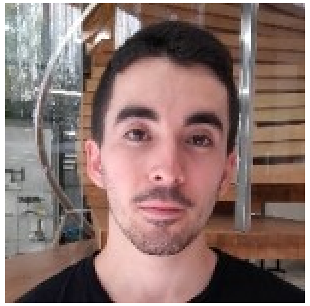
Plasma/liquid interactions in the case of low pressure misty plasmas used to deposit Nanocomposite thin films

PhD, 2017-20



PhD, 2020-

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Context

One step deposition of nanocomposite thin films with nm size Nanoparticles (NP) homogeneously distributed in a matrix

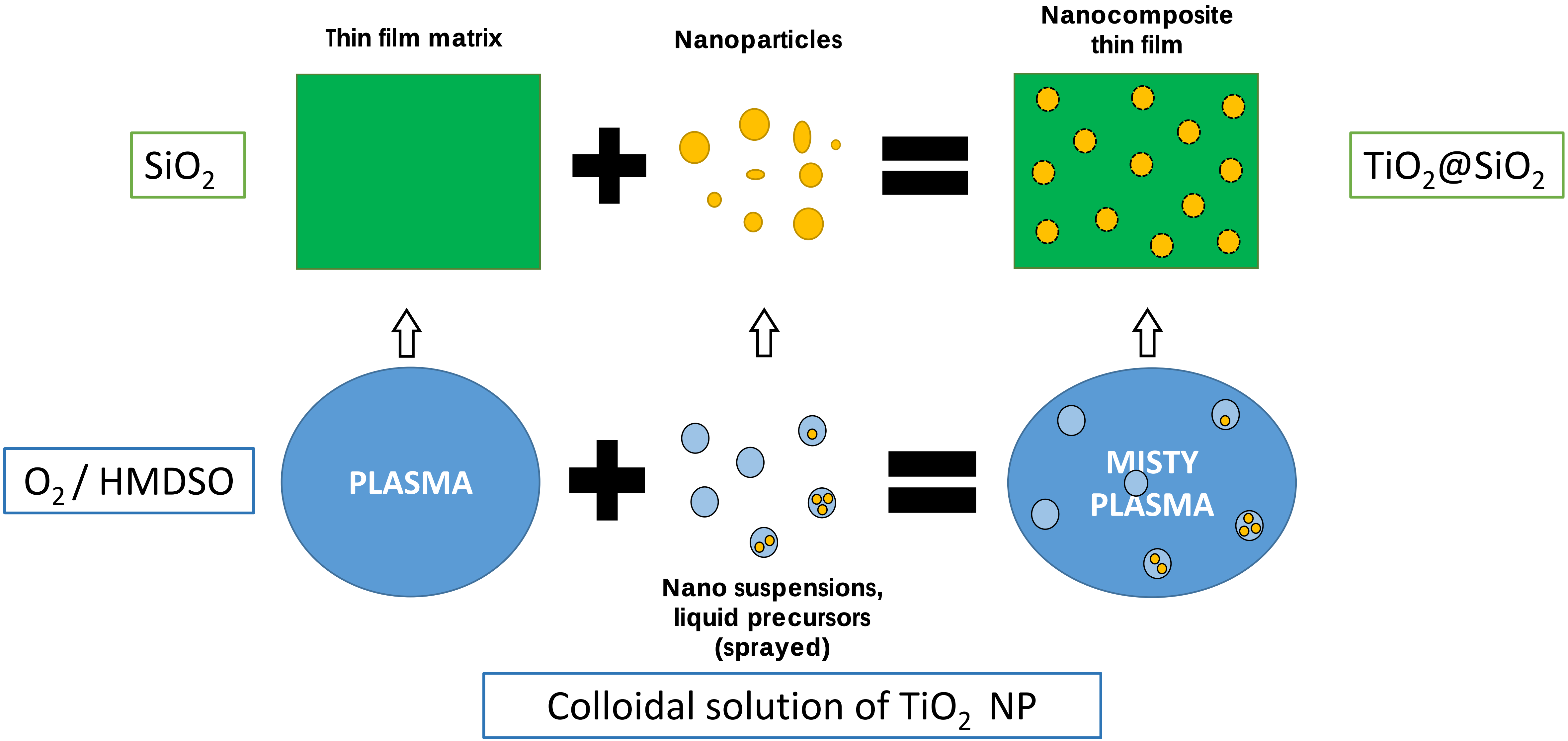
Strategy (to avoid NP charging and agglomeration in the plasma):
injection of liquid droplets of a colloidal solution (NP in a solvent) in a plasma (used to deposit the matrix)

