Study of various configurations of Micro Hollow Cathode Discharges in Ar/N_2 used for boron nitride PECVD

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Joint GEC-IOPS / OLTPD seminar – March 7, 2023

Team in LSPM

- Colleagues:

Xavier Aubert, Ovidiu Brinza, Kristaq Gazeli, Laurent Invernizzi, Guillaume Lombardi, Vianney Mille, Swaminathan Prasanna, Alexandre Tallaire, Ludovic William

- Post-docs:
  - Hiba Kabbara (2018-2019)
  - Manoel Jacquemin (2021-2022)


- PhD students:
  - Salima Kasri (2015-2019)
  - Alice Remigy (2019 – 2022)
  - Belkacem Menacer (2022 -)



Collaborations

- Colleagues from LPGP: Gérard Beauville, Michel Fleury, Stéphane Pasquiers, Joao Santos Sousa
- Colleagues from synchrotron SOLEIL: Nelson de Oliveira and Laurent Nahon
- Colleagues from LTM and LIPhy: Nader Sadeghi
- Colleagues from MPQ: Clément Barraud and Maria Luisa Della Rocca

Agenda of the presentation

I. Introduction

II. Deposition of boron nitride by PECVD: description of the process and few deposition results

III. Atomic nitrogen production in the microplasma source

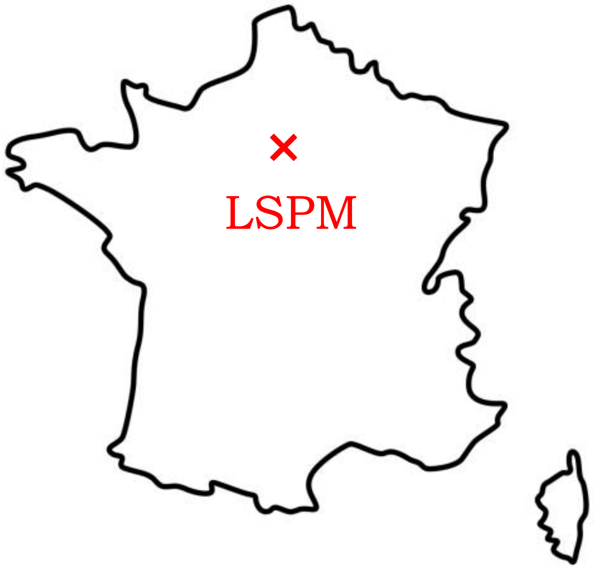
IV. Atomic nitrogen transport in the deposition chamber

V. Conclusion and perspectives

My laboratory: LSPM

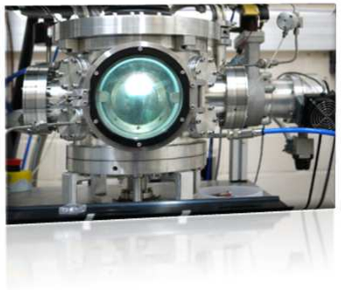
- Laboratory of Process and Material Sciences; created January 1st, 2011

- Located in France, in the north of Paris

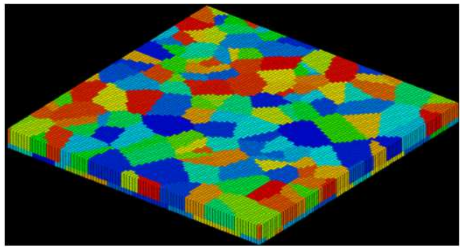


LSPM: few numbers

- 85 permanent positions:
  - 10 CNRS researchers
  - 55 associated professors/professors
  - 20 engineers/technicians/administrators



- 45 PhD students and post-docs

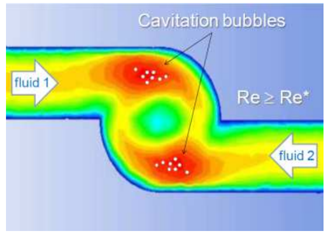


- 4/5 PhD government grants/year

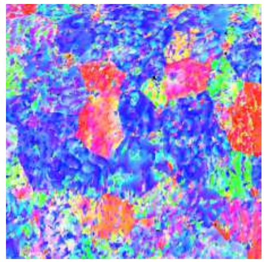
LSPM: scientific axis

- <u>3 scientific axis</u>:

1) Development of elaboration and transformation process of materials



2) Structural caracteristics and properties of materials



3) Integration of materials in systems, devices and process

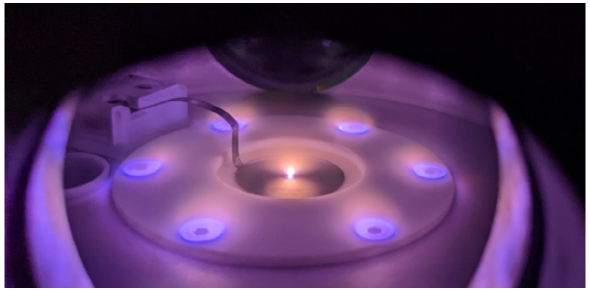
University Sorbonne Paris Nord

University Sorbonne Paris Nord

University Sorbonne Paris Nord

- 5 campus
- 26000 students
- 28 laboratories
- 1500 assistant professors and professors
- 730 people in the administration and technical staff

Deposition of Boron Nitride by microplasmas: process description



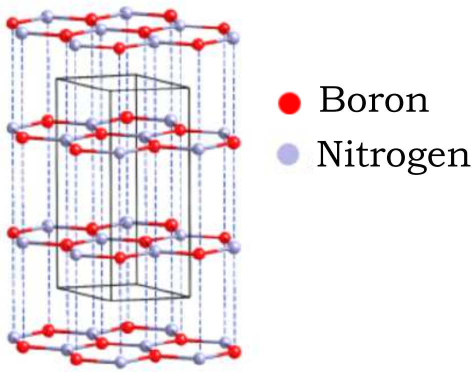
Context

- New research axis since 2016 in LSPM: "Microplasmas for innovative materials".
- Idea: choice of a material and a versatile process
  → control of the morphological and structural characteristics of the films
- Goals:
  - To develop an efficient new plasma reactor for the deposition of high potential materials on large surfaces, easily adaptable to established technologies
  - To optimize the quality of the deposited layers by understanding the mechanisms involved in growth processes using reactive plasmas
- Target material: hexagonal boron-nitride (h-BN)

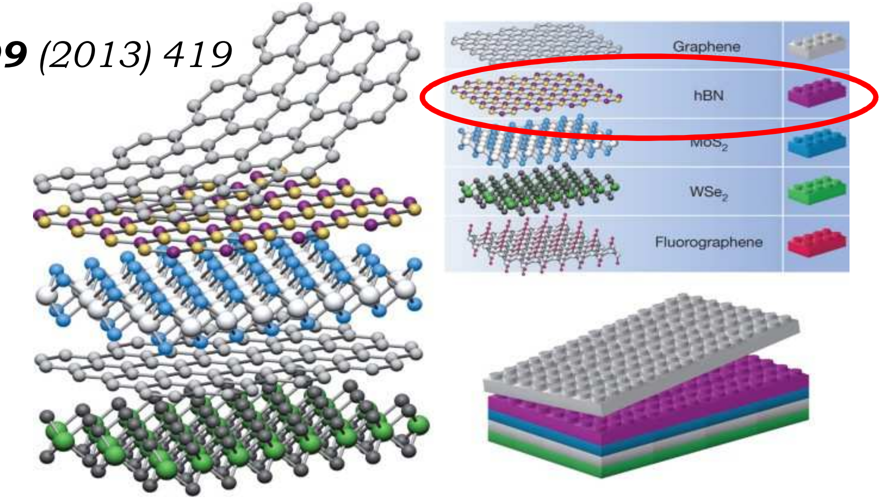
Why h-BN?

- Large band gap, thermally and chemically stable, ideal substrate for graphene.

Griem et al. Nature ***499*** *(2013) 419*



h-BN (sp^2)

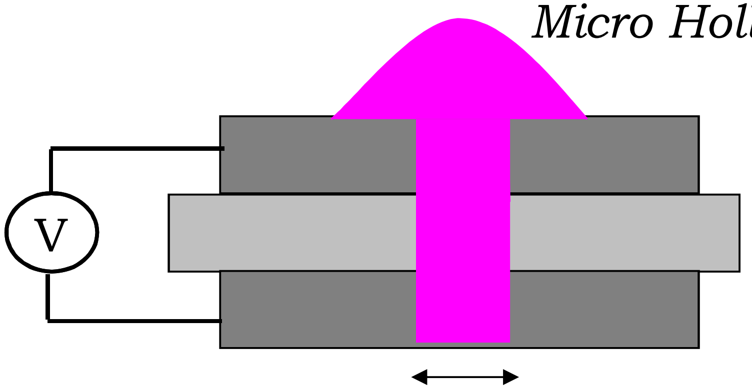


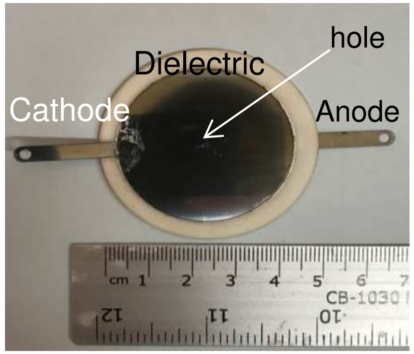
Van der Waals heterostructures

- Strategic material highly demanded for electronic and optoelectronic applications, also quantum technologies.
- But the development of applications based on this material is still held back by the poor availability of high-quality epitaxial films on large areas → new process based on microplasmas.

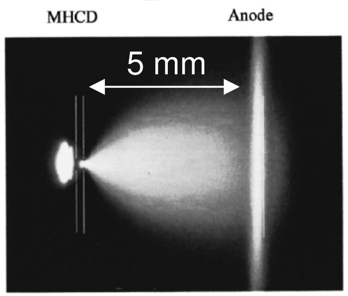
Why MHCD?

Micro Hollow Cathode Discharges



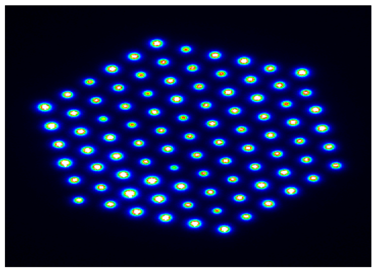


- Low temperature plasma: reduction of the deposition temperature compared to conventional processes.
- Production of high electron density: high degree of dissociation of nitrogen.
- Deposition on large surfaces: MCSD and array of MHCDs.



Ar
160 Torr

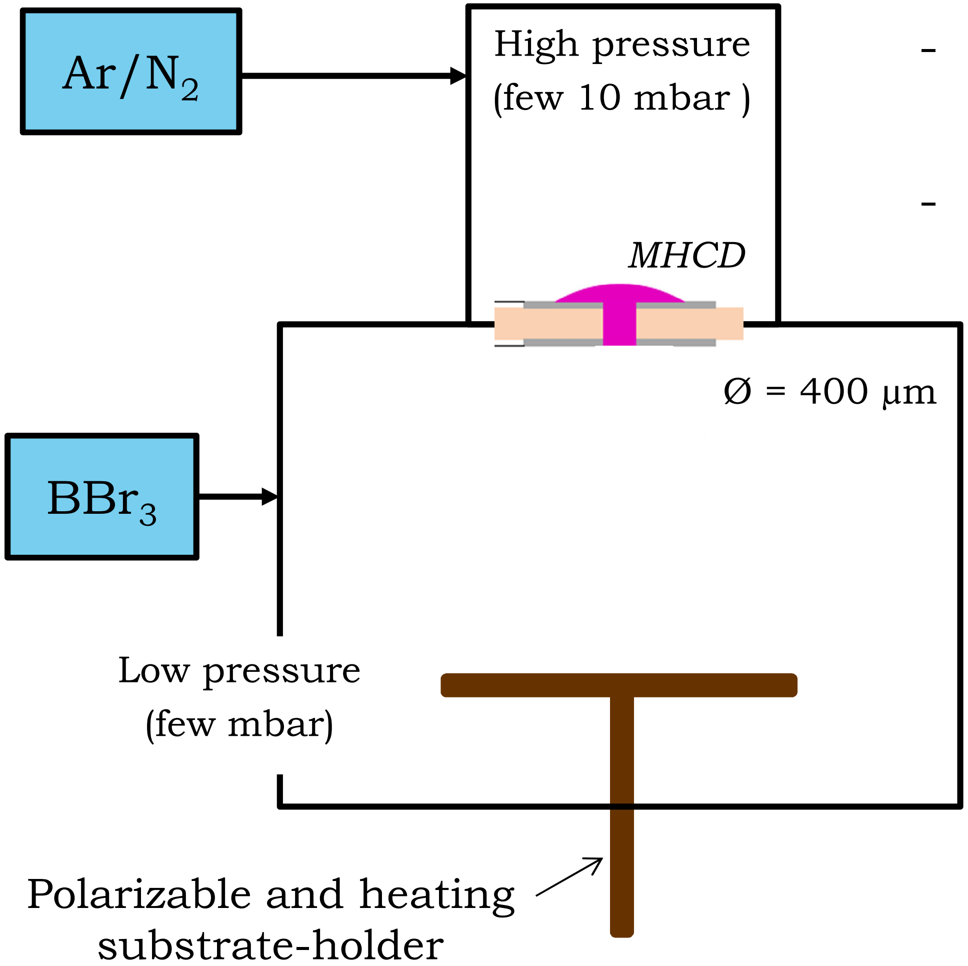
Stark et al. PPCF ***85*** *(1999) 2075*
Makasheva et al. PPCF ***49*** *(2007) B233*



