I NOVANT'ANNI DEL PROF. BELLOBONO

Deposizione di strutture di TiO2 gerarchicamente organizzate ad elevate area superficiale

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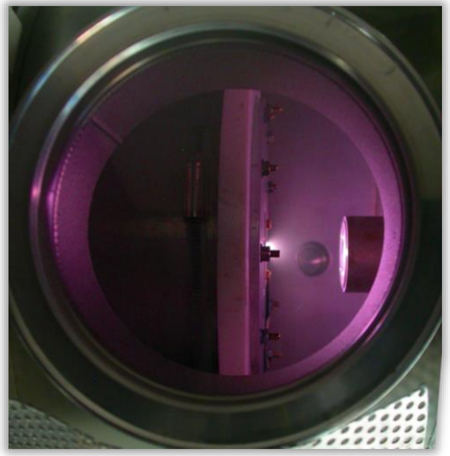

Nanostructured thin film

Nanostructures in a thin film can…
Greatly enhance mechanical, electrical, optical, catalytic properties
But…
requires a tailoring of the building blocks and of the growth process

Chemical Vapour Deposition (CVD)

Physical Vapour Deposition (PVD)

Nanostructured thin film

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Chemical Vapour Deposition (CVD)

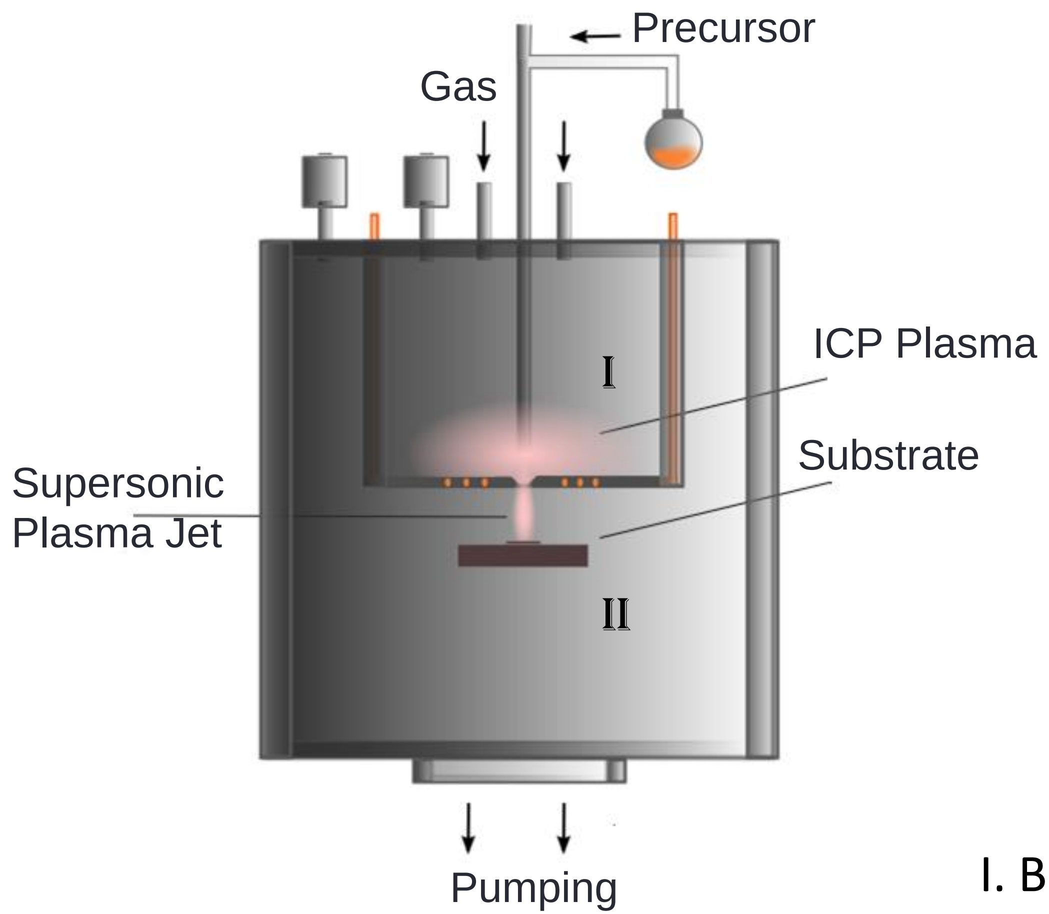
Physical Vapour Deposition (PVD)

Ideal technique:

- Control on nanostructure
- Control on chemical composition
- Efficient
- Flexibile
- Up-scalable

Plasma Assisted Supersonic Jet Deposition

STRATEGY: to separate the process in two different steps



I : ICP plasma
precursor dissociation
particle formation
(control of purity)

II : Supersonic Jet
particles acceleration
(control of particle nucleation and morphology)