$\Rightarrow$ NP are transported inside the droplet up to the substrate (avoiding plasma/NP interactions)

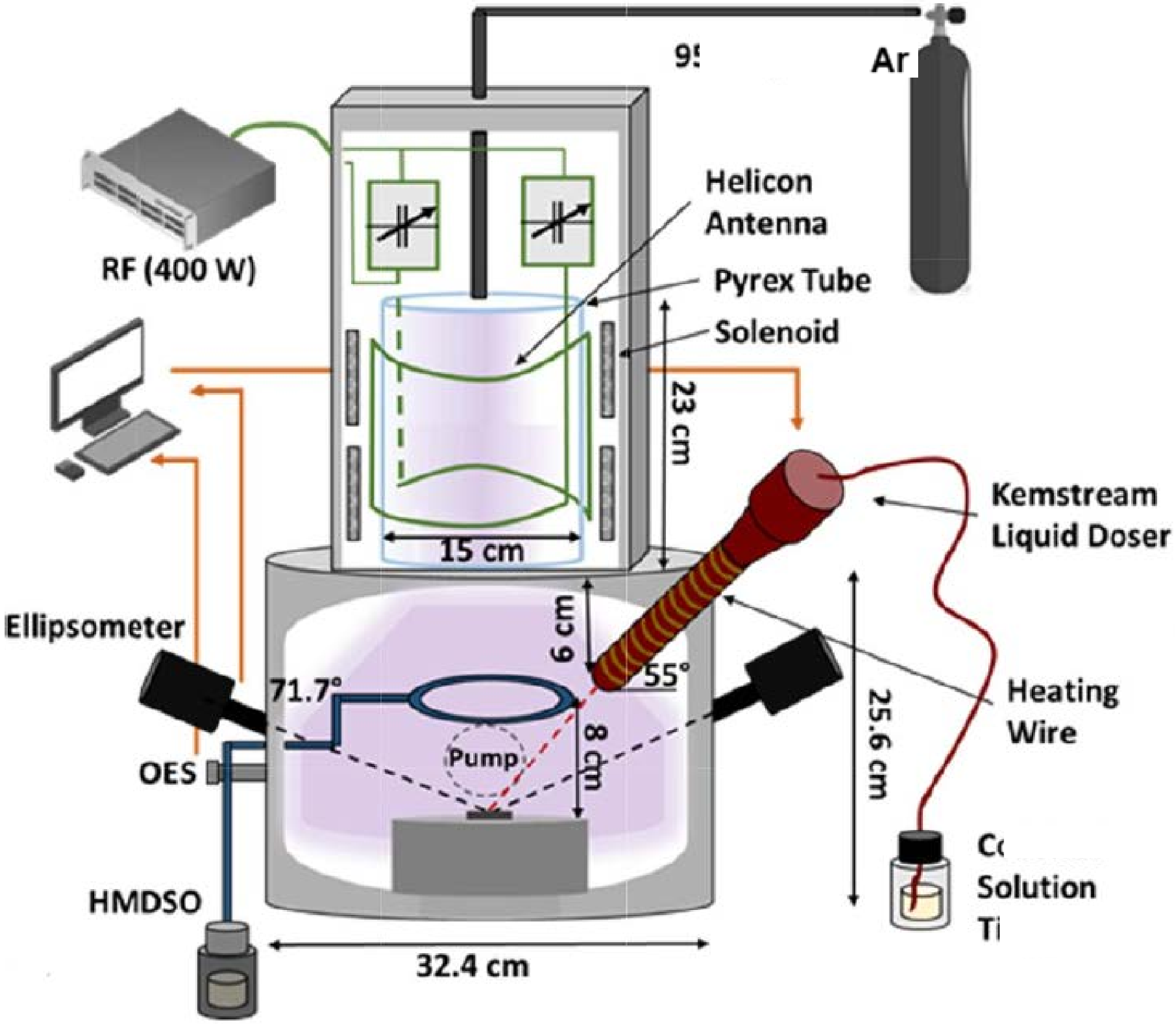
$\Rightarrow$ BUT : **plasma / liquid (droplet) interactions** : charging, evaporation…

Hybrid Approaches coupling sol-gel and plasma for the deposition of oxide-based nanocomposite thin films: A review,
M. Mitronika, A. Granier, A. Goullet, M. Richard-Plouet, **SN Applied Sciences** 3:665 (2021)

Nancomposites and misty plasmas



Methods – Low pressure misty plasma

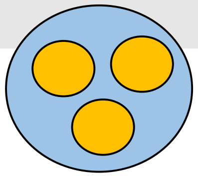


Mitronika *et al.* J. Phys. D: Appl. Phys. **54** 085206 (2021)