Pulsed
power supply

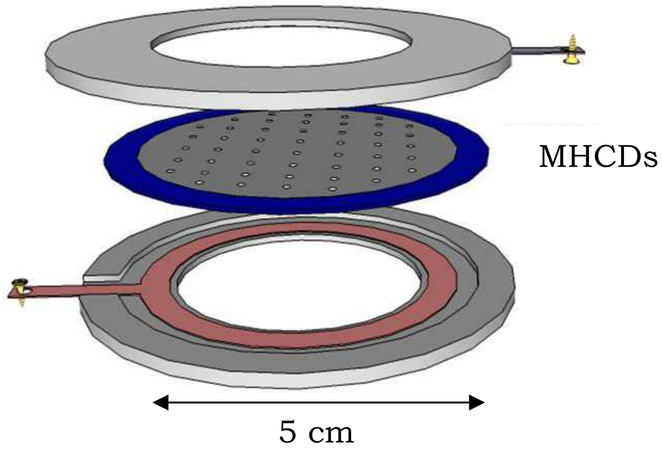
91 MHCDs in pure N_2

PECVD process

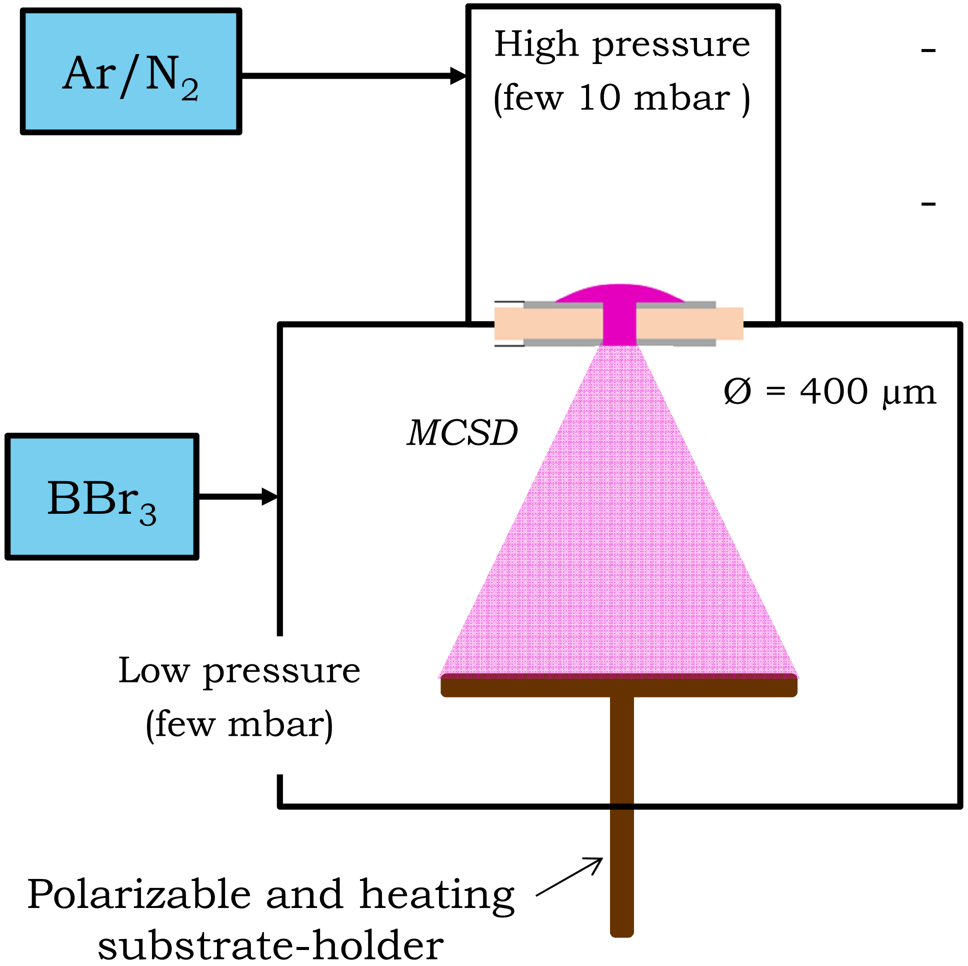


- Higher pressure upstream chamber
  → dissociation of N_2
- Lower pressure downstream chamber
  → limitation of N recombination

Gluing and laser drilling



PECVD process



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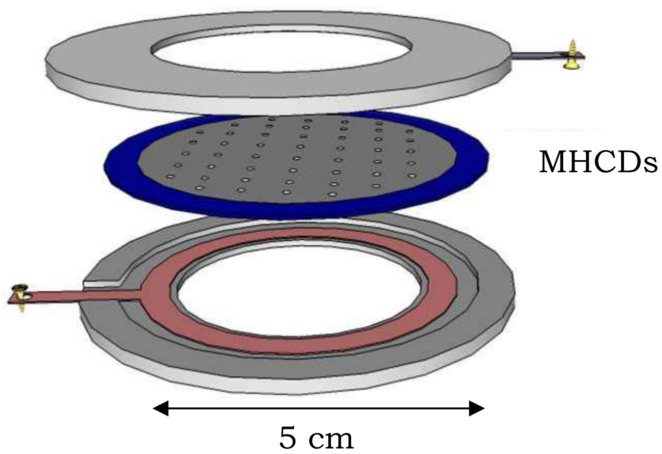
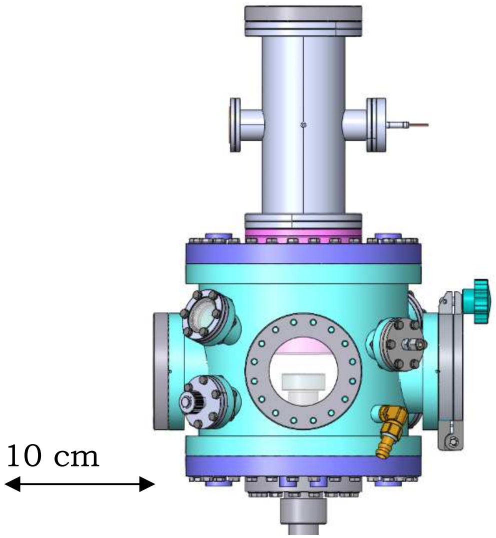


Developed reactors

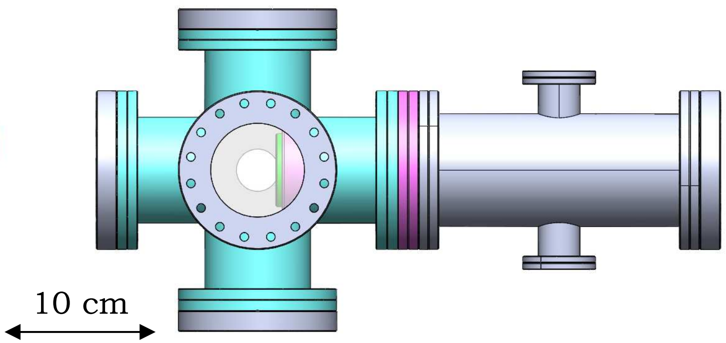
Design of the pulsed power supply

Optimal plasma conditions for deposition

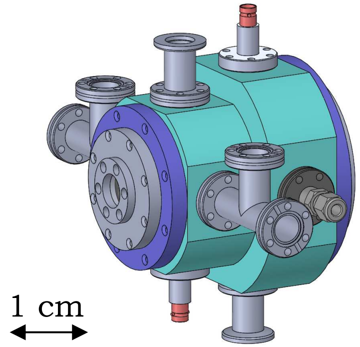
Deposition reactor



Matrix reactor



1 MHCD reactor



h-BN deposition	**Optimization of a MHCD matrix**	**Fundamental study of one MHCD in reactive gas**
Excitation by a ns pulsed high voltage Ar/N_2 discharge + boron precursor : BBr_3	Excitation by a ns pulsed high voltage Ar/N_2 discharge	DC excitation Ar/N_2 discharge

Developed reactors

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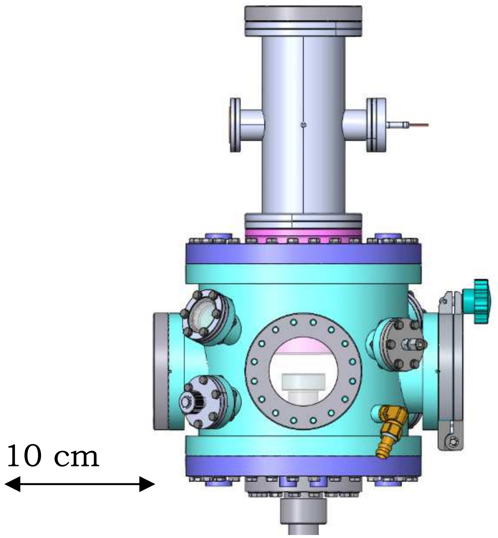
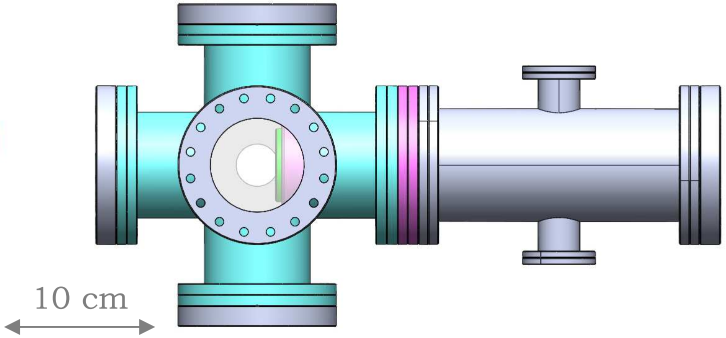
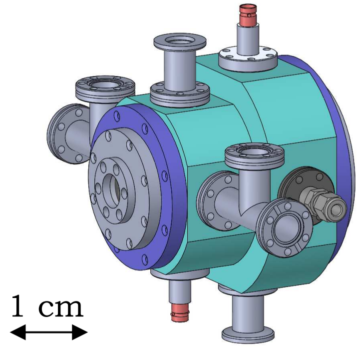
Deposition reactor	Matrix reactor	1 MHCD reactor







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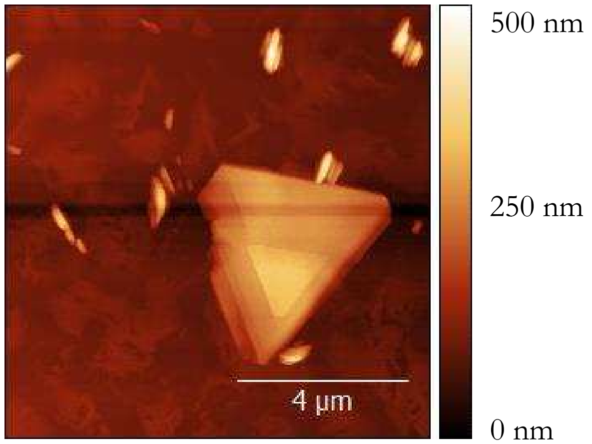
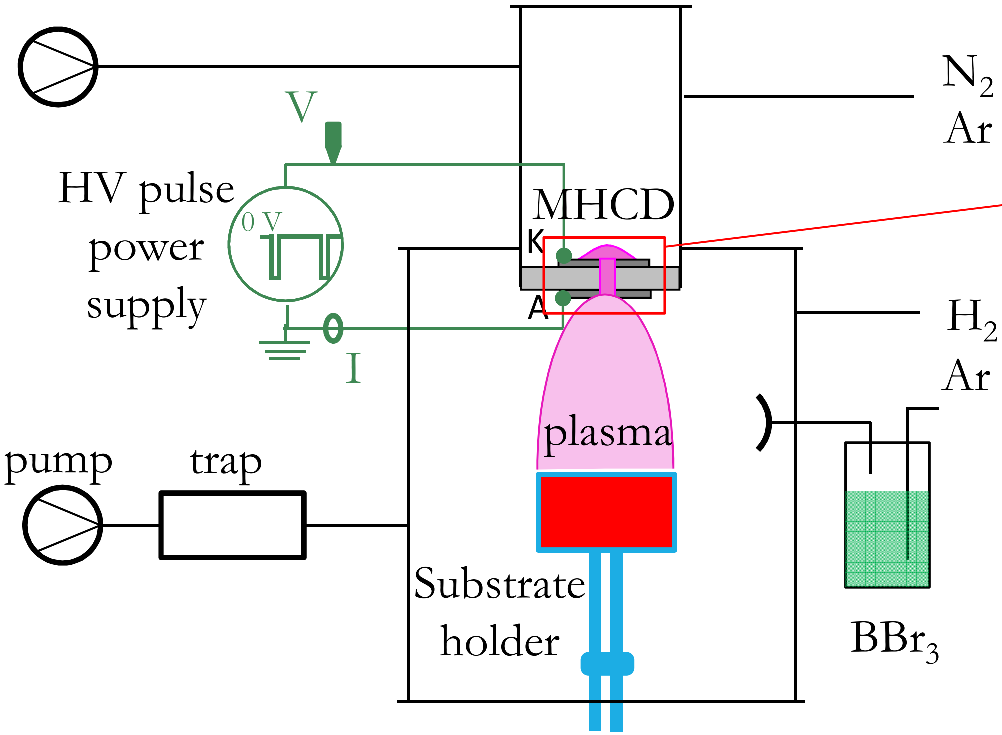
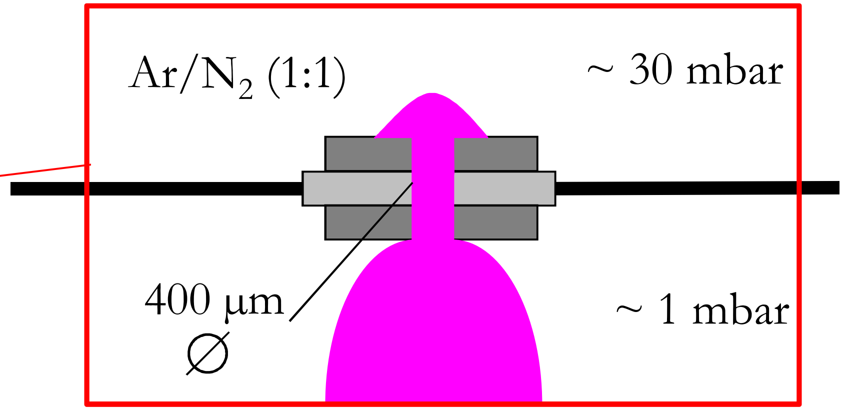
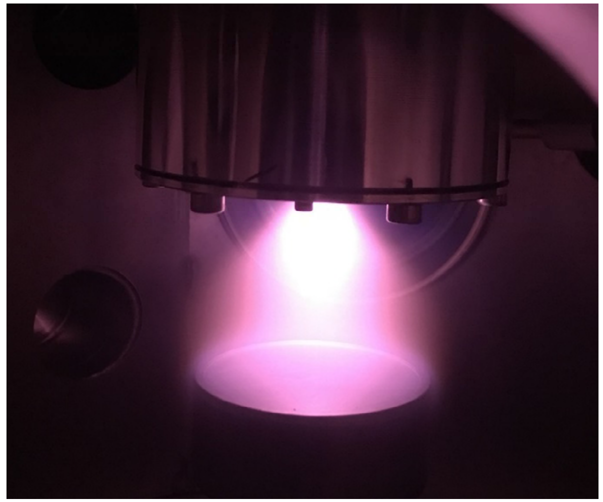
Deposition reactor: few results



Experimental setup for h-BN deposition







Expansion covering all the substrate

<u>Working conditions</u> :

