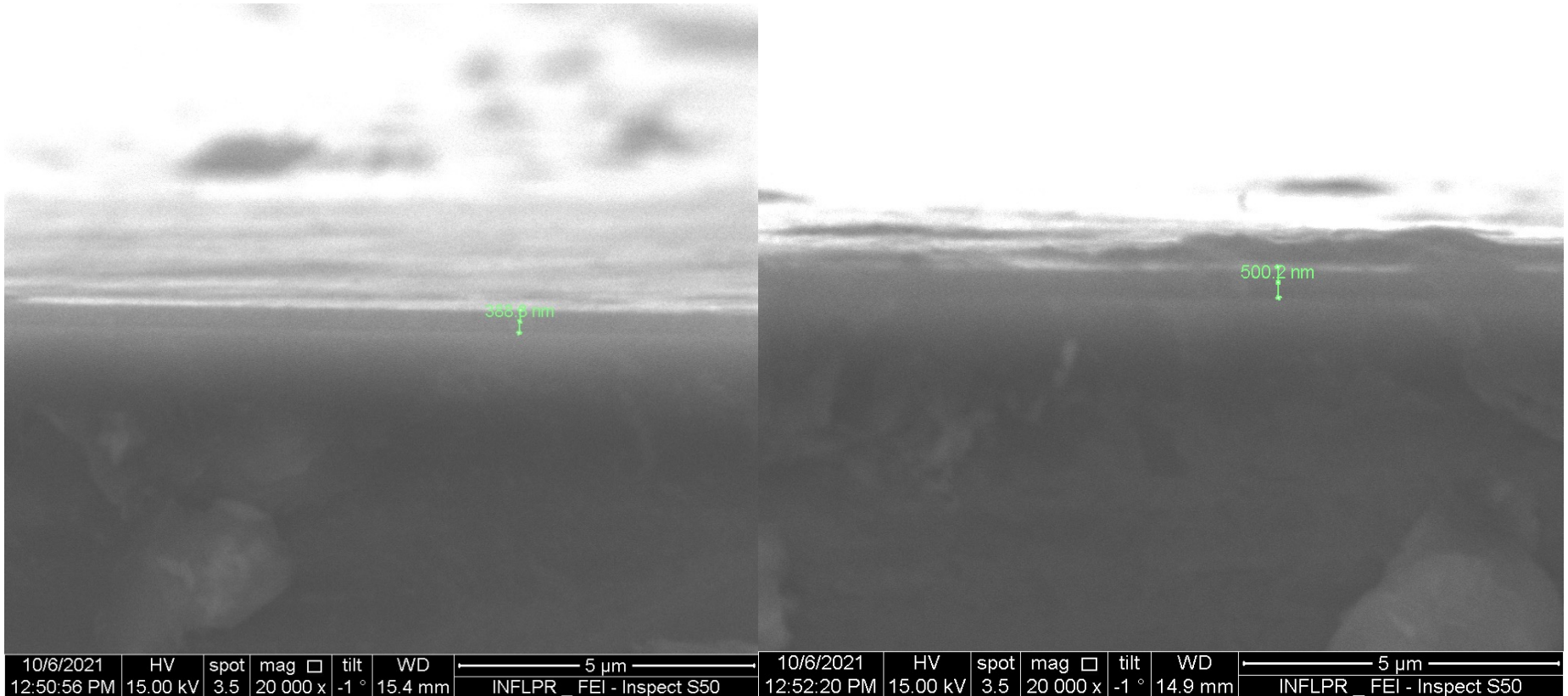


Heat ramp during the coating for a JET Like pulse simulation

Sample requirements under the SPB4 Production of Be containing coatings : 2021-2023

1. **Nov. 2021:** Be with D or H ~20%, 5 microns thick – 110 samples in total, thermally treated
2. **Nov 2021:** Be 20 microns layer, no gas, R.T. and 200 C during deposition: 12 Samples
3. **Feb 2022:** Be+O+D (5, 10 and 20 D at%) – 16 samples
4. **June 2022:** Be+D (10 D at%) 4 different temperatures: - 44 samples
5. **July 2023:** Be O D and Be O H, ~20%, 5 microns thick – 192 samples in total, thermally treated

Production of Be-based coatings - pre-characterization of the samples



SEM images for Be co-depositions on Si substrate – thickness calibration

Production of Be-based coatings - pre-characterization of the samples

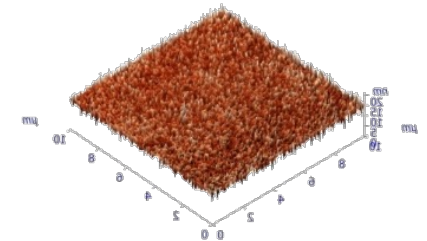
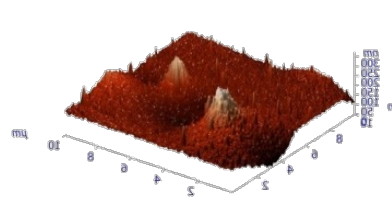
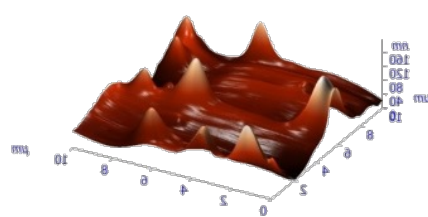
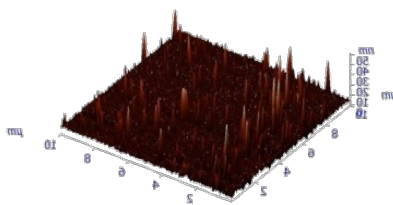
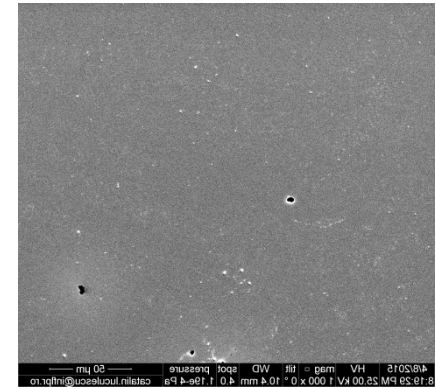
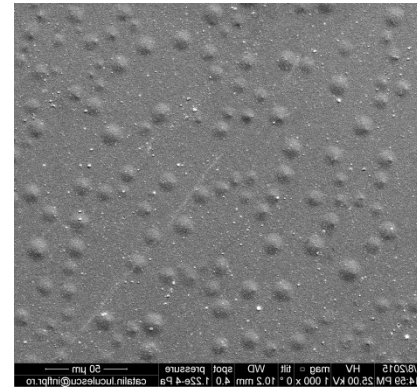
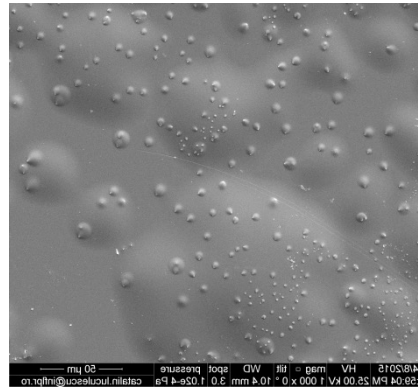
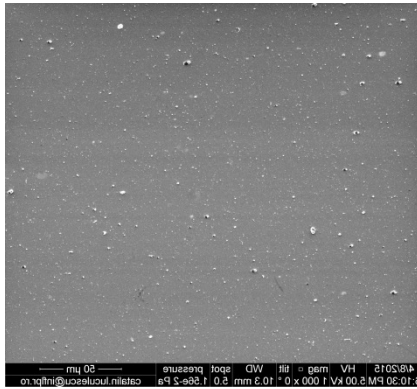


Be-D

W-D

Be-W-D

Be-W-D-N

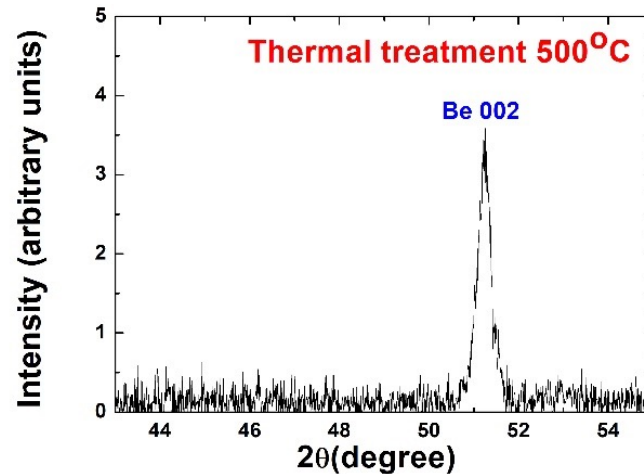
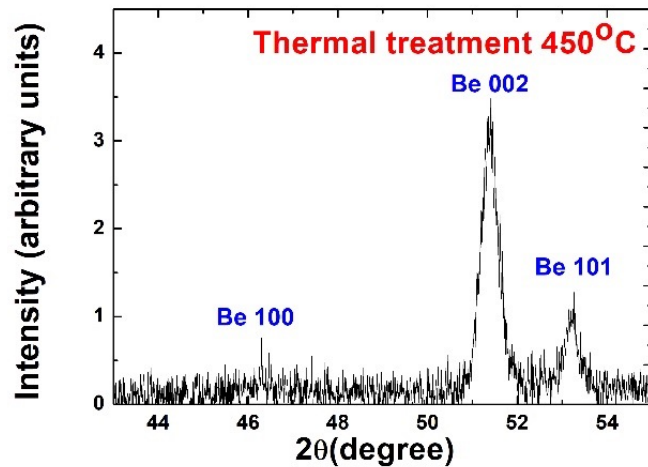
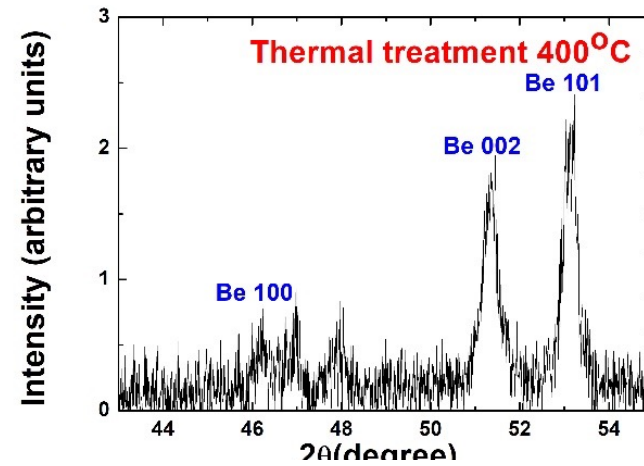
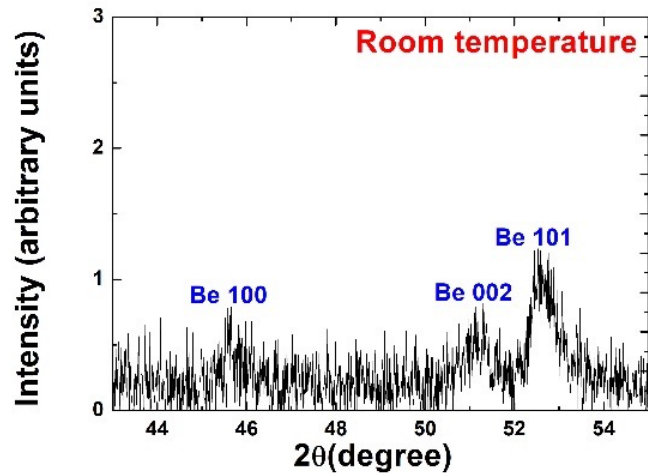


SEM and AFM 3D images for
Be-D, W-D, Be-W-D and Be-W-D-N

Production of Be-based coatings - pre-characterization of the samples



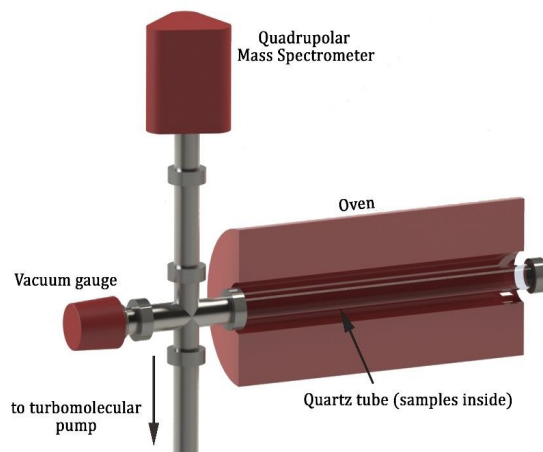
XRD Measurements



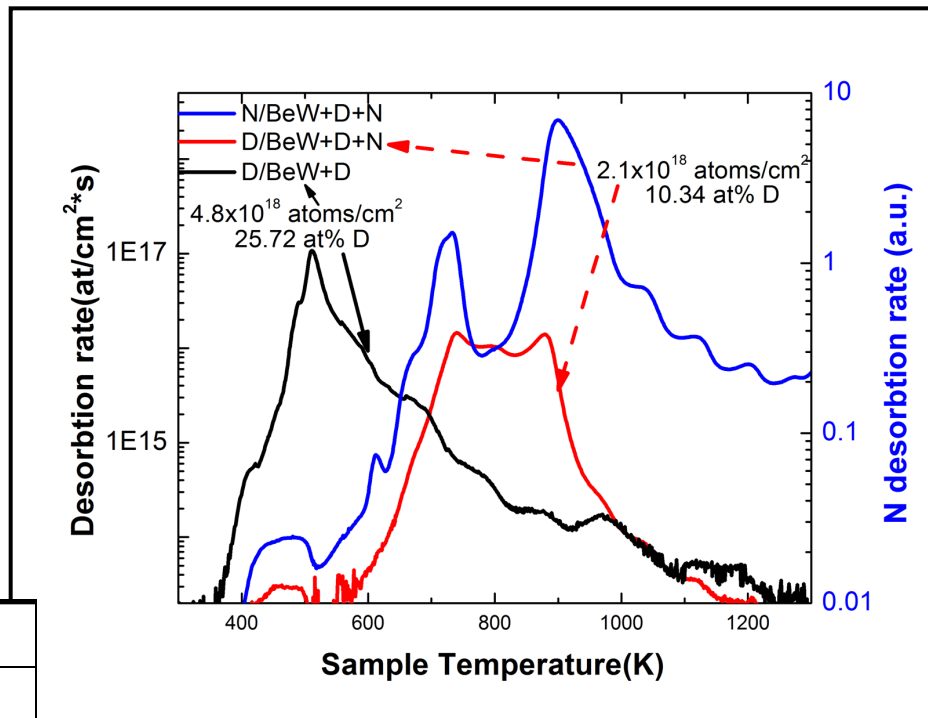
Production of Be-based coatings - pre-characterization of the samples



TDS Measurements



Experimental setup for TDS measurements



D and N release measured using TDS of mixed Be-W-D and Be-W-D-N films deposited on silicon

D release measured using TDS

Sample	D 10^{17} cm^{-2}	D (%)
W + D/Si	1.82	9.20
BeW + D/Si	1.39	3.93
BeW + D + N/Si	2.88	6.00
BeW + D/Mo	477	25.72
BeW + D + N/Mo	213	10.34

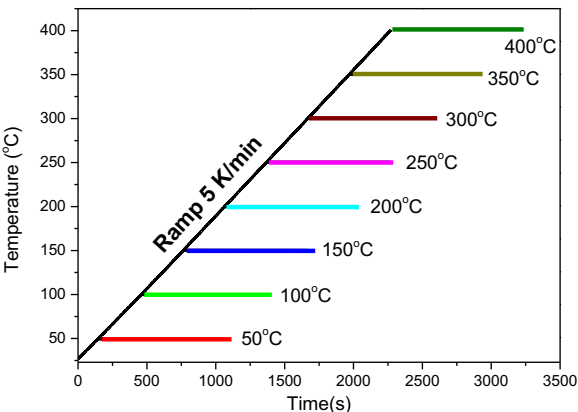


SPB 4: Production of reference coatings 2021-2022:

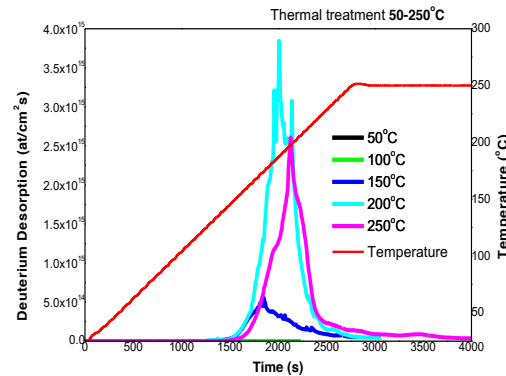
Be-based reference coatings:

- Be with D and H ~20%, 5 microns thick – 110 samples in total, thermally treated
- Be 20 microns layer, no gas; R.T. and 200 C during deposition: 12 Samples

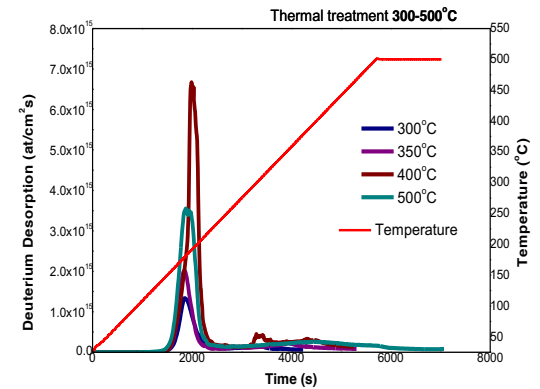
Thermal treatment and TDS Results:



Thermal Treatment operation for Be-D and Be-H sample



Deuterium release from Be-D layers on W substrates



Deuterium release from Be-D layers on tungsten substrates

XRD, TDS, SEM measurements were performed in order to have preliminary information on samples structure and morphology.