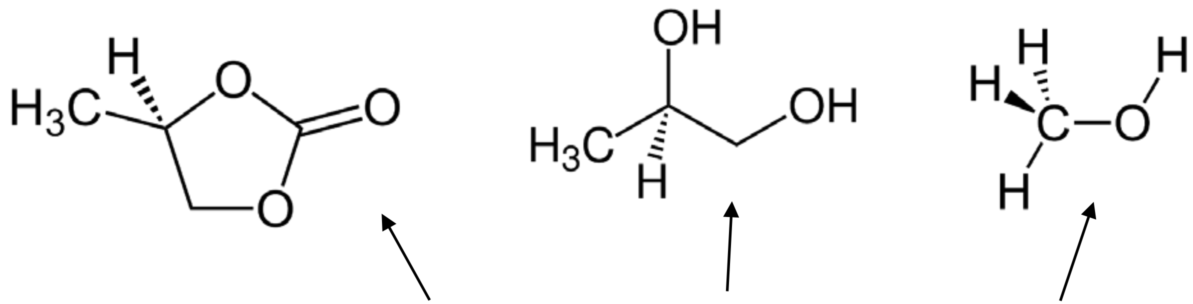
EXPERIMENTAL CONDITIONS	
Solvents	Methanol – MeOH – CH_4O Propylene Carbonate – PC – $C_4H_6O_3$
Injection time	1 ms
Injection flow	~1 μL/ms
Temperature	300 K to 423 K
Gas flow	oxygen 24 sccm, HMDSO : 0.11 sccm
Base Pressure	**3 mTorr**

Mitronika *et al.* Thin Solid Films, **709,** 138212 (2020)

Colloidal solution



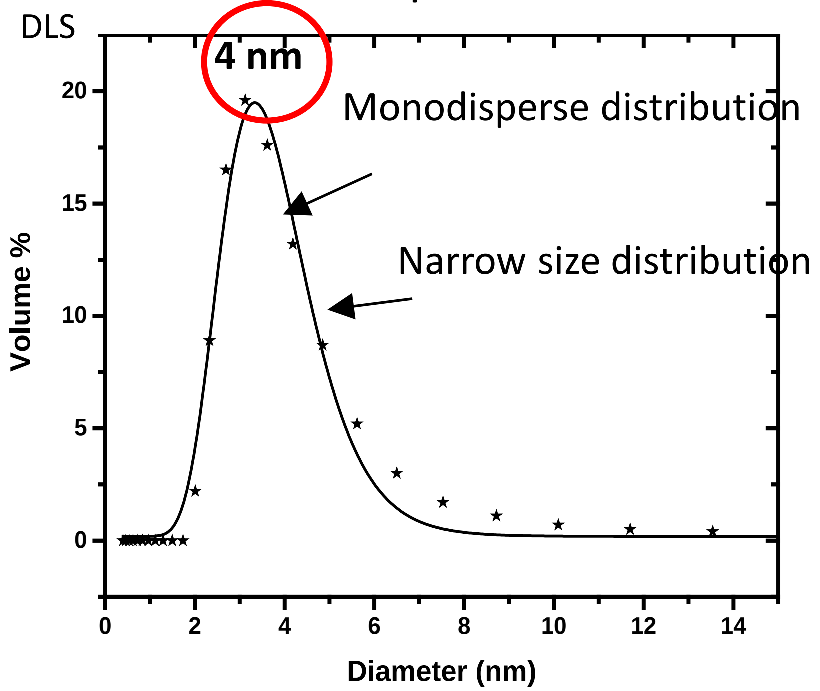
Solvent



	Propylene carbonate PC	Propylene Glycol PG	Methanol
Boiling point (°C)	242	188	65
Vapor pressure (Pa)	4	11	12300
Volatility	-	-	+++

Methanol added to the initial PC/PG colloidal solution in order to increase the solvent volatility