Pulse 1 kV, 500 ns, 10 kHz, 71-120 µJ/pulse

BBr_3 flux: 2 µmol/sec

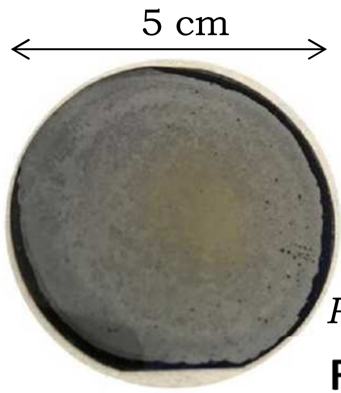
V_{SH}: 230 V and T_{SH}: 600-950°C

$P_{deposition\ chamber}$: 0.7-1.2 mbar

Substrates: (0001) sapphire, (111) or (100) Si

Deposition results

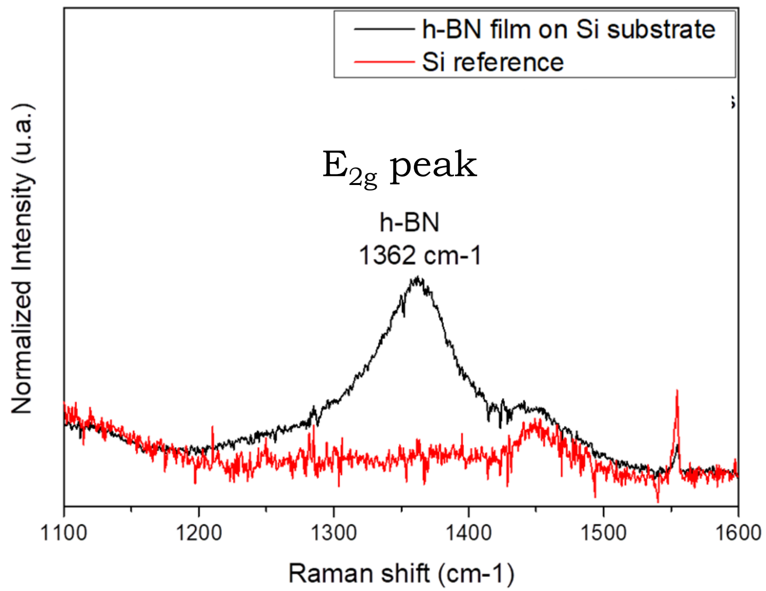
- Deposition on 2-inch silicon (Duration: 2-7h)
- Clear signature of h-BN at 1362 cm^{-1} ⇨ Proof of feasibility
- Deposition rate: v ~ 35 nm/h
- Crystalline quality probably moderate considering the broad Raman line at half maximum
- Chemical composition: 55% of B and 45% of N (very close concentration)
- Effect of the distance MHCD/substrate



Film deposited on 2-inch Si wafer covering almost all the surface

Photography

Raman spectroscopy :



H. Kabbara et al, APL 116 (2020) 171902

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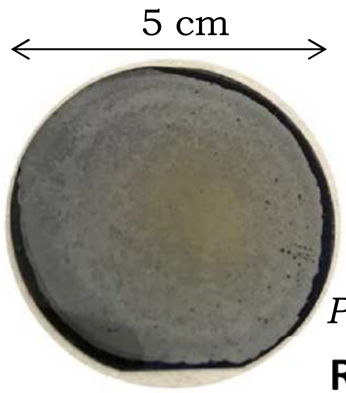
Optimisation of the process → study of the discharge: density of N in particular



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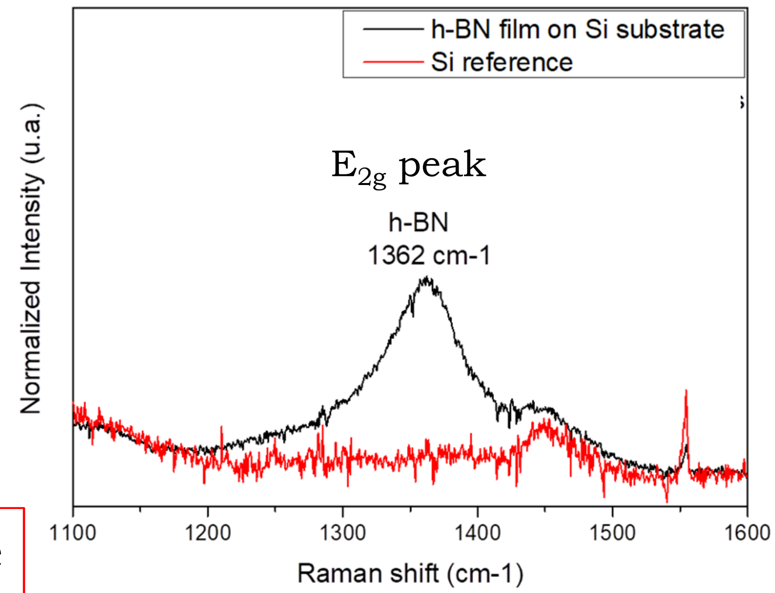


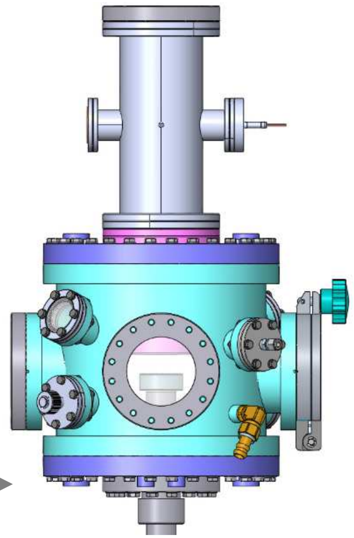
H. Kabbara et al, APL 116 (2020) 171902

Developed reactors

Design of the pulsed power supply

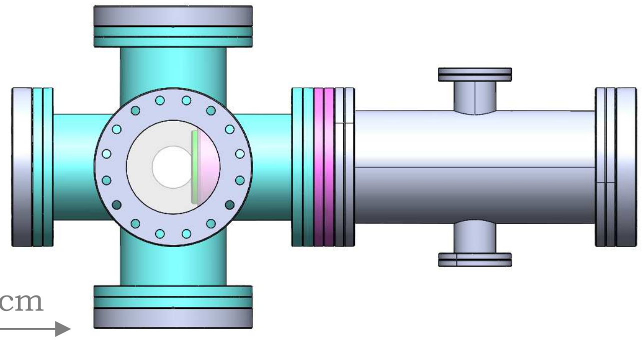
Optimal plasma conditions for deposition

Deposition reactor



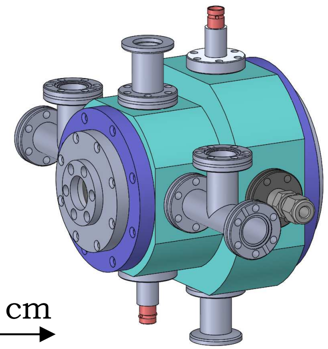
10 cm

Matrix reactor



10 cm

1 MHCD reactor



1 cm

Alice Remigy thesis

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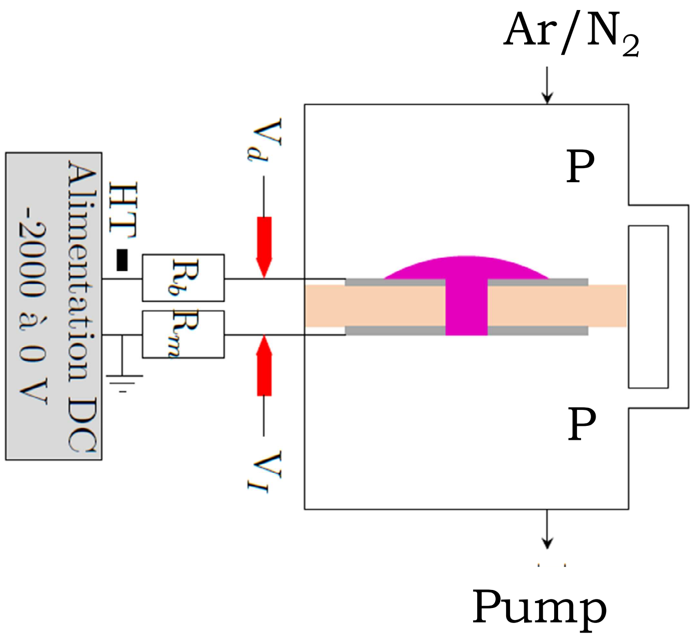
Excitation by a ns pulsed high voltage	Excitation by a ns pulsed high voltage	DC excitation
Ar/N_2 discharge + boron precursor : BBr_3	Ar/N_2 discharge	Ar/N_2 discharge

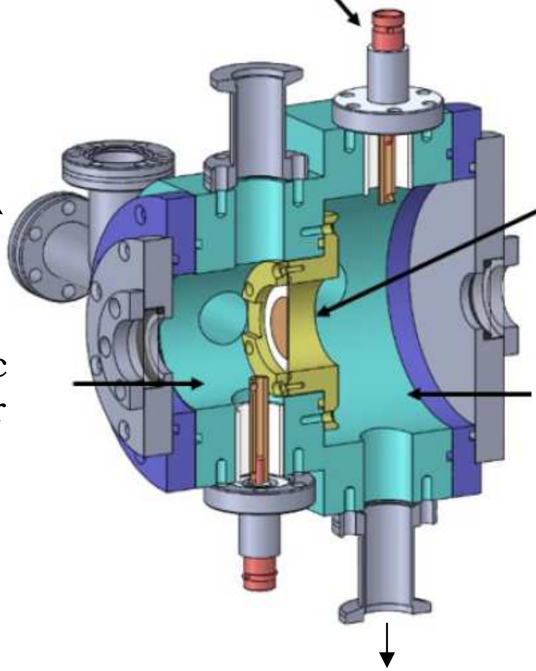
Study of the 1 MHCD reactor: production of atomic nitrogen

MHCD configuration



Same pressure in the two chambers of the reactor

Tools



- Electrical characterization → discharge resistance
- VUV Fourier transform absorption spectro. (SOLEIL synchrotron) and TALIF → atomic nitrogen density

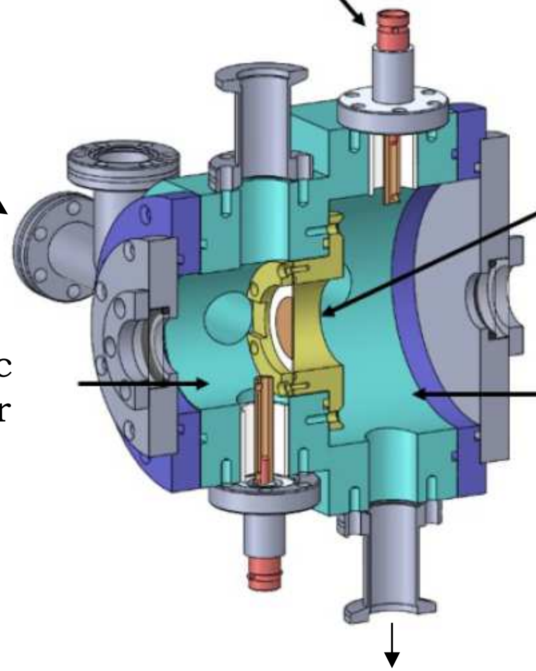
SOLEIL SYNCHROTRON   DESIRS

- OES → electron density and gas temperature
- Absorption spectroscopy → metastable argon density

LPP

- Global model 0D

Tools



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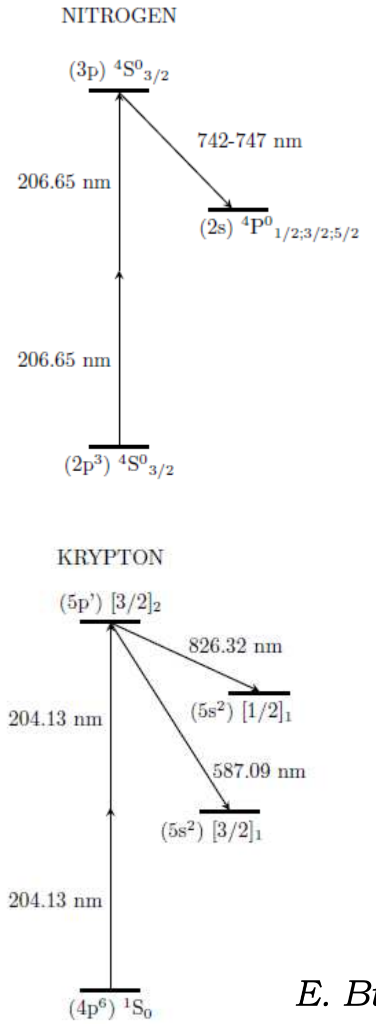
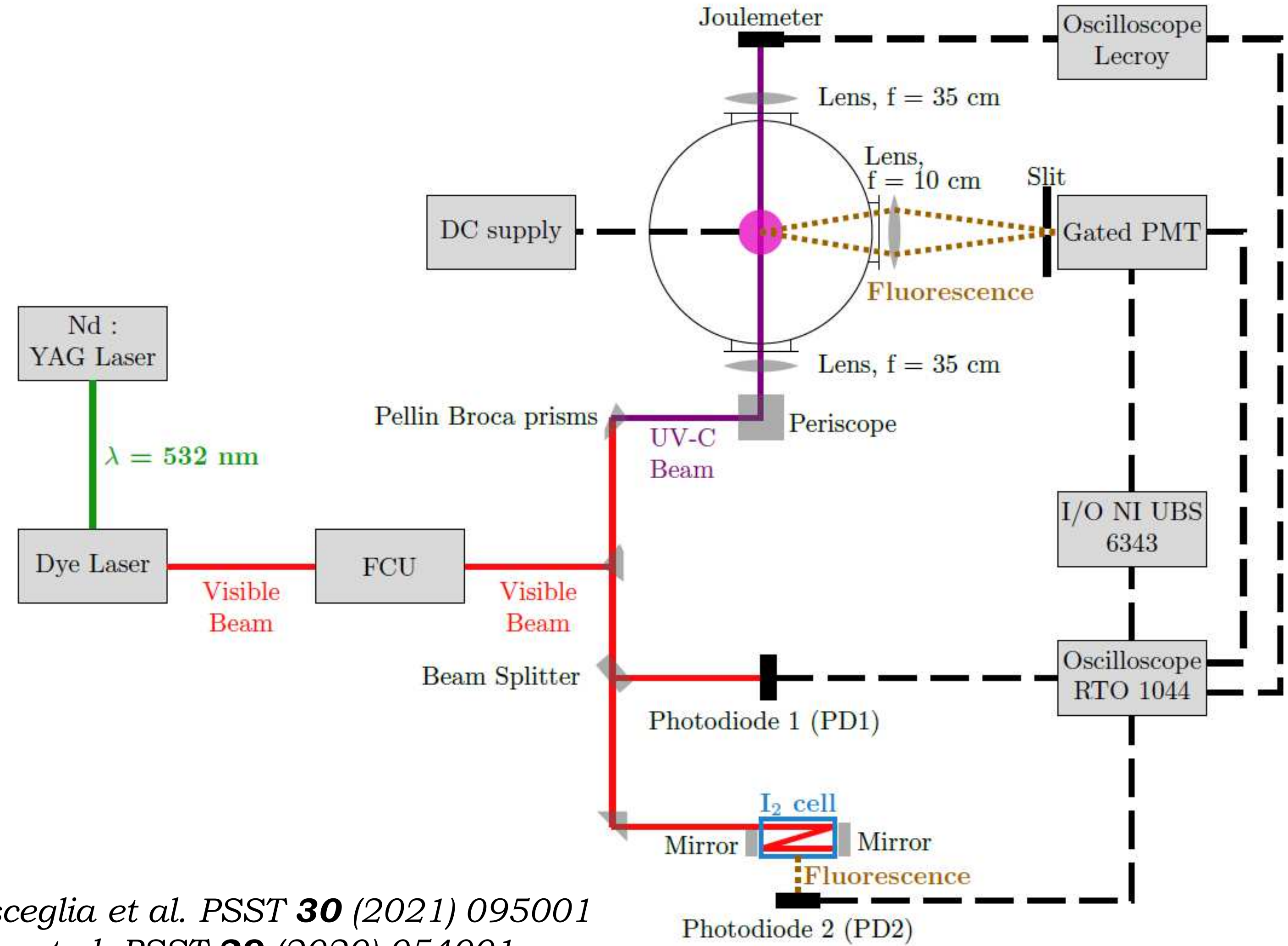
Two photon Absorption Laser Induced Fluorescence (TALIF)

