SP F - IAP experiments. Boron plasma coatings and boronization studies.

Plama coatings – plasma parameters vs. film properties

C. Porosnicu, P. Dinca, B. Butoi, O. G. Pompilian, C. Staicu, B. Solomonea, C. P. Lungu

Approaches for surface coating with Boron by PECVD at low and high deposition rates using diborane as precursor

S. Vizireanu, G. Dinescu, D. Stoica, T. Acsente, V. Satulu, G. Dinescu, F. Dumitrache, Marius Dumitru, G. Morjan

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Plama coatings – plasma parameters vs. film properties

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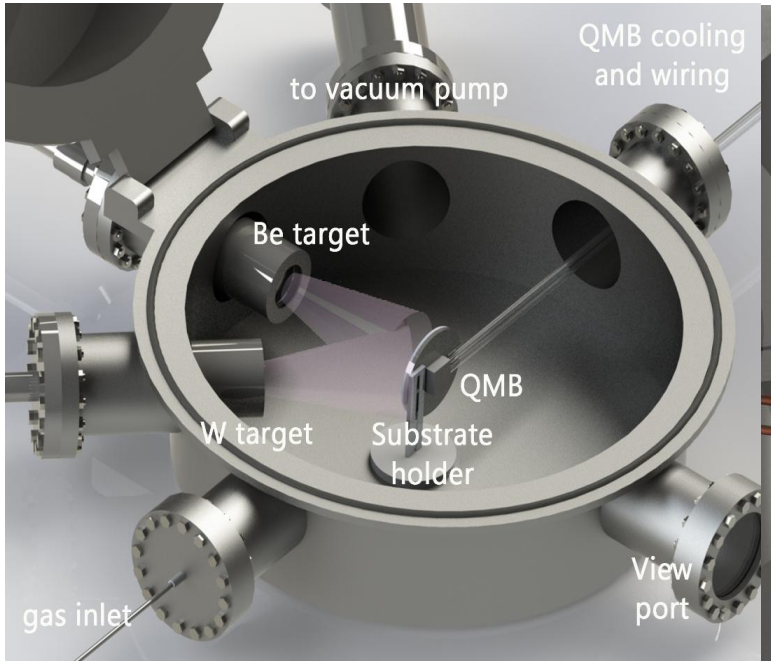
IAP-Romania

Outline

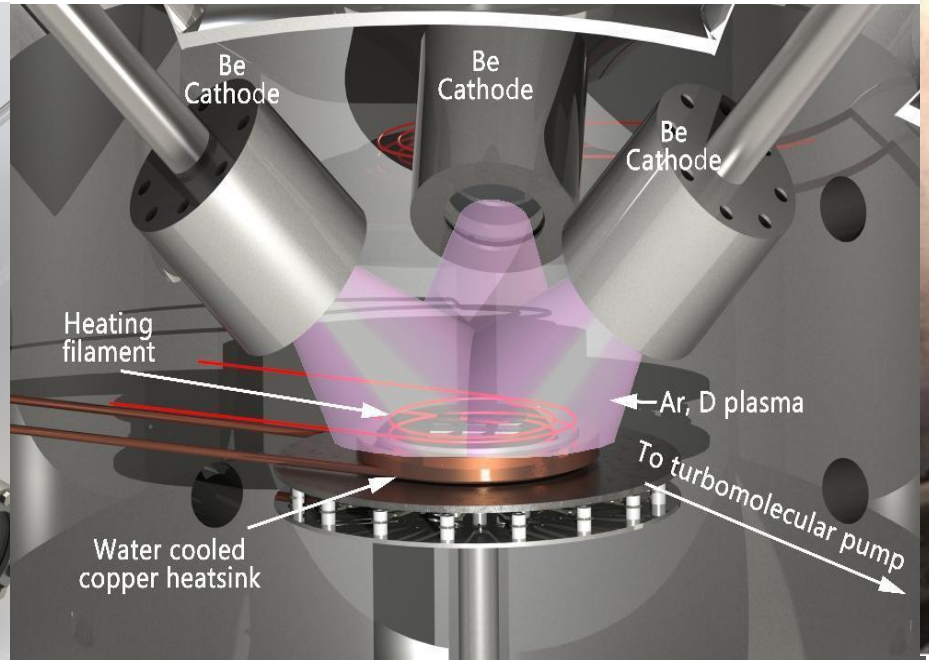
1. Boron coatings capabilities
2. Coating setups: TVA, HiPIMS, RF MS
3. Results form the B layers production task in 2025 under SBP4
4. Plasma characterisation - ion energy measurements
5. Prospects for studying B layers under SPF. Proposal of an experimental plan

From Be/D to B/D coating process – setups available

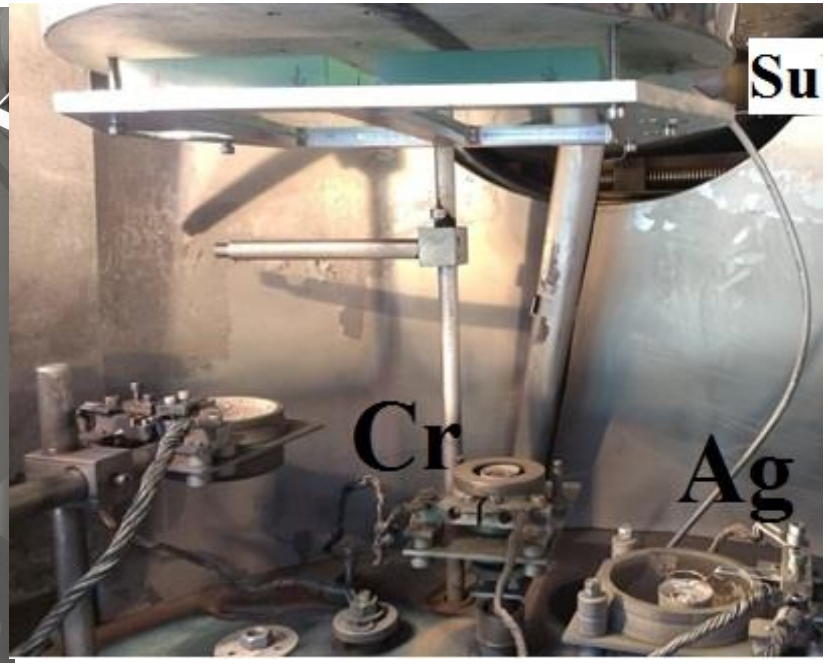
All the setups and experience used for Be was redirected to B



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



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



*TVA Deposition system used for obtaining **B** (/W). layers*

2024 was dedicated in setup and coating recipe development and plasma charactherisation methods

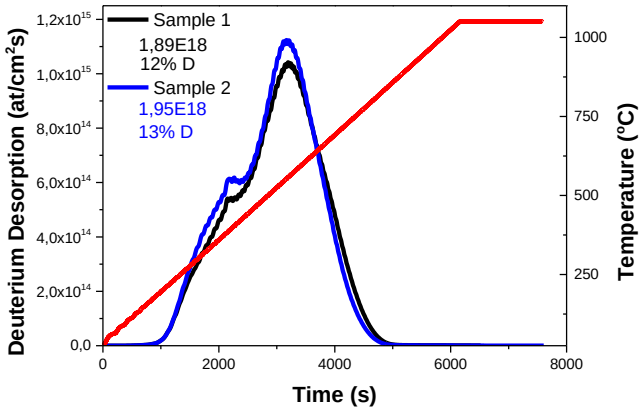
Results form the B layers production taskin 2025 under SBP4

Pre-deposition. Calibration

Coating parameters

- 4x Si substrates
- 2 RF sources opperated at 100W each
- Working pressure: $1x10^{-2}$mbar
- Ar flow= 20sccm
- D_2 flow= 20 sccm

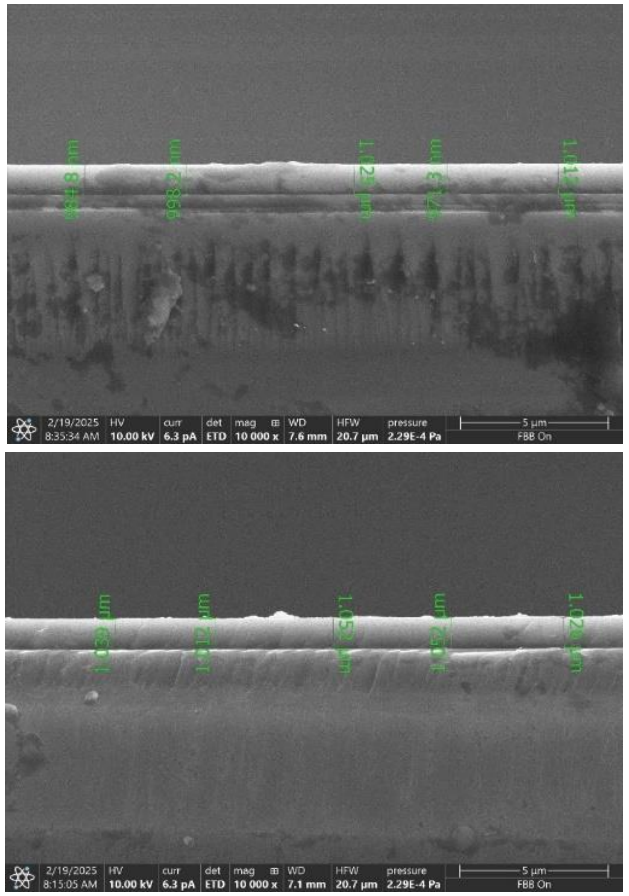
In situ photo of the deposition



TDS results (D concentration and quantity)

Measurements

- SEM cross-section
- TDS



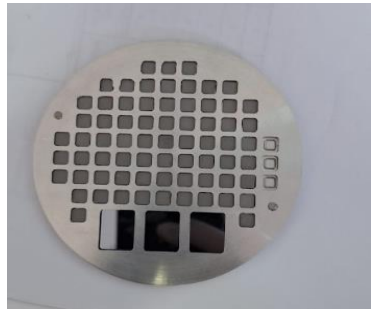
Cross-section-SEM results

Results form the B layers production taskin 2025 under SBP4

Boron+D2(10%) 5µm

Preparation of 5x5 mm^2 W samples coated with $B+D_2(10\%)$
Subject to thermal treatment post-coating

- 60 tungsten substrates 5x5 mm
- 2 RF sources opperated at 100W each
- Working pressure: $1x10^{-2}$mbar
- Ar flow= 20sccm
- D_2 flow= 20 sccm

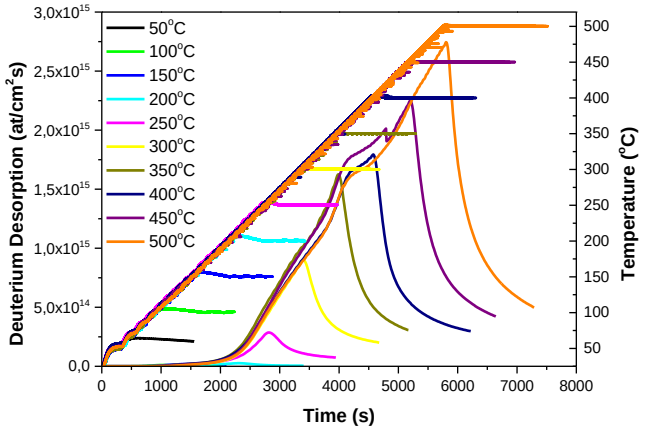


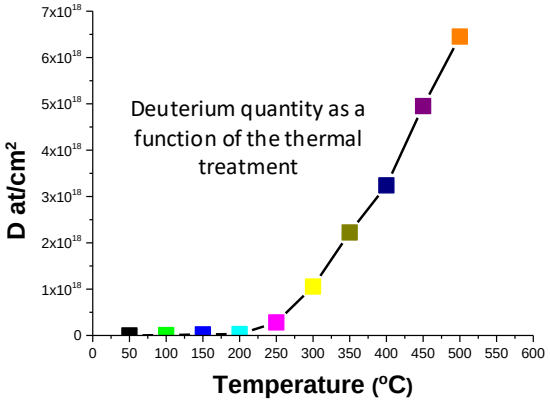
Sample holder

In situ photo of the deposition

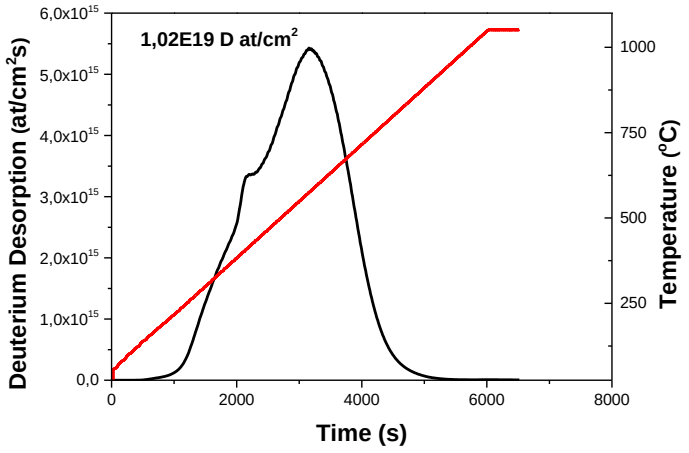
Thermal Treatment- 50°C- 500°C_Ramp 5°C/min