TiO_2 Nanoparticles

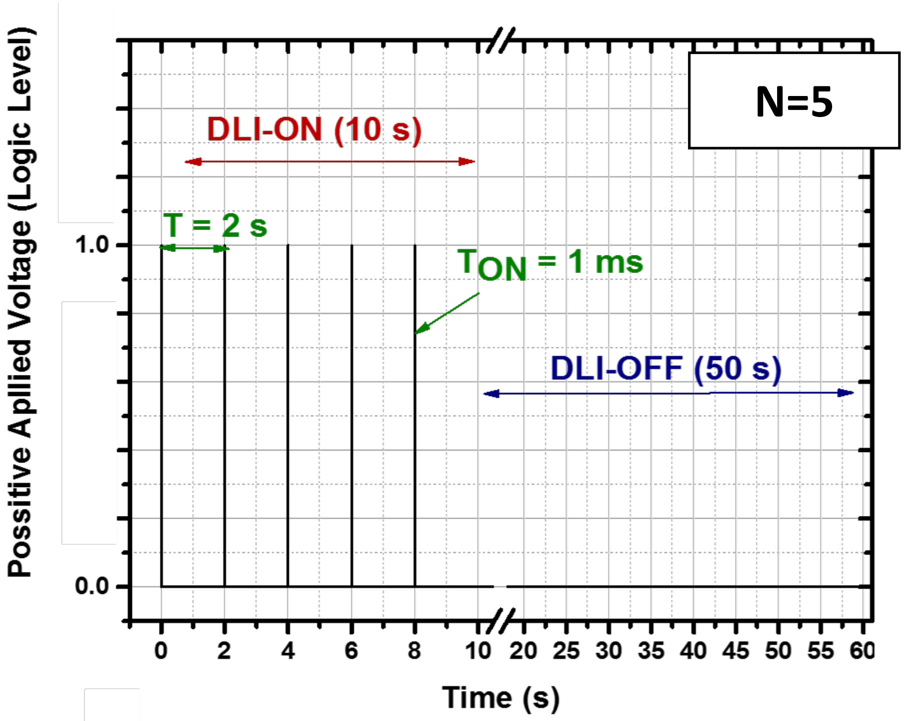


M. El Kass et al. ChemPhysChem. 18 (2017) 2390–2396

Arkadiuz Karpinski, PhD, 2011

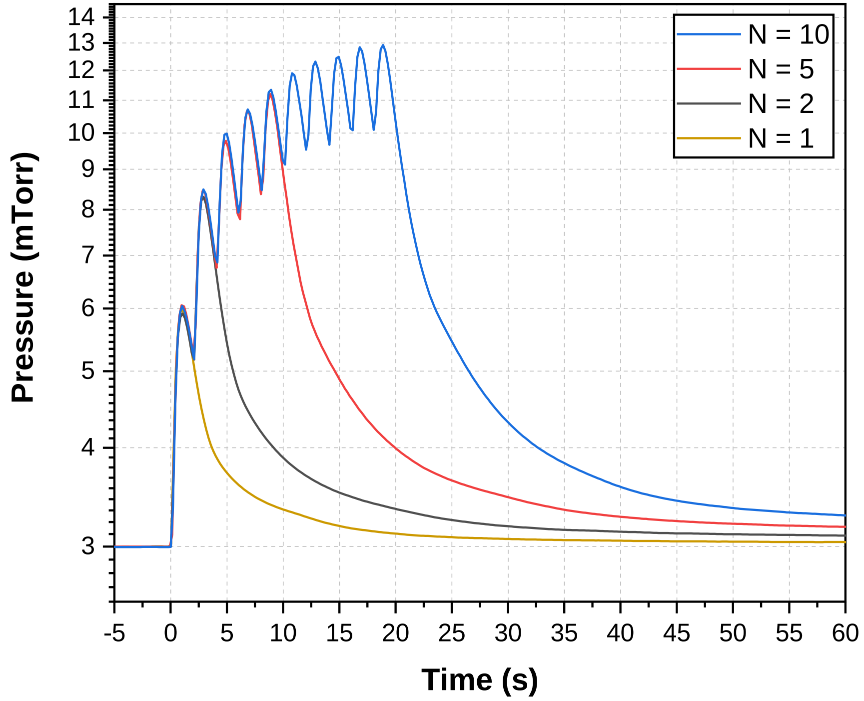
Colloidal solution injection : Iterative mode

Pulsed Direct Liquid Injection
f=0.5 Hz
Injector open for 1 ms, T_{ON}
Off for 2 s, T=2 s