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- 4. June 2022**: Be+D (10 D at%) 4 different temperatures: - 44 samples.

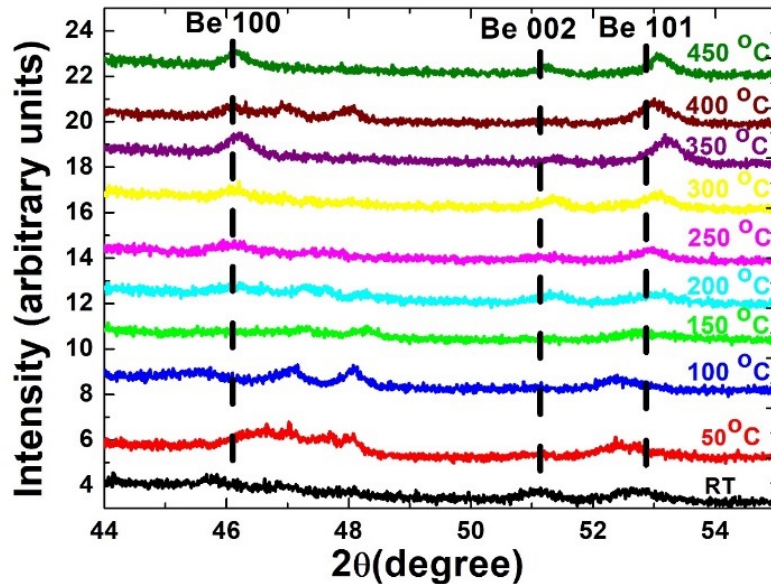
All the samples were shipped, analysis finished.

SPB 4: Production of Be reference coatings:

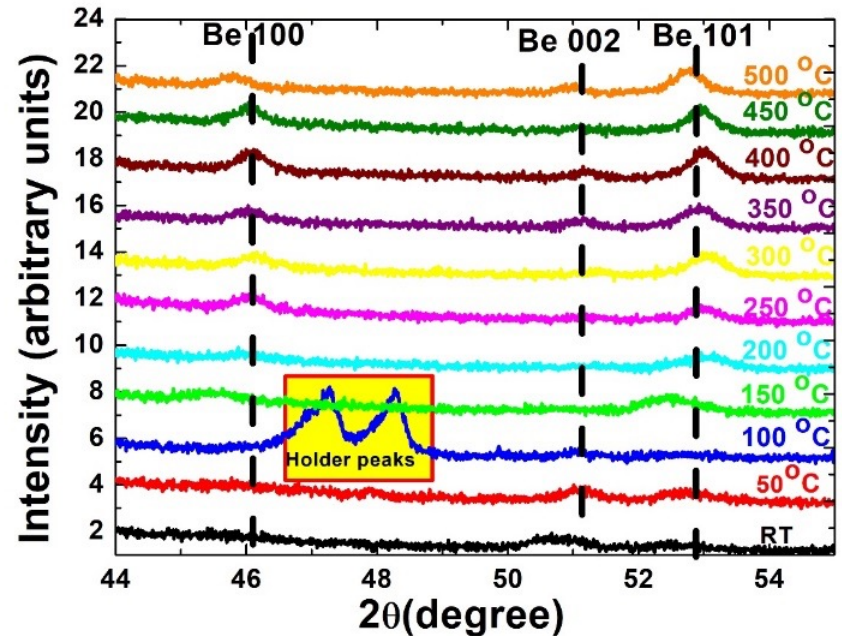


Be with D and H ~20%, 5 microns thick – 110 samples in total, thermally treated

XRD measurements



Be-D diffraction curves



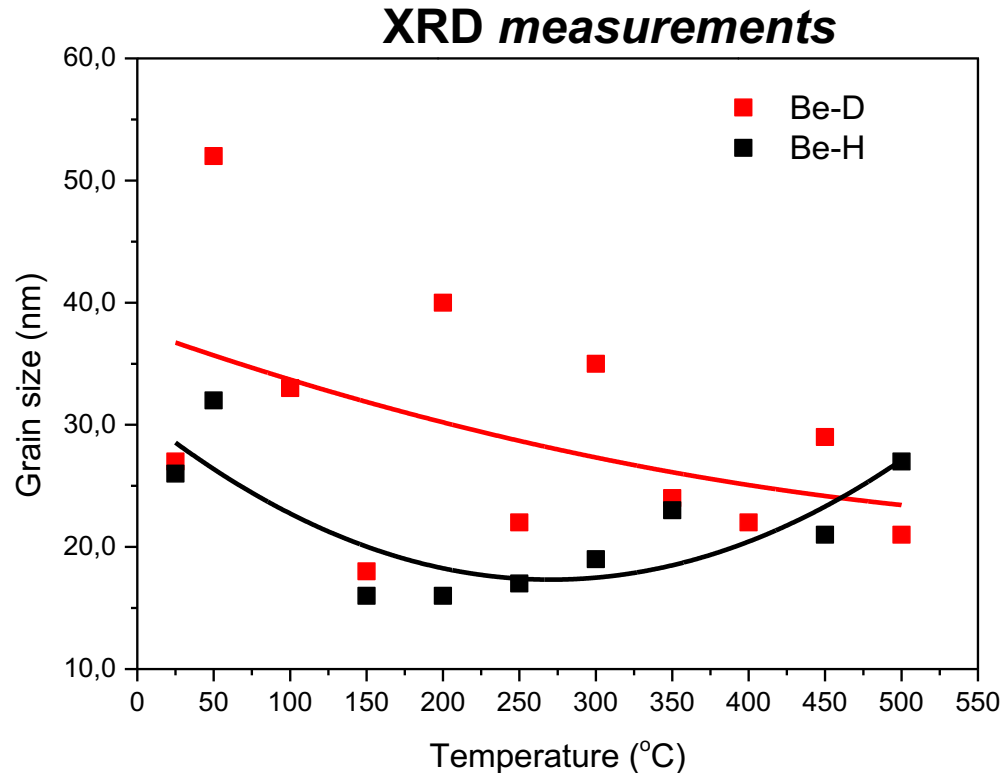
Be-H diffraction curves

- Shift (0.4°) of the 101 peak \rightarrow higher angles for T. T. samples $> 300^\circ\text{C}$. \Rightarrow Tensile stress
- Source of the tensile stress \Rightarrow coating process, released during the T. T..
- Grainsize: 18 to 52 nm with a decrease with T. T. temperature increase. Exception at 50°C for Be-D sample.
- Corroborates with Raman measurements

SPB 4: Production of Be reference coatings:



Be with D and H ~20%, 5 microns thick – 110 samples in total, thermally treated



Grain size variation extracted from the Be-D and Be-H diffraction curves

- Shift (0.4°) of the 101 peak \rightarrow higher angles for T. T. samples $> 300^\circ\text{C}$. \Rightarrow Tensile stress
- Source of the tensile stress \Rightarrow coating process, released during the T. T..
- Grainsize: 18 to 52 nm with a decrease with T. T. temperature increase. Exception at 50°C for Be-D sample.
- Corroborates with Raman measurements done

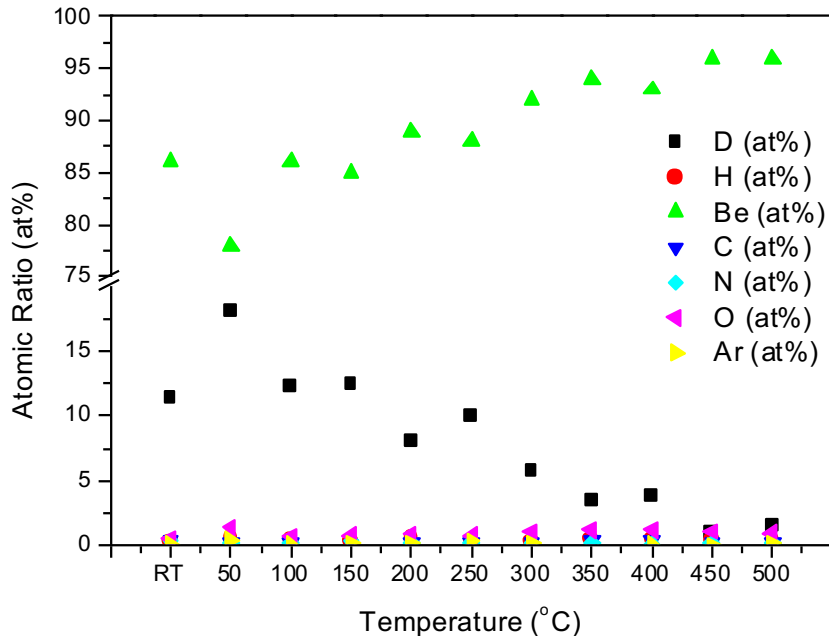
SPB 4: Production of Be reference coatings:



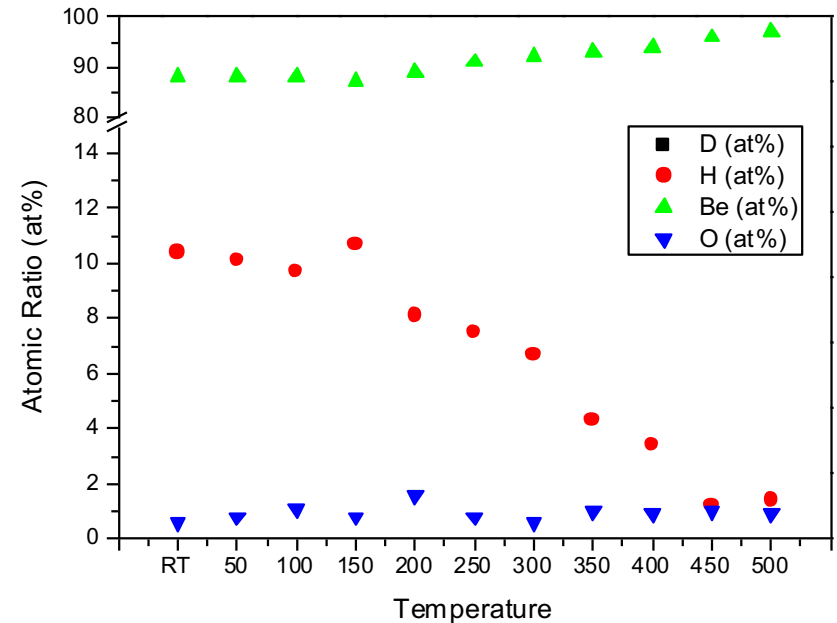
Be with D and H ~20%, 5 microns thick – 110 samples in total, thermally treated

HIERDA measurements

Performed at RBI (Many thanks to Iva Bogdabovici)



Be-D diffraction curves and depth profiles from HIERDA



Be-H depth profiles from HIERDA

- D or H ratio drop with the T. T. temperature
- Oxygen below 1 %
- ~10 % H isotope at room temperature
- No other impurities => High quality confirmation of the coatings

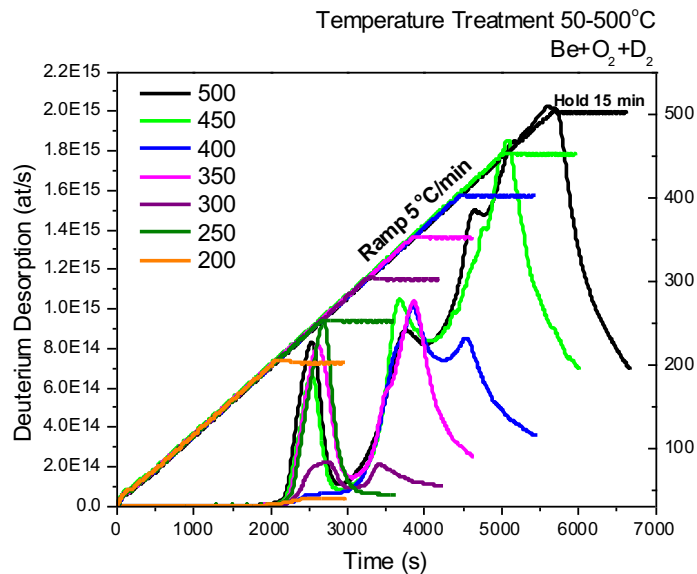


SPB 4: Production of Be reference coatings:

Samples produced in 2023

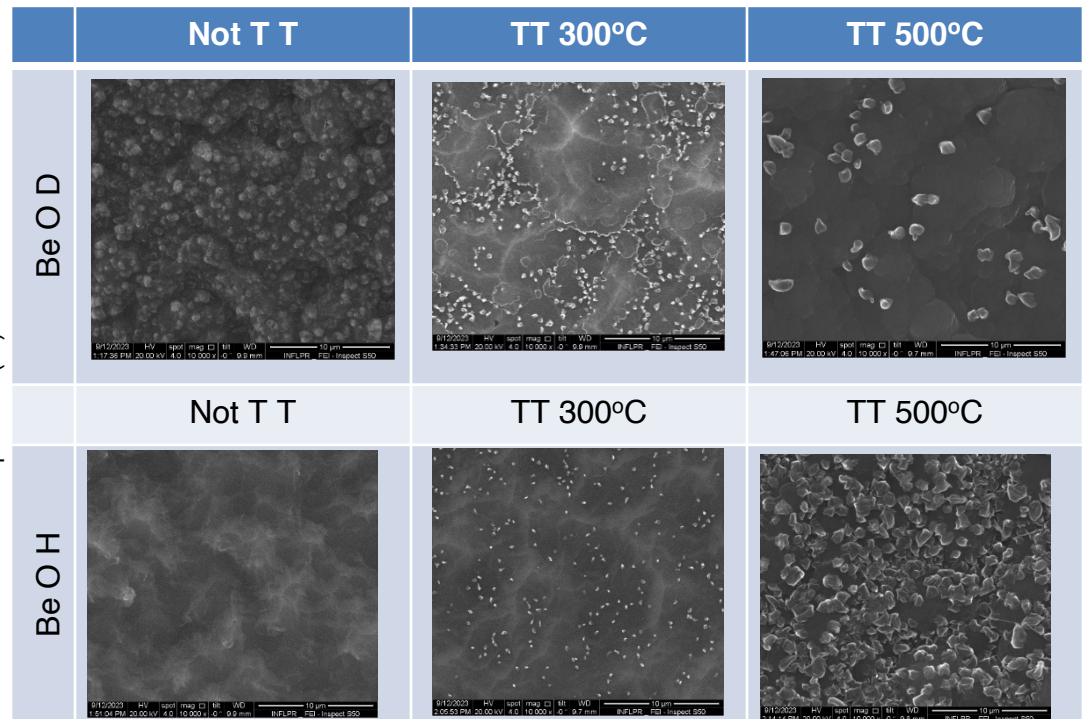
- 1. May 2022:** Be+O+H – 186 samples; **May 2022:** Be+O+D - 186 samples
- 2. June 2023** – Thermal treatment up to 500°C, 50°C step, 15 minutes hold
XRD, TDS, SEM measurements were performed in order to have preliminary information on samples structure and morphology.