TDS measurement during Thermal Treatment





TDS result on B+D2_1050°C



Temperature (°C)	D released (at/cm²)	D released during the TT (%)
50	7.45E+14	0.01
100	8.25E+15	0.08
150	2.21E+16	0.22
200	2.98E+16	0.29
250	2.82E+17	2.76
300	1.06E+18	10.39
350	2.22E+18	21.76
400	3.24E+18	31.76
450	4.95E+18	48.53
500	6.45E+18	63.24
1050	1.02E+19	100.00

Results form the B layers production taskin 2025 under SBP4

Boron deposition (100nm)

- 12 tungsten substrates 10x10 mm
- 2 RF sources opperated at 100W each
- Working pressure: $1x10^{-2}$mbar
- Ar flow= 20sccm
- D_2 flow= 20 sccm

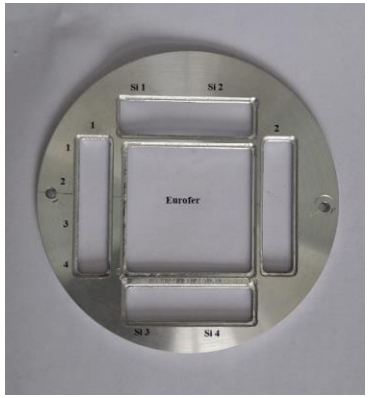
In situ photo of the deposition

Sample holder

Boron deposition (5µm) with and witout D

- 8 tungsten substrates
- Eurofer ϕ 40 mm
- 2 RF sources opperated at 100W each
- Working pressure: $1x10^{-2}$mbar
- Ar flow= 20sccm
- D_2 flow= 20 sccm

In situ photo of the deposition



Sample holder

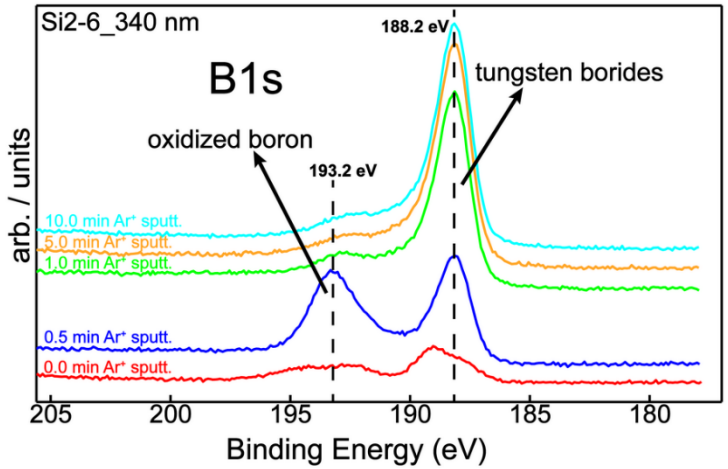
All samples were stable after the deposition (kept in vacuum).
Analisys (TDS, XRD,SEM, etc.) will be performed in April at IAP.
Samples to be sent this week (24-28 March) to the laboratories - sealed bags in vacuum, according to the matrix.

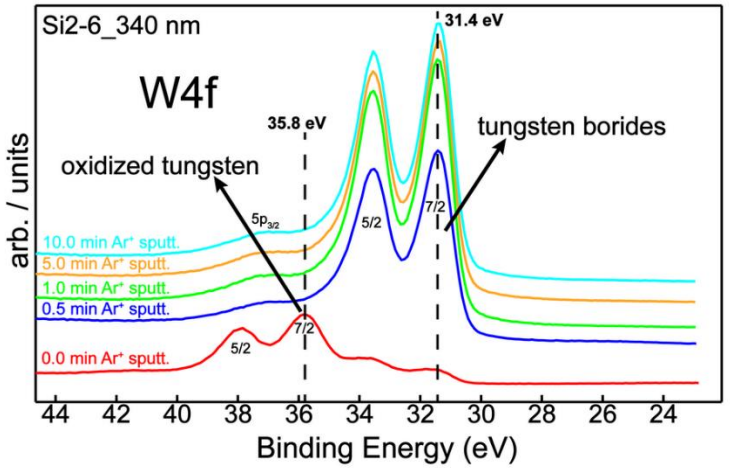
XPS on tungsten-boride formation

Request for tungsten boride layers from Penn State University (A. Marin) under a PSU - WEST collaboration.

Samples coated by TVA – task performed.

TVA parameters variation- W/B coatings with and without boride formation





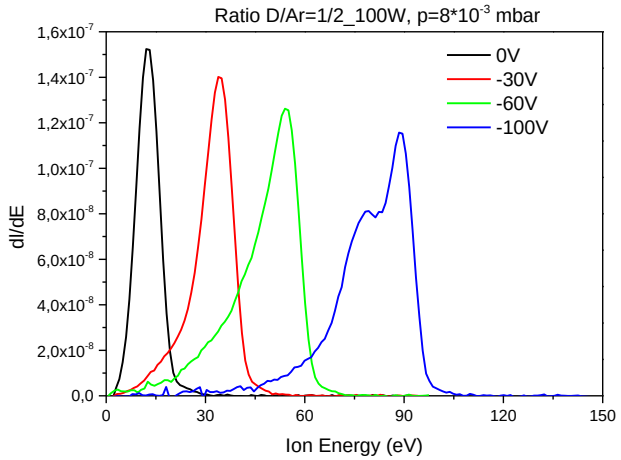
Elemental relative concentrations (at. %)

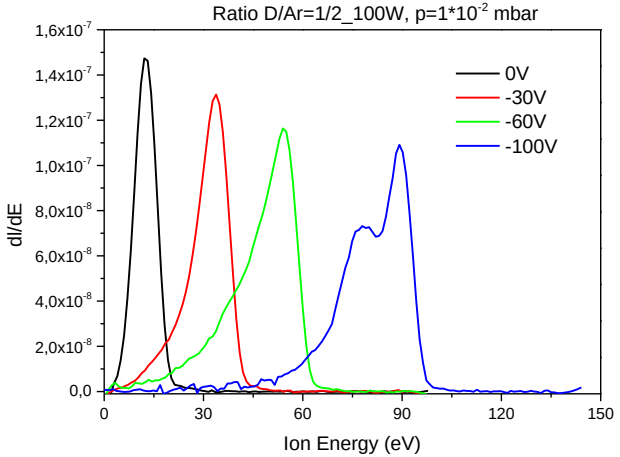
Si2-6_340 nm	B1s	C1s	O1s	W4f	B/W
0.0 min sputtering	15.1	45.3	32.9	6.7	2.3
0.5 min sputtering	45.9	-	38.8	15.3	3.0
1.0 min sputtering	58.3	-	15.8	25.9	2.3
5.0 min sputtering	63.0	-	13.5	23.5	2.7
10.0 min sputtering	63.3	-	13.1	23.6	2.7

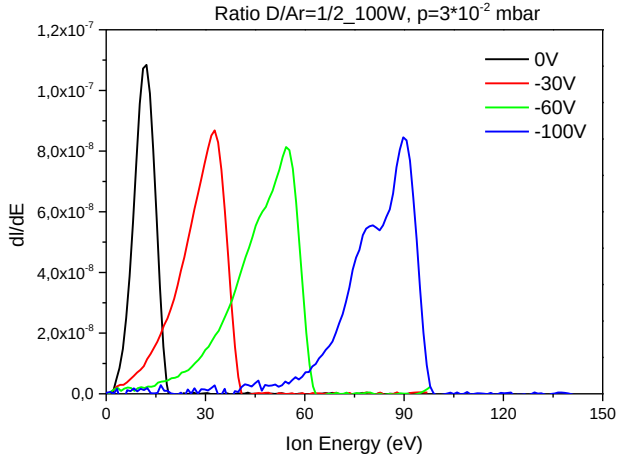
Plasma characterisation - Ion energy measurements

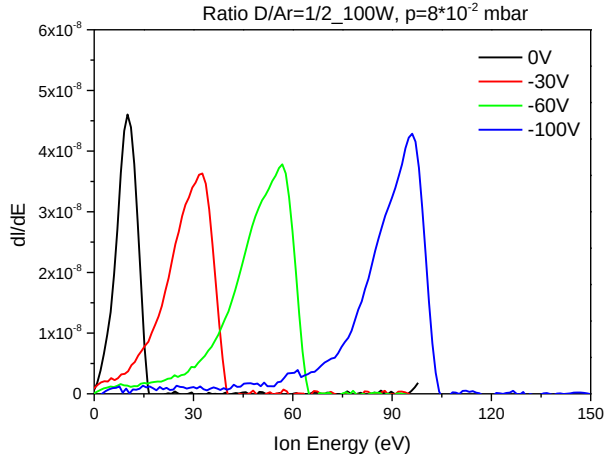
RF plasma, P= 100W

BIAS voltage influence – several pressures





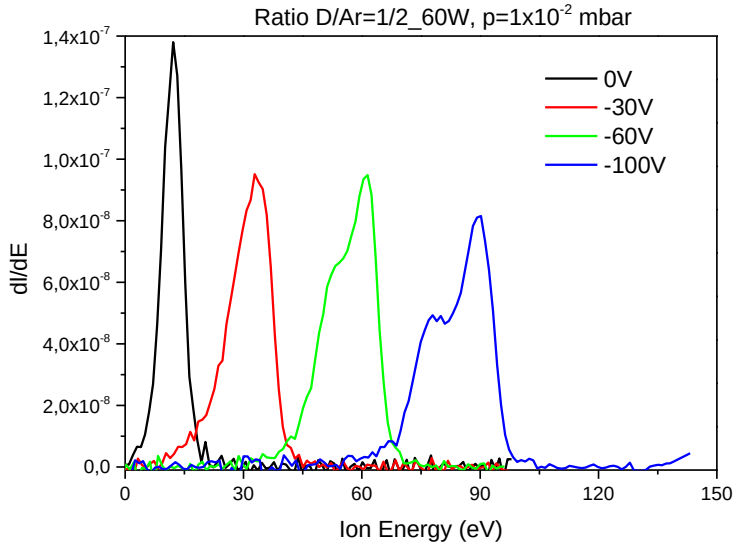


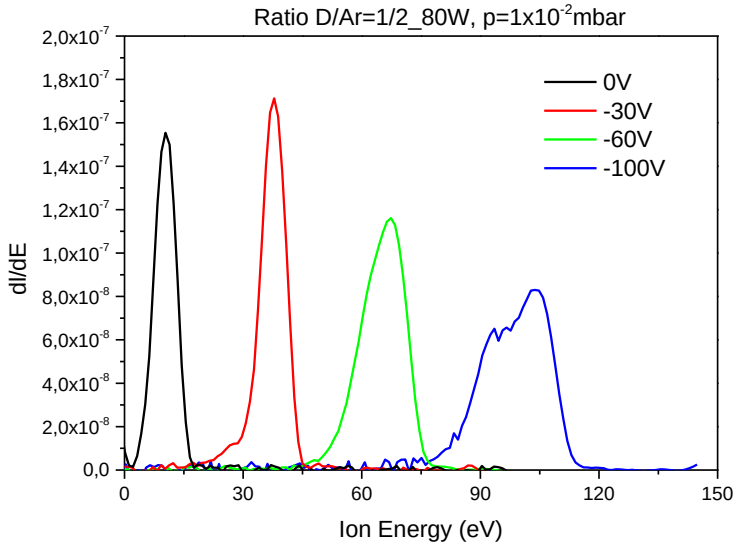


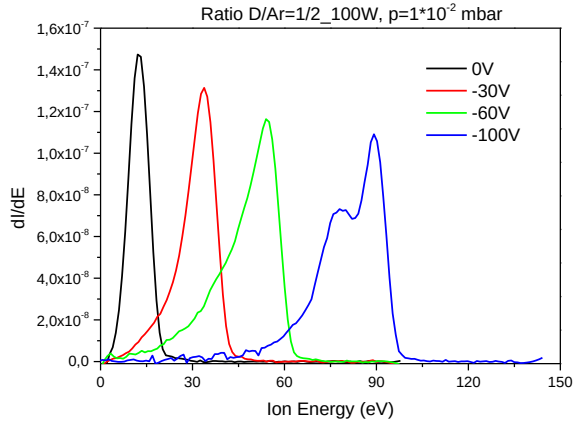
Plasma characterisation - Ion energy measurements