Mitronika et al. J. Phys. D: Appl. Phys., 2021, 54, 085206

P_{init} = 3 mTorr, Plasma O_2/HMDSO continuously ON



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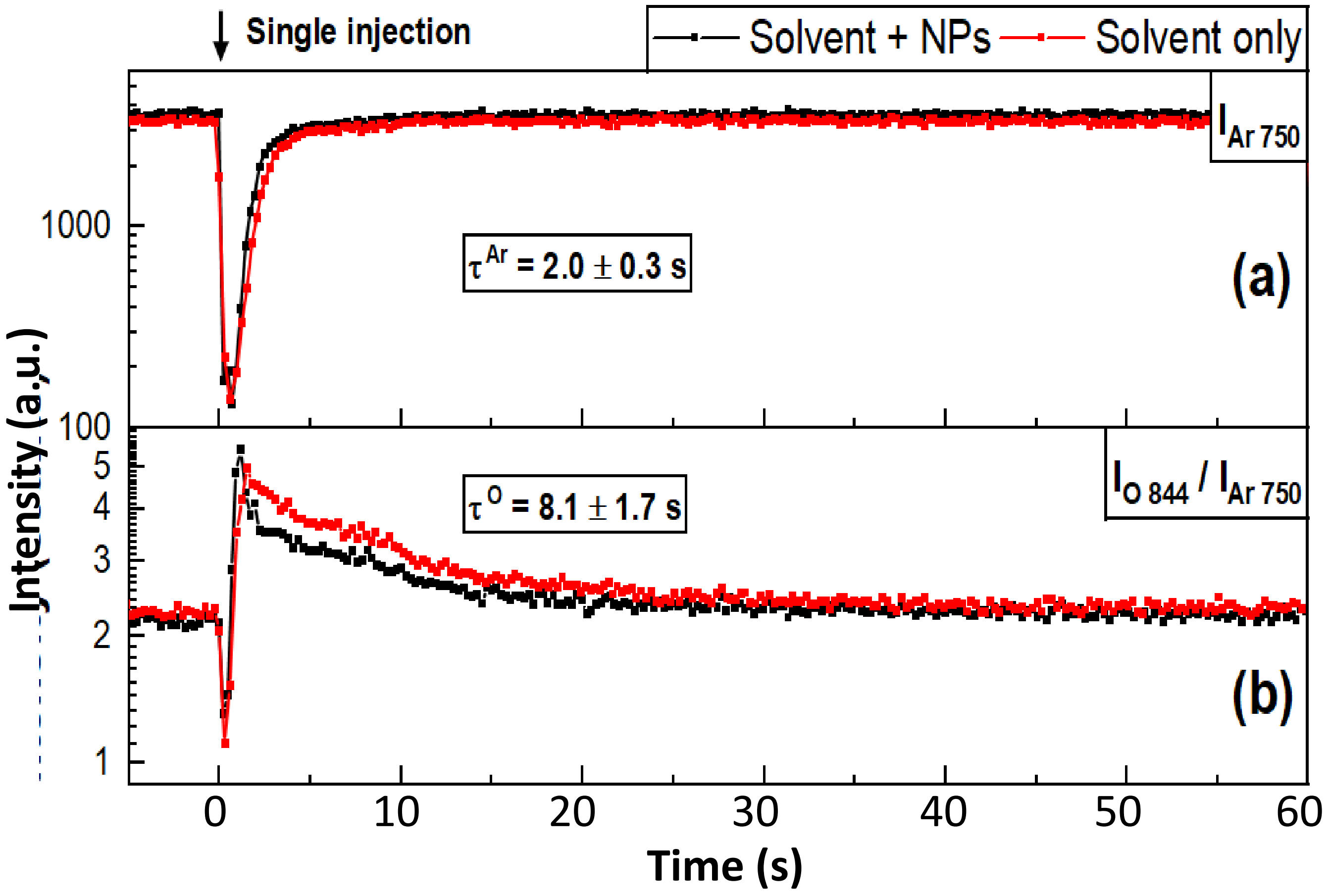
Time resolved optical emission spectroscopy (N=1)

N=1



Chouteau, S. et al. J. Phys. D: Appl. Phys., 55 505303 (2022)
doi.org/10.1088/1361-6463/ac9ac2

- ➢ same variations of I_{Ar} and I_O/I_{Ar} with and without NPs in the solvent

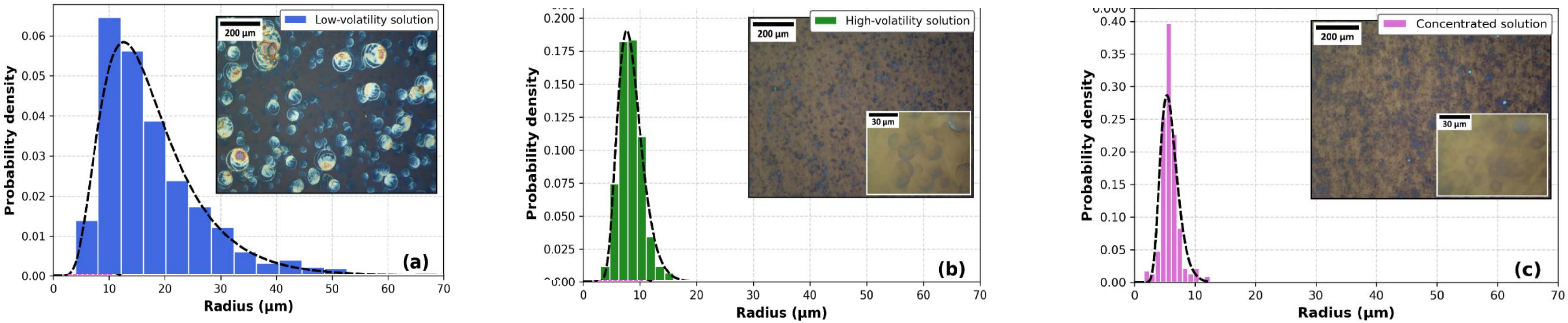
→ **NPs remain inside the droplets and do not interact with the plasma**