Thermal treatment and TDS during the treatment



Thermal Treatment operation for Be-O- D samples

SEM images aquired after the thermal treatment



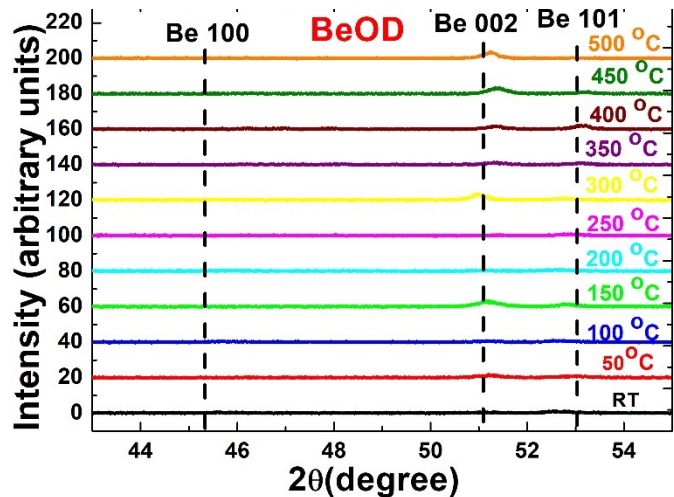
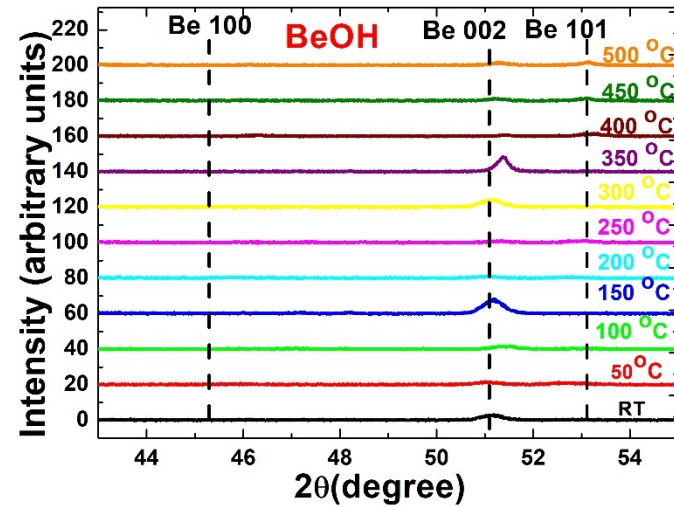
Grain formation starts at 250°C. More intense for H containing BeO layers



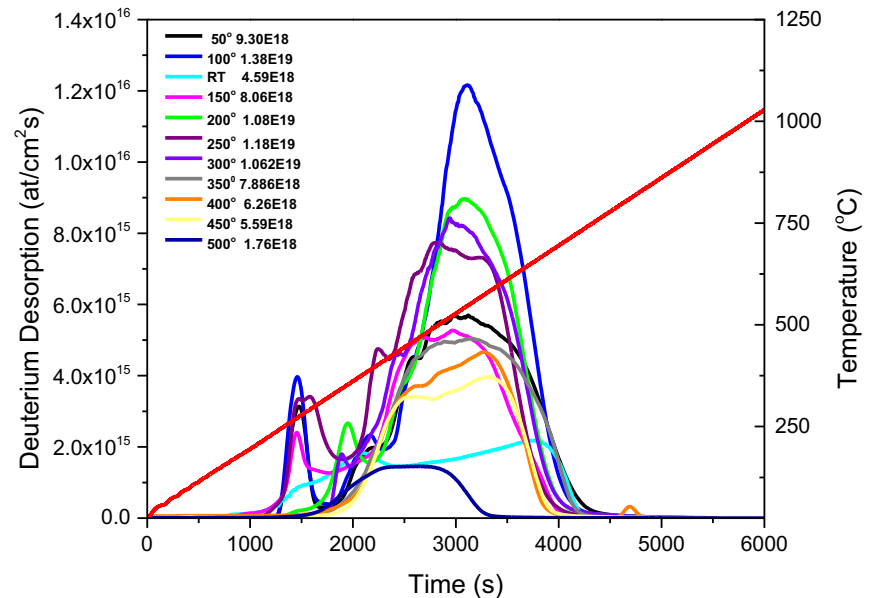
SPB 4: Production of Be reference coatings:

XRD and TDS results

XRD was performed on all types of samples as presented below.



TDS measurements finished



XRD and TDS data are available and interpreted.

A comparison between no O containing samples from 2022 and the ones just produced **is necessary** and will be performed.



Samples requirements for PWIE SP B 4 and production status:

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5. **July 2023:** Be O D and Be O H, ~20%, 5 microns thick – 192 samples in total, thermally treated

Pre-characterization before sample delivery:

XRD, TDS, SEM measurements were performed in order to have preliminary information on samples structure and morphology.

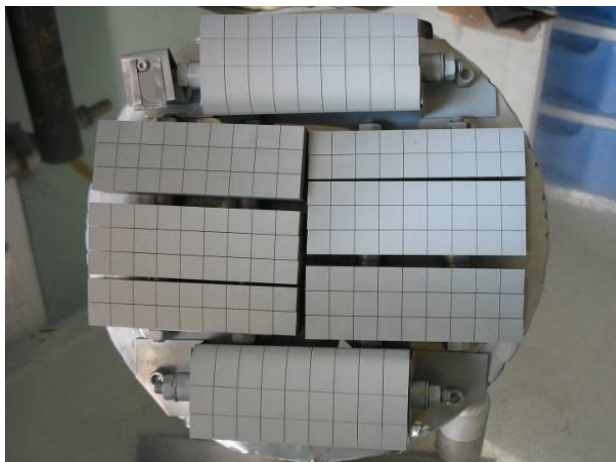
Alongside with IBA and Raman – measurements certified the samples high quality

Consistent database on D retention and release for Be containing co-deposited layers

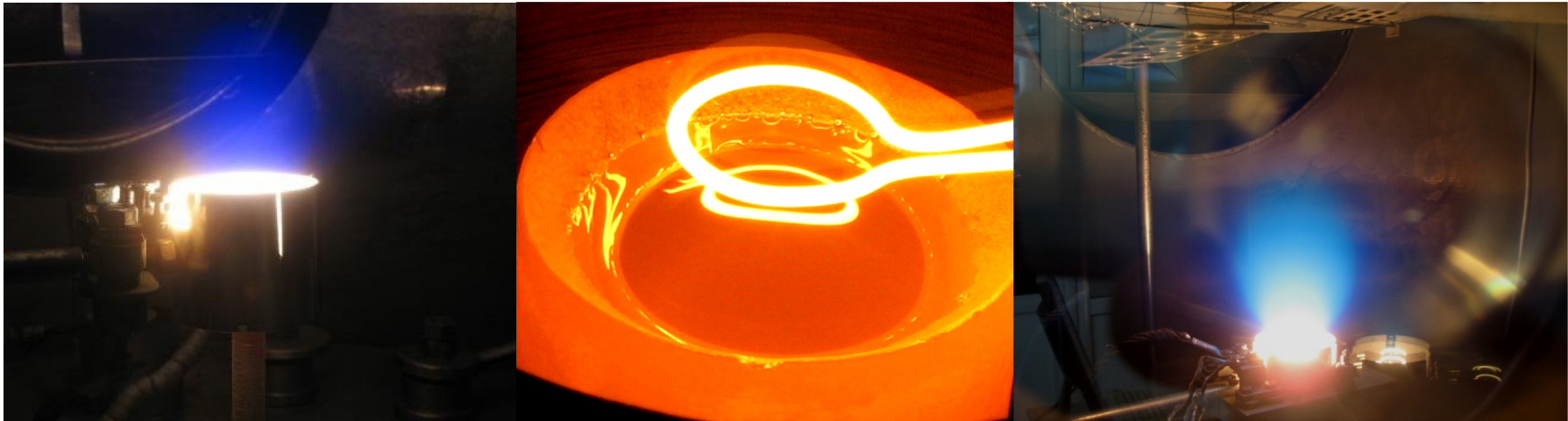
We need to include results on 2023 samples : thermal treated O containing BeD and BeH layers. We are collecting data.

Discussions are underway to resolve some results discrepancies.

From Be/D to B/D and T experiments

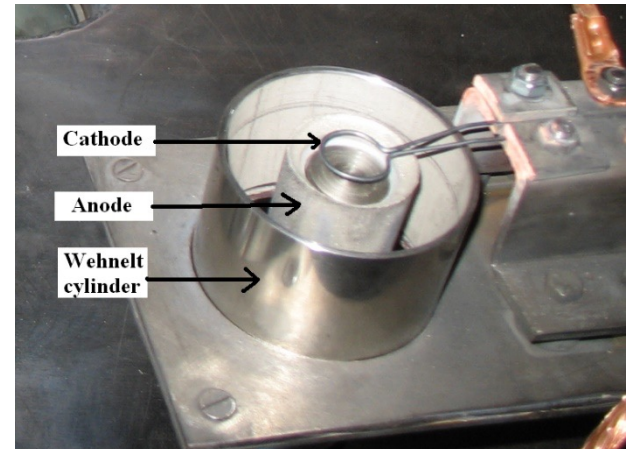


From Be/D to B/D and T experiments

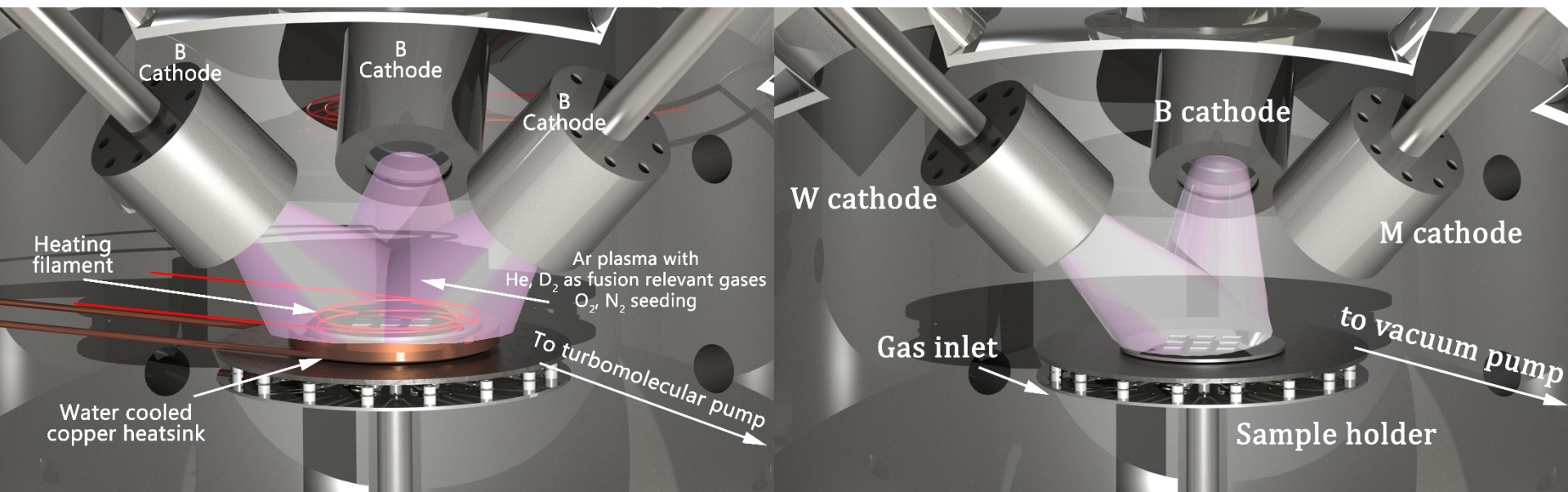


Boron coatings were successfully performed in the past (2009). Pure 50 microns layers

**5 microns more realistic maximum thickness target
Suitable for large coating surfaces (up to 600mm diameter).**



From Be/D to B/D and T experiments



*Schematic description of the coating system used for **B**-D (H, O)) layer deposition*

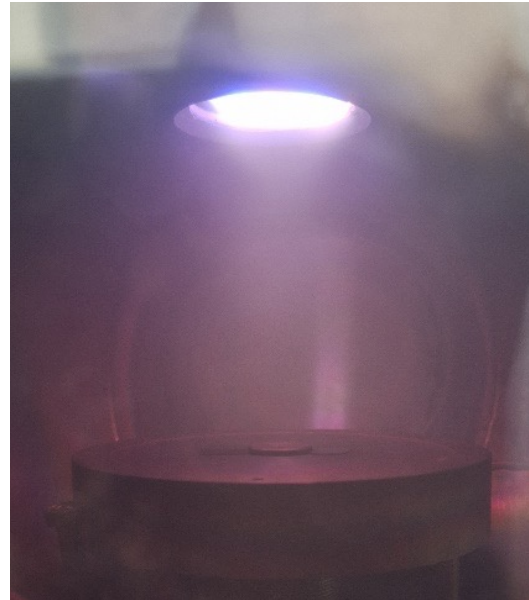
*Deposition system used for obtaining **B** (-C, W, etc.)-D/H/O/etc layers*



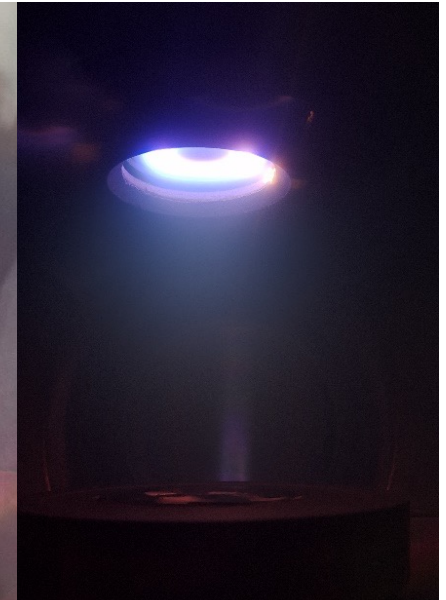
Sample Preparation

- Boron target
- Ar+D₂ mixt gas
- Magnetron sputtering in radio frequency mode
- Desired thickness of 500 nm
- Working parameter varied:
 - Pressure
 - Gas flow
 - Substrates temperature
 - BIAS voltage applied on substrates

RF MS plasma



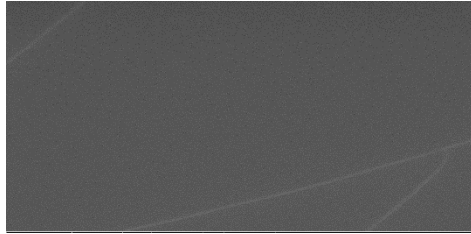
HiPIMS plasma



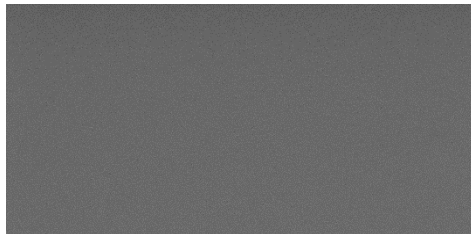


SEM Measurements

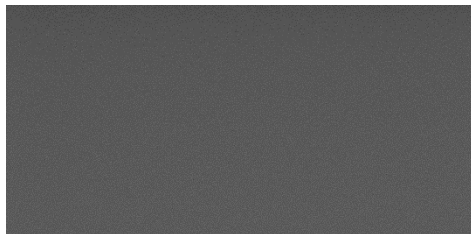
● Deuterium flux variation:



a. Ar:D=5:1

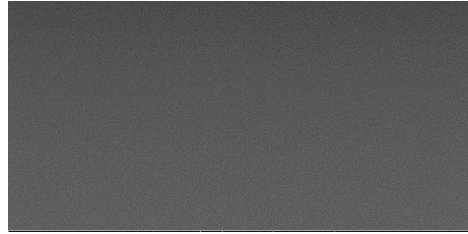


b. Ar:D=2:1

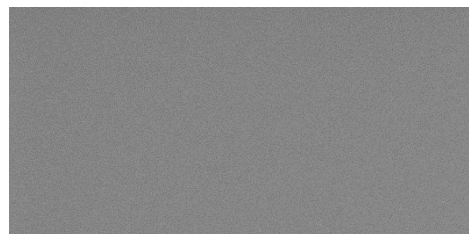


c. Ar:D=1:1

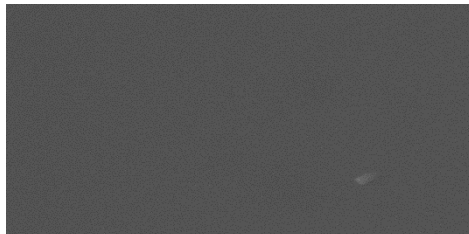
● Pressure variation:



a. $8 \cdot 10^{-3}$ mbar

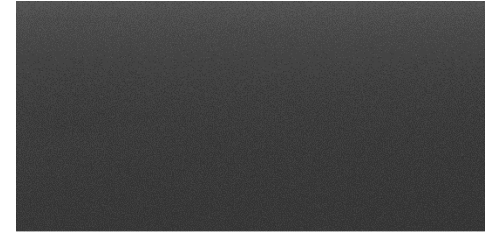


b. $3 \cdot 10^{-2}$ mbar

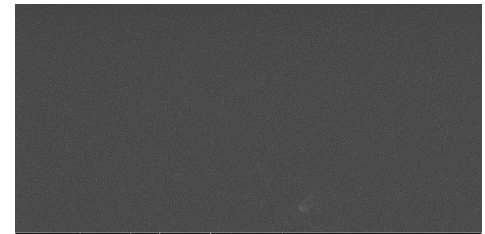


c. $8 \cdot 10^{-2}$ mbar

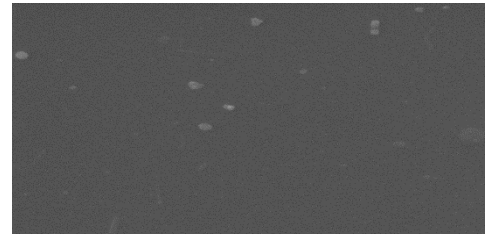
● BIAS applied on substrates variation:



a. 30V



b. 60V



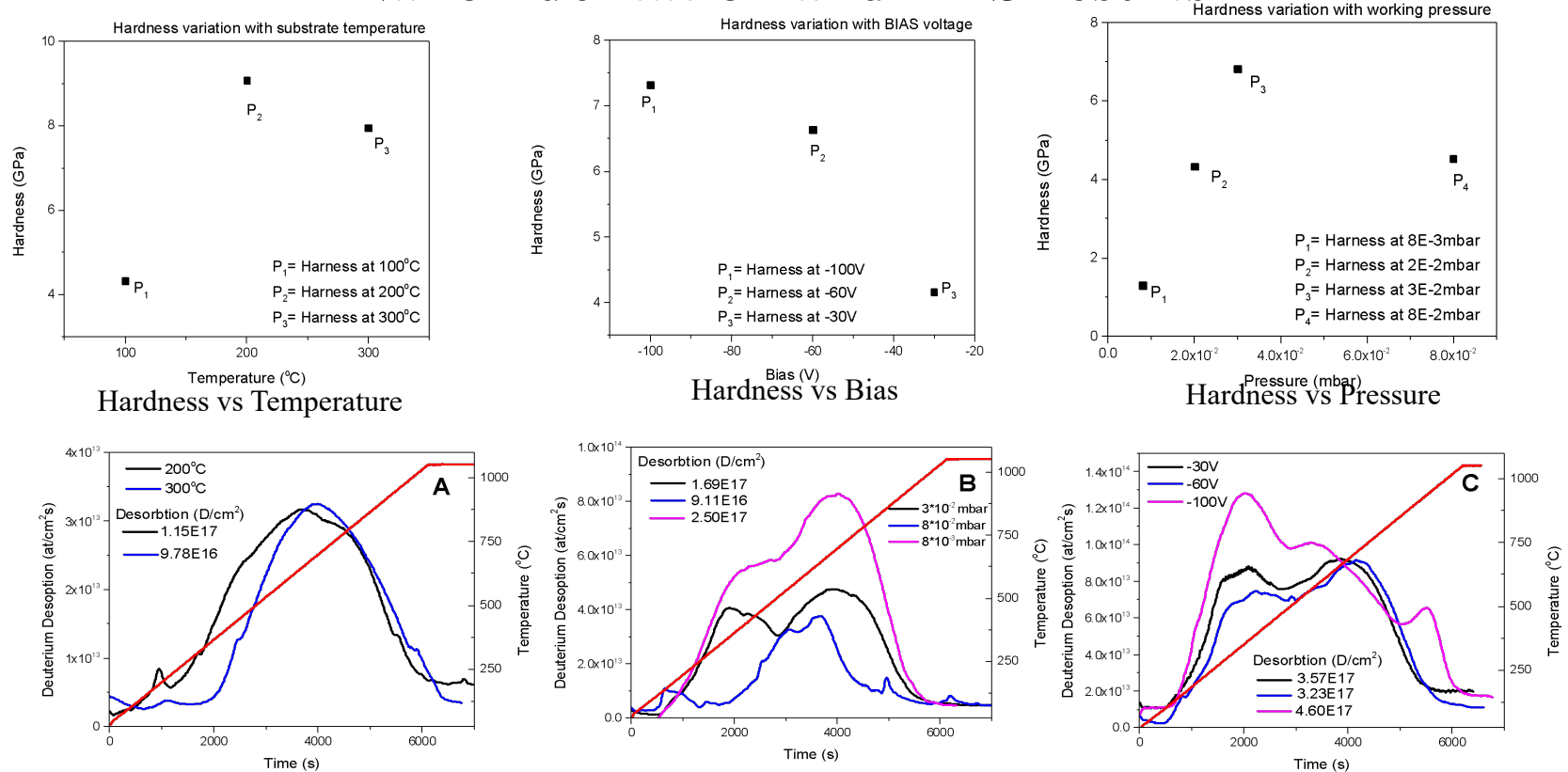
c. 100V

Prospects for studying B layers – Preliminary results

Deuterium release behavior from B-D layers in varying working conditions



Nanoindentation and TDS results



- We performed the study on 500nm B-D co-deposited layers by RF - MS.
- SEM images shows that the sample surface is free of roughness.
- Hardness is affected by the deposition condition. The highest value (9GPa) was obtained at the temperature of 200°C.
- TDS measurements determined a strong relationship between deposition conditions and the total amount of deuterium released from the samples.

Prospects for studying B layers – Preliminary results



Deuterium release behavior from B-D layers in varying working conditions

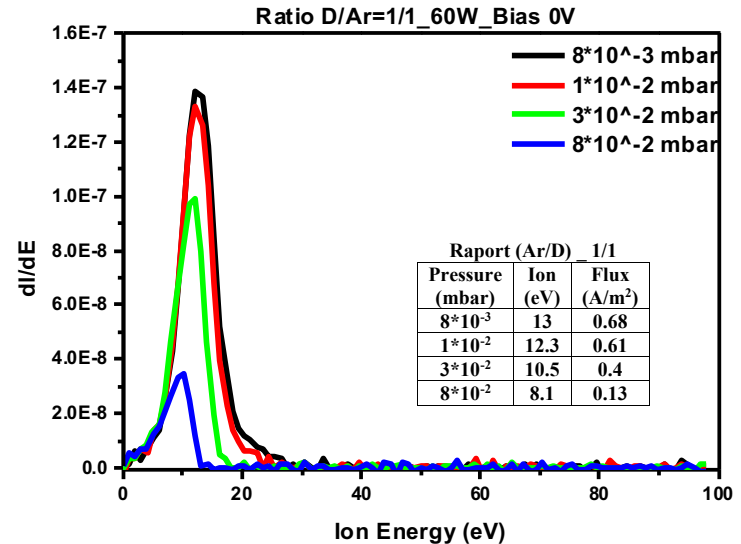
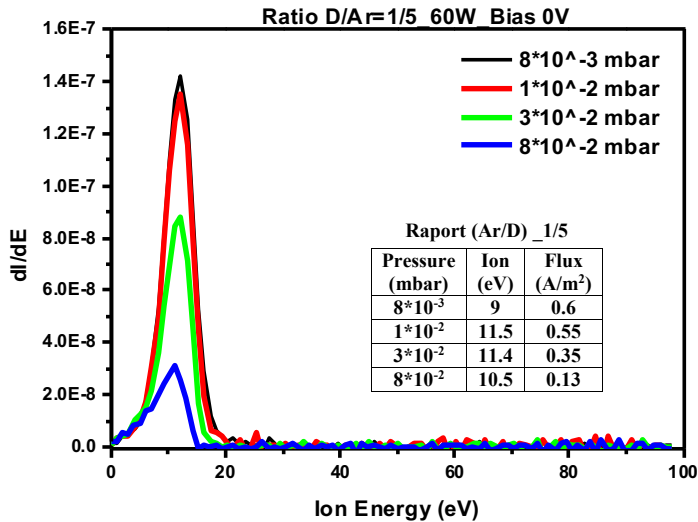
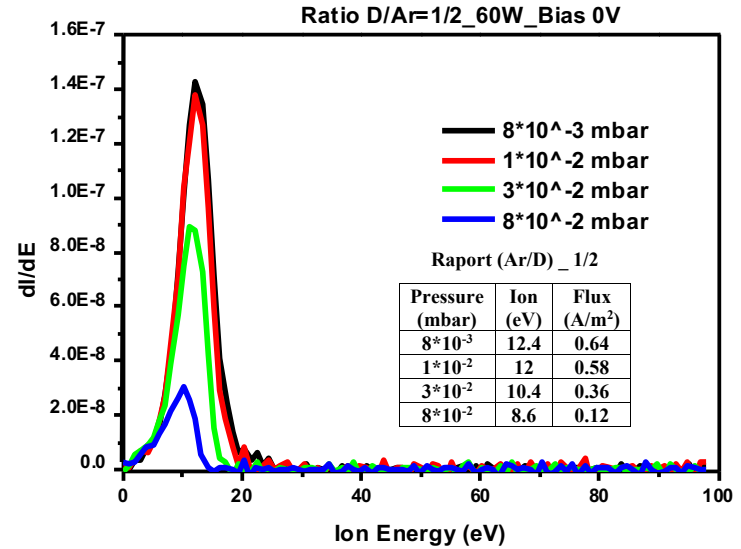
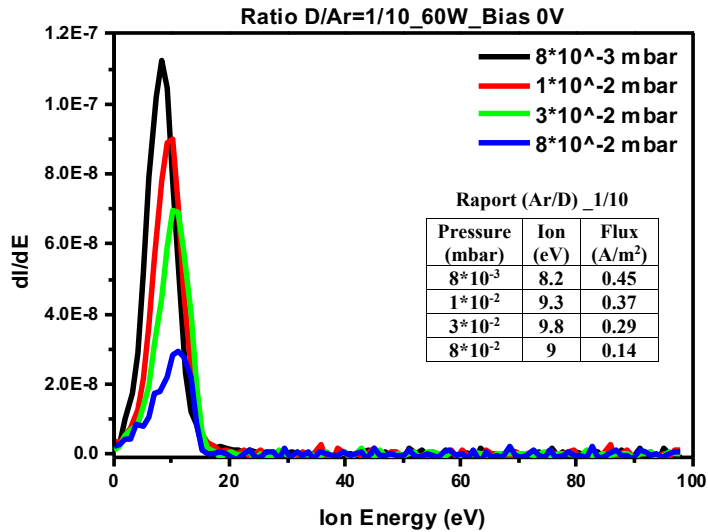
Deuterium trapped inside the samples during the coating process

Deposition Conditions	D ₂ :Ar (ratio)	Pressure (mbar)	Temperature (°C)	Bias (V)	D ratio normalized to the dimension and cross
D ₂ :Ar (ratio)	1:10	1x10 ⁻²	Room Temperature	0V	4,1%
	1:5				-
	1:2				4,76%
	1:1				8,59%
Pressure (mbar)	1:1	8x10 ⁻³	Room Temperature	0V	3%
		3x10 ⁻²			4%
		8x10 ⁻²			1,4%
Temperature (°C)	1:1	1x10 ⁻²	200°C	0V	1,74%
			300°C		1,8%
Bias (V)	1:1	1x10 ⁻²	Room Temperature	-30V	3,88%
				-60V	4,94%
				-100V	6,61%

Ion energy measurements for B-Ar-D MS plasma



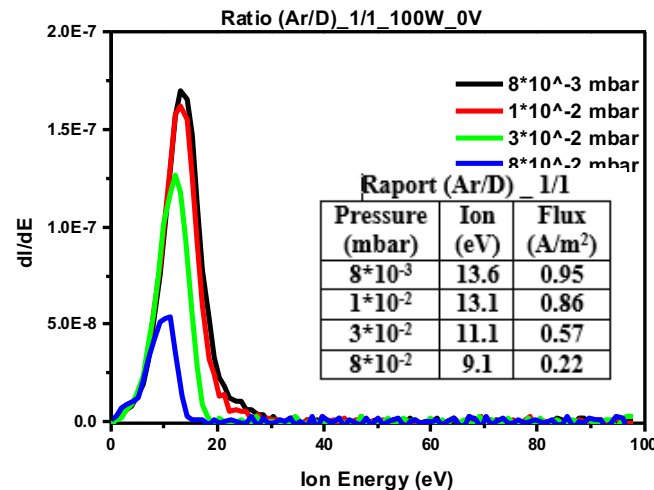
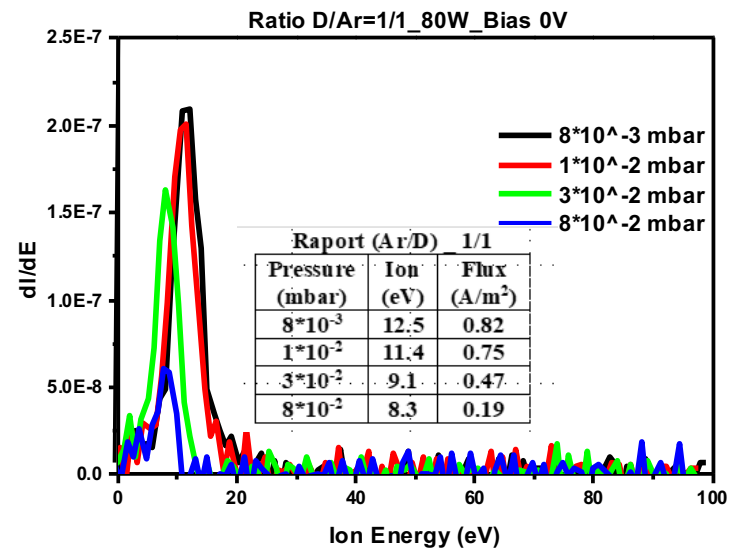
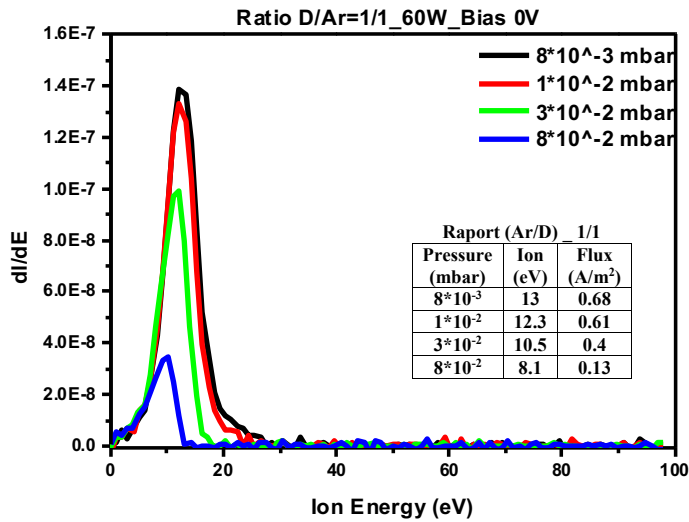
B+Ar+D, P=60W, D:Ar=from 1/10 to 1/1, pressure varied