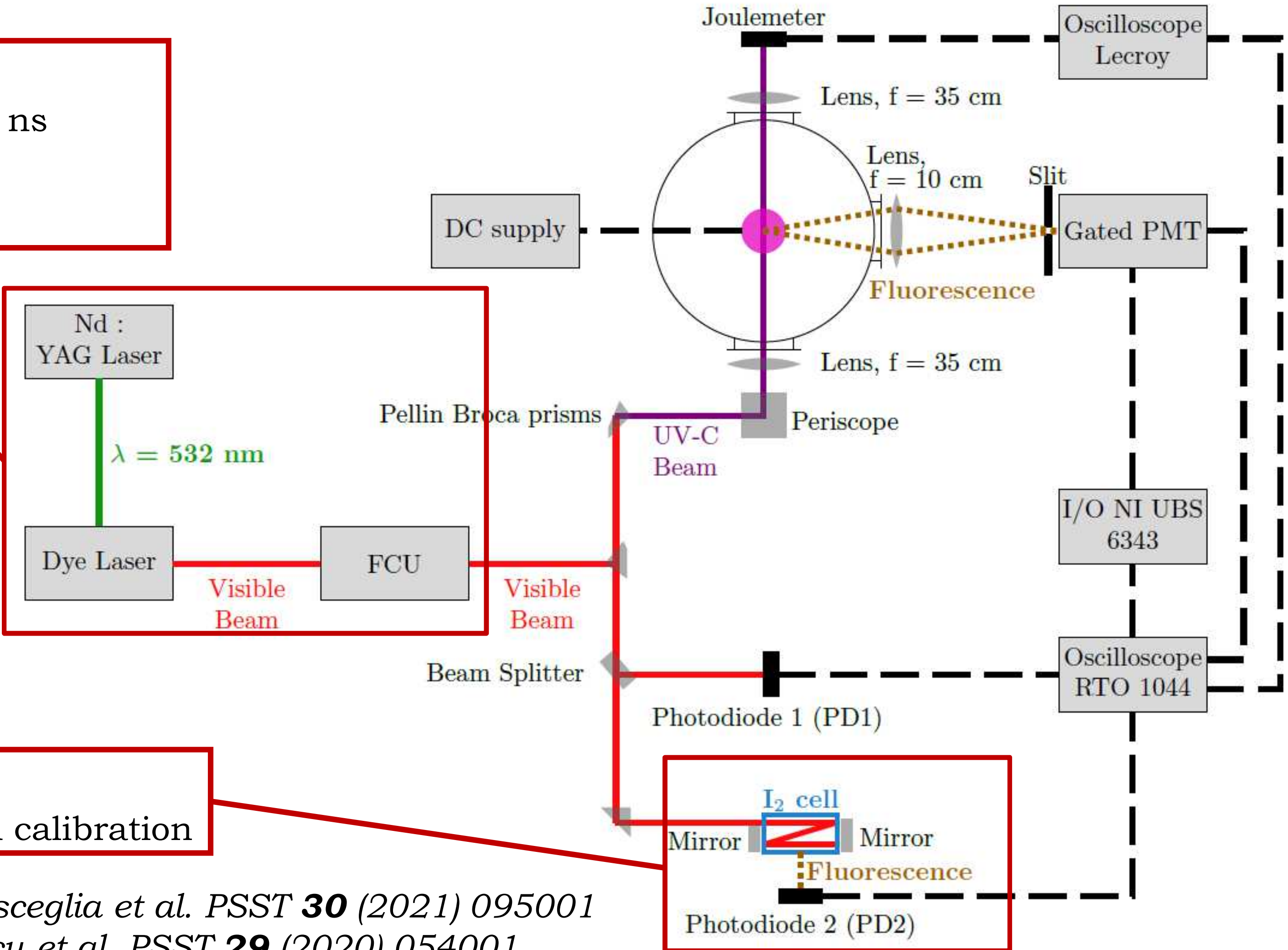




E. Bisceglia et al. PSST ***30*** *(2021) 095001*
Stancu et al. PSST ***29*** *(2020) 054001*

Two photon Absorption Laser Induced Fluorescence (TALIF)

ns-Laser
- Pulse width : 10 ns
- 10 Hz
- 2.5 mJ/pulse



Iodine cell
- Wavelength calibration

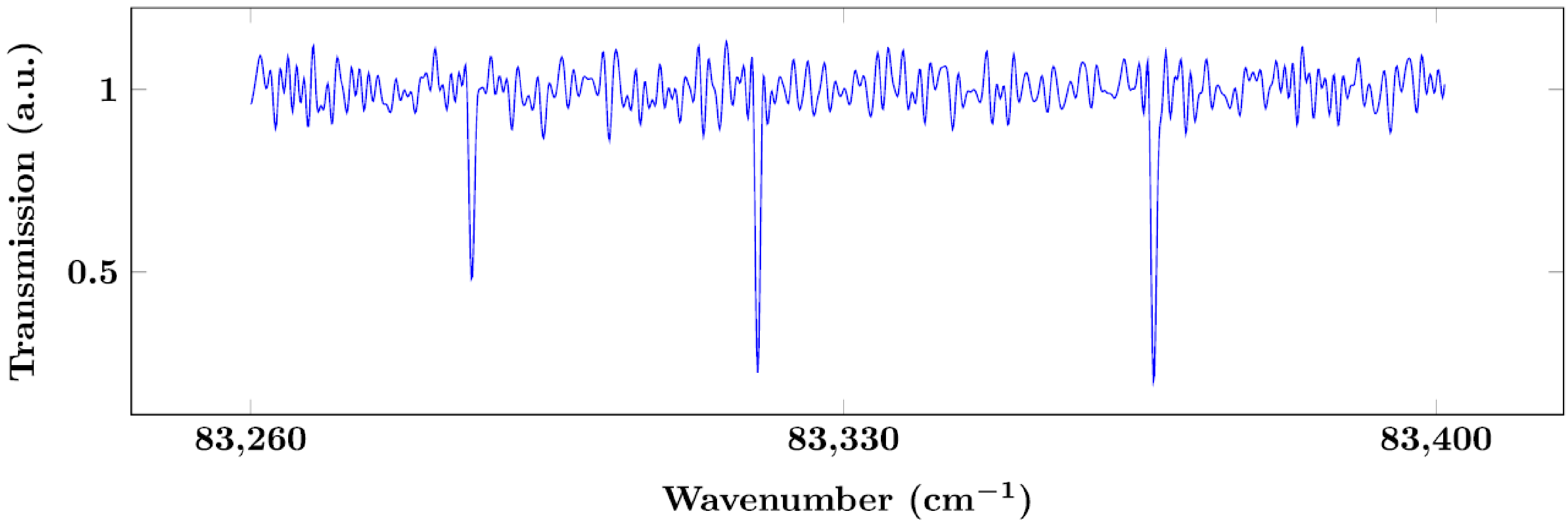
*E. Bisceglia et al. PSST **30** (2021) 095001*
*Stancu et al. PSST **29** (2020) 054001*

Fourier transform absorption spectroscopy (FTS VUV)

- Direct measurement of N in the ground state studying the transitions in the vacuum UV.

*K. Niemi et al. APL **103** (2013) 034102*
*Dumitrache et al. PSST **31** (2022) 015004*

- Probed transition (120 nm): N ($2p^3\ ^4S_{3/2}$)→ Triplet N ($3s\ ^4P_{1/2,\ 3/2,\ 5/2}$)



Example of a normalized non deconvoluted transmission spectrum

Global model

- Volume-averaged (0D) model: temporal variations of volume-averaged quantities (densities and temperature)

- Particle balance:

$$\frac{dn_\alpha}{dt} = G_\alpha - P_\alpha$$

- Electron power balance:

$$\frac{d}{dt}\left(\frac{3}{2}n_e e T_e\right) = P_{\mathrm{abs}} - P_{\mathrm{dis}}$$

Global model

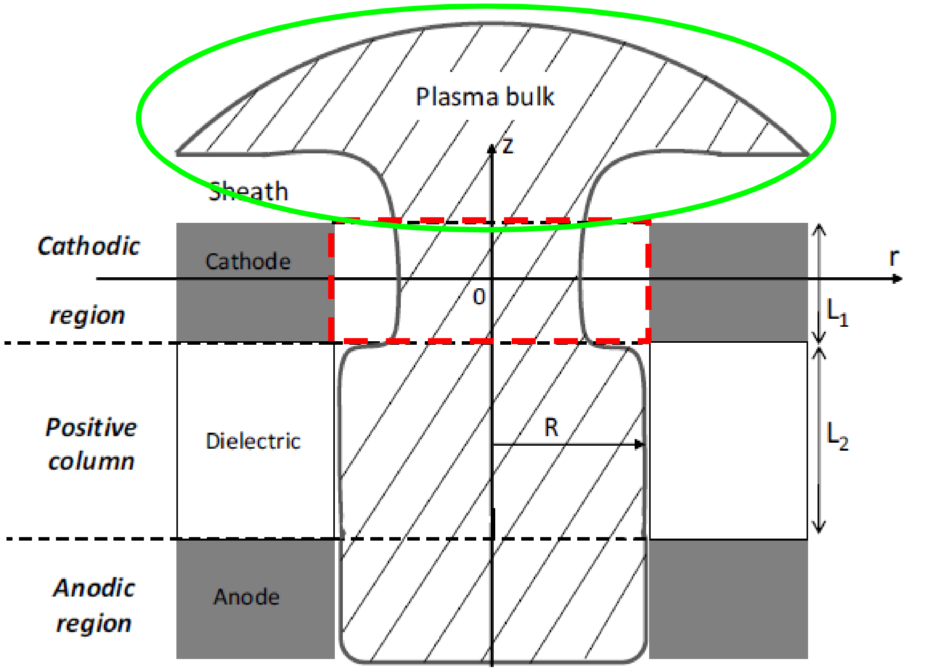
Power balance:

Modelisation of the cathodic region

$$P_{\text{abs}} = \frac{A}{S_C} \kappa I_d V_d$$

Fraction of power absorbed by the electrons:

$$\kappa = \frac{\bar{P}_e}{\bar{P}_e + \bar{P}_i} \simeq \frac{1}{1+\gamma} \frac{1}{\ln(1+\frac{1}{\gamma})}$$



C. Lazzaroni et al. PSST **20** (2011) 055004

Particle balance:

Electropositive plasma: Ar-N_2 mixture

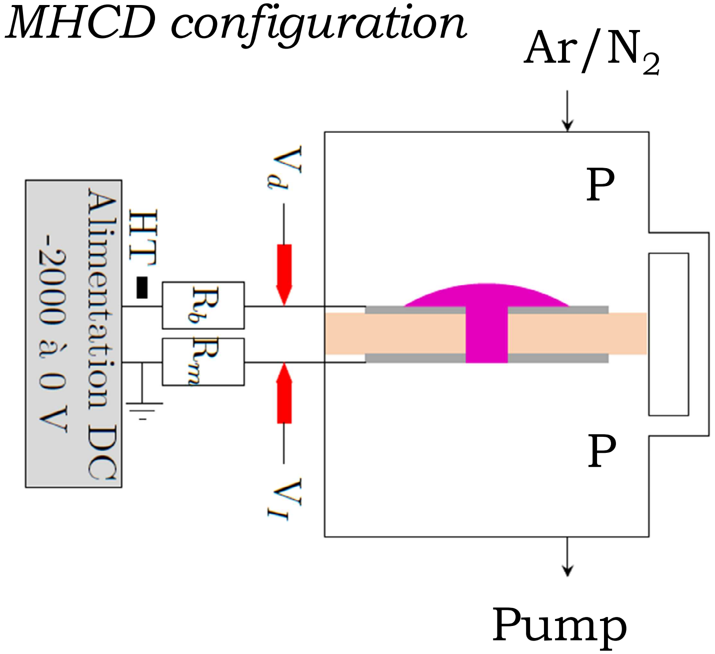
- 14 species
- 69 volume reactions
- T_g=470 K