- ➢ Srong decrease of I_{Ar} upon solvent injection related to the pressure increase and the associated decrease in n_e and T_e

- ➢ I_O/I_{Ar} representative of O atom density :
  - Initial decrease => oxydation reactions
  - Increase attributed to a change in O recombination at the wall due to surface reactions (such as H_2O adsorption)

Size of the droplet imprints on the surface

(N=10, 60 mn deposition)



PC/PG/methanol : 20 / 55 / 25 (volume fractions)

PC/PG/methanol : 7 / 18 / 75 (volume fractions)

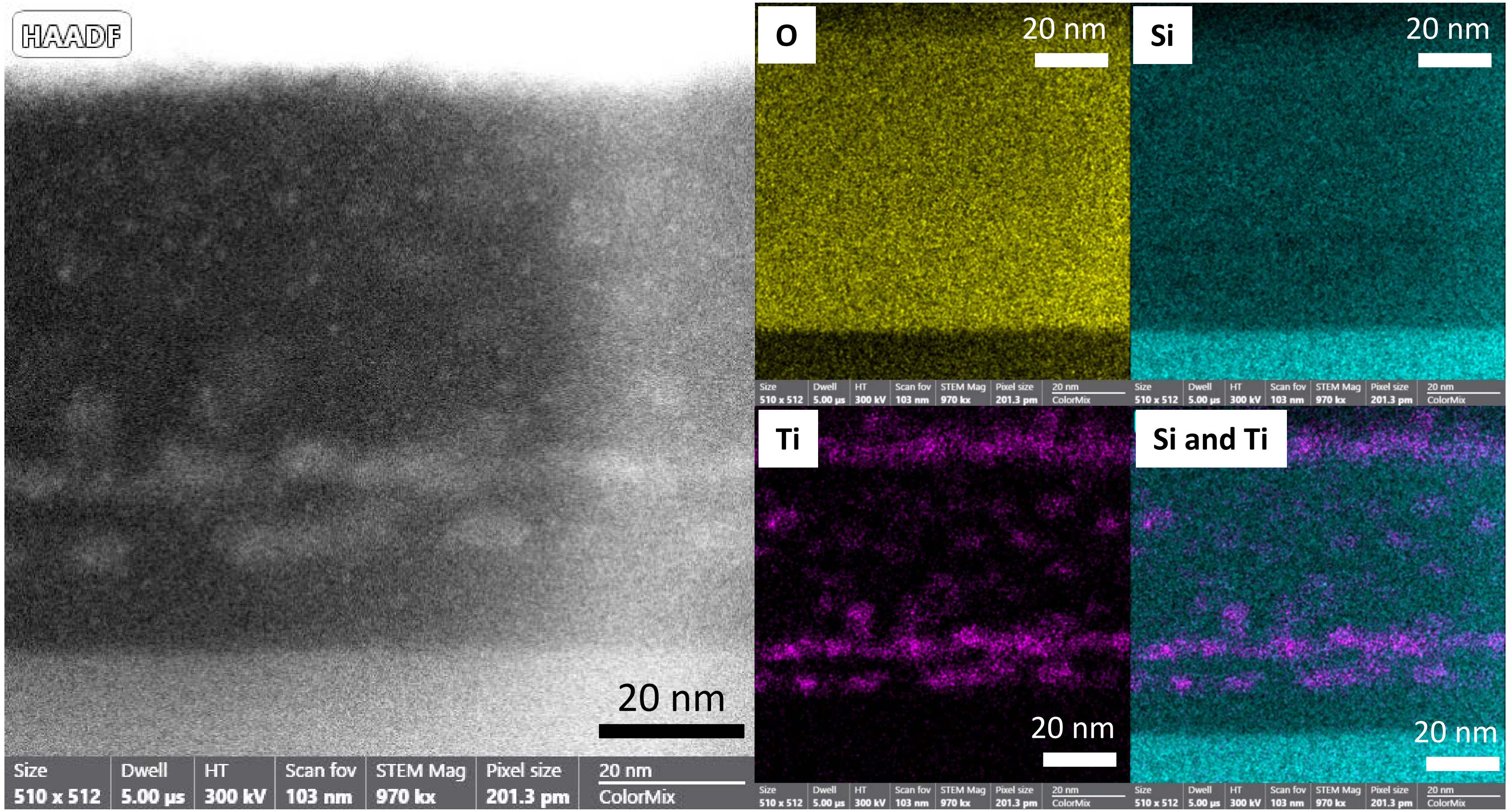
PC/PG/methanol : 11 / 9 / 80 (volume fractions)