Ion energy measurements for B-Ar-D MS plasma



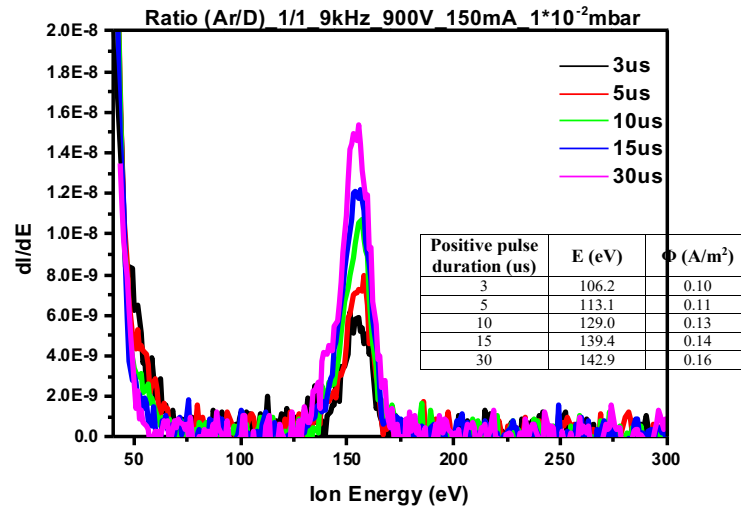
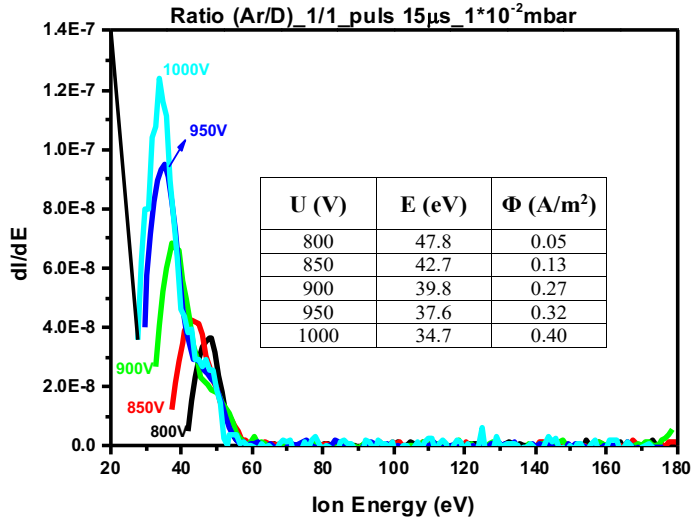
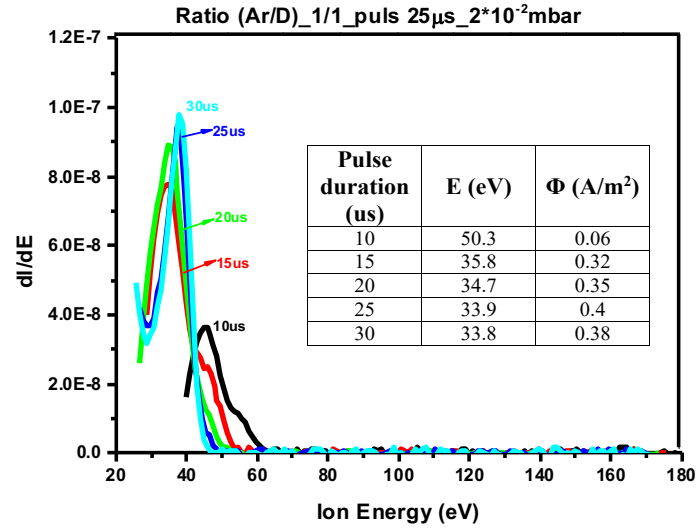
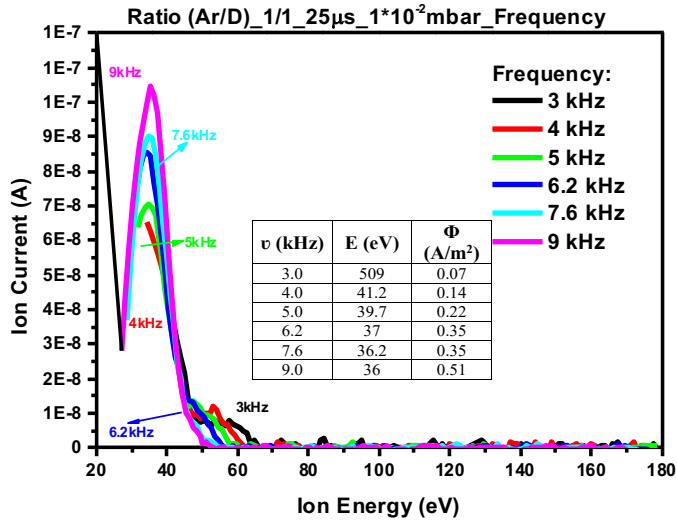
B+Ar+D, P=30, 60, 100 W, D:Ar=from 1/10 to 1/1, pressure varried



Ion energy measurements for B-Ar-D MS plasma



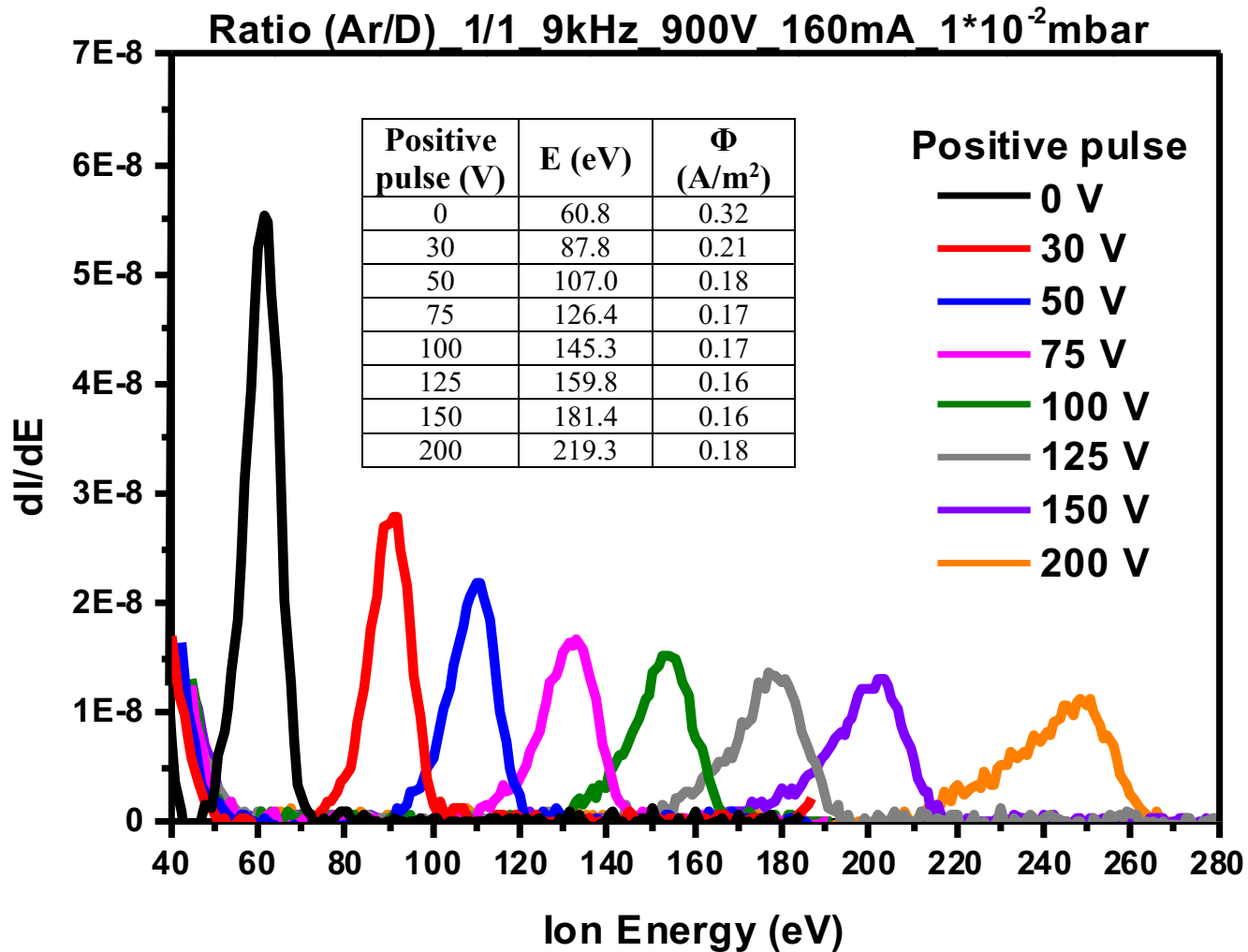
B+Ar+D, Ar/D: 1/1, HiPIMS MP, Frequency varried



Ion energy measurements for B-Ar-D MS plasma



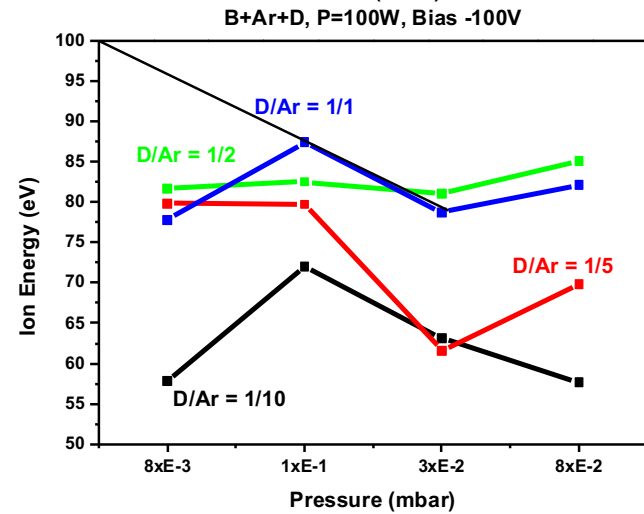
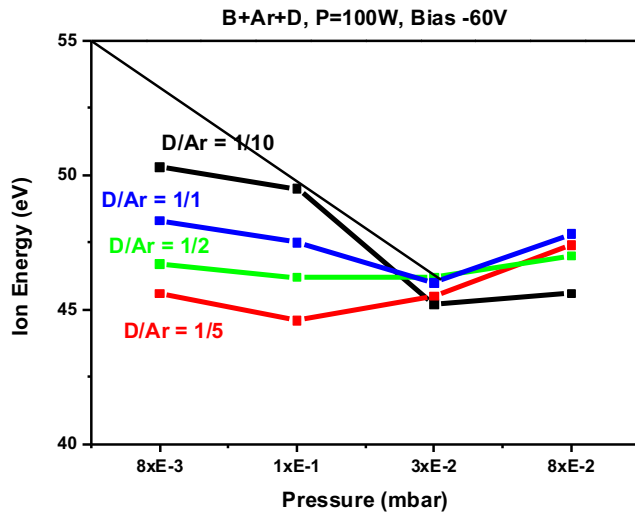
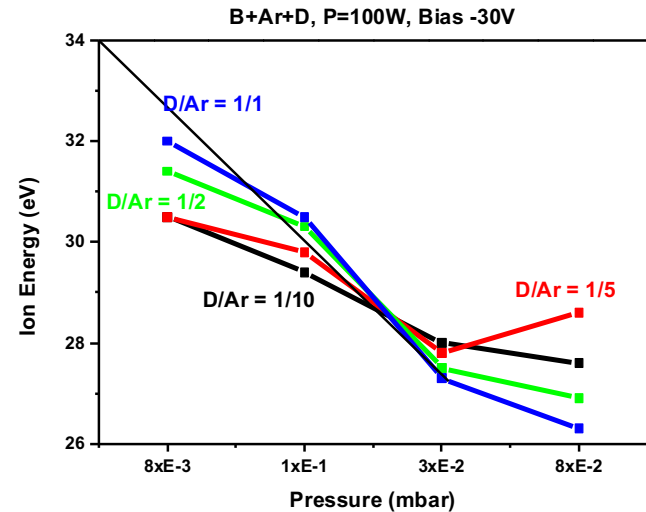
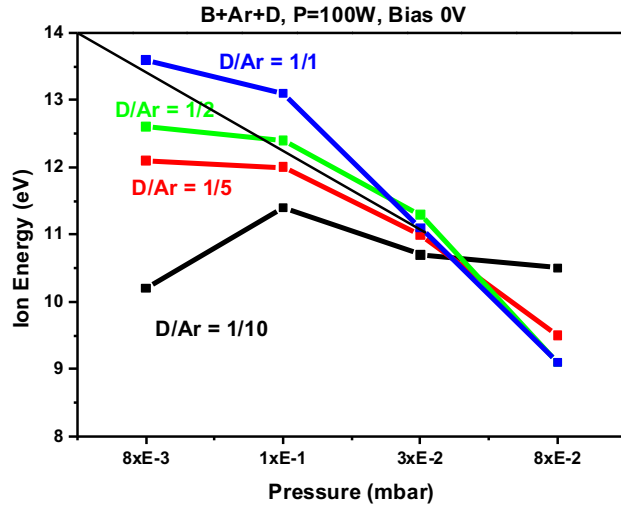
B+Ar+D, Ar/D: 1/1, $p=1 \times 10^{-2}$, HiPIMS BP, Positive pulse varied



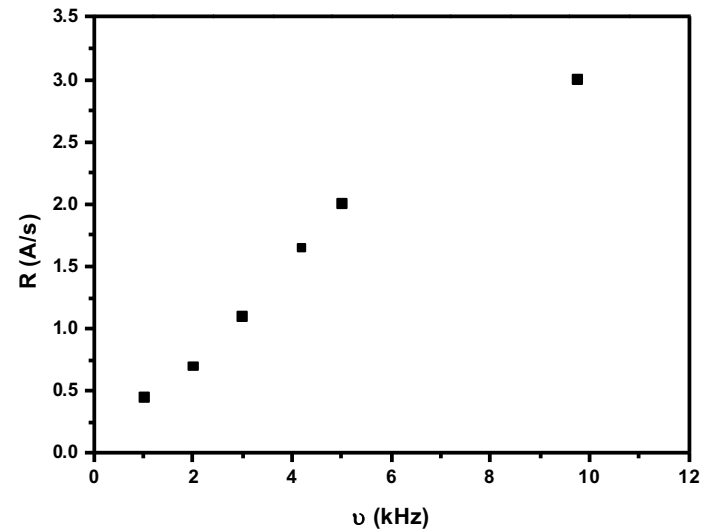
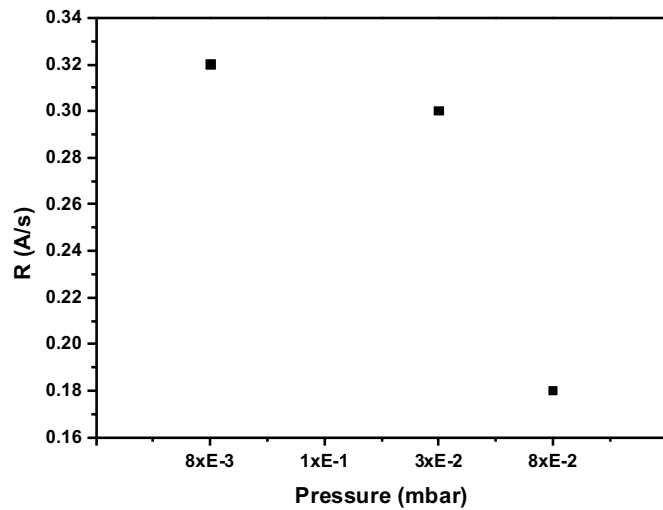
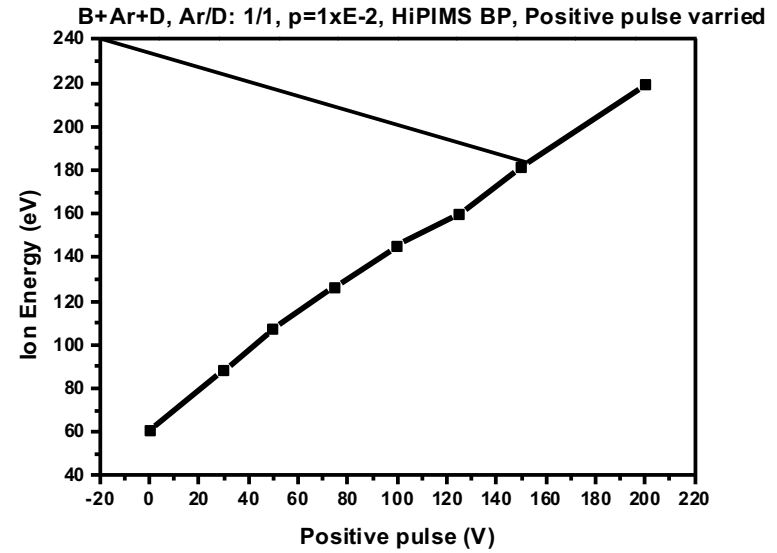
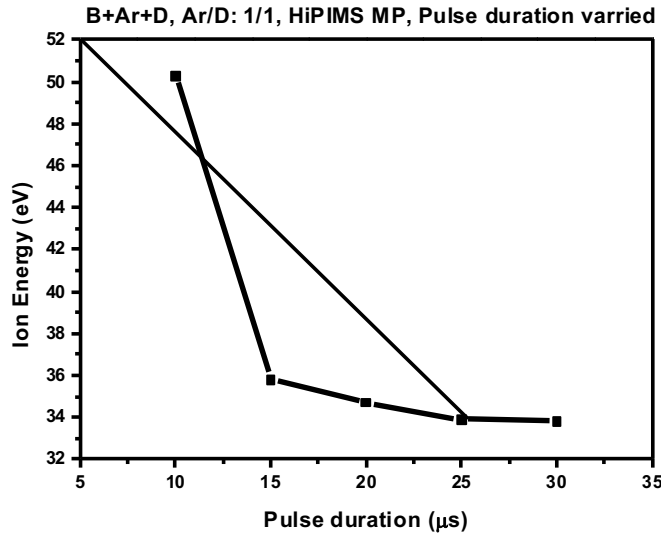
Ion energy measurements for B-Ar-D MS plasma



RF B+Ar+D plasma , P=100W



Ion energy and deposition rate measurements for B-Ar-D MS plasma





Workplan for production of B layers

- ✓ Repeat the exercise [performed with CEA in 2022 and 2023](#):
 - **2024**: BD and BH with high H and D content (more than 10%), thermally treated from 50 to 500°C
 - **2025**: Oxygen addition to the same set of samples
- ✓ Samples for [permeation studies under SP C](#) as follows:
 - **2024**: different thickness samples 500 to 5000 nm, pure B
 - **2025**: gaseous inclusions of the types of samples
- ✓ For micromechanical measurements and water exposure to check the [delamination behavior of B surface layers exposed to boiling water](#)
 - **2024**: B-coated W substrates, 12×15×1 mm³, 5 μm, dense and porous
 - **2025**: boron with D 10 % of 10×10×1 mm³ samples
- ✓ **Additionally**: B+W (pure and D doped) composite coatings for [re-deposition studies](#)
- ✓ Analysis of the produced coatings using **SEM, TDS, XRD, Sputtered XPS and nanoindentation**

Deliverables:

Database of **B** containing deposited layers; **D/B ratio** versus plasma conditions. **Fuel removal efficiency** assessment on boron containing layers.