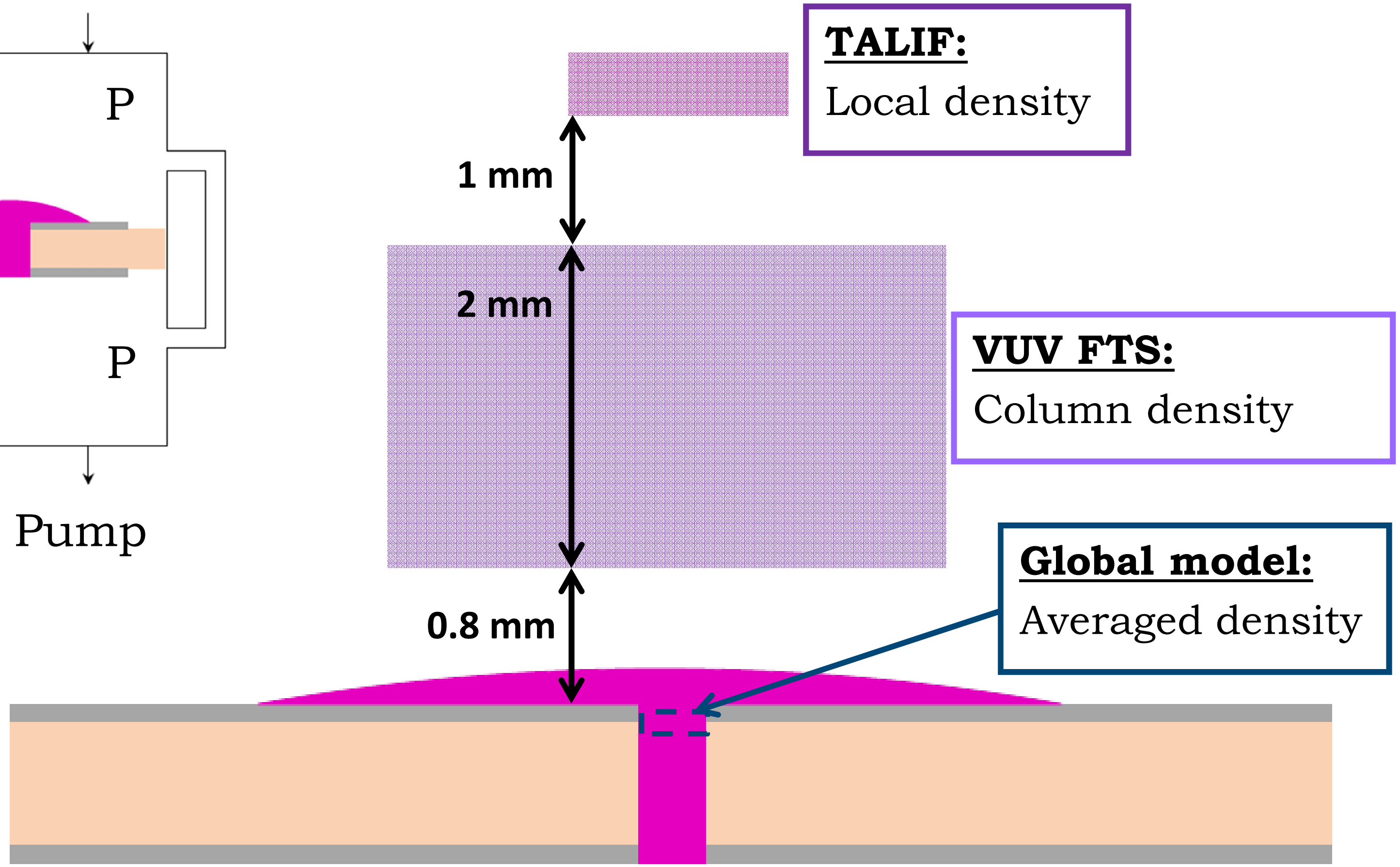
14 considered species:

Ar, Ar^+, Ar_2^+, Ar^m, Ar^r, Ar^{4p}, N_2, N, N_2^+, N_4^+, $N_2(A)$, $N_2(B)$, $N_2(C)$ and e^-

Experiments/model comparison?

MHCD configuration

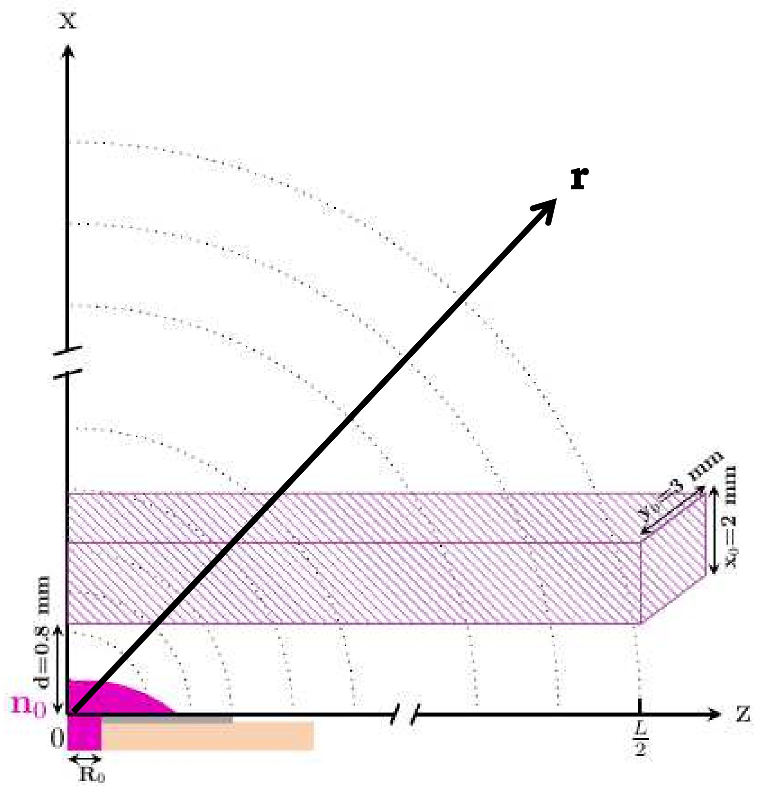




Model of diffusion: n(r)

→ VUV FTS measurements: estimation of the absorption length to get the N density from the column density

→ Comparison of n_N measurements by FTS and TALIF



Diffusion equation and N atom conservation equation:

$$\Gamma(r) = -D\frac{\partial n(r)}{\partial r} \qquad div\vec{\Gamma} = 0$$

$$n(r) = \frac{R_0 n_0}{r}$$

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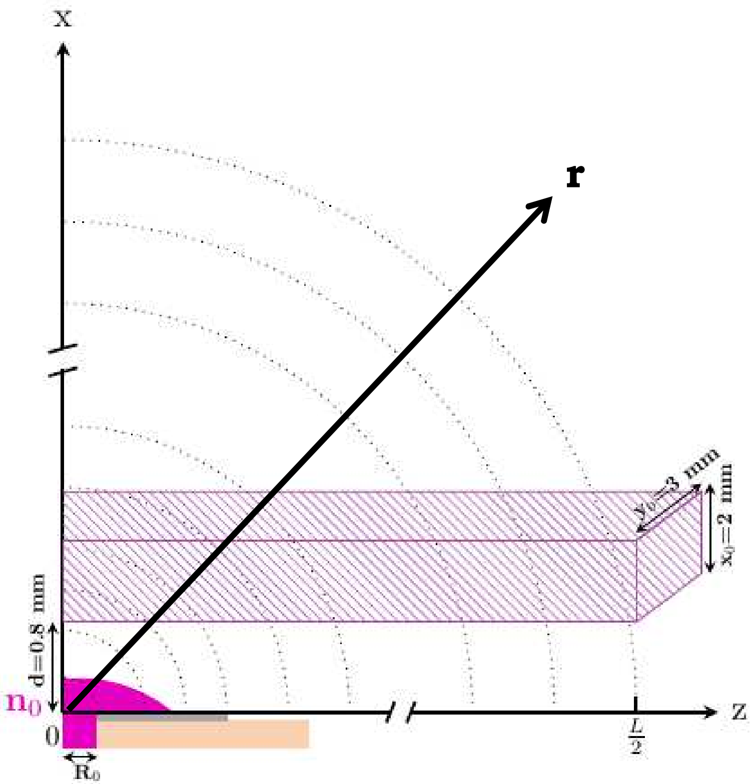
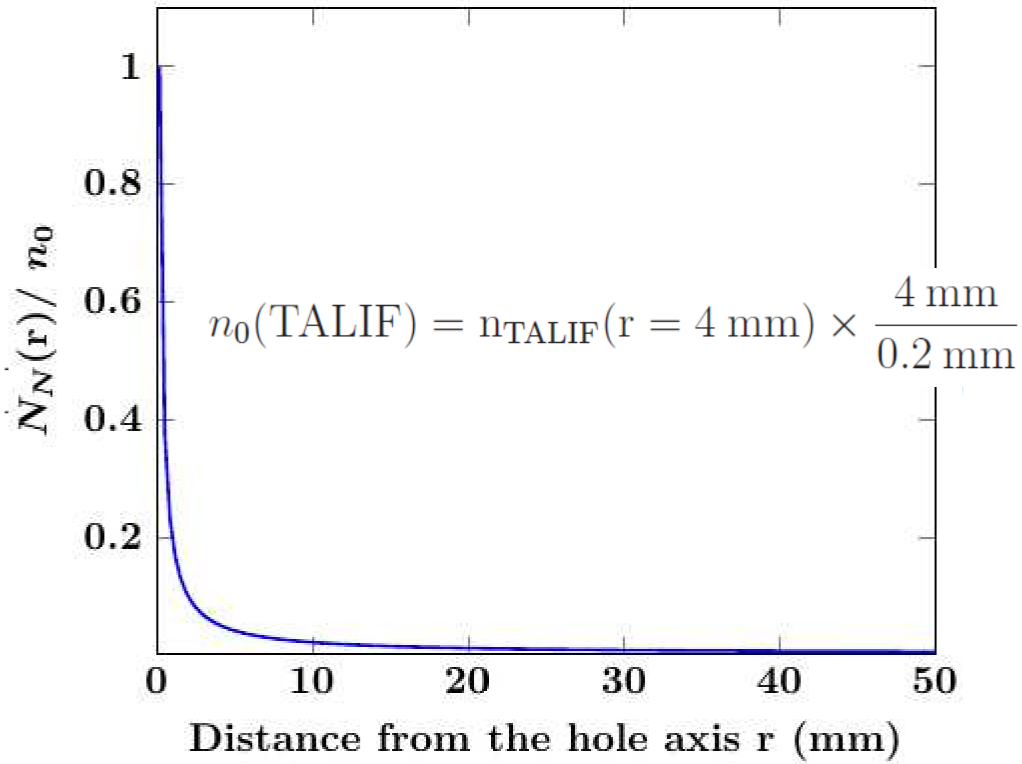




Model of diffusion: eff. absorption length

- Density in cartesian coordinates: $n(x,y,z) = \dfrac{R_0 n_0}{\sqrt{x^2+y^2+z^2}}$

- Density profile integrated on the probed volume by the beam
  → effective absorption length $l_{abs}(N)$

$$Abs(\sigma) = \frac{k(\sigma)}{x_0 y_0}\int_d^{d+x_0}\int_{-y_0/2}^{y_0/2}\int_{-L/2}^{L/2} n(x,y,z)\,dx\,dy\,dz$$

$$Abs(\sigma) = k(\sigma)n_0\frac{R_0}{x_0 y_0}\int_d^{d+x_0}\int_{-y_0/2}^{y_0/2}\int_{-L/2}^{L/2}\frac{1}{\sqrt{x^2+y^2+z^2}}\,dx\,dy\,dz$$

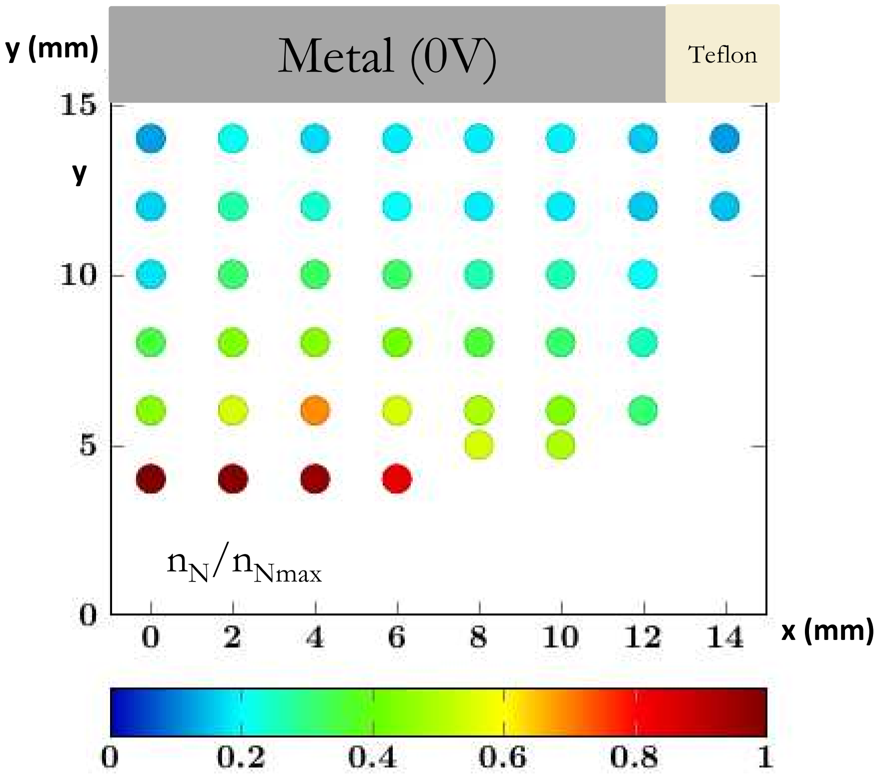
$$Abs(\sigma) = k(\sigma)n_0 l_{\rm abs}(N)$$

- Numerical integration → $l_{abs}(N)$=1.58 mm and $n_{\rm FTS} = n_0 = n_N(\mathrm{r} = R_0)$

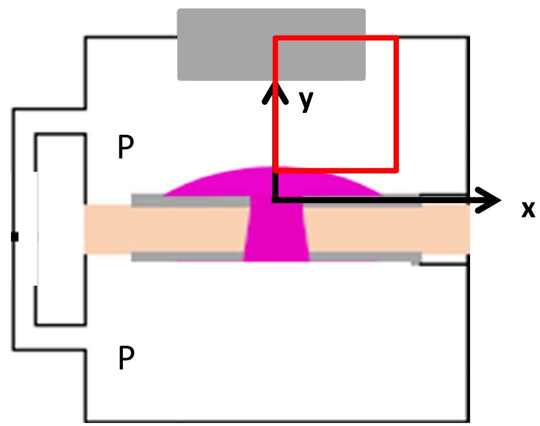
A. Remigy et al. J. Phys. D ***55*** *(2022) 105202*