RF plasma, P= 1e-02 mbar

BIAS voltage influence – several RF Powers



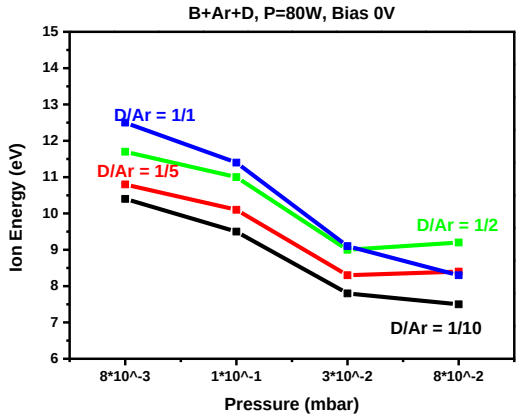


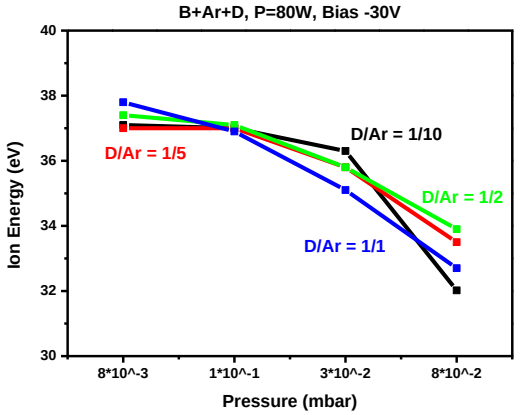


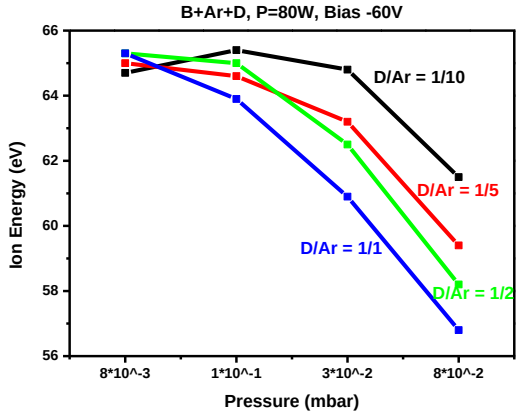
Plasma characterisation - Ion energy measurements

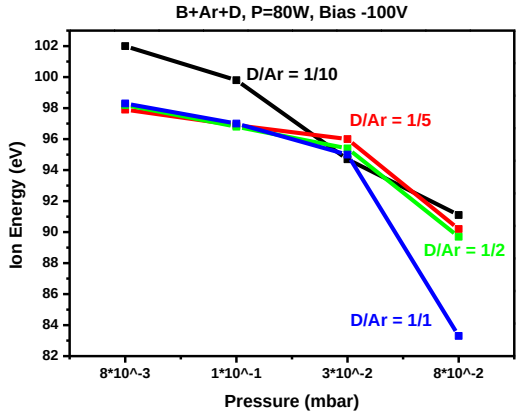
RF plasma, Ion energy overview

BIAS, pressure and D/Ar ratio



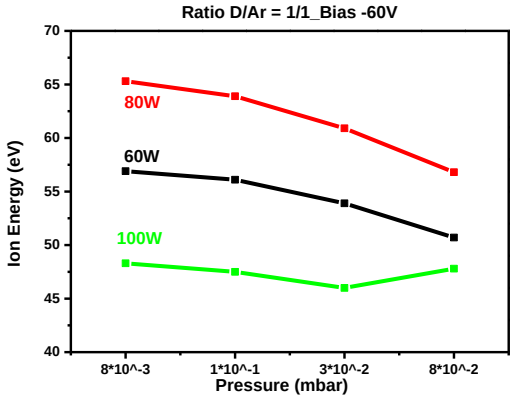


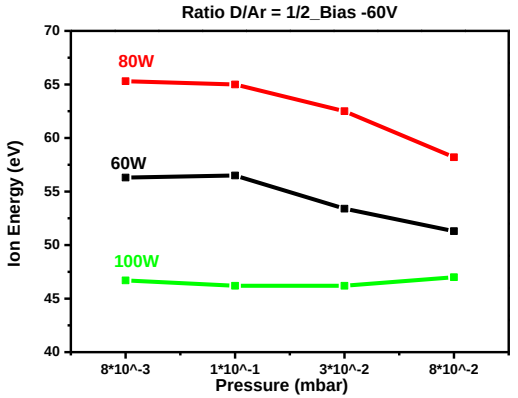


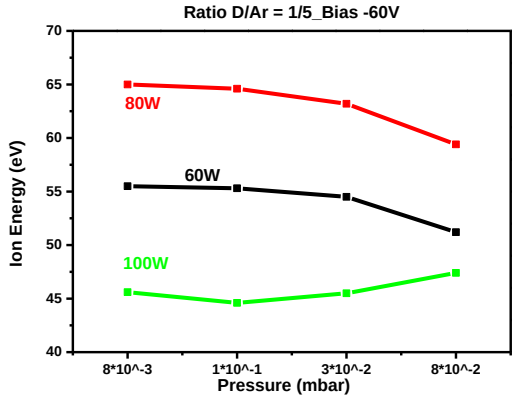


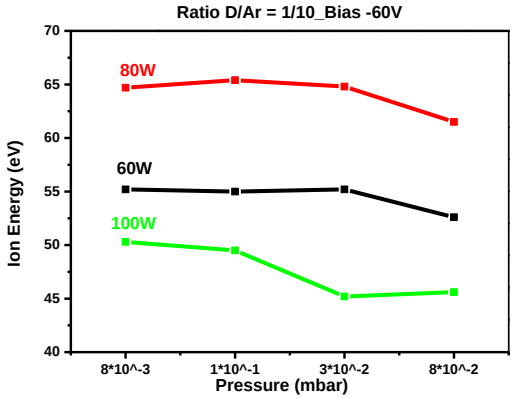
Plasma characterisation - Ion energy measurements

RF plasma, Ion energy overview
RF power, pressure and D/Ar ratio







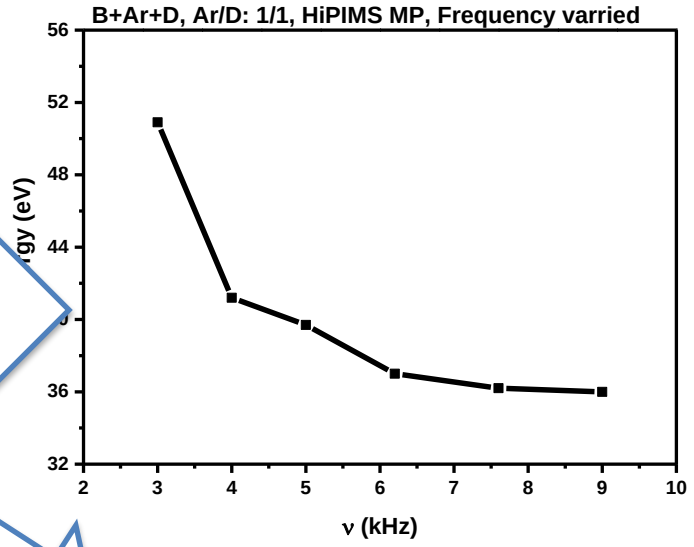


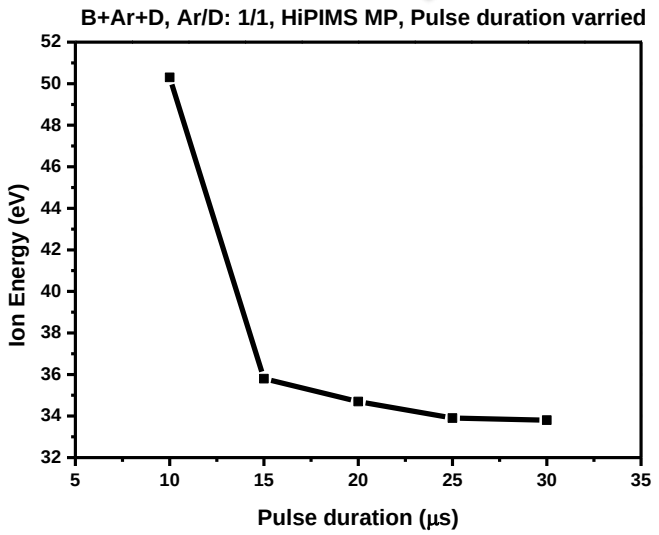
Plasma characterisation - Ion energy measurements

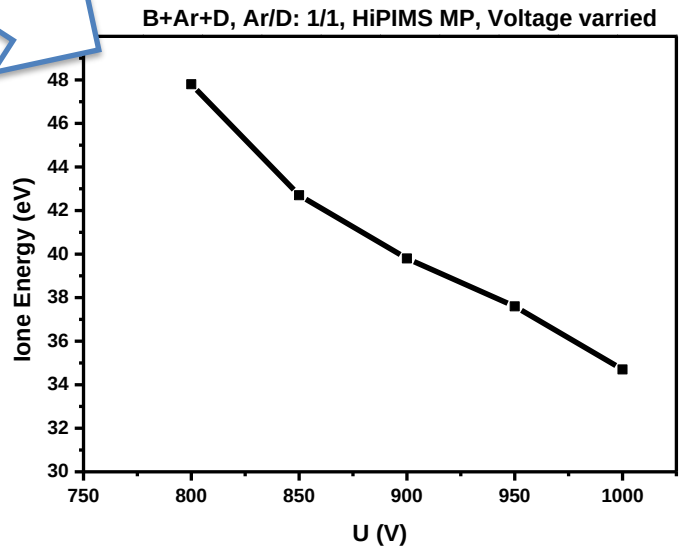
HiPIMS MP

B+Ar+D, Ar/D: 1/1

Frequency
Voltage
Pulse duration



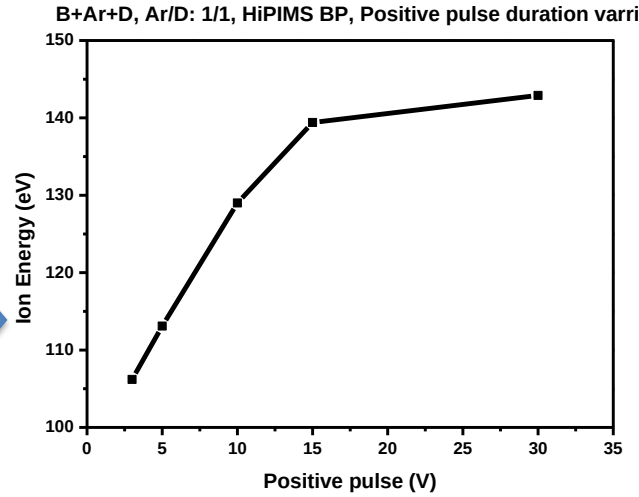




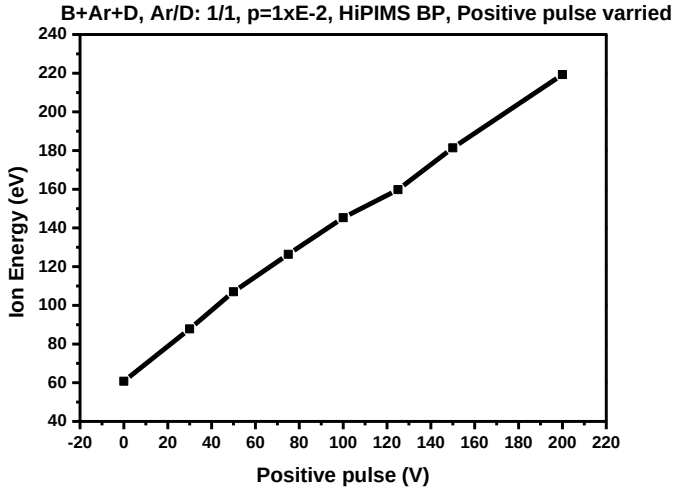
Plasma characterisation - Ion energy measurements

B+Ar+D, Ar/D: 1/1,
Bipolar HiPIMS,

Positive pulse duration varried



Positive pulse voltage varried



Prospects for studying B layers under SPF
Proposal of an experimental plan - Example and ideas:

Different aproach than under SPB: Focus on plasma parameters instead of coating properties.

Parameters to be varied:		
RF-MS parameters (Input power)		Pressure (1e-03 – 1e-01 mbar)
HiPIMS MP and BP plasma parameters (Pulse duration and frequency, voltage for negative and positive pulse)		Acceleration voltage (0 to-200V for MS;-700V for TVA),
TVA parameters (voltage and current)		D/Ar ratio (1/20 – 1/1)

For each set of parameters, very well defined plasma characterization
Ionisation degree (Langmuir probe), Ion energy (IEDF), species identification (MS, OES), etc.

Sistematic study

Fixed plasma parameters – well characterized plasma => what will we obtain??
stability, morphology, composition, adhesion, hardness, fuel retention

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

Approaches for surface coating with Boron by PECVD at low and high deposition rates using diborane as precursor

S. Vizireanu, D. Stoica, T. Acsente, V. Satulu, **G. Dinescu, F. Dumitrache,** Marius Dumitru, G. Morjan

IAP-Romania

Outline

- **Experimental capabilities at INFLPR for plasma and laser CVD in diborane;**
  - PECVD configurations used for boron deposition;
  - Laser pyrolysis configuration used for preparation of B based nanoparticles;
- **Experimental parameters and sample labelling;**
- **Results on Glow discharge (GD-) samples: Surface morphology;**
- **Results on Plasma jet (J-) samples: Surface morphology;**
- **Time stability of boron samples on Si substrates;**
- **Boron samples deposited on W substrates;**
- **Boron samples deposited for various temperatures;**
- **Boron samples composition- XPS investigation;**
- **Conclusions and future plans.**

Experimental capability at INFLPR for a boronization in diborane

Advantages: PECVD boron samples can be similar to those used in tokamak walls after boronization
Drawback: difficulties in diborane manipulation

Caution!!!

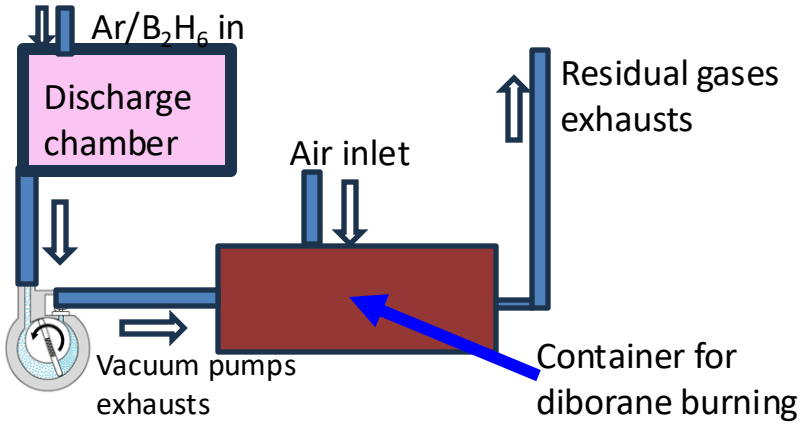
High toxicity: needs special health and safety equipment.
- **TLV** (Threshold Limit Values) **=0.1 ppm;**
- immediately dangerous at 40 ppm.

Flammable gas: auto ignition in air at temperature ~ 40°C.
Special procedures must be followed to prevent hazard.

Details for handling diborane B2H6

- We used a mixture of **B_2H_6/H_2 at ratio 1/10** in vacuum;
- **Non-used B_2H_6 is burning** before exhausting;
- Dedicated mass-flow controllers;
- Diborane detection sensors.
- More safety measure must be implemented

One essential component of the deposition system is the container in which we burn the flammable gas. At INFLPR this container was used before for burning silane **SiH_4** and lately for **B_2H_6** for boron doping by laser pyrolysis [1].



[1]. Balas M.; Dumitrache F. et al, Nanomaterials 2018, 8, 495
https://doi.org/10.3390/nano8070495

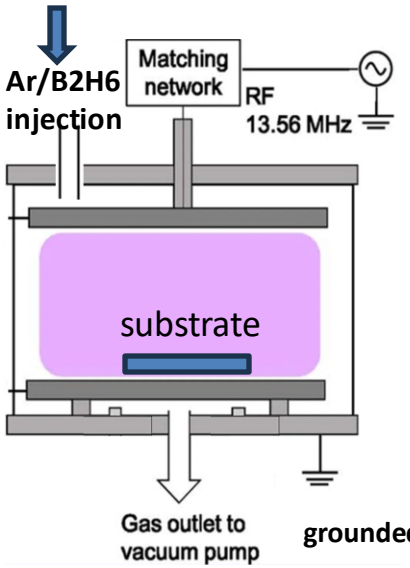
Two PECVD configurations used for boron deposition

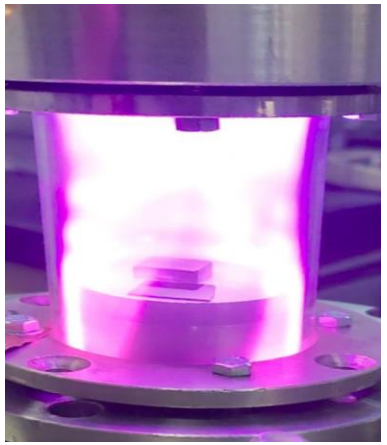
Glow discharge (GD) configuration

Set-up glass tube+ 2 parallel plate electrodes (50 mm and distance in between electrode 60 mm

Carrier gas: Ar and Precursor: H2/B2H6

Variable parameters: RF power, Flow rates, pressure, deposition time, Substrate: Si, W





grounded holder and chamber

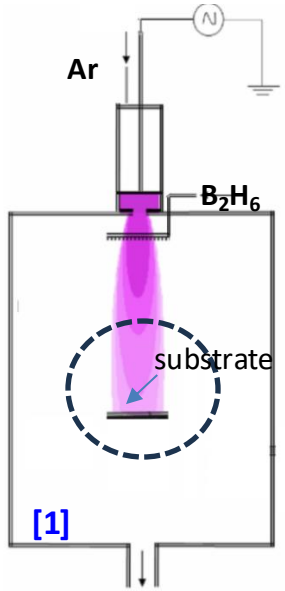
RF plasma jet (J) configuration

Set-up steel vessel +Jet plasma source used before for PECVD of nanostructure carbon

Carrier gas: Ar and Precursor: H2/B2H6

Variable Working parameters:

RF power, Nozzle substrate distance, flow rates , Pressure, Deposition time, Temperature, Substrate: Si, W



Images of the plasma jet in Ar / B_2H_6

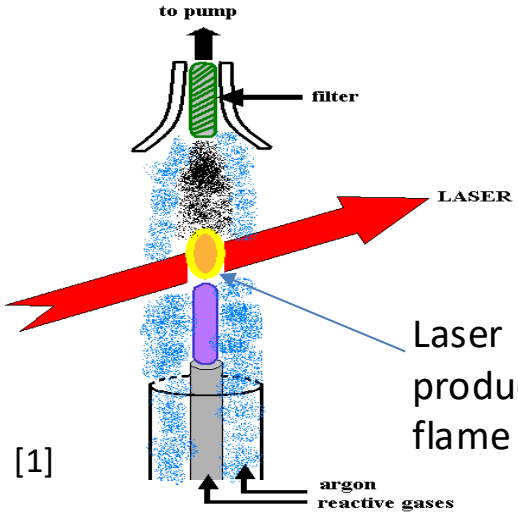
Gas ratio: **Ar/Diborane**

1000/5 (sccm)

300/5 (sccm)

[1]. S. Vizireanu et al, Plasma Sources Science & Technology 19, 034016, 2010.

Laser pyrolysis used for Boron based nanoparticles

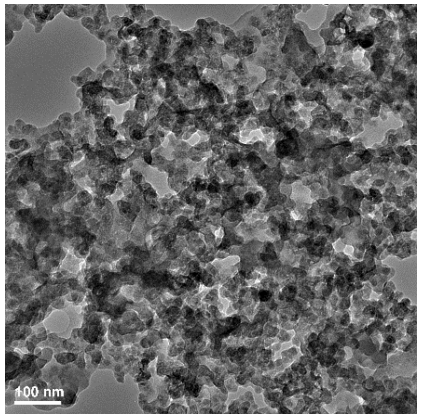


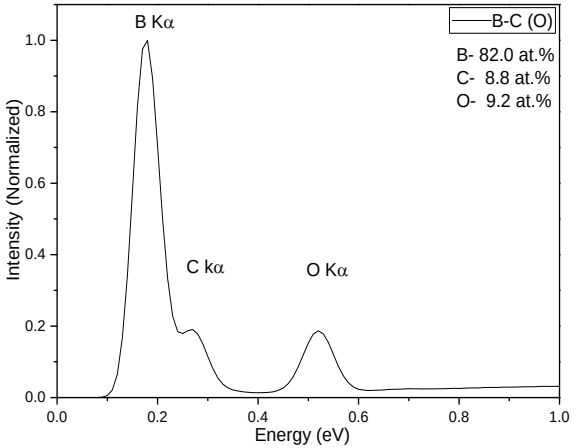
[1]

Experimental method: laser pyrolysis
B_2H_6 was used as B precursors

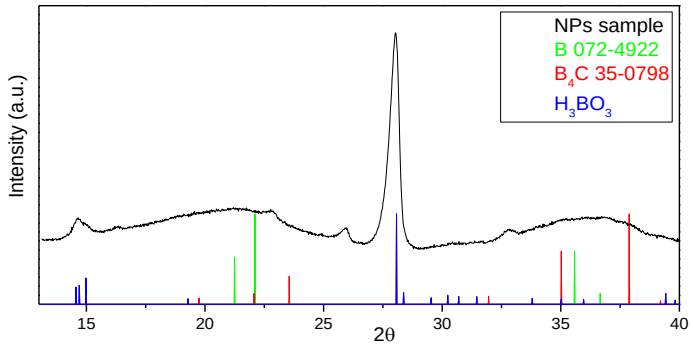
Specific **synthesis of Boron rich NPs: B-C** (O) NPs

Reactive mixture: B_2H_6 / C_2H_2/ C_2H_4: 8/1/3 (sccm), T_{flame}=780 °C





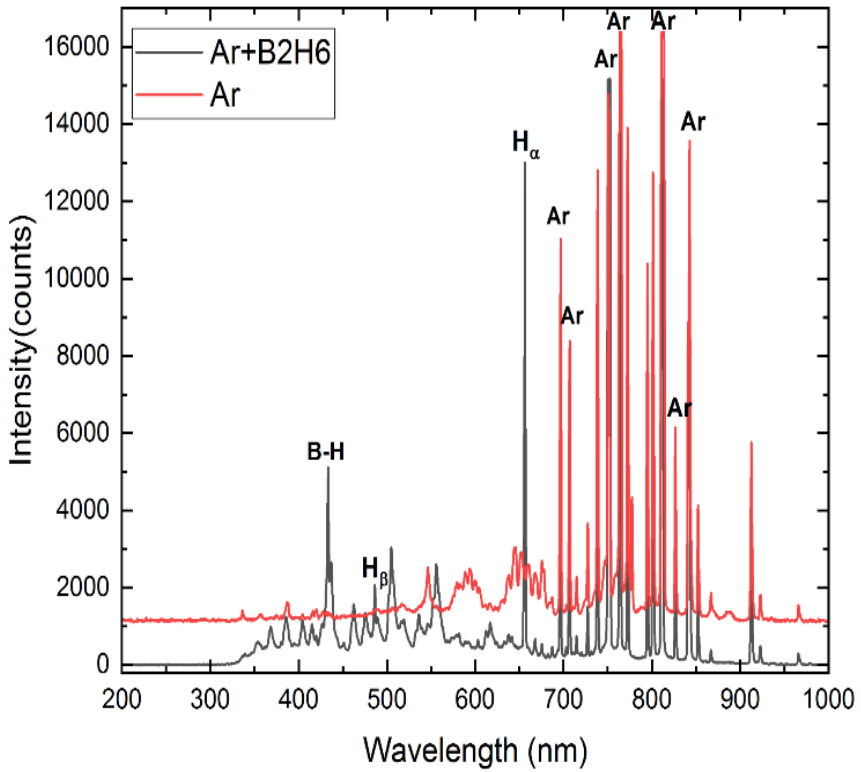
Advantages:
✓pure and reproducible nano-products
✓extremely fine and monodisperse powders (d < 30 nm);
✓continuous synthesis **with high rate~<u>1-10 g/h</u>;**
✓ **<u>B doped materials, B carbide and nitride: (Fe,Ti, Si) borides</u>**.



XRD diffractogram of $B_{4+x}C$-O NPs NPs /Laser pyrolysis

[1]. Balas M.; Dumitrache F. et al, Nanomaterials 2018, 8, 495 https://doi.org/10.3390/nano8070495

Preliminary Ar/B_2H_6 plasma jet investigation



OES in plasma jet of Ar/diborane mixture

Plasma jet Ar/ B_2H_6 at 1000/5

Plasma +Optical fiber+ Optical multichannel analyzer+ acquisition

OES investigations show the presence the Argon lines, and BH bands, H_α and H_β lines in plasma jet after introduction of 5 sccm of diborane.

Further investigations: Detailed studies follow after

I will mount a quartz window.

-**OES study** of He or D_2/diborane plasma in various condition.

-**OES study** of boron films in interaction with plasma.

-**Mass spectrometry study of boron** films in interaction with plasma. Study of species during sputtering of boron layers in **D_2/H_2 plasma**

Experimental parameters and samples labels

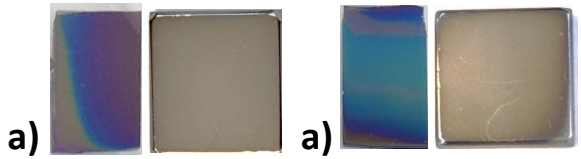
Labelling of samples:

H-samples at High Ar flow (1000 sccm)+5sccm B_2H_6

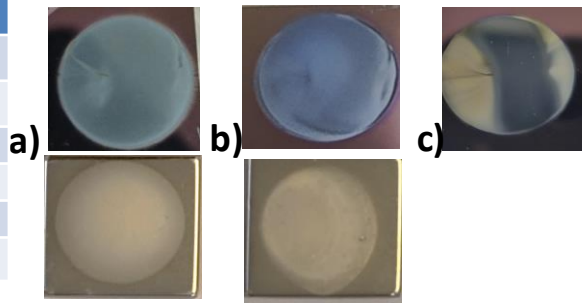
L-samples at Low Ar flow (300 sccm) +5sccm B_2H_6

Samples label	Ar [sccm]	B2H6 [sccm]	Deposition press. [mbar]	Time [min.]	Temper. Degree C
1. Set I- Samples deposits by Glow Discharge (GD-samples)					
GD-H	1000	5	0.7	10	
GD-L	300	5	0.4	10	
2 Set II Samples deposits by plasma Jet (J-samples)					
J-H	1000	5	0.7	10	
J-L	300	5	0.4	10	
J-H-RT	1000	5	0.73	10	47 ^{O}C
J-H-400C	1000	5	0.72	10	400 ^{O}C
J-H-600C	1000	5	0.71	10	600 ^{O}C
J-H-700C	1000	5	0.71	10	700 ^{O}C

a)



Pictures of samples a) GD-H and b) GD-L on Si and W substrates



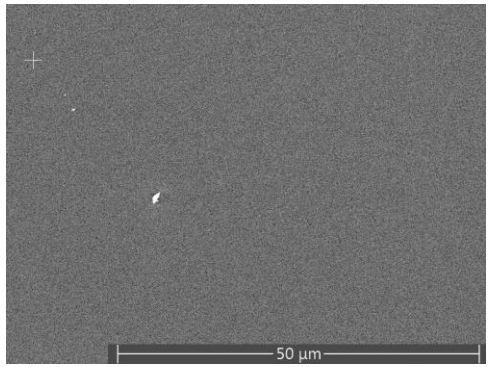
Pictures of samples a) J-H; b) J-L and c) to an intermediate Ar flow (500 sccm)

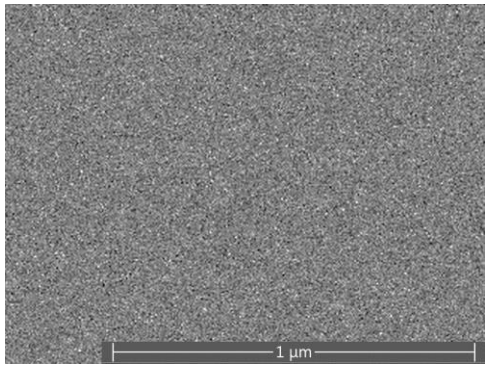
There are fixed parameters like RF power 100W, precursors kept always at the same flow values diborane: H2/B2H6 = 5 sccm

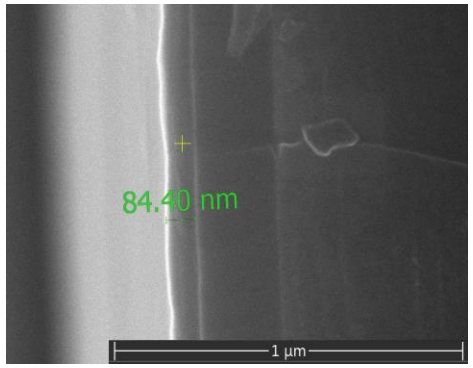
Glow discharge GD-samples: Surface morphology

SEM investigation results: top view and cross sections

Time:10 minutes, thickness ~84 nm

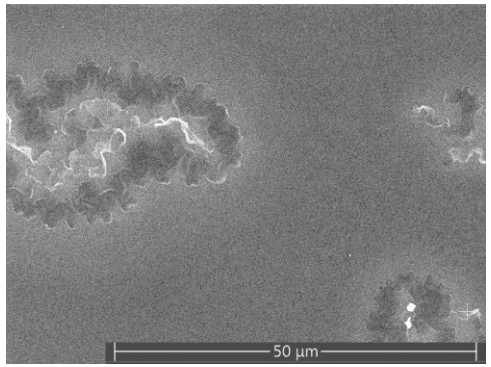


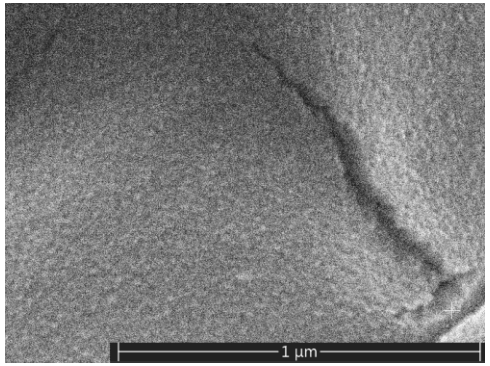


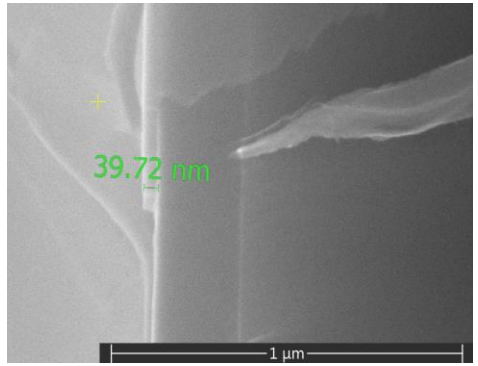


Smooth films
Deposit. rate: **8.4 nm/min**

GD-H on Si in **Ar/B2H6** ratio 1000/5 sccm top and cross section



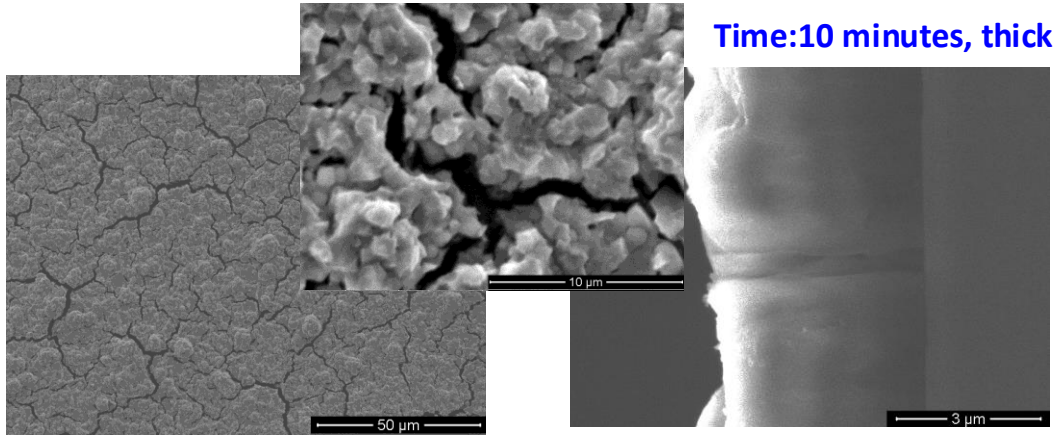




Smooth films
Deposit. rate: 4 nm/min

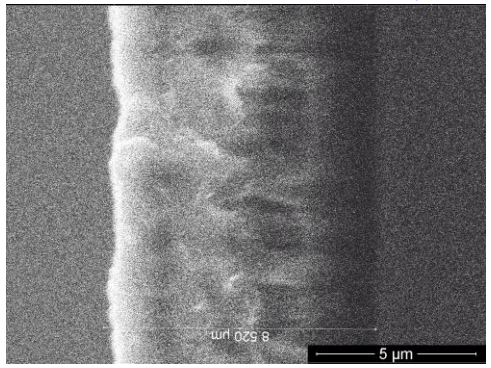
GD-L, on Si from **Ar/B2H6** ratio 300/5 sccm- Thickness: **40 nm**

Plasma jet (J) samples: Surface morphology

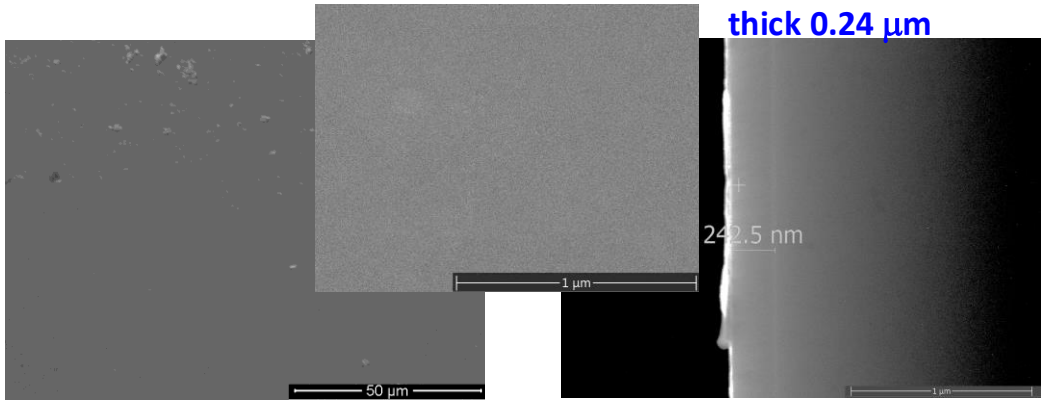


Time:10 minutes, thick 4.1 µm

Time: 30 minutes, thick 8.5 µm

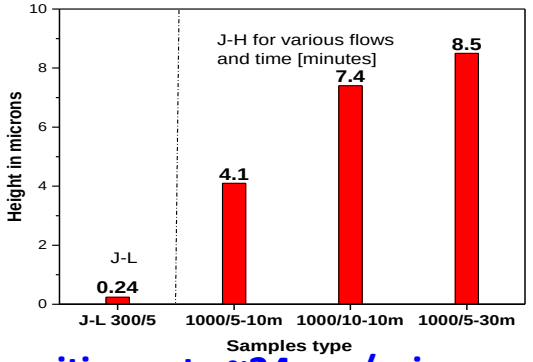


SEM images of J-H 1000/5 sccm top and cross section. **J-H samples are rough.**



thick 0.24 µm

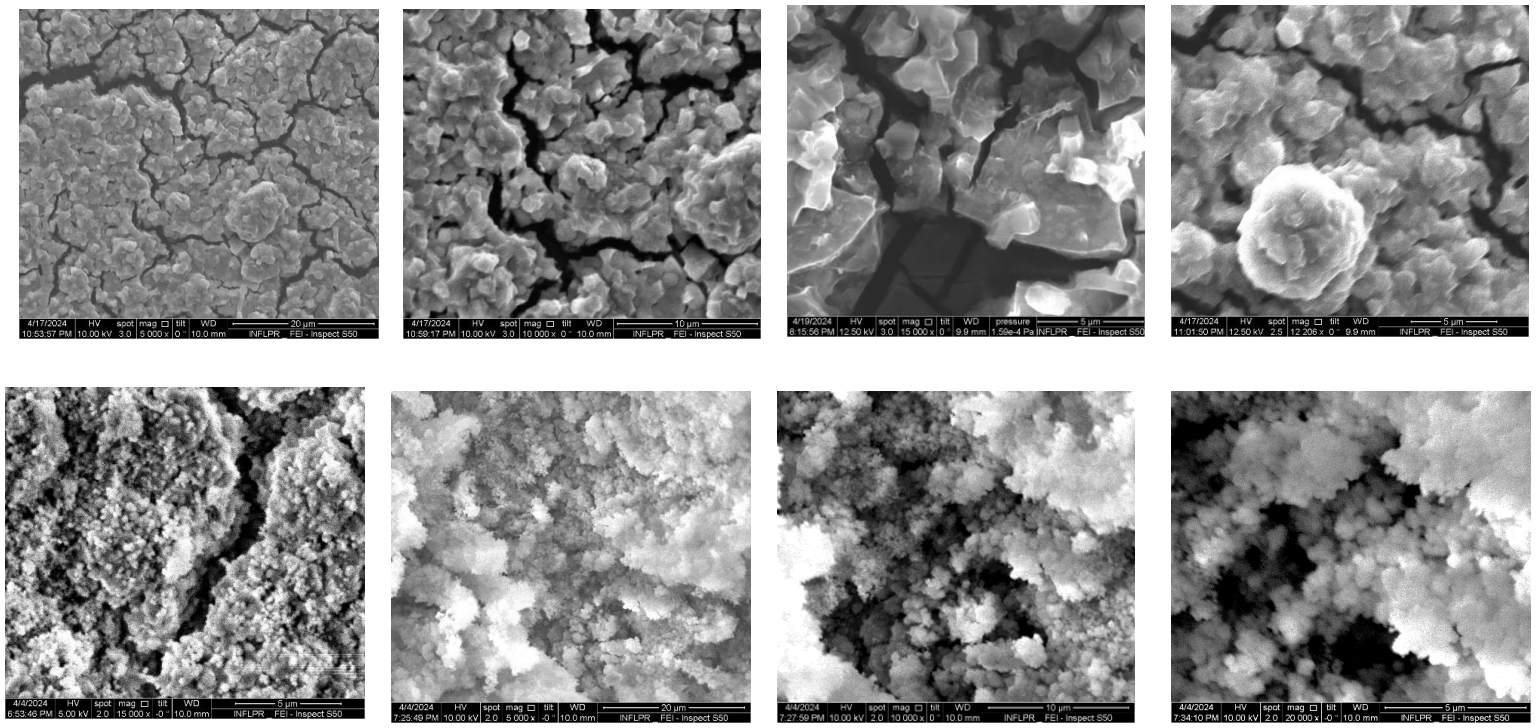
Deposition rate of J-H samples at about **400 nm/min**



SEM images of J-L samples 300/5 sccm J-L samples are smooth and small deposition rate ~24 nm/min

J-H samples. Details on morphology

case of J-H: for high Ar flows, the sample are very rough and irregular

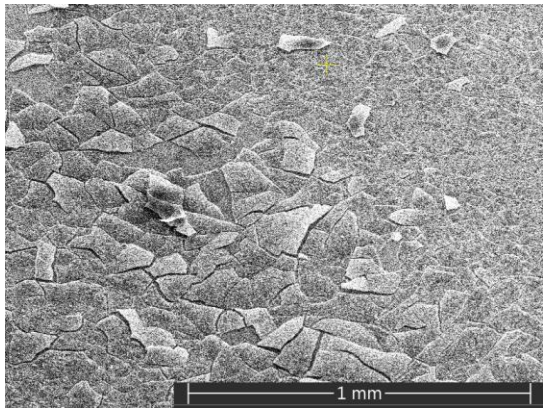


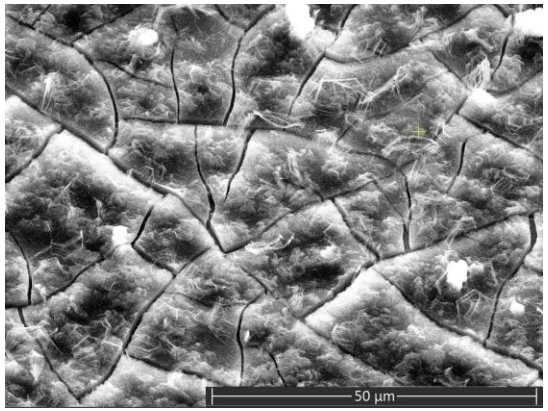
Thick layer present many cracks and sponge-like morphology
At the film edges, a whitish color is observed, the film are oxidized and nanoparticles appear

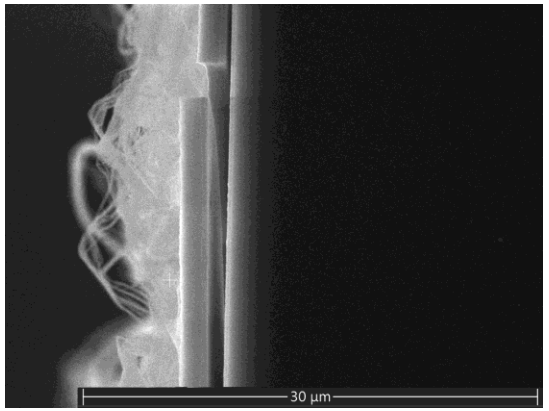
Time stability: J-H sample on substrates Si

Adhesion behaviour in time (after 6 months)
of thick film deposited at (Ar/B_2H_6 1000/10 sccm)

Initial SEM

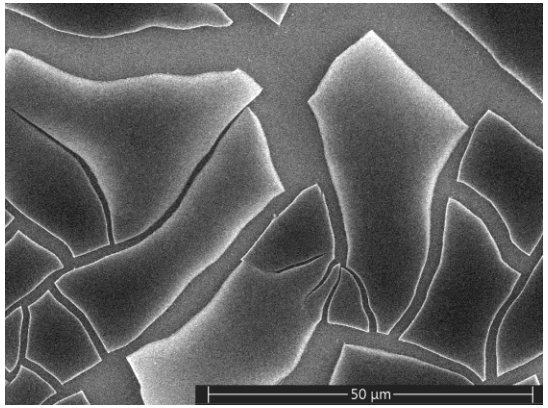


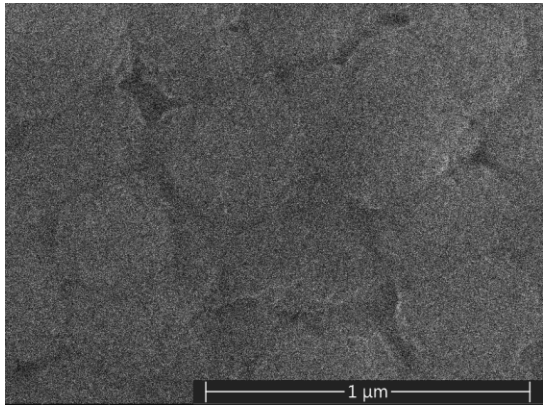




SEM images of J-H sample after 6 month.

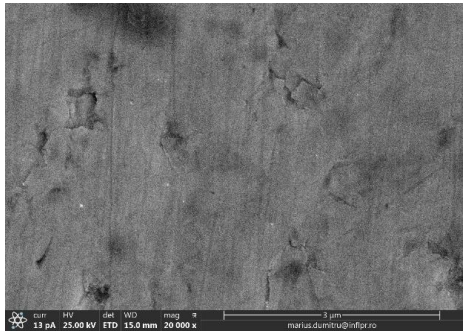
Boron films are delaminated Exfoliation of thick layer can be observed after 6 months



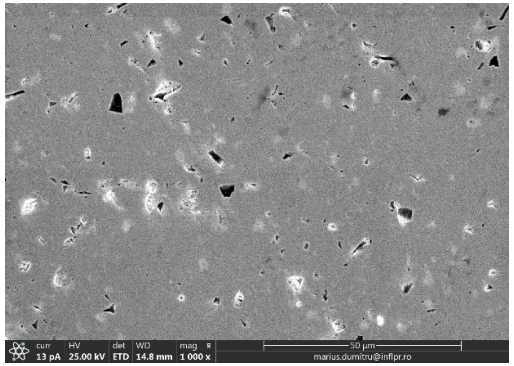


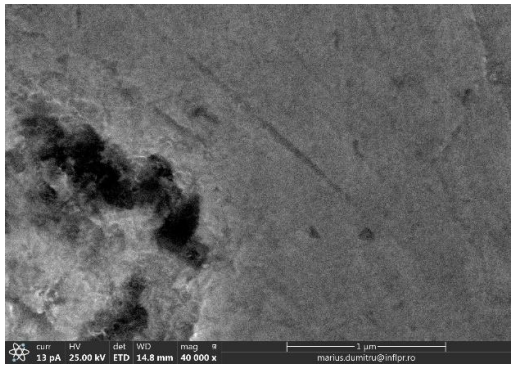
Boron-GD samples on W substrates

SEM image GD boron films onto W substrate- measured after 6 month



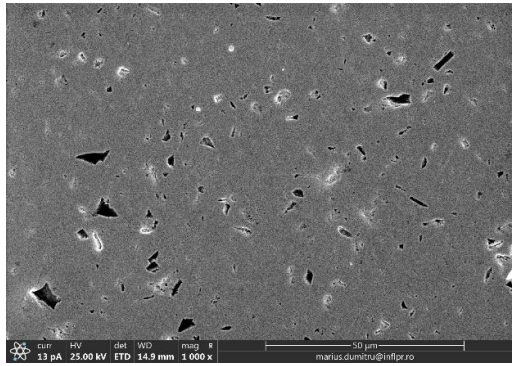
SEM image of the polished W substrate

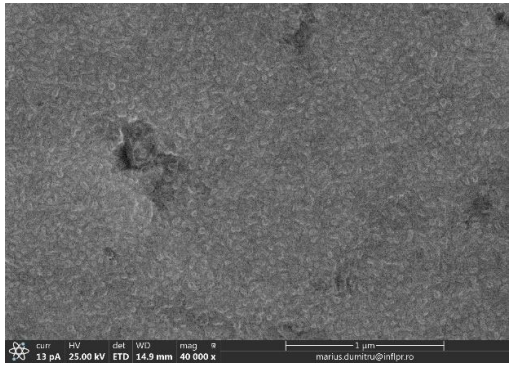




Conformal film

GD-H on W in Ar/B_2H_6 at 1000/5 layers (about 84 nm onto Si) :



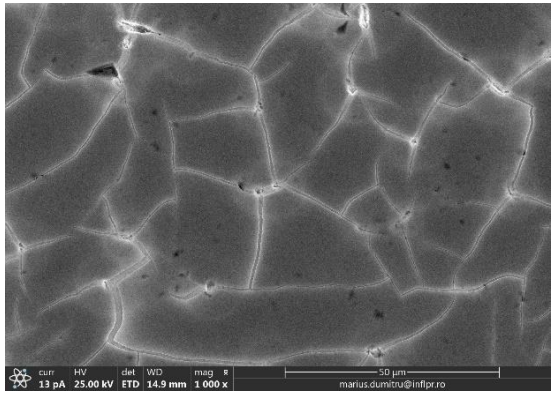


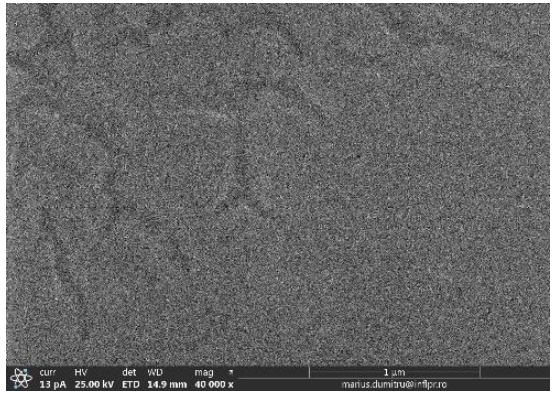
No delamination are observed

GD-L on W in Ar/B_2H_6 at 200/5 (layers of about 40 nm onto Si)

Boron-J samples on W substrates

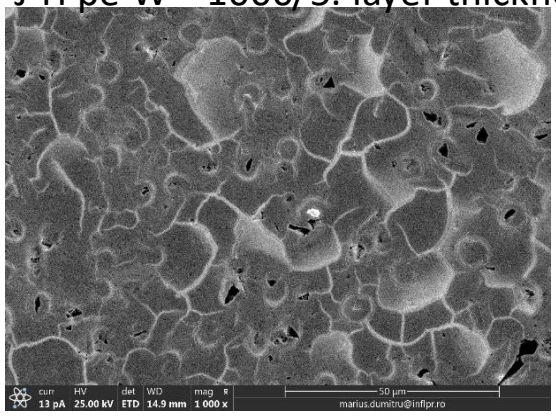
SEM image Jet boron films onto W substrate- measured after 6 months

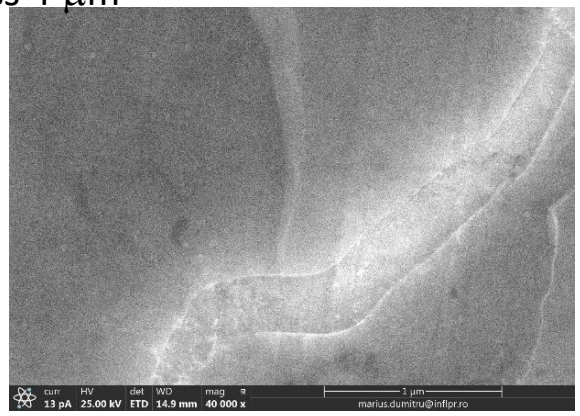




J-H pe W 1000/5: layer thickness 4 µm

cracks in the film are observed , however the layer does not completely delaminate





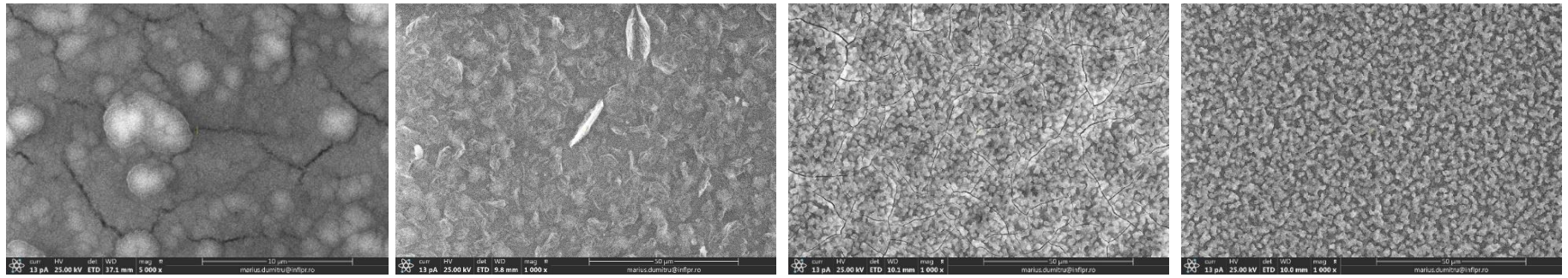
J-L on W 300/5: layer thickness 240 nm

Delamination or flakes deposition?

We have SEM only after 6 month for J-L on W

Boron-J-H samples obtain for various temperatures

Room Temp. 400 C 600 C 700 C

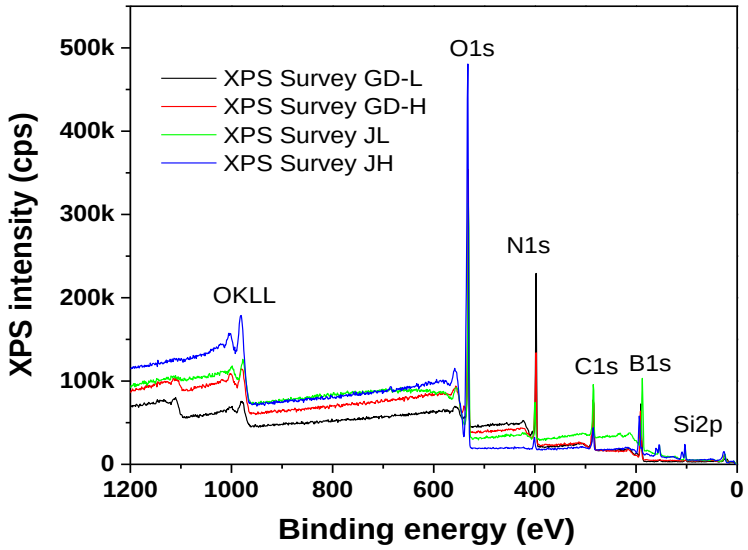


Room Temp. 400 C 600 C 700 C

SEM images of J-H (Ar/B2H6 at ratio 1000/5 sccm, 100 W for 10 minutes at various temperatures.

The boron films are nanostructured at high temperatures. Nano-flakes and nanotubes are observed after 400 C and sponge like nano-structures are visible at 600 and 700 C.

XPS investigation- survey spectra and elemental composition



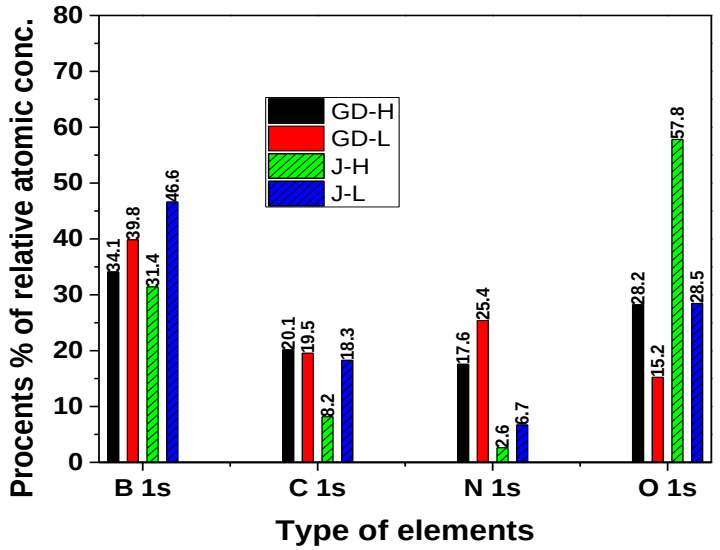
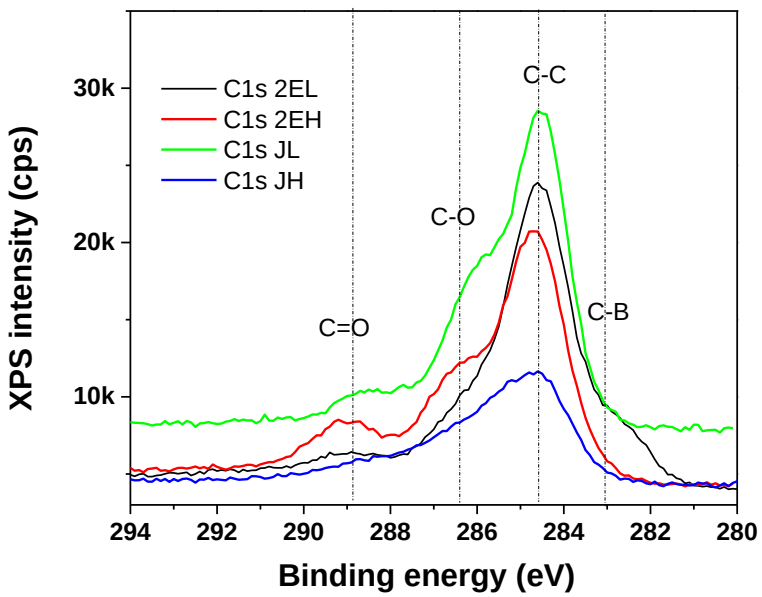


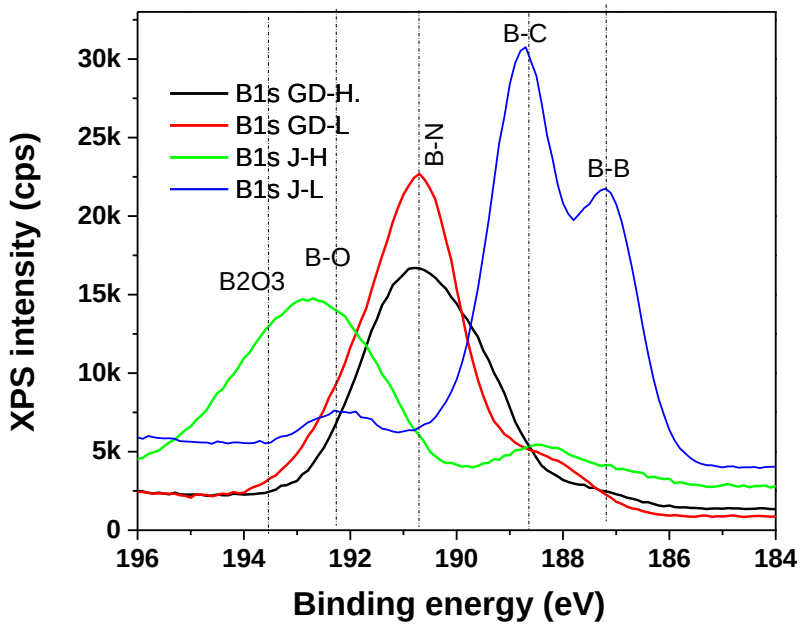
Table with relative atomic concentration of elements in the samples

	GD-H	GD-L	J-H	J-L
B 1s	34.1	39.8	31.4	46.6
C 1s	20.1	19.5	8.2	18.3
N 1s	17.6	25.4	2.6	6.7
O 1s	28.2	15.2	57.8	28.5

- Boron, carbon, nitrogen and oxygen elements;
- **Boron is dominant element;**
- High Ar flow rate led to a smaller B content and samples oxidation compared to L-rate;
- Lower Nitrogen and Carbon content in Jets sample;
- Oxides and nitride from air leaks and exposure.

XPS investigation- High resolution in C1s and B1s regions and bonding types

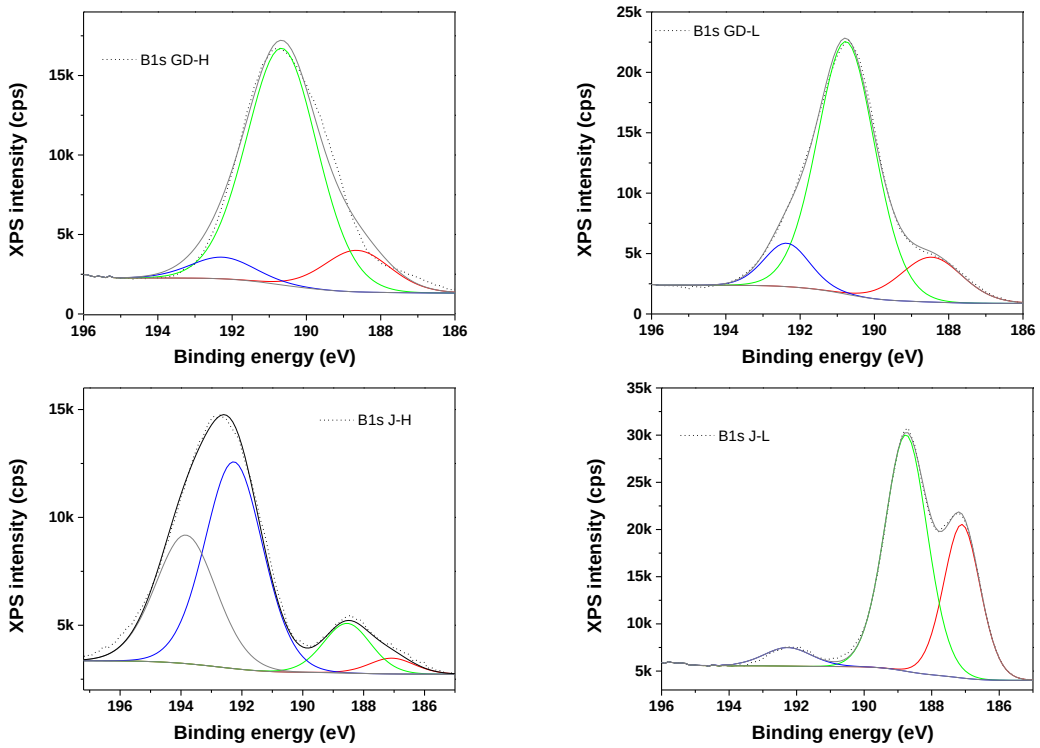




High resolution XPS spectra in the C1s and B1s region.

After calibration to C1s peak we observed various bond type of Carbon and Born atoms in the PECVD sample.

Boron bonds type - B1s region deconvolution

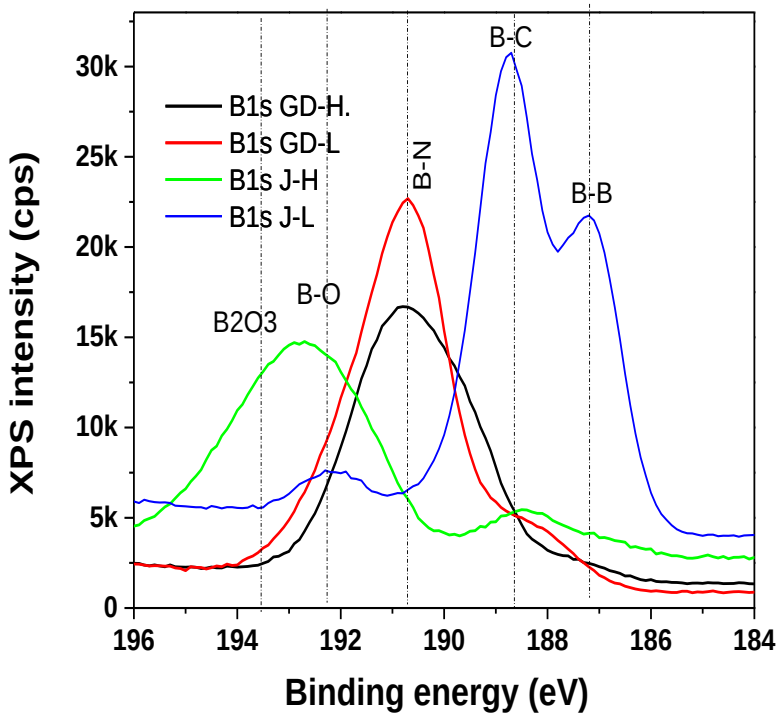


Bond type	Binding en.[eV]
(B-B),	187.2 ±0.1
(B-C);	188.5±0.1
(B-N),	190.8±0.1
(B-O subox.)	192.4±0.1
B_2O_3	193.5±0.1

Deconvolution of high resolution XPS spectra in B1s region (binding energies found in the literature)

XPS investigation- High resolution in B1s regions

and bonding types and their percentage



High resolution XPS spectra in the B1s region

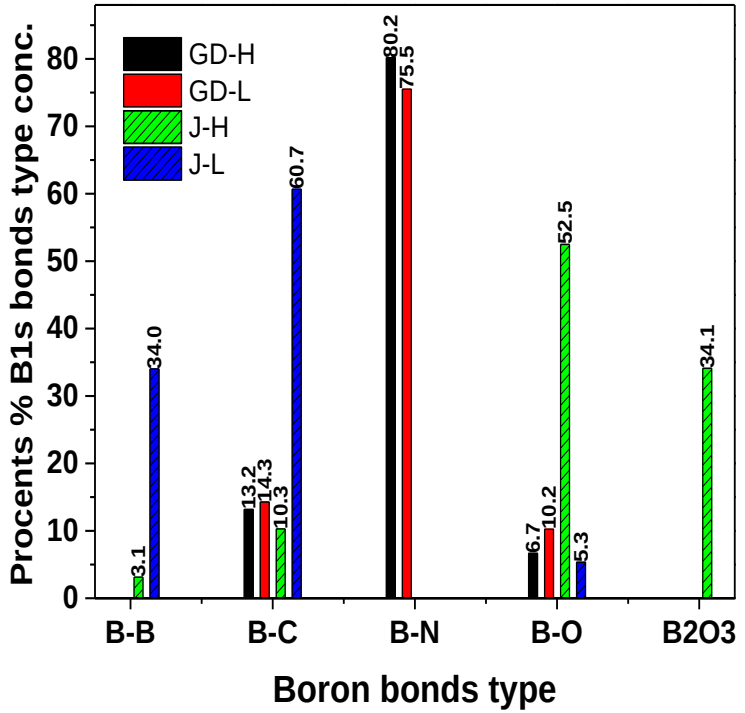


Diagram with percentages of B1s components

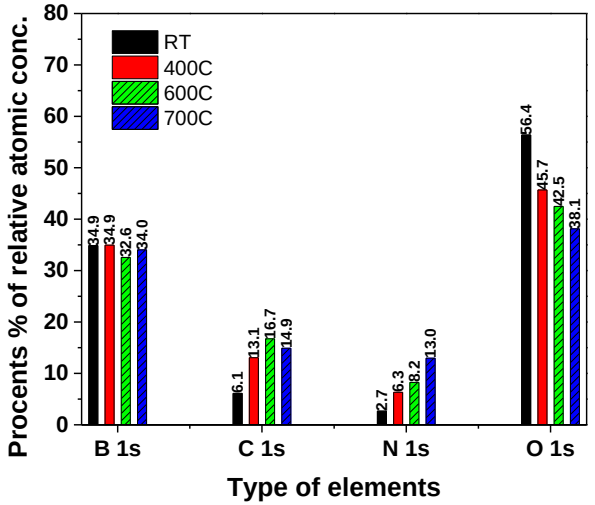
J-L contain metallic boron and J-H shows the most oxidized boron.

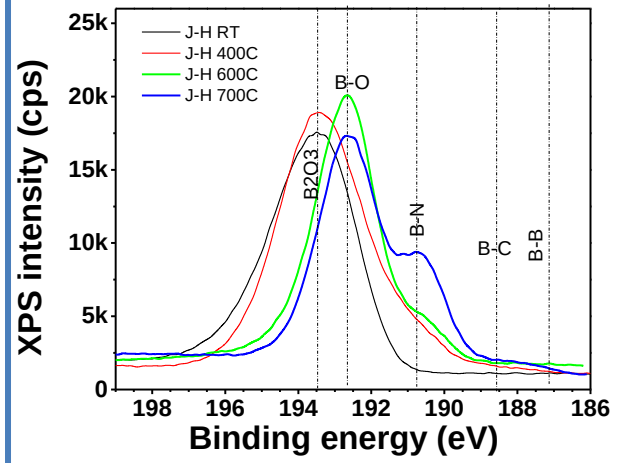
GD samples presents boron nitride bond type because of poor vacuum - mechanical pumps.

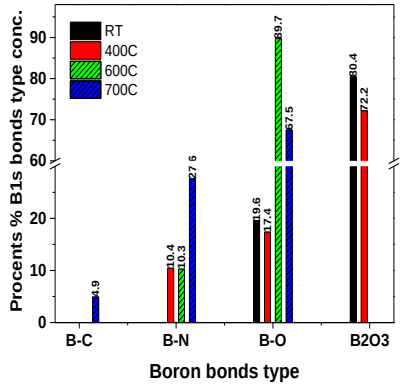
Composition of boron PECVD samples for various temperatures

Table with elemental composition from survey spectra for boron at various temperature

	RT	400C	600C	700C
B 1s	34.9	34.9	32.6	34.0
C 1s	6.1	13.1	16.7	14.9
N 1s	2.7	6.3	8.2	13.0
O 1s	56.4	45.7	42.5	38.1







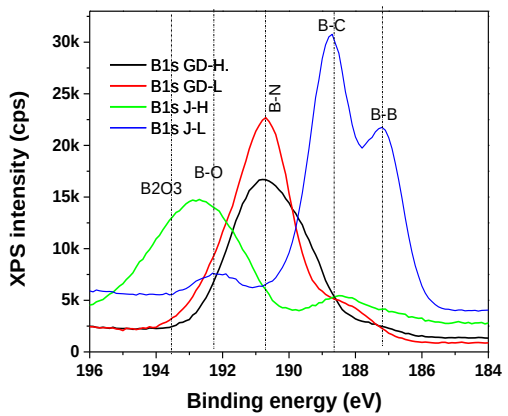
High resolution XPS spectra in the B1s region of samples deposited at various temperature.
Samples present oxidized boron.

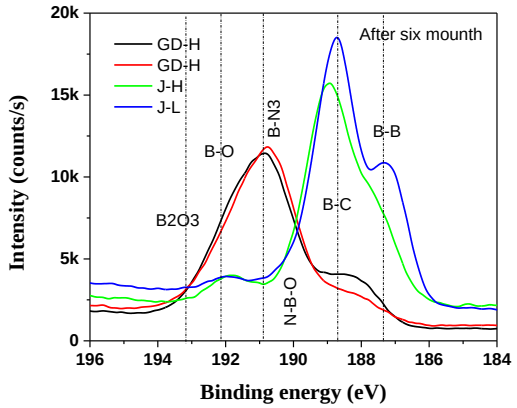
Time stability of composition in time

(*after 6 months*, substrates Si)

Table with elemental composition of initial and after 6 months of boron samples obtained by GD and plasma Jet

	GD-H	*+6 m*	GD-L	*+6 m*	J-H	*+6 m*	J-L	*+6 m*
B 1s	**34.1**	*34.0*	**39.8**	*31.8*	**31.4**	*31.1*	**46.6**	*39.8*
C 1s	**20.1**	*27.2*	**19.5**	*28.6*	**8.2**	*26.4*	**18.3**	*30.9*
N 1s	**17.6**	*19.7*	**25.4**	*18.7*	**2.6**	*7.4*	**6.7**	*6.3*
O 1s	**28.2**	*19.1*	**15.2**	*21.0*	**57.8**	*35.1*	**28.5**	*23.0*





High resolution XPS spectra in the B1s region of boron PECVD samples measure after days and 6 months.

We can observed variation in B, C, N and O concentration.
The GD samples that presents **boron nitride bonds** are quite stable because are difficult to oxidize over time.
In the J-L samples that contain B-B and B-C remains almost the same shape.

Conclusions

- We demonstrated that we can obtain boron layers by PECVD in Ar/B_2H_6 mixture;
- High deposition rate for **jet** (~400 nm/min) and low rate for **glow discharge** (4-8 nm/min);
- Good adhesion of the thin B layers on W surface, and low adhesion on Si wafers;
- For thin boron film the morphology remains stable in time (both GD-L and J-L at Low Ar);
- The boron films **are nanostructured at high temperatures;**
- The composition of boron layers deposited by PECVD from diborane contains in various concentrations B, C, N and O elements.
- In the **Jets** samples we have **metallic boron and oxide bonds type**, while in the **GD** samples we found mostly **boron nitride bonds type**. The boron bonds type seems to be preserved after 6 months, except J-H samples which are quite spongy (not compact);
- Modification of the composition of boron layers are observed in time.

Future plans

Infrastructure:

- Improving the work safety by inserting higher sensitivity diborane detectors, new system for burning the pumps exhaust;
- Optimization of the deposition setups (high vacuum pumping systems, mass flow controllers, diborane bottles – also with He, or D_2, quartz windows for OES);
- Development of new diborane discharge configurations relevant for fusion (we have know-how in designing of new plasma sources with injection for PECVD).

Research

- Study of the boronization process (efficiency, species formed, influence of impurities) using diborane or other boron containing precursors by PECVD. Use diagnostics and characterization techniques for:
  -Species formed during sputtering of boron layers in D2/H2 plasma (Optical emission spectroscopy and mass spectrometry available);
  -Properties of Boron films deposited by PECVD using diborane (morphology, composition, adhesion, hardness, resilience to sputtering etc).
- Identification of the critical issues in boronization, of interest for fusion technology: process, adhesion, time stability, behaviour in respect to sputtering;
- Identification of the needs for PECVD preparation of thick/thin Boron layers for materials study (substrate types, pre-treatment, thickness, etc).