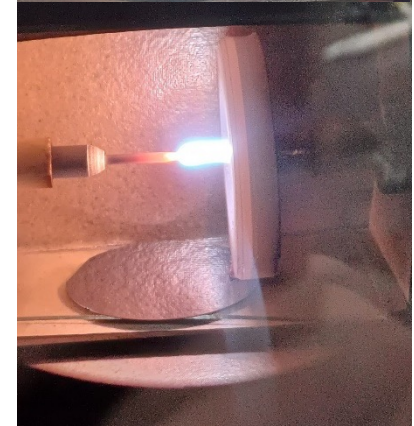
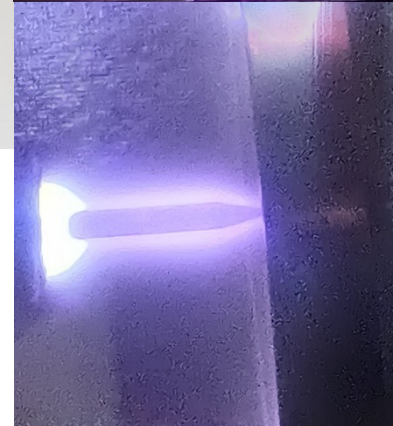
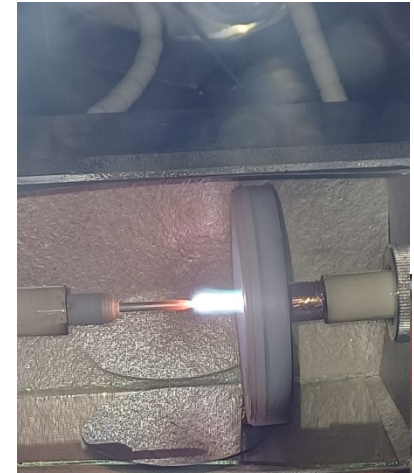
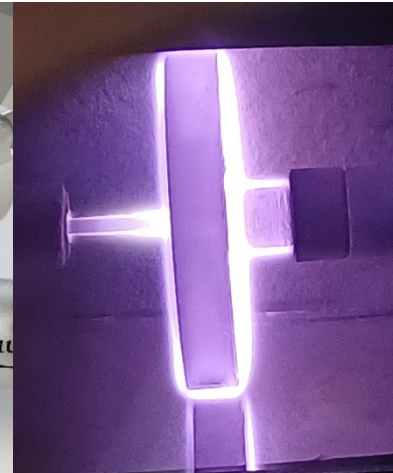
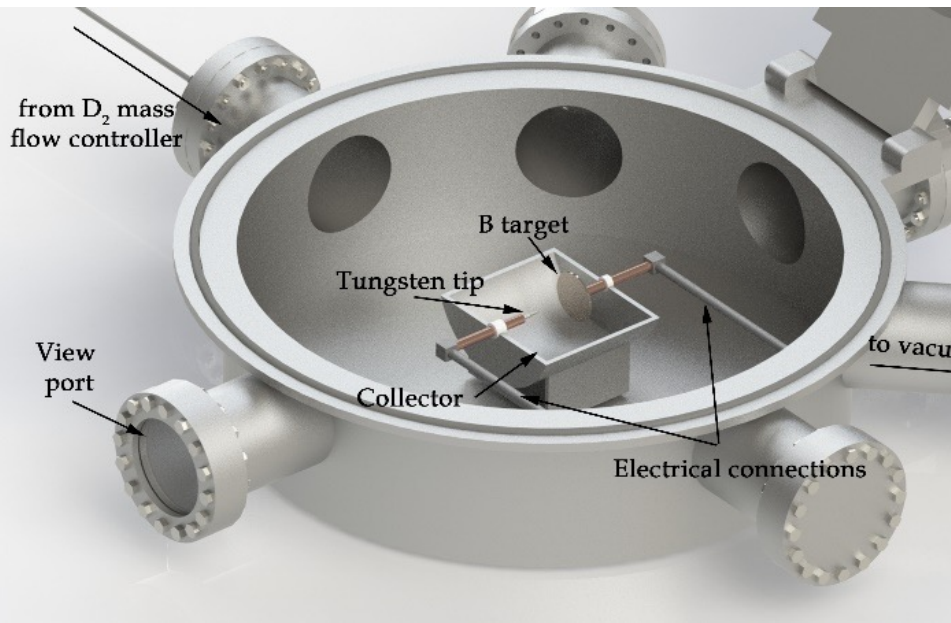
Samples to be produced for any other experiments suggested by laboratories.



SPB 4: Production of B samples for lab experiments

Glow discharge

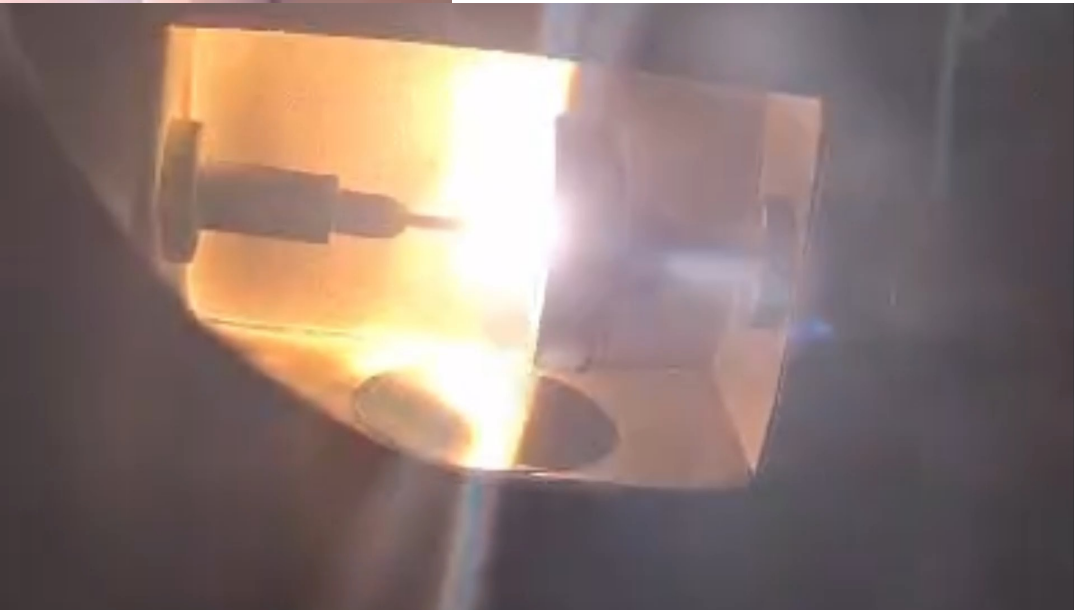
Aching discharge



Apparatus: a DC / pulsed reactor working in deuterium or H₂/D₂ mixture gas. Addition of water and air will be performed.
An arc discharge was ignited between a 1 inch B plate and a W tip.



Arching – No B collected



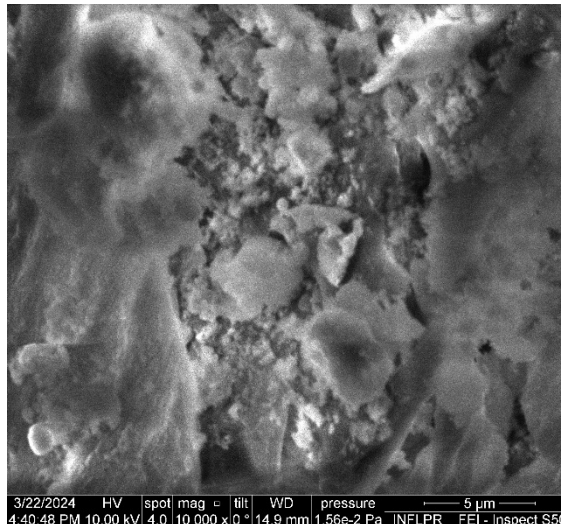
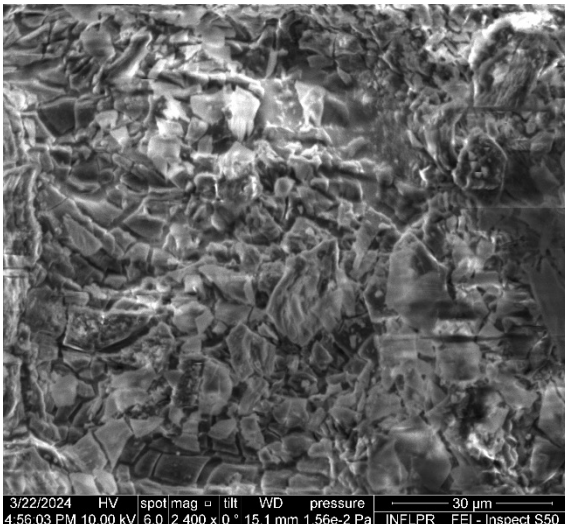
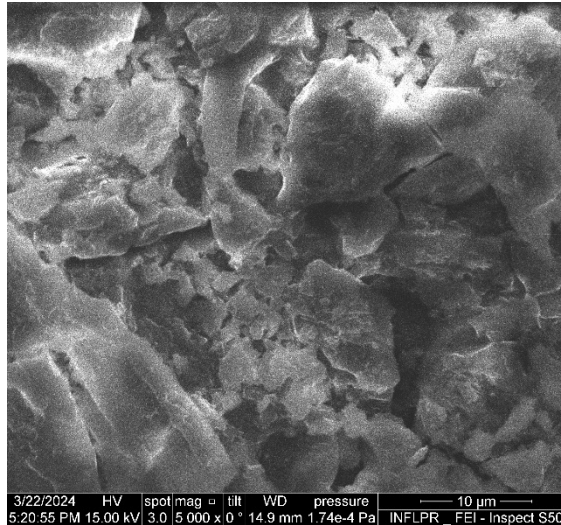
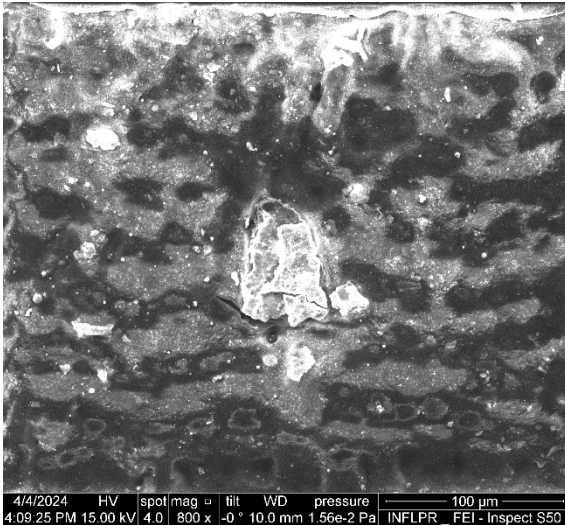
Arching – B collected
See the droplets



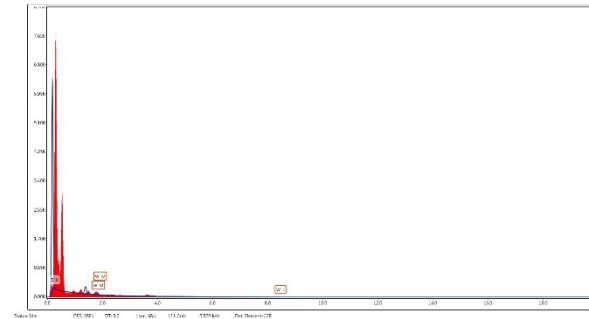


SPB 4: Production of B samples for lab experiments

Boron particles produced by arching



EDS shows W as the only “impurity” (W tip)



Several dimensions and shapes
Very large amount of B present
Parametric study in terms of productivity rate vs pressure, discharge parameters, gasses used, etc.
will be performed in 2024



Workplan for dust

- ✓ Investigations of **B dust production using the plasma-arc device**
 - **2024:** systematic study on B dust particle formation and size with the arc parameters
 - **Productivity rate vs. pressure, electric parameters, gasses used, etc.**
 - **2025:** extend the studies to dust with gaseous addition (air leak and water vapors)
 - Characterization using SEM, TDS, XPS → **calling for XRD collaboration**
- ✓ Investigations of B/W mixed and pure W **dust production using the plasma-arc device**
 - **2024:** B/W mixture particle formation by usage of pure B or B/W composite coating on W substrate, as well as W dust production by plasma arching.
 - **2025:** extend the studies to dust with gaseous addition (D, He, etc, air leak and water vapors)
 - Characterization using SEM, TDS, XPS → **calling for XRD collaboration**



Sample production capabilities

- TVA – up to 3 plasma sources, low gas amount intake – best for pure layers – 5-5000nm
- MS (DC, RF, HiPIMS, BP HiPIMS) – up to 7 magnetrons at once, up to 3 gasses intake - 5-5000nm
- Post coating plasma exposure – GD, Plasma torch, etc.
- T facility – experiments and sample handling from July 2024

Pure B, B/D, B/W/D, different gaseous addition, several parameters variation (T, P, ion energy, thickness, gas fluxes, discharge type)

Characterisation: SEM/EDS, XRD, XPS, TDS, T surface monitoring, nanoindentation, XPS

- LIBS/LIA QMS – first tryouts on B/D codeposits successful.
- Linear plasma device with in-situ LIBS – from late 2025

Sample preparation facility already fully equipped for boron containing coatings. Tritium facility included inside the current BeHF can be used for boron. Preliminary data available for capability demonstration

Prospects for studying B layers capabilities – Proposal of an experimental plan - Example and ideas



Typical pure B layers – 100nm or more

- characterisation and ready for implantation
- interphase study (B unstable at B-W interface)
- plasma torch exposed (various parameters)- TDS
- tritiation - TDS

Codeposited B-D layers

- different thicknesses, temperatures, pressures, plasma type etc,

Repeat the exercise with other more complicated systems (W, C, O, He, Ne, N intake)

Work plan has to be established by SP Leaders under SPB, SPC, SP D, SPX and SPF3 since the need of a *“database of artificial B layers for physics studies: stability, fuel content, and release”*

Collaboration with CEA

Etienne HODILLE

- Corroboration of TDS and diffusion reactions – MHIMS code – understand the D retention in B – PhD Student from Romania

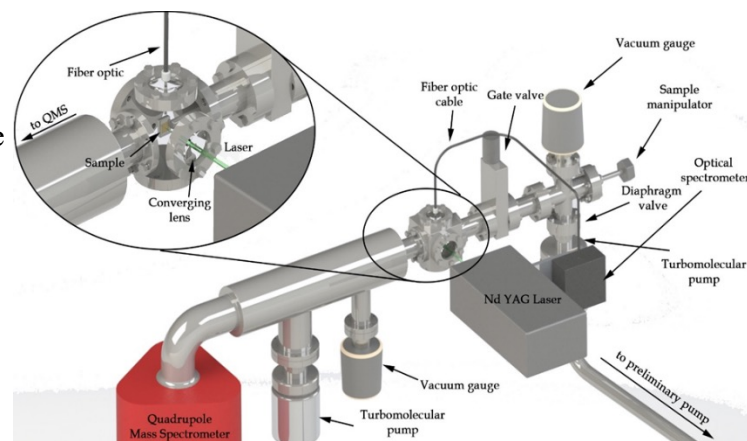
SPB 4: Production of B samples for lab experiments



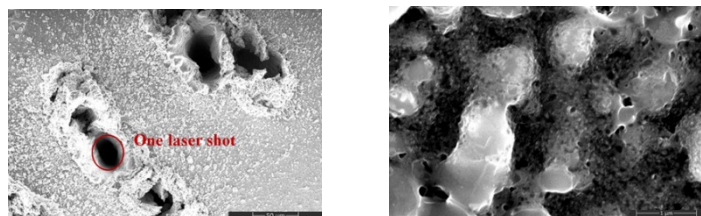
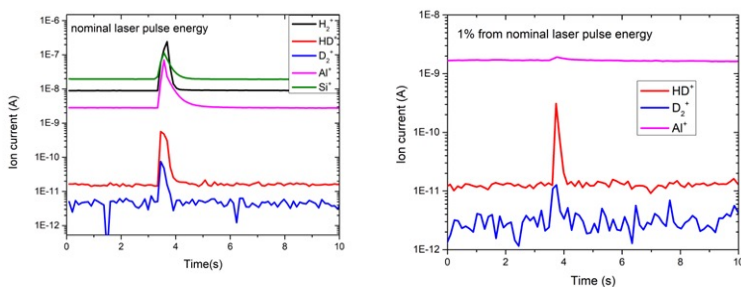
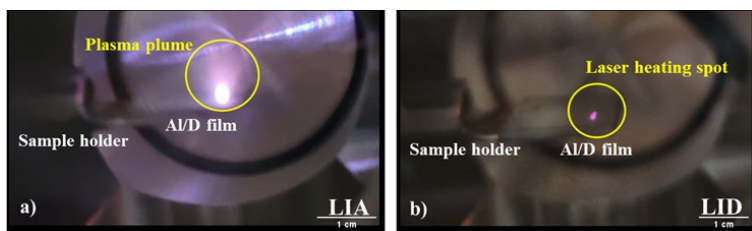
Other experimental capabilities

H isotopes release measurements LIBS, LIA-QMS and LID-QMS

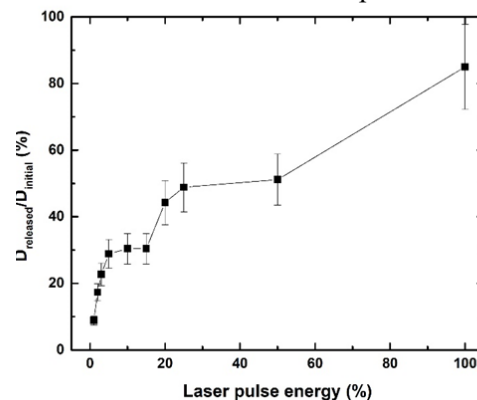
- Q-switched laser / 1 kHz / wavelengths of 1053 nm/ pulse duration: 10 ± 3 ns, the nominal pulse energy - 350 μ J, and nominal laser fluence was around 84×10^{-4} J/cm².
- QMS and OES simultaneously measurements.
- LIA-QMS and LID-QMS calibration was performed for D₂
- Cross correlation between TDS and LIDS/LIBS



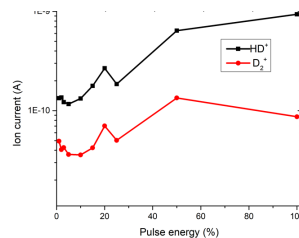
Experimental setup for LIA and LID analysis by QMS and OES.