Spatial mapping of N by TALIF

Conditions: 80% N_2 - 20% Ar, 1.6 mA, 50 mbar



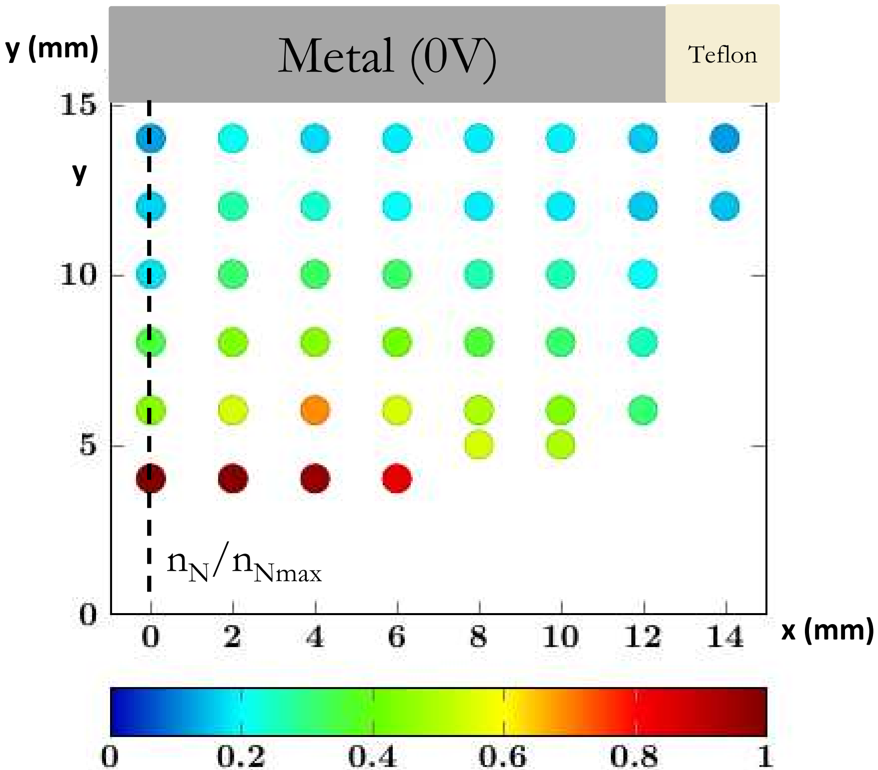
$n_{Nmax} = 5.65.10^{19}$ m^{-3}



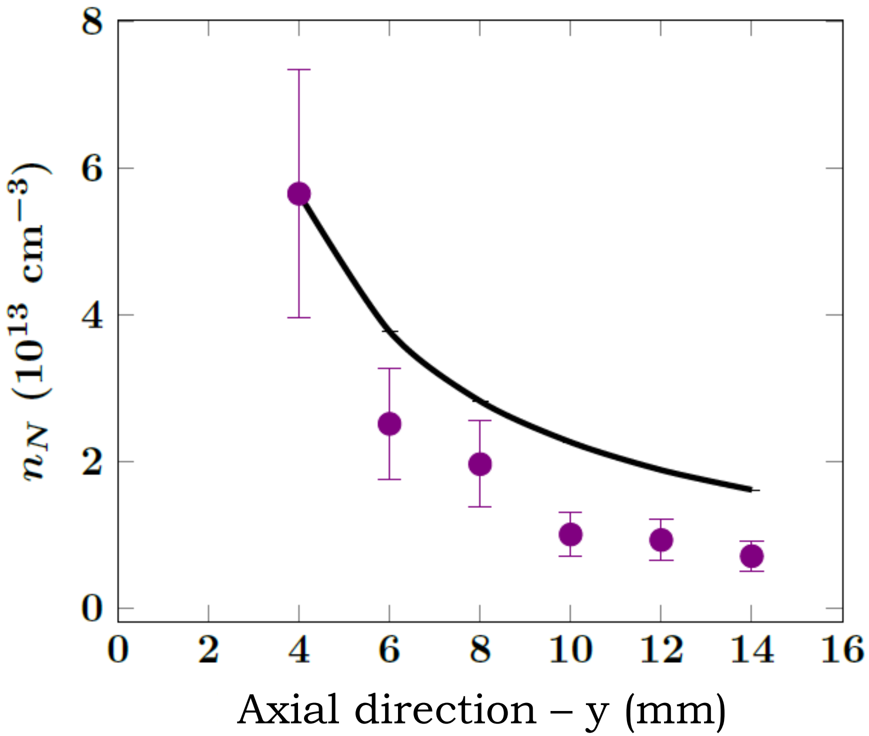
- High density near the cathode surface and then fast decay

Spatial mapping of N by TALIF

Conditions: 80% N_2 - 20% Ar, 1.6 mA, 50 mbar

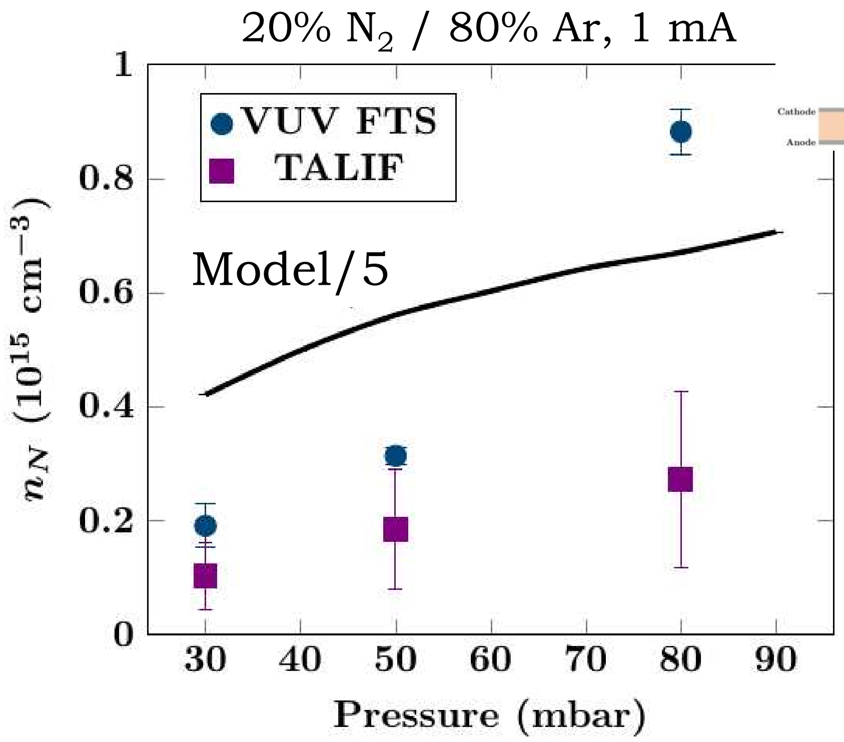


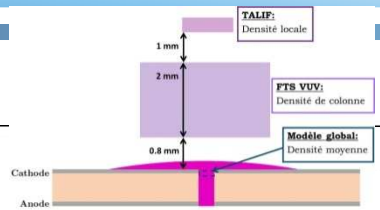
$n_{Nmax} = 5.65.10^{19}\ m^{-3}$

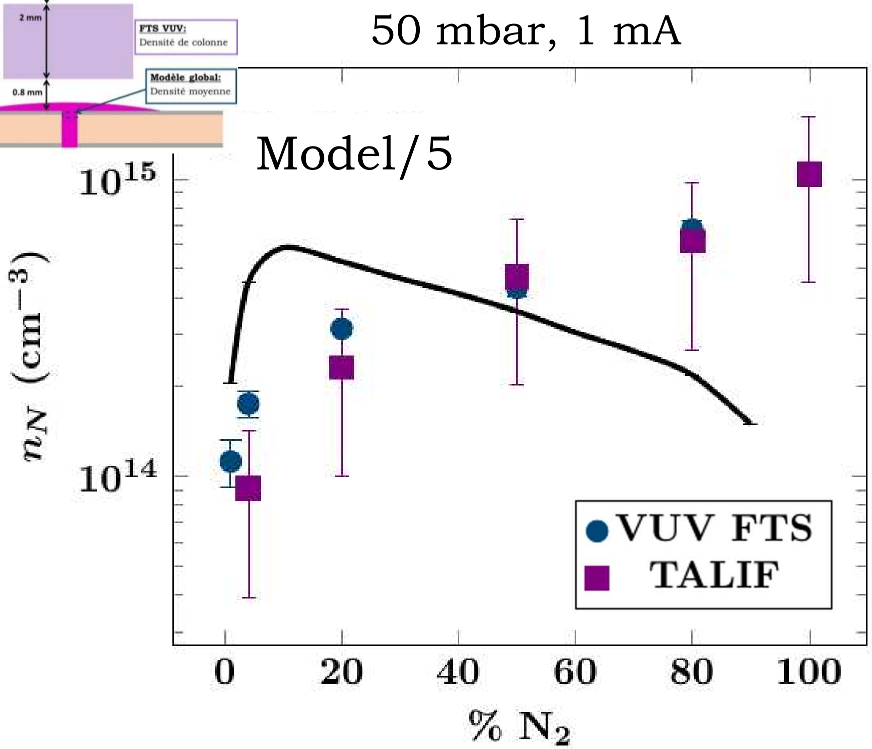


- High density near the cathode surface and then fast decay
- Decrease in agreement with the diffusion model

n_N: effect of pressure and dilution



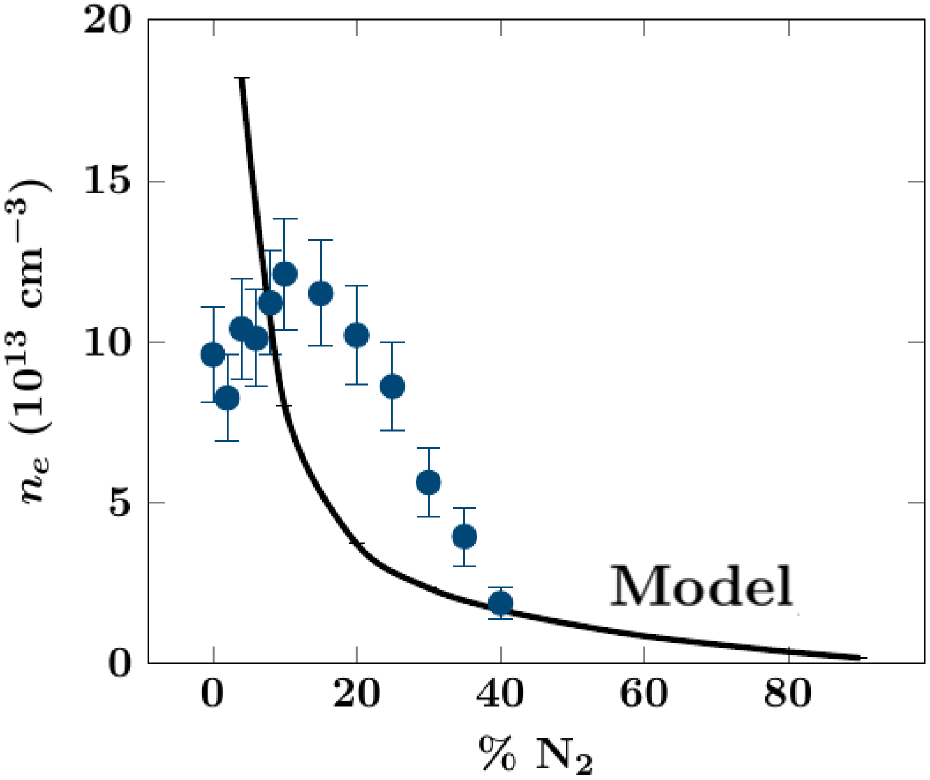


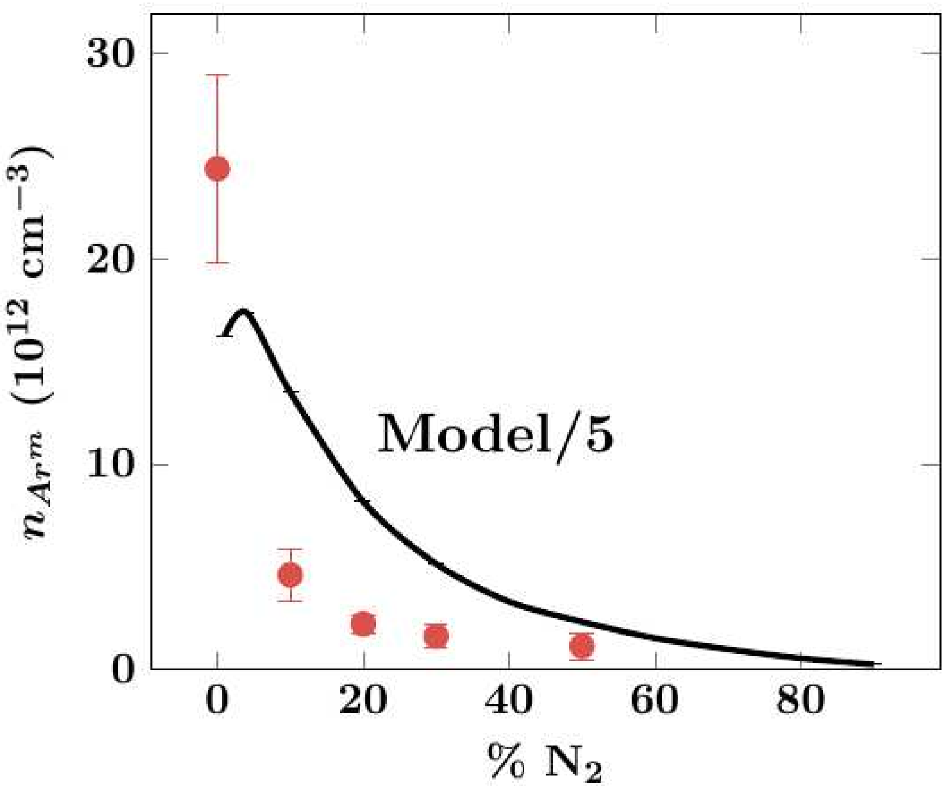


- Good agreement between TALIF and FTS; higher calculated densities
- Increase of the density with pressure and % of N_2; discrepancy between the two technics at higher pressure
- Opposite trend model/experiments at high % of N_2

n_N: effect of dilution

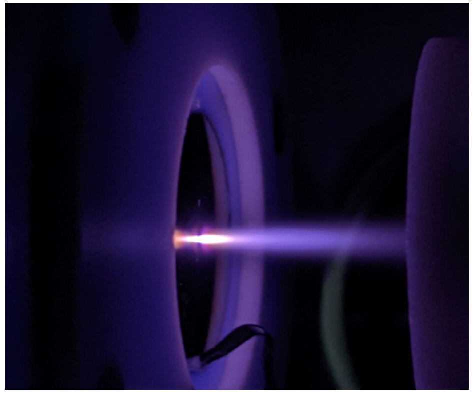
50 mbar, 1 mA





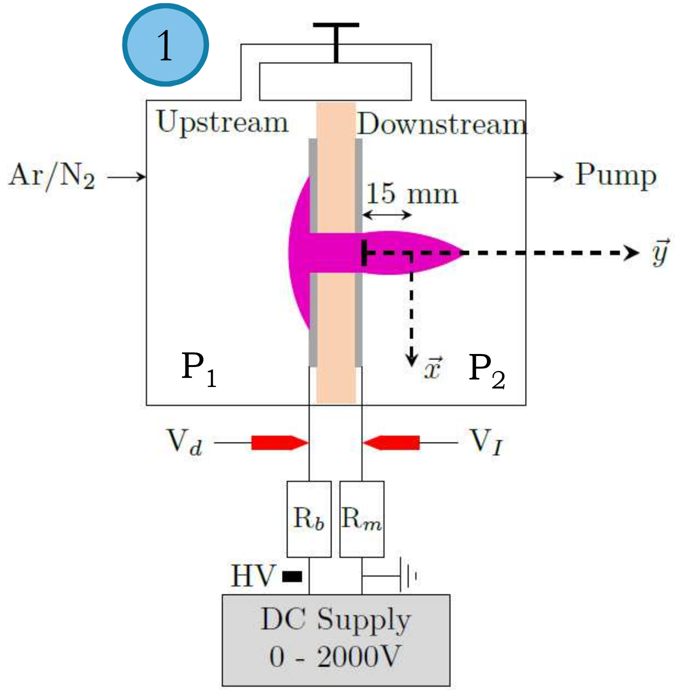
Decrease of n_e and n_{Arm} + increase of N_2^0 → optimum of % N_2 for n_N?