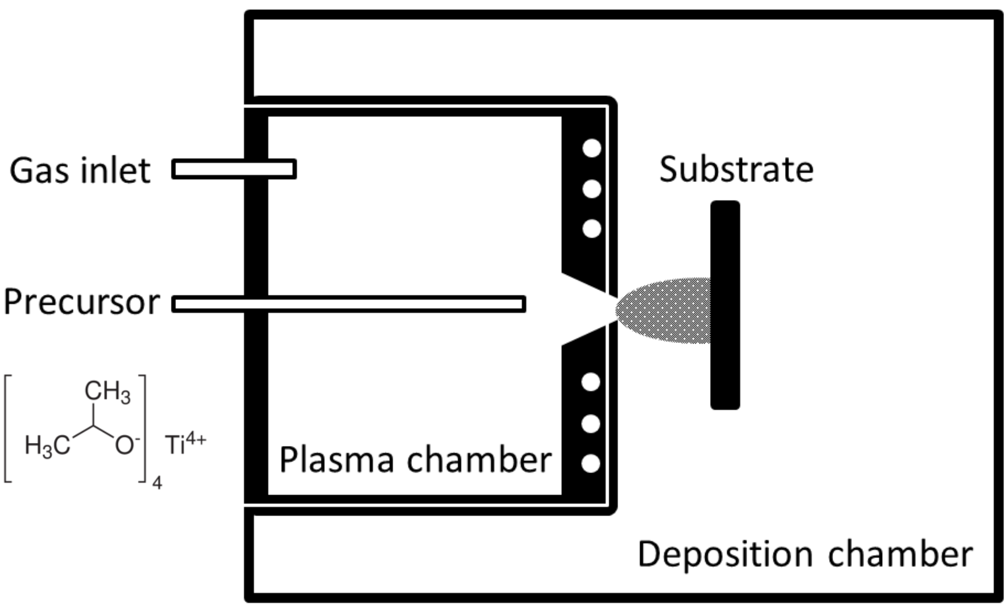
titanium precursors for tests

I. Biganzoli, *J. Mod. Phys.* , 2012

PA-SJD Plasma Reactor

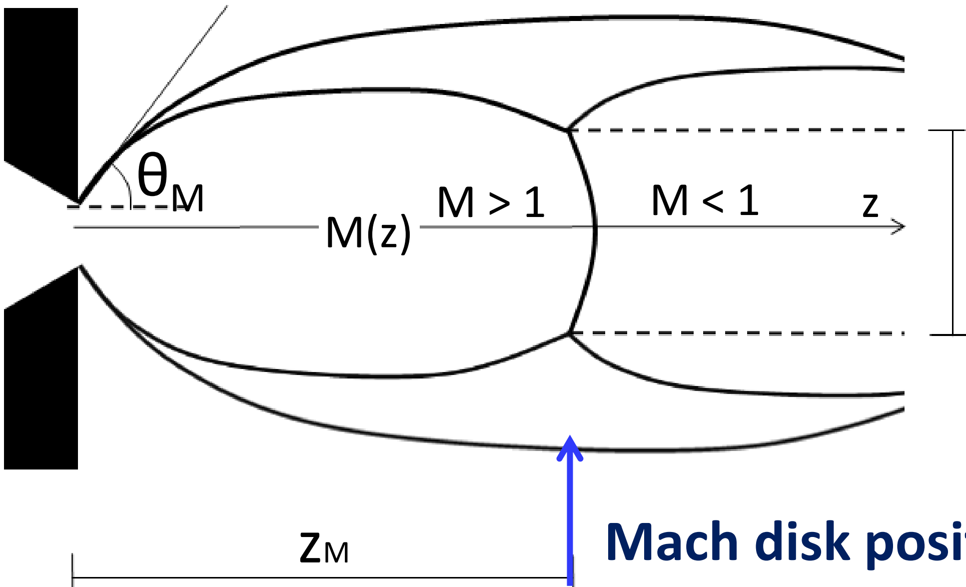
ICP plasma

- High density $Ar\text{-}O_2$ plasma at low pressure
- Low potential inside the chamber
- Control on precursor oxidation and dissociation



$Ar\text{-}O_2$ mixture	2:3
P_{plasma}	10 Pa
$P_{deposition}$	0.1-8 Pa
13.56 MHz Power	450 W
Temperature	500 K
TTIP precursor flow	0.5 g/h

PA-SJD Supersonic Jet



$$v_{crit} = \sqrt{\frac{2\,\gamma k_B T_0}{(\gamma - 1)m}}$$

$$\theta_M = 5.3\ R^{0.6}$$

$$z_M = 0.67\ D\sqrt{R}$$

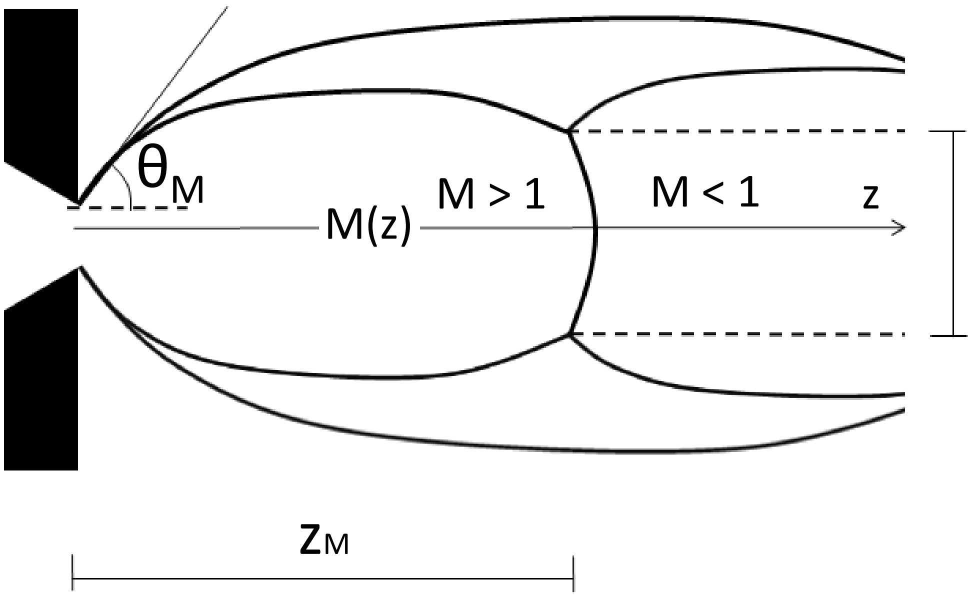
D = nozzle diameter
R = pressure ratio
T_0= inlet temperature