- LIA 100 % from nominal laser pulse energy.
- LID 1 % from nominal laser pulse energy.



9 % efficiency for D release by LID process and 85 % efficiency for D release by LIA process considering that TDS has 100% efficiency



The HD⁺ and D₂⁺ ion currents dependence on laser pulse energy

Spectrochimica Acta Part B: Atomic Spectroscopy 206 (2023) 106774



Considerations on hydrogen isotopes release from thin films by laser induced ablation and laser induced desorption techniques

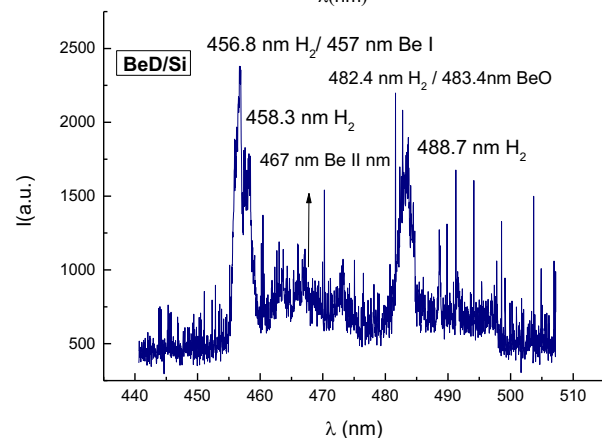
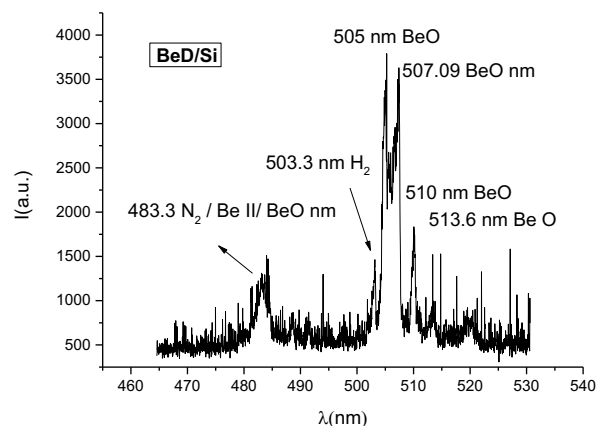
Sasa-Alexandra Yehia-Alexe ^{a,b}, Andreea Groza ^{a,†}, Mihai Serbanescu ^a, Maria Elena Zarif ^{a,c}, Bogdan Bita ^{a,b}, Paul Dinca ^a, Bogdan Butoi ^a, Corneliu Staicu ^{a,b}, Corneliu Porosnicu ^a





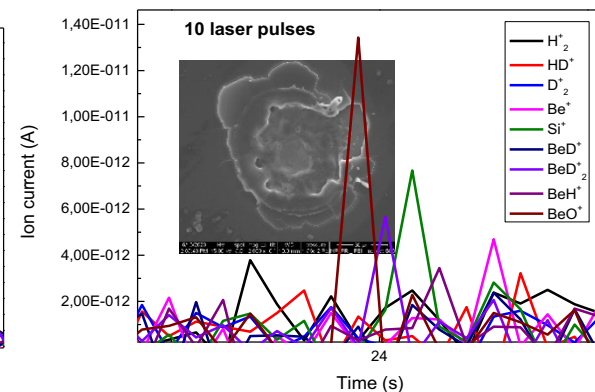
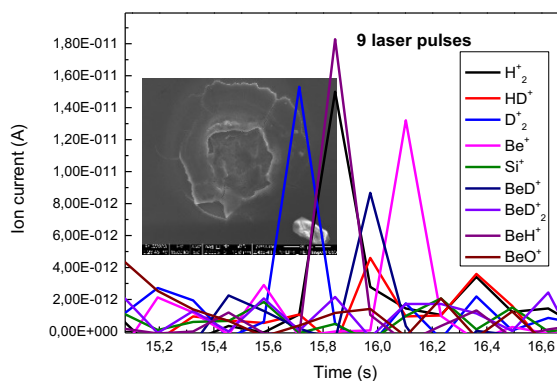
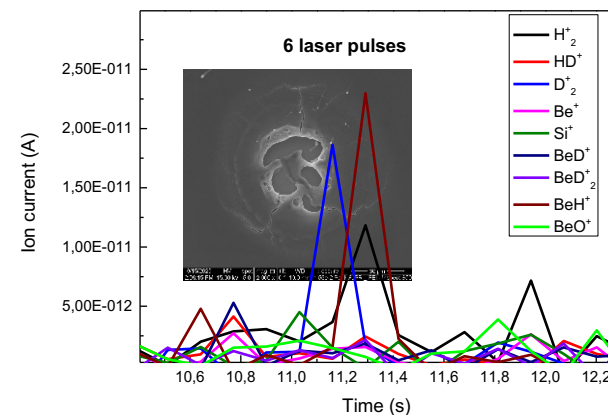
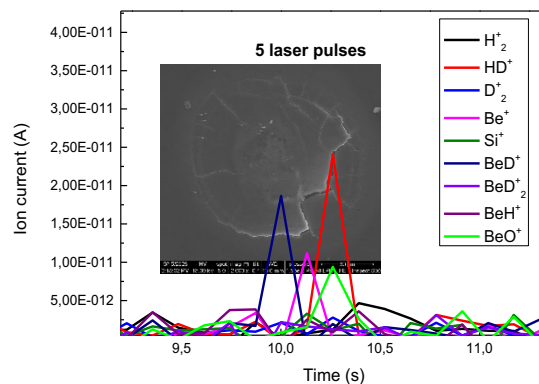
Other experimental capabilities

Preliminary results on deuterium release from BeD/Si layers by laser induced ablation/desorption - QMS and OES techniques



Evidence of BeO, BeH and H₂/D₂ optical emission bands during laser ablation of BeD/Si samples

Selectivity in the detection of components as function of number of laser pulses



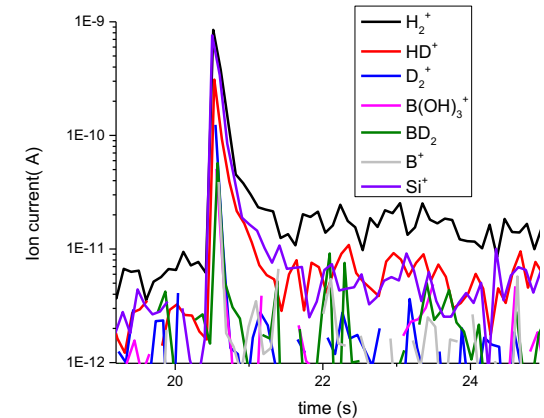
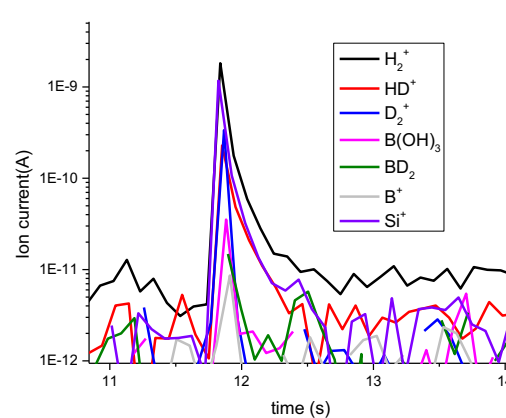
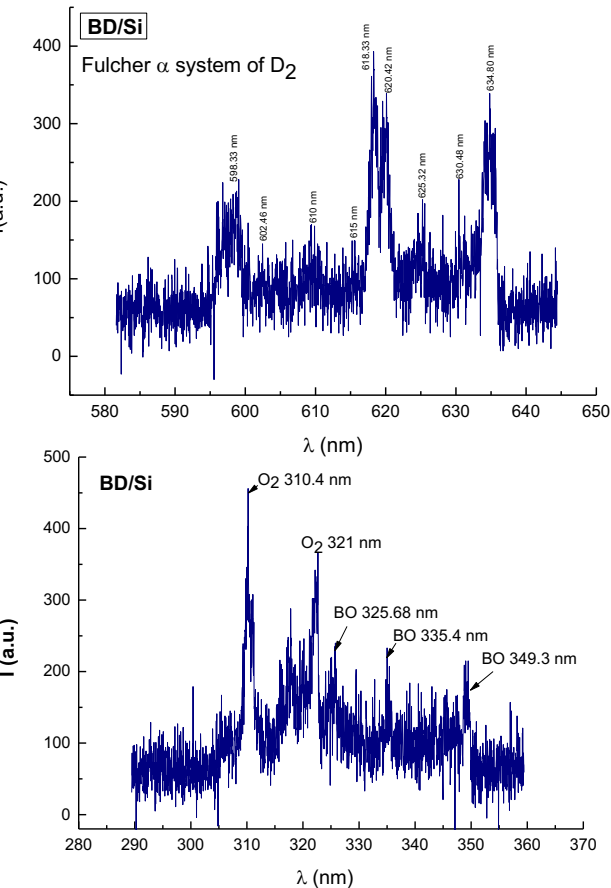
Mass spectral analysis of components produced by laser ablation and laser desorption of BeD/Si samples

SPB 4: Production of B samples for lab experiments



Other experimental capabilities

Preliminary results for deuterium release from BD/Si layers by laser induced ablation/desorption – QMS and OES techniques



Mass spectral analysis of components produced by laser ablation and laser desorption of BD/Si layers

Evidence of BO and H_2/D_2 optical emission bands during laser ablation of BD/Si samples

From Be/D to B/D and T experiments



Coroboration of TDS and diffusion reactions – MHIMS code

Etienne HODILLE from CEA

QUESTION:
A Rate equation model for D desorption from Boron codeposited layer relevant for WEST and/or ITER?

Bulk model

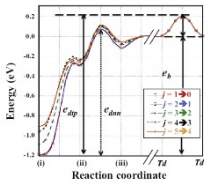
$$\frac{\partial c_m}{\partial t} = \nabla \cdot (\mathbf{D}(\mathbf{T}) \cdot \nabla c_m) - \sum_i \left(\frac{\partial c_{t,i}}{\partial t} \right) + S_{\text{ext}}(H, H^+)$$

$$\frac{\partial c_{t,i}}{\partial t} = -\mathbf{v}_i(\mathbf{T}) \cdot c_{t,i} + \mathbf{v}_m(\mathbf{T}) \cdot c_m \cdot (\mathbf{n}_i - c_{t,i})$$

Surface

$$\frac{dc_{\text{surf}}}{dt} = \Gamma_{\text{stick}}(H_2, H) - 2\mathbf{v}_{\text{des}}(\mathbf{T})c_{\text{surf}}^2 - \lambda \frac{\partial c_m}{\partial t} \Big|_{x=0}$$

N. Fernandez et al., Acta Mater. 94 (2015)
H in vac in W



V_1D_n	E_{dt}
V_1D_1	1.43 eV
V_1D_2	1.42 eV
V_1D_3	1.25 eV
V_1D_4	1.17 eV
V_1D_5	1.11 eV
V_1D_6	0.86 eV

Activation energy of elementary processes

Diffusion-reaction Code MHIMS

Conditions tokamak

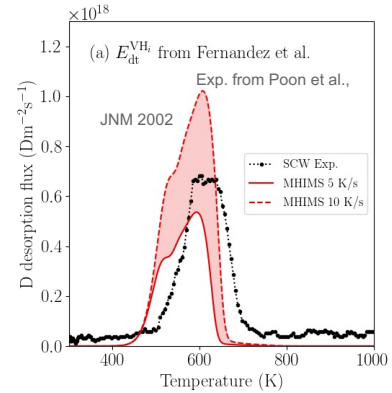
Desorption

Geometry Plasma fluxes

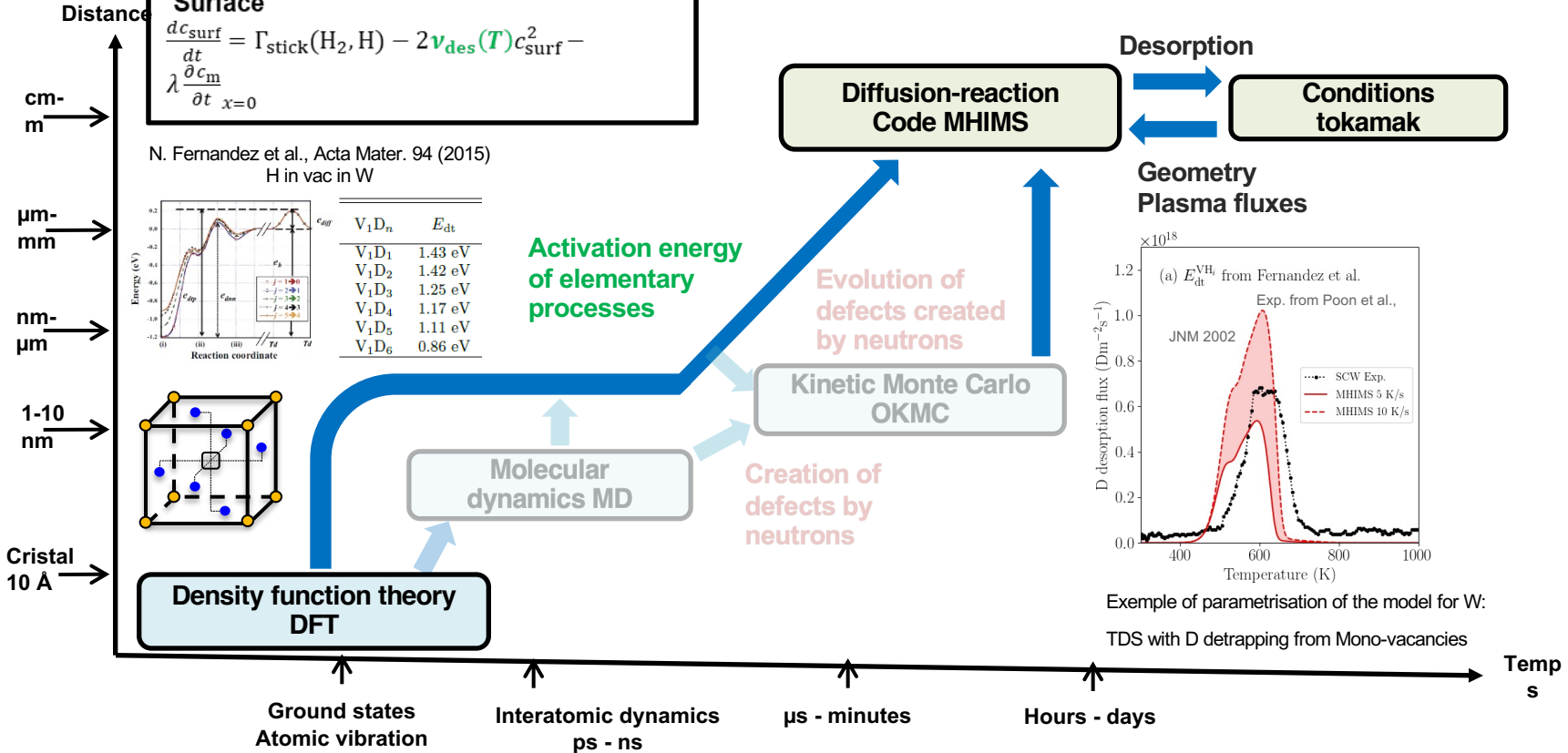
Kinetic Monte Carlo OKMC

Molecular dynamics MD

Density function theory DFT



Example of parametrisation of the model for W: TDS with D detrapping from Mono-vacancies