Study of the 1 MHCD reactor: transport of atomic nitrogen



Experimental setups for the MHCD characterization

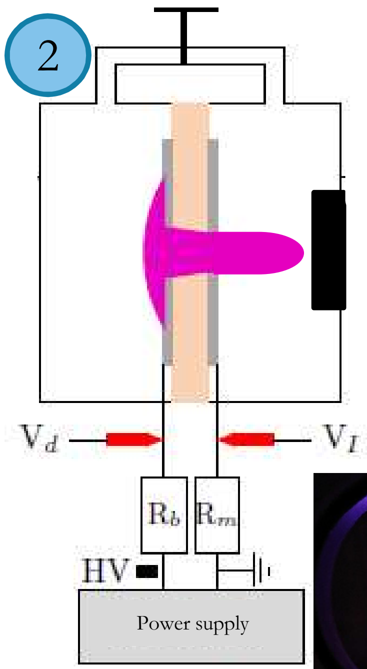
Free jet configuration

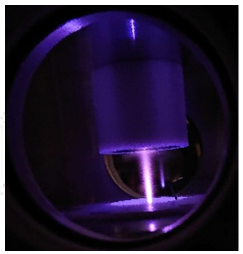


MHCD jet without a 3rd electrode

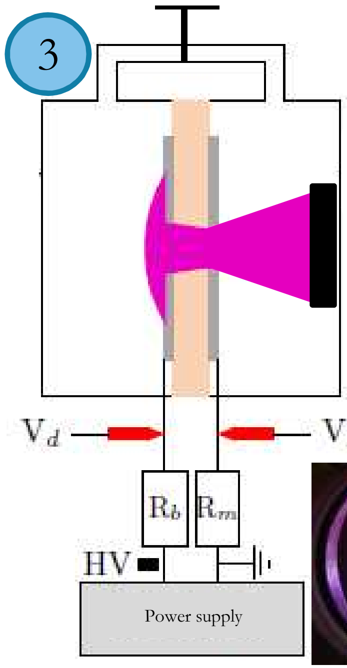
30 mbar < P_1 < 110 mbar
1 mbar < P_2 < 10 mbar

Jet configuration





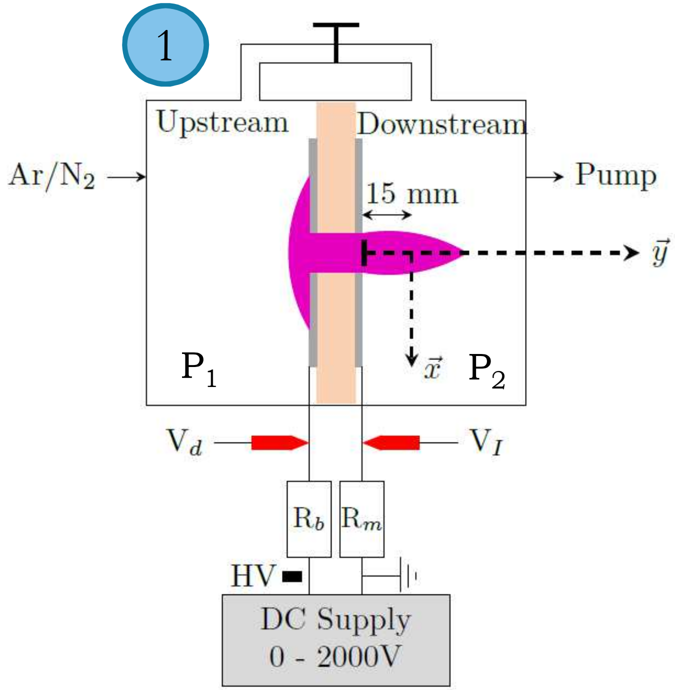
MCSD configuration



MHCD jet with a 3rd electrode:
1.5 cm between the MHCD and the 3rd electrode
MHCD jet / MCSD
(Substrate holder not polarized / polarized)

Experimental setups for the MHCD characterization

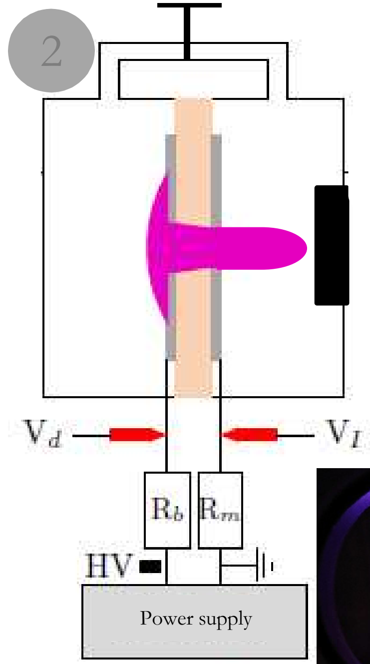
Free jet configuration

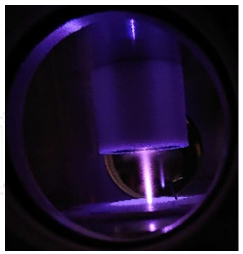


MHCD jet without a 3rd electrode

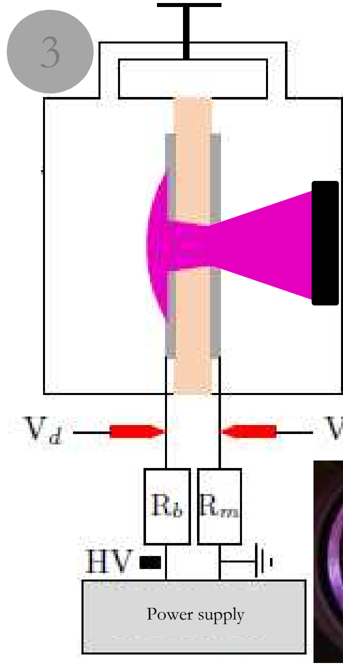
30 mbar < P_1 < 110 mbar
1 mbar < P_2 < 10 mbar

Jet configuration





MCSD configuration

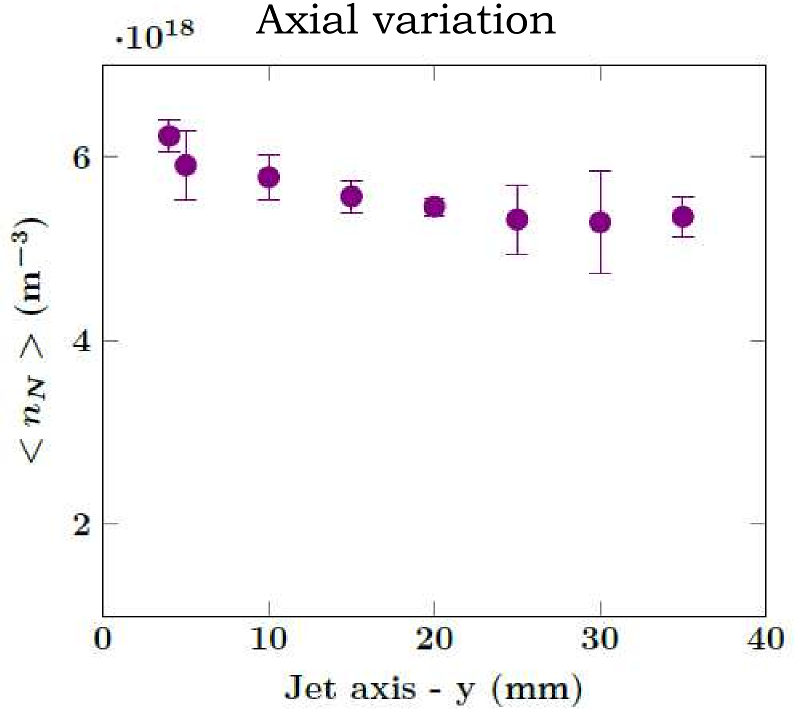


MHCD jet with a 3rd electrode:
1.5 cm between the MHCD and the 3rd electrode
MHCD jet / MCSD
(Substrate holder not polarized / polarized)

Spatial mapping of N

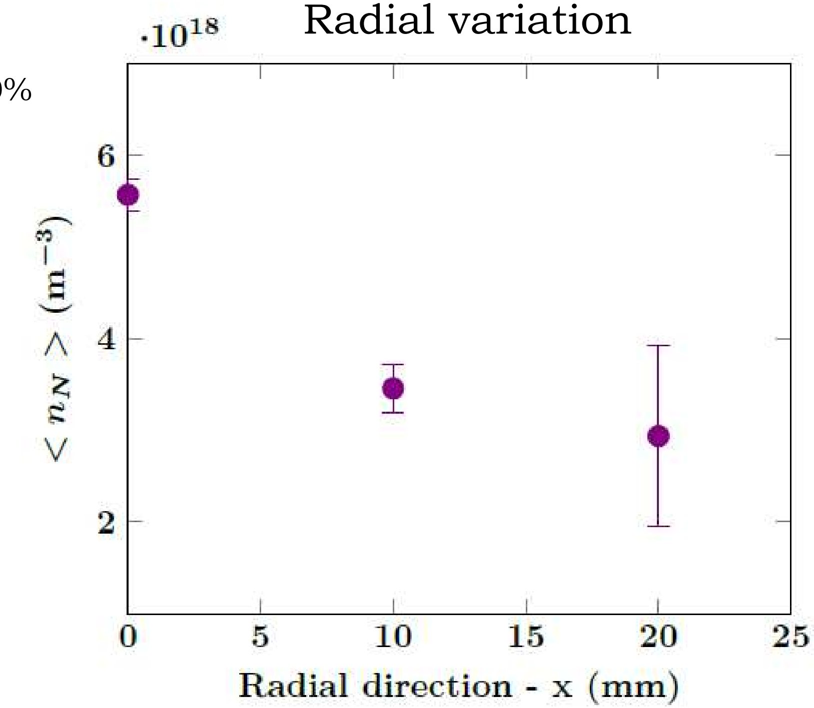
1

Axial variation



P_1 = 50 mbar
P_2 = 1 mbar
N_2 fraction = 20%
I_d = 1.6 mA

Radial variation

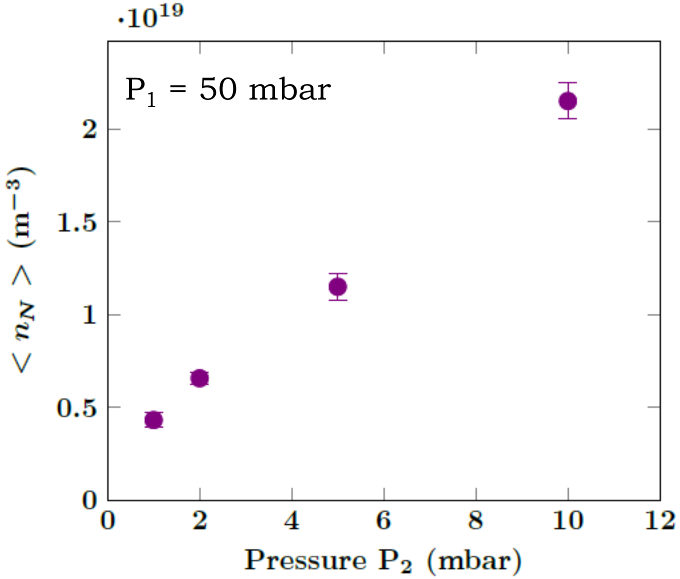


*A. Remigy et al. PoP **29** (2022) 113508*

- Density of N atoms almost constant along the jet axis: decrease of 16% over 35 mm
→ Production in the cathodic region and transport along the anodic chamber due to the pressure differential
- Decrease of the density along the radial direction: density 2 times lower at x=20 mm
→ could be overcome using an array of holes (MHCDs in parallel)

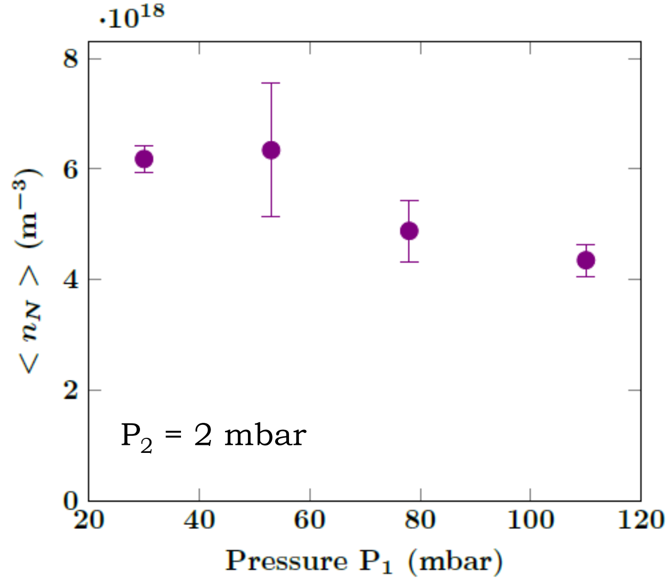
Effect of the pressures

1



- n_N 4 times higher when P_2 increases by a factor of 10

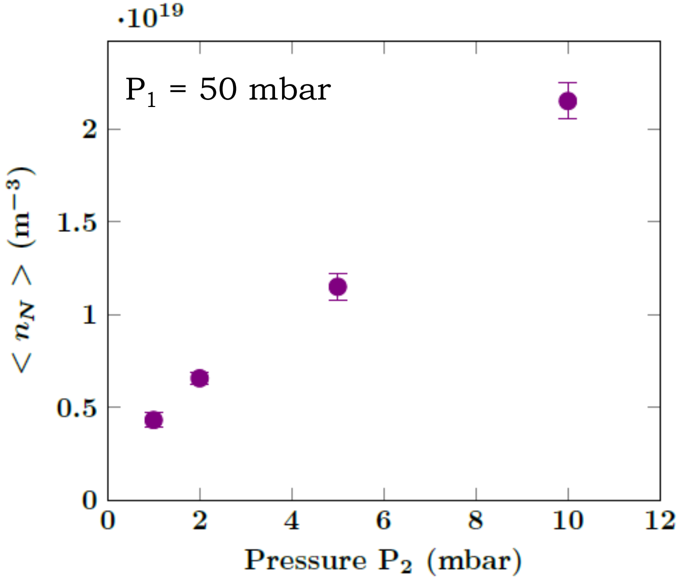
- The time spent by the gas mixture in the cathodic region increases with P_2