Mach disk position beyond which the gas speed decreases abruptly

Free gas isentropic expansion $R=(P_{pla}/P_{dep})>2$

- Mach number $(v_{gas}/v_{sound}) > 1$
- Pressure, density and temperature decrease
- Particle velocities quickly reach v_{crit} (longitudinal velocity)

PA-SJD Supersonic Jet



Mach disk position

D = nozzle diameter
R = pressure ratio

D = 6.9 mm
2 < R < 40
1 < M < 8
6.5 mm < Z_M < 29 mm
v_{crit}=750 m/s for Argon

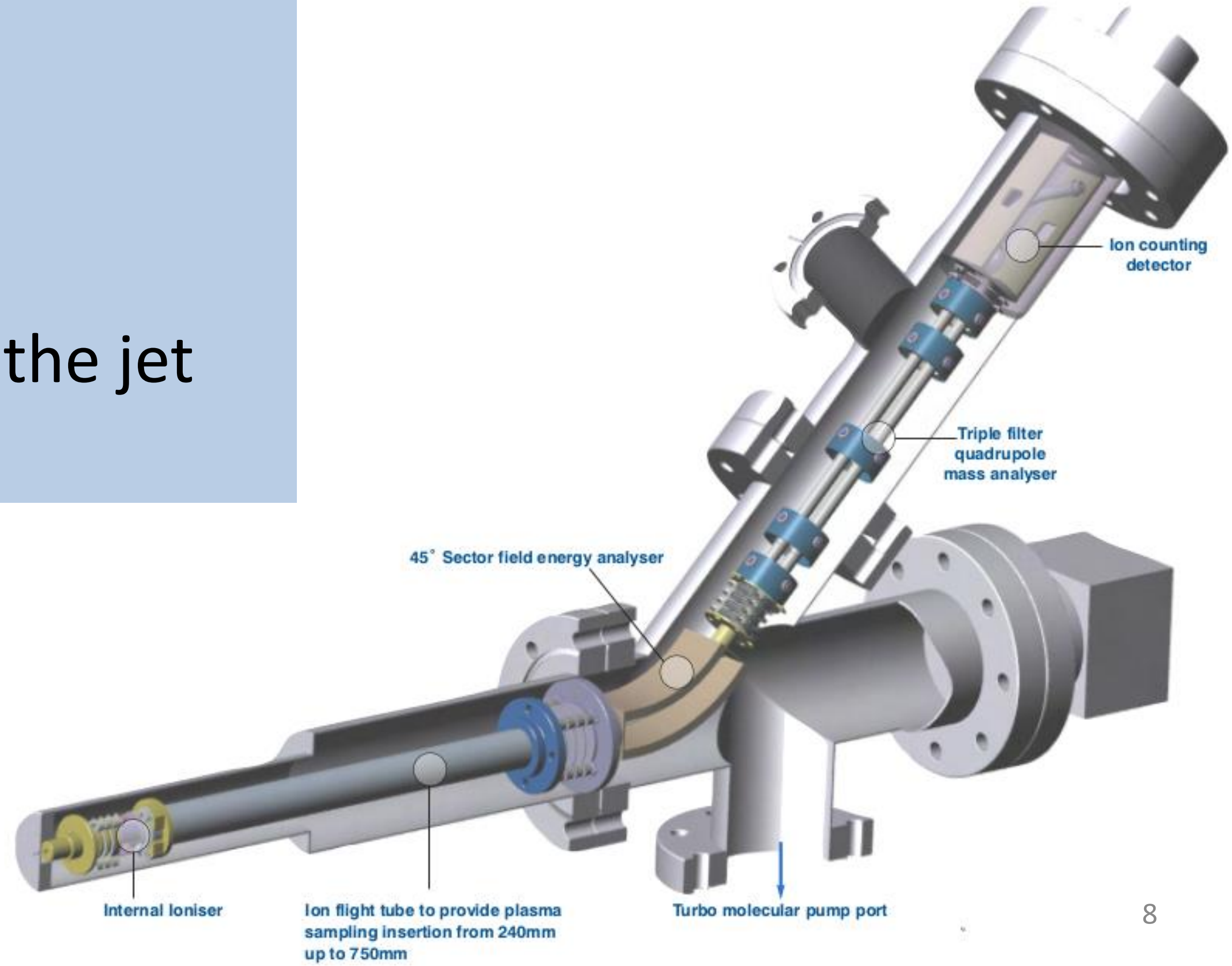
<u>inside the Mach cone:</u>

- Oriented jet ($v_{//} >> v_{\perp}$)
- Nanoparticles acceleration (energy to promote organized structures)
- Controlled nucleation (low collisionality to avoid <u>aggregation</u>)