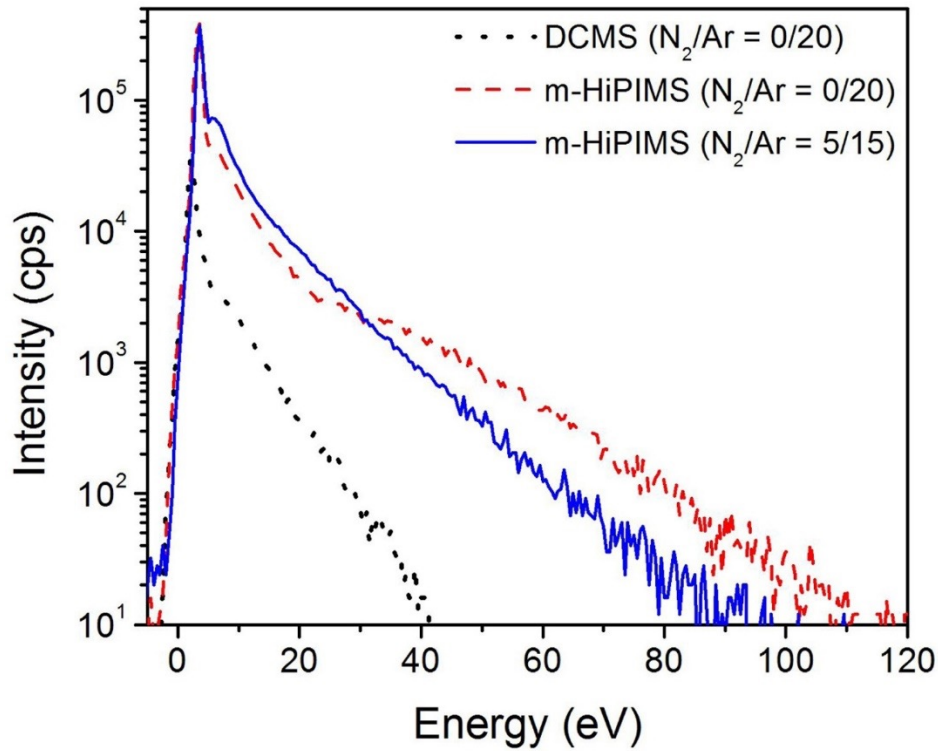
Extra slides

Plasma parameters – National funded PostDoc - Paul Dinca
Short pulse HiPIMS advantages

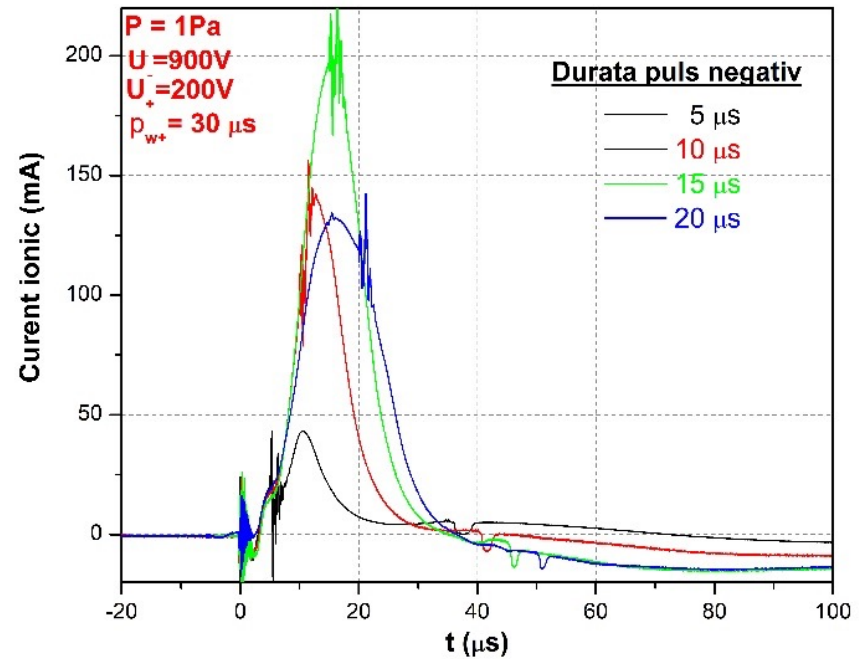


Magnetron sputtering plasma regimes available

DCMS **sp-HiPIMS**
RF – 13.56MHz BP-HiPIMS



Ion energy distribution function



Ion saturation current vs pulse length

Extra slides

Plasma parameters – National funded PostDoc - Paul Dinca

Bipolar short pulse HiPIMS advantages – Measurements on Be/D and Be/D/N magnetrons



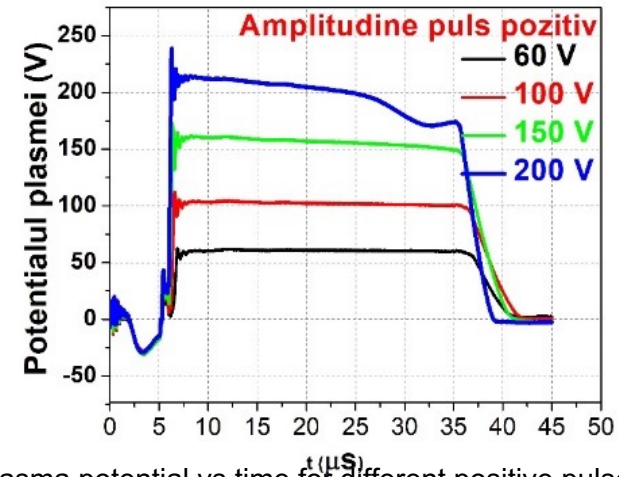
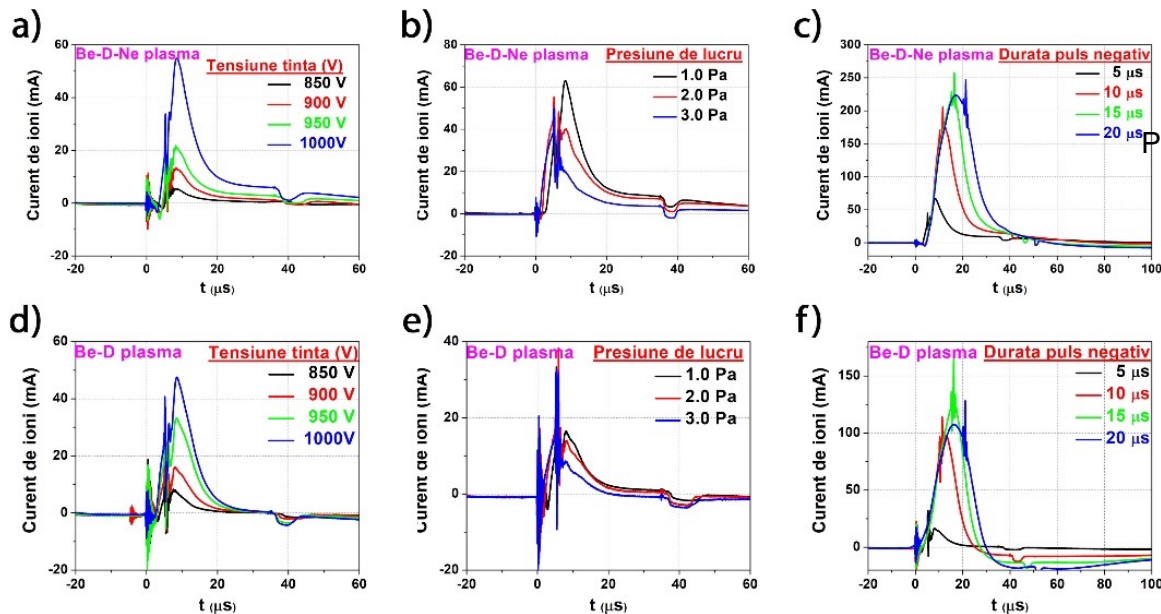
Magnetron sputtering plasma regimes available

DCMS

RF – 13.56MHz

sp-HiPIMS

BP-HiPIMS



Plasma potential vs time for different positive pulses

Ion current distribution for the Be/D and Be/D/N plasmas



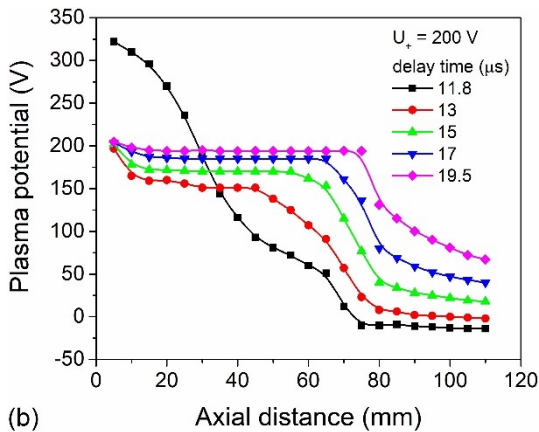
Extra slides

Bipolar short pulse HiPIMS advantages

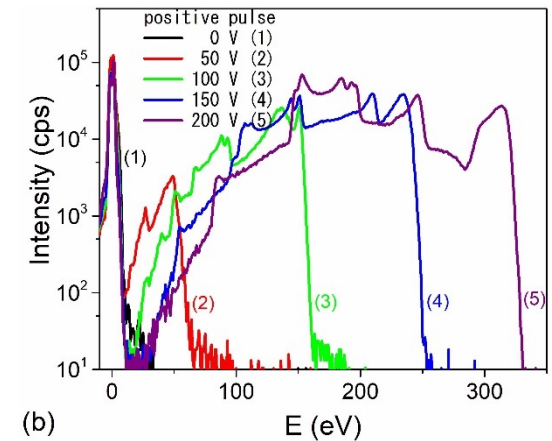
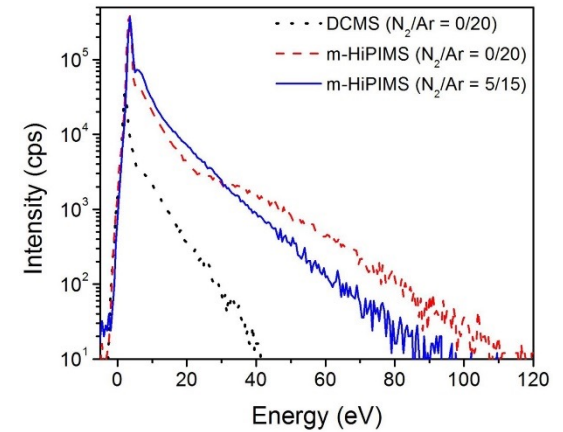
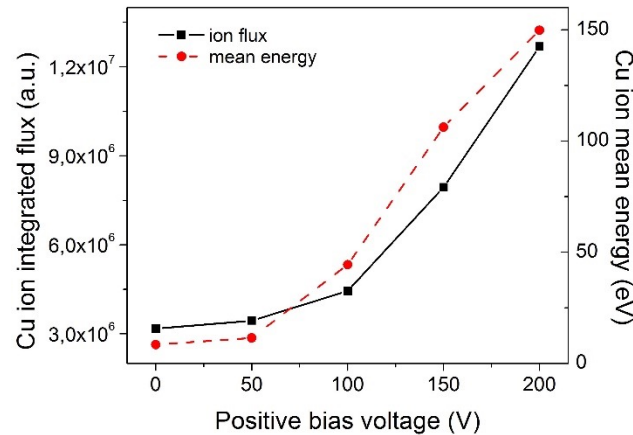
Magnetron sputtering plasma regimes available

DCMS
RF – 13.56MHz

sp-HiPIMS
BP-HiPIMS



(b)



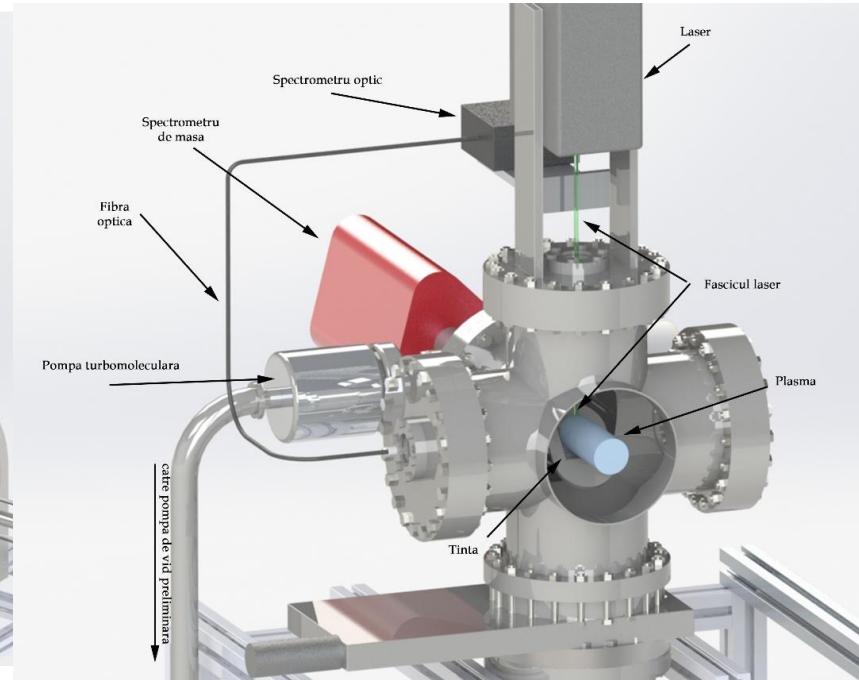
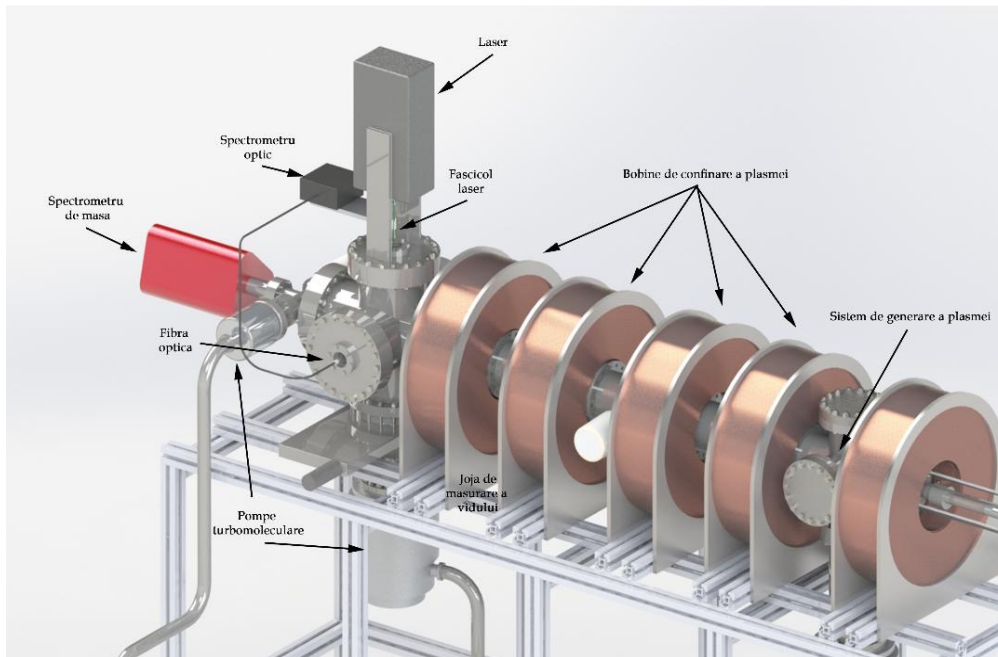
(b)

Data published in Surface and Coatings Technology, [359](#), 2019, 97

Ion energy distribution functions



Plasma linear device with insitu LIA/LID QMS and OES



Funding successfully acquired. Project starts in July 2024
Optimistic operation time: late 2025