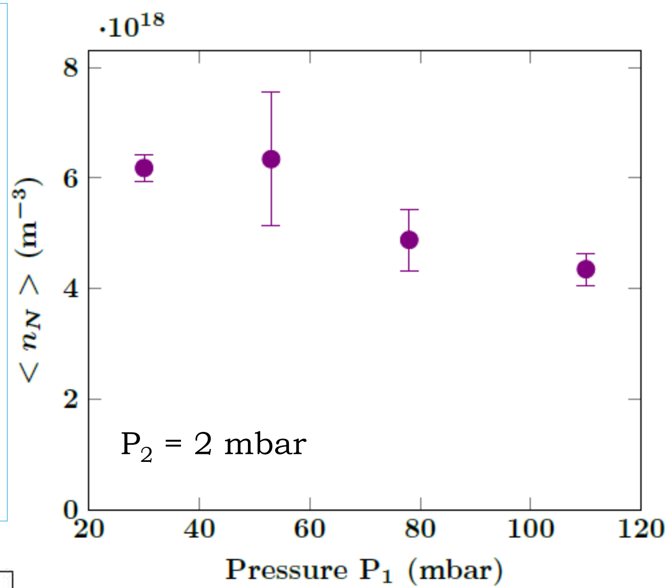
- n_N decreases with P_1
- Effect of P_1 lower than that of P_2 (decrease of 30% over a range of pressure of 80 mbar)
- Decrease of the N atom density with the increase of the pressure differential, in both cases → residence time?

Effect of the pressures

1

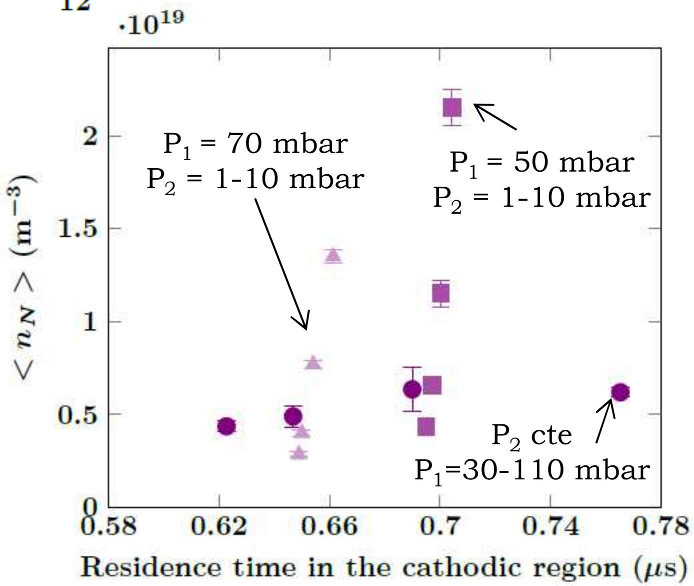


- No general correlation between the residence time and n_N
- Role of the residence time negligible even if for P_2 cte, effect probably compensated by a higher n_N at higher pressure
- Larger impact on n_N of P_2, related to the jet turbulences



- n_N 4 times higher when P_2 increases by a factor of 10

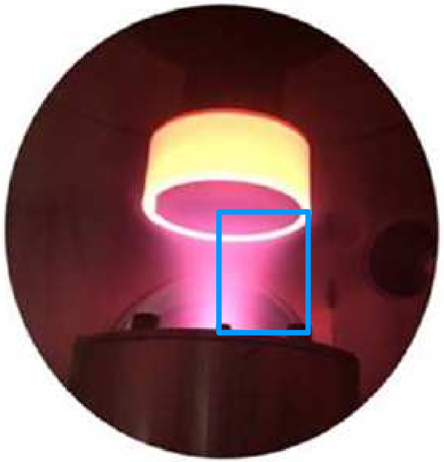
- The time spent by the gas mixture in the cathodic region increases with P_2

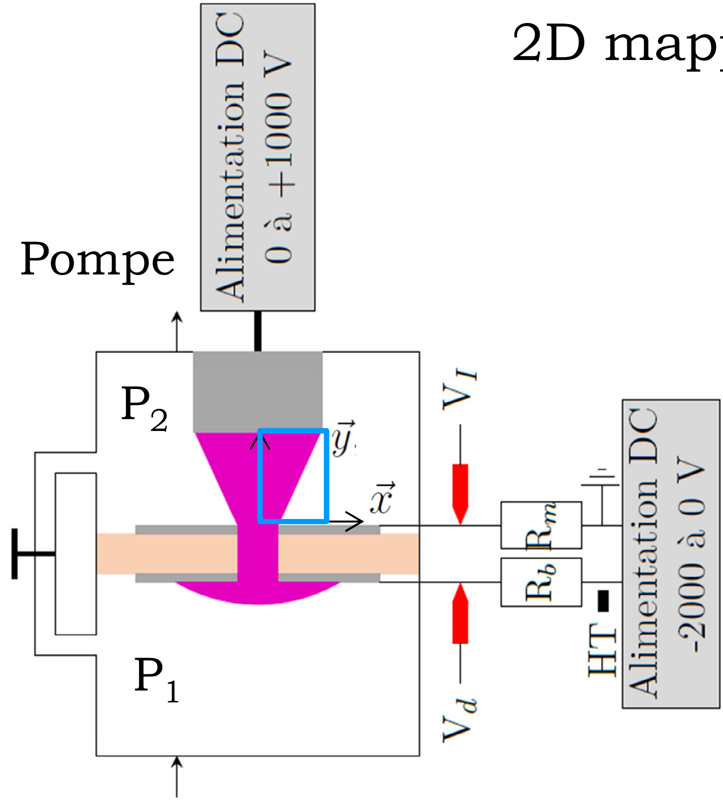


- n_N decreases with P_1
- Effect of P_1 lower than that of P_2 (decrease of 30% over a range of pressure of 80 mbar)
- Decrease of the N atom density with the increase of the pressure differential, in both cases → residence time?

n_N in the deposition chamber ② ③

2D mapping of n_N by TALIF



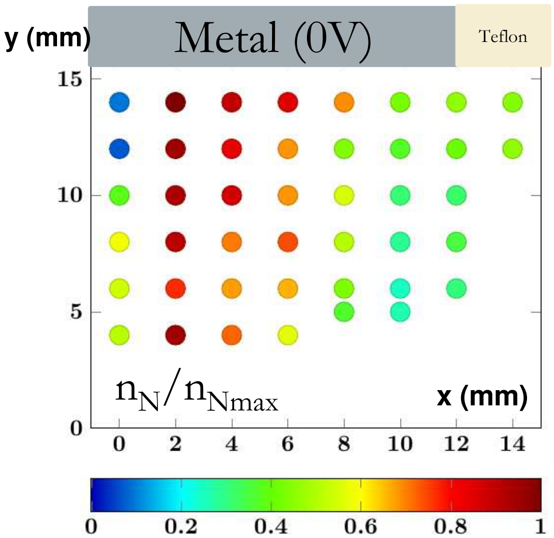


Configurations jet + MCSD

Spatial mapping of N: jet configuration

2

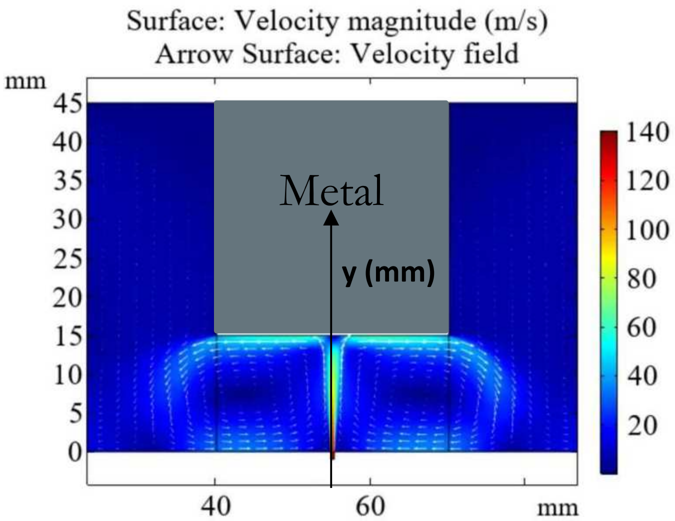
Conditions: 80% N_2 - 20% Ar, 26 sccm, 30 mbar – 10 mbar



$n_{Nmax} = 2{,}99.10^{19}\ m^{-3}$

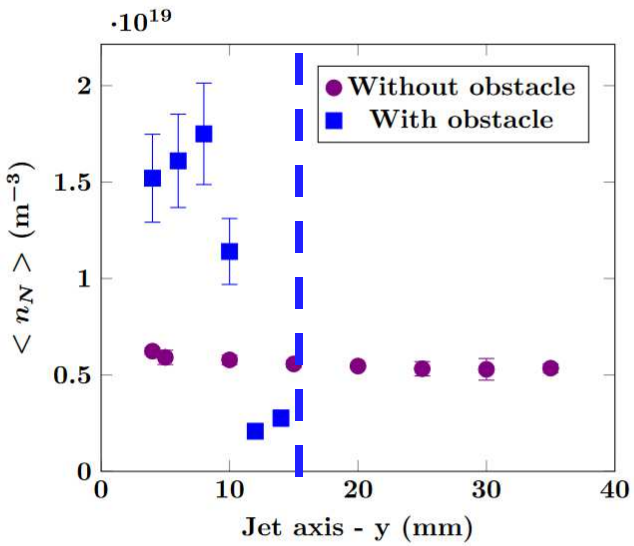
I_d= 1.6 mA

$I_{3ème\ électrode}$= 0 mA



O. Gazeli, University of Cyprus, PV Technology

Comsol simulation: 100% Ar

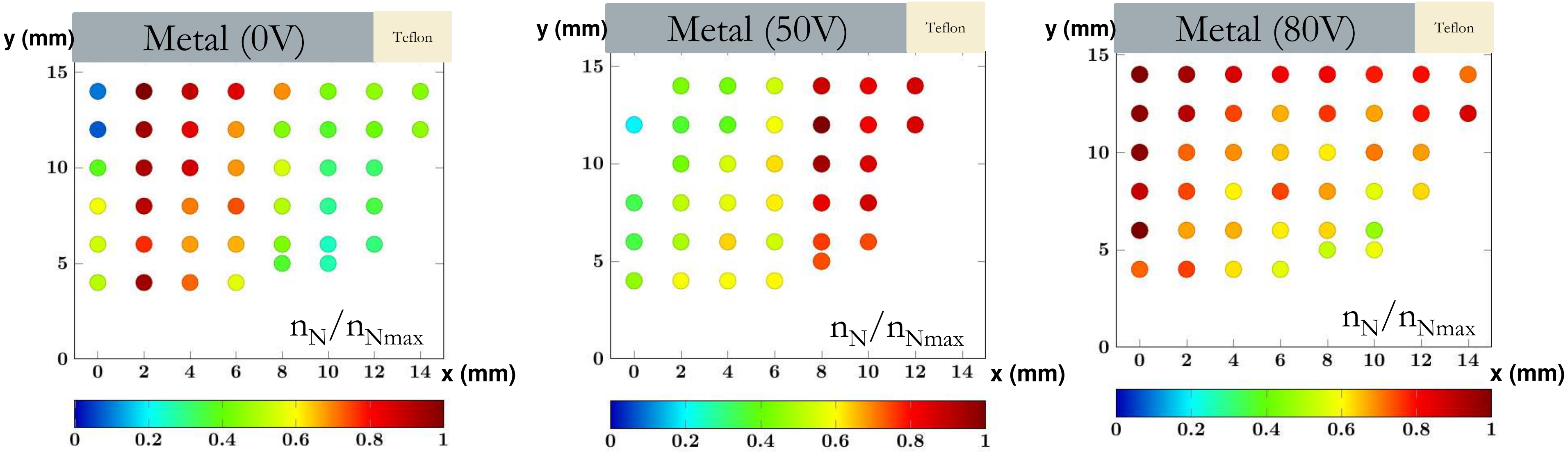


- With an obstacle: depletion in the center → gas flow
- In that case we do not have a film deposition

Spatial mapping of N: MCSD

3

Conditions: 80% N_2 - 20% Ar, 26 sccm, 30 mbar – 10 mbar



$n_{Nmax} = 2{,}99.10^{19}\ m^{-3}$

I_d= 1.6 mA
$I_{3rd\ electrode}$= 0 mA

$n_{Nmax} = 1{,}95.10^{19}\ m^{-3}$

I_d= 1.4 mA
$I_{3rd\ electrode}$= 0.27 mA

$n_{Nmax} = 2{,}37.10^{19}\ m^{-3}$

I_d= 0.62 mA
$I_{3rd\ electrode}$= 1.12 mA

- Mode transition required to homogenize the density
- Almost homogenous density over the whole substrate

Conclusion

- MHCD is an effective way to produce high densities of N atoms and cover a high area substrate homogenously → low cost process for h-BN deposition

- Small impact of P_1 on n_N, larger effect of P_2: great impact of fluid effects, more than the expected effect of the resident time

- Presence of N atoms near the substrate not enough for a deposition : bias needed

- 3rd electrode polarized with a voltage high enough to have more current flowing through the second anode → homogenous density on the substrate + dissociation of boron precursor?

Perspectives

- Future deposition experiments: increase of the pressure in the deposition chamber (P_2) and variation of the bias on the substrate holder

- Improvement of the global model: chemistry of discharge → vibrational levels of N_2, eedf in presence of N_2 → Boltzmann's solver, treatment of the wall losses → analytical model of the sheath (+ comparison to PIC simulations)

- Focus on B atoms (mapping in the deposition chamber) + modelisation of the gas flow → design of the future reactor (new MHCD source, new heating system of the substrate holder)

Thanks for your attention

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Alice Remigy is looking for a post-doc position from August 1st 2023:
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