Experiments :

Methanol fraction ↗ → decrease in droplet imprint size
(→ more homogeneous NP distribution in the film)

Structure of the TiO_2-SiO_2 NC film

STEM cross section, HAADF and EDX



Conditions: 75% MeOH solution, 60 min deposition at N=10

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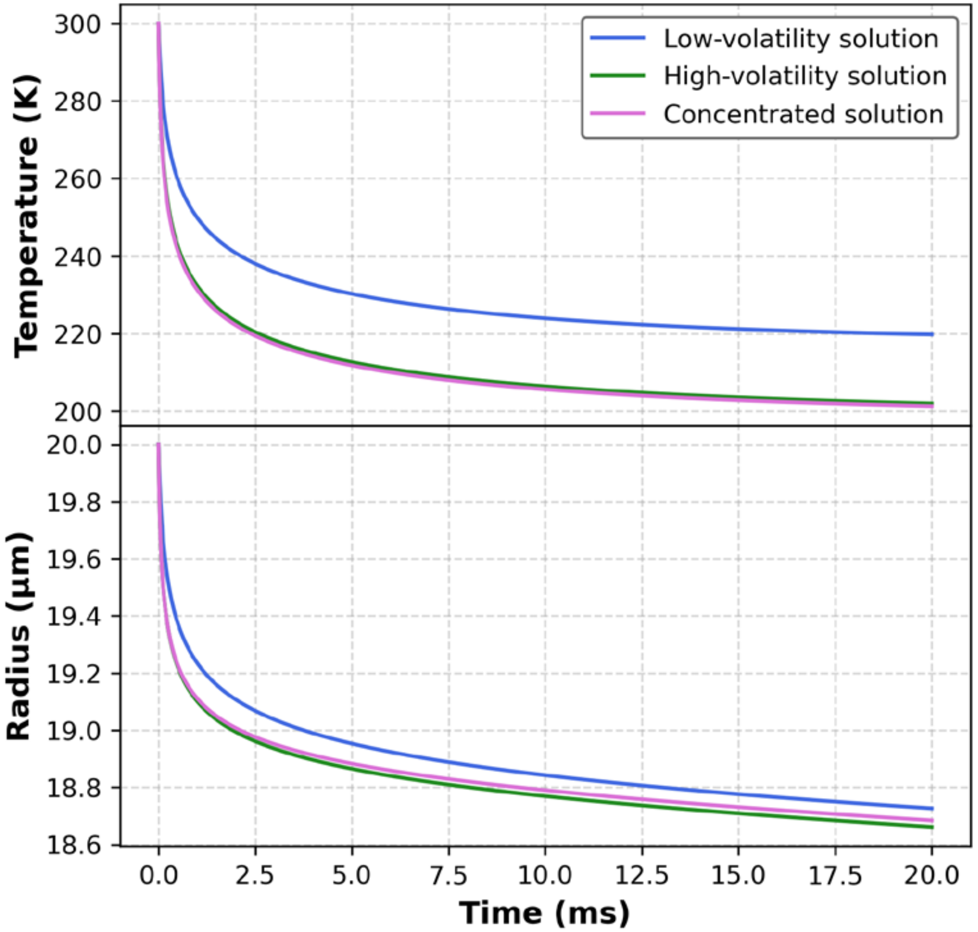
- Si and O homogeneously distributed through the film
- Ti-rich areas from *coffee rings* clearly visible
- Their height roughly matches a single NP (5 nm)

Et que dit la « modelisation » sur l'évaporation d'une goutte dans le plasma ?