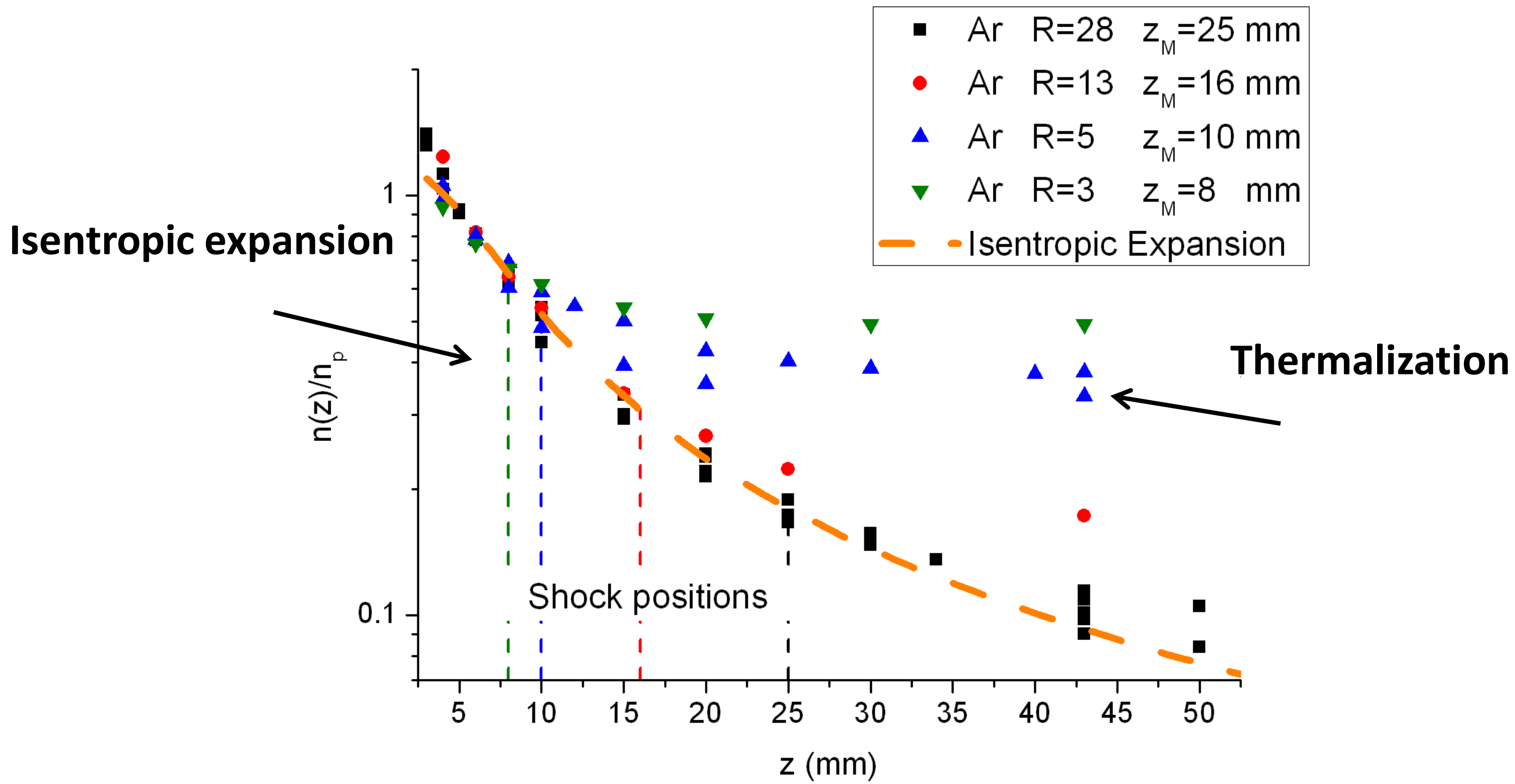
Quadrupole Mass Spectrometry Diagnostic

In situ, real time diagnostic

- Neutrals
- Ions
- Radicals
- IEDF
- Movable along the jet centerline



Neutral gas profile



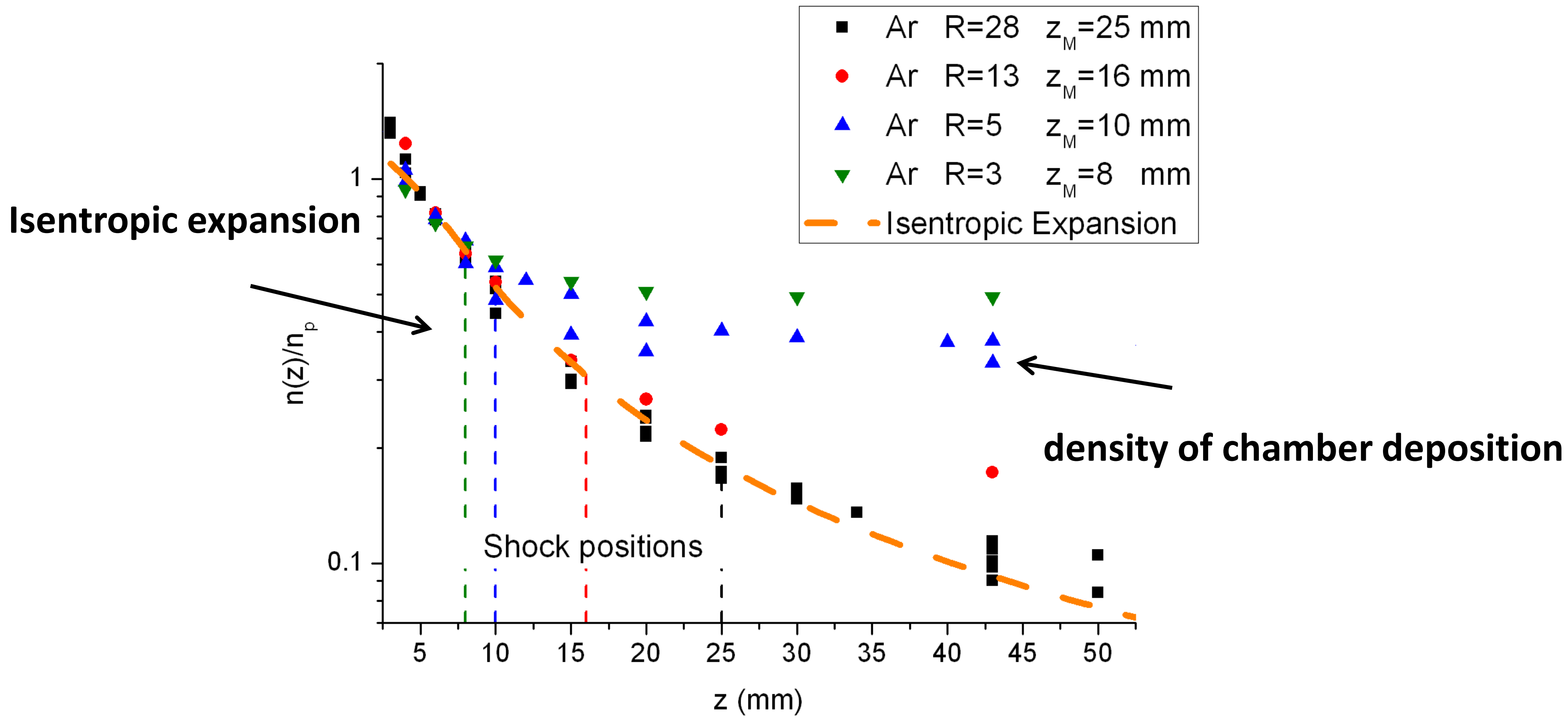
Isentropic expansion:

$$\frac{n(z)}{n_p} = \left(1.44\left(\frac{z}{D}\right)^2 - 0.65\left(\frac{z}{D}\right) + 0.87\right)^{-1/\gamma}$$

Mach disk position:

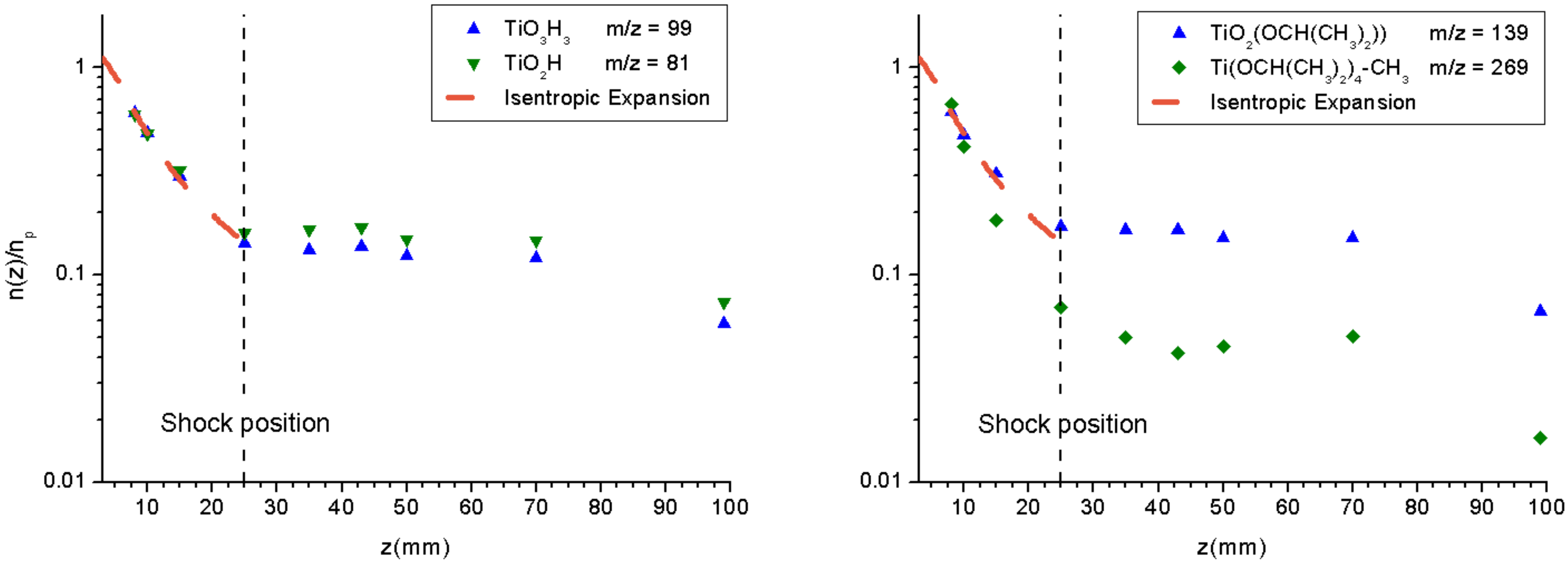
$$z_M = 0.67\ D\sqrt{R}$$

Neutral gas profile



- Low collisional $\lambda \approx 10$ mm
- High speed $v \approx 600\text{-}750$ m/s
- Directional

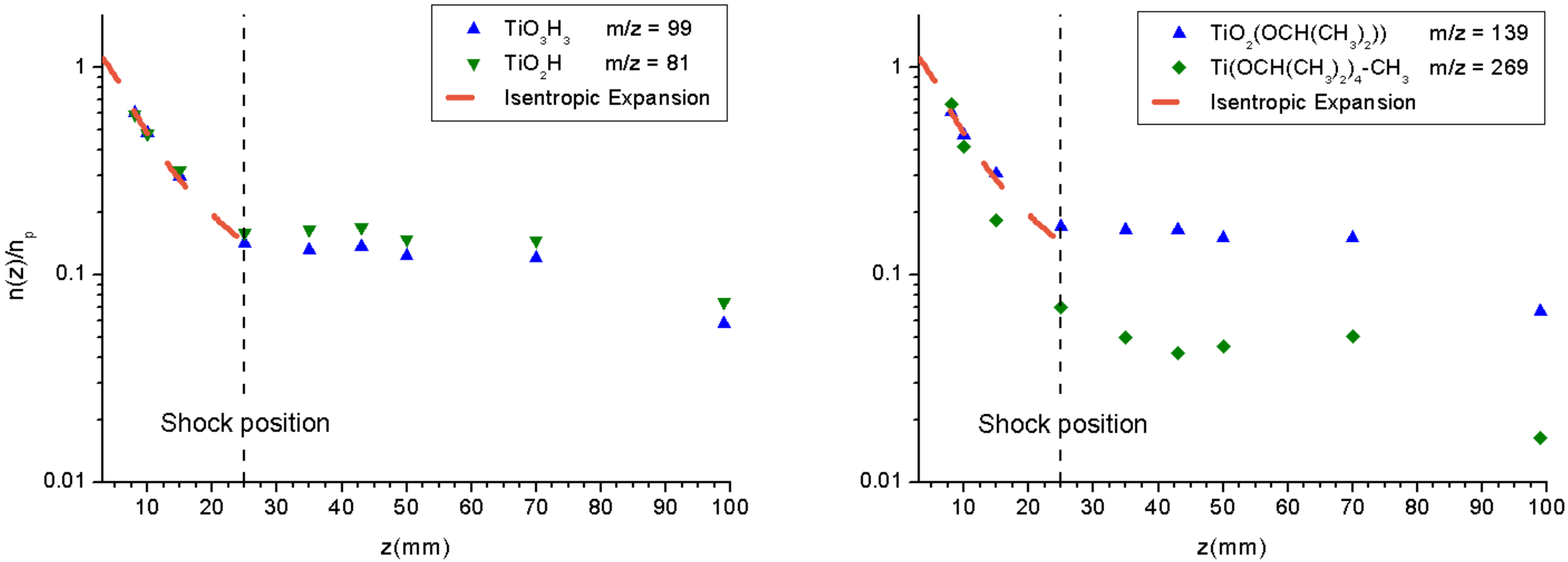
Seeded jet



- TiO_x seeds follow isentropic expansion
- Drag forces and inertia determine the NP acceleration and deceleration (300 m/s -750 m/s)

Results confirm a supersonic jet acceleration of Titanium molecules diluted into the gas mixture

Seeded jet



We operate inside the Mach cone in the well oriented jet, where nanoparticles can be accelerated up to a speed of 750 m/s and their aggregation can be controlled and reduced (~10 nm particle size) do to the low collisionality

Film properties vs set-up parameters

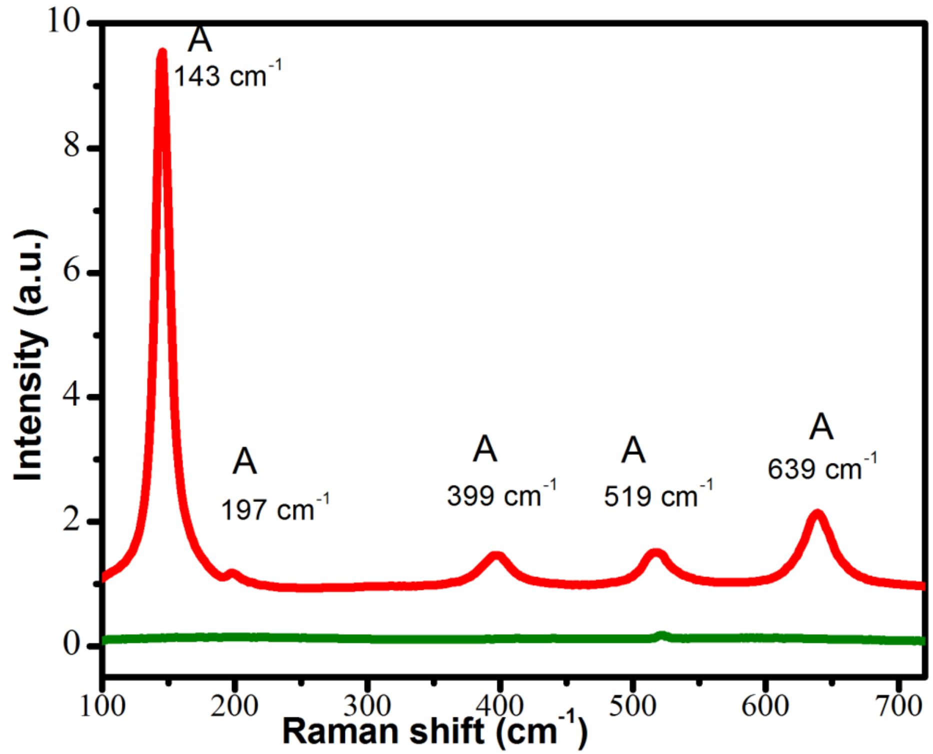
- TiO_x particles, created in the plasma chamber, impact on a substrate yielding the growth of the thin film

The film morphology depends on:

- Particle density in supersonic jet → precursor flow rate (T)
- Particles energy → nozzle design and compression ratio (R)
- Substrate position with respect to the Mach disk (z)
- Substrate roughness

The film chemical composition depends on chemical reactions in the plasma chamber (Ar O_2 mixture, RF Power)

Film Chemical properties



RAMAN spectrum of synthesized TiO_2 film before (green) and after (red) annealing

Upon annealing Raman analysis shows the complete transformation in Anatase, with a high purity level of the TiO2 films (as indicated by the red peaks)

Film Deposition rates

Deposition rate is affected by multiple factors:

Nozzle-Substrate position (z)

Precursor flow rate (T=40-55 °C)

Supersonic jet parameter (R)

Deposition rates

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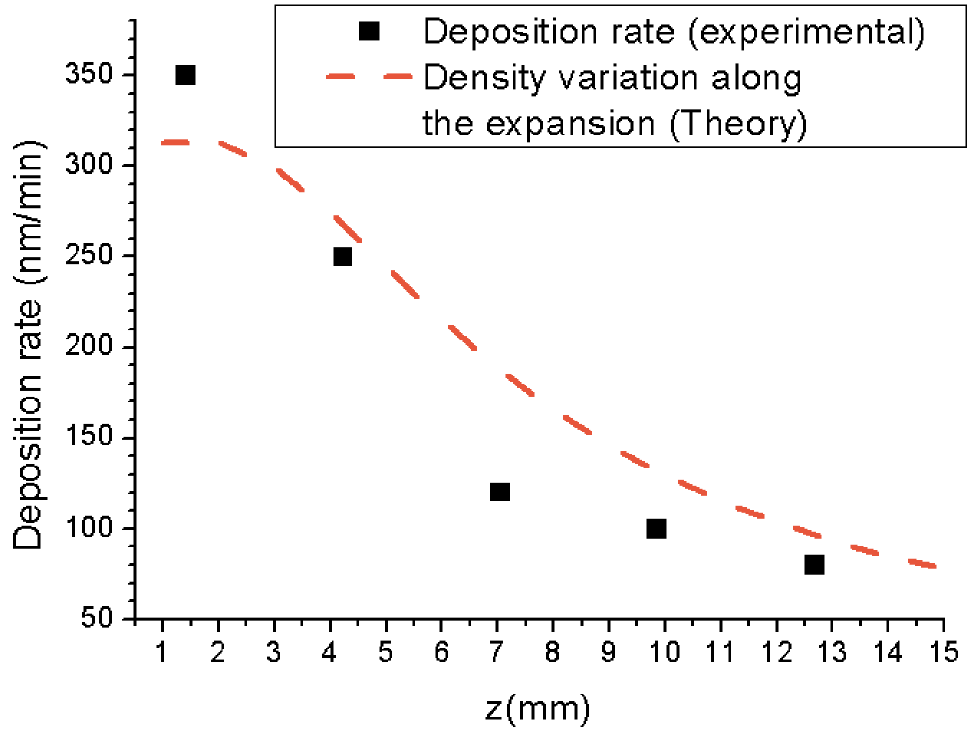
- Nozzle-Substrate position (z)
- Precursor flow rate (T=40-55 °C)
- Supersonic jet parameter (R)

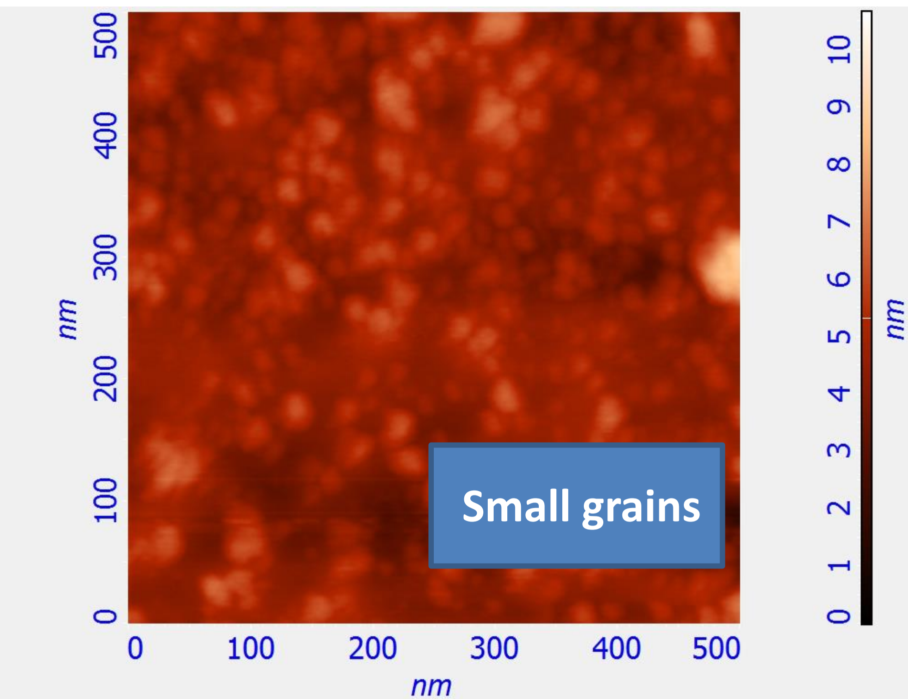


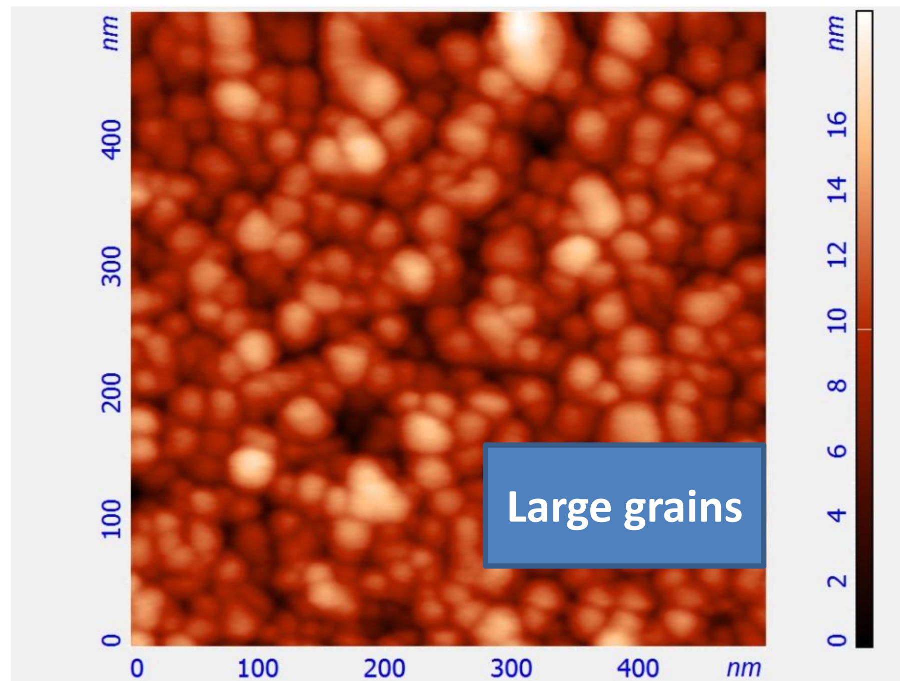
- **Typical deposition rates from tens nm/min to several hundreds nm/minute**
- **It is possible to deposit films between ~50 nm to ~10 μm thickness**

Film porosity

Distance nozzle- substrate: 14 mm
Low Precursor flow rate: 40 °C
Thickness: 80 nm (16 %)
Deposition rate: 8 nm/min
Low Relative porosity:13%

Distance nozzle- substrate: 9 mm
High Precursor flow rate: 49 °C
Thickness: 350 nm (12%)
Deposition rate: 144 nm/min
High Relative porosity:35%



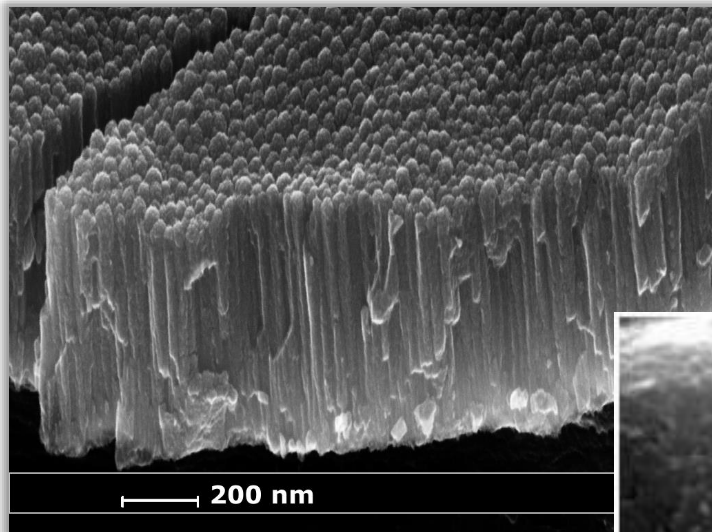


Relative porosity evaluated as vacuum percentage respect to a T_iO_2 bulk by means of an ellipsometer

Film morphology SEM

Substrate inside the jet

- High speed NP
- Well oriented jet
- Low collision
- high deposition rates
- directional structures