Transport d'une goutte de PC/PG/methanol de 20 µm de diamètre



S. Chouteau et al, under review

Transfert Radiatifs

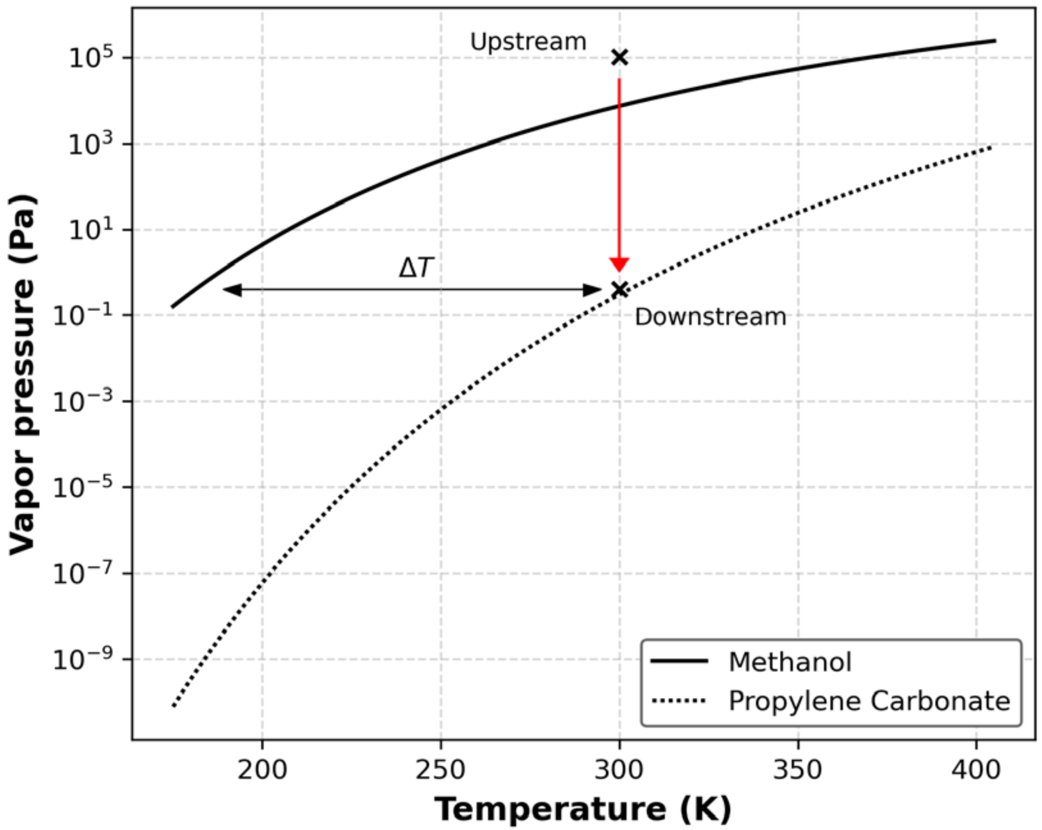
Refroidissement par évaporation

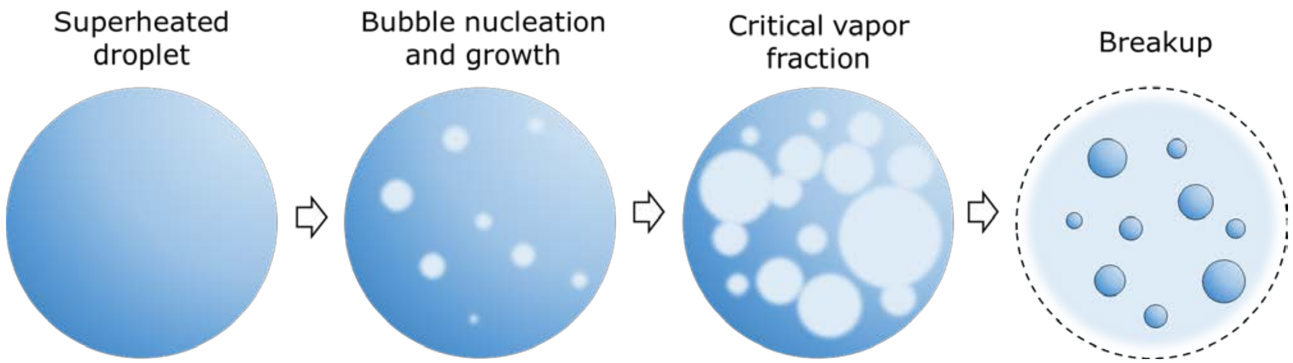
$$J_{net} = \sigma\left(T_g^4 - T_d^4\right) + \frac{1}{4} n_O v_{th,O} E_{rec,O} - \sum_i x_i \Gamma_{evap,i} \frac{H_{vap,i}}{N_A}$$

Chauffage par recombinaison des atomes d'oxygène

Refroidissement => bloque l'évaporation de la goutte

Flash boiling process





- Superheating states in liquids trigger so-called flash boiling processes
- At 3 mTorr, methanol is already highly superheated at 300 K. Greater temperatures will not bring any significant changes.
- On the other hand, PC is not superheated at room temperature. Heating during the injection triggers flash boiling in the PC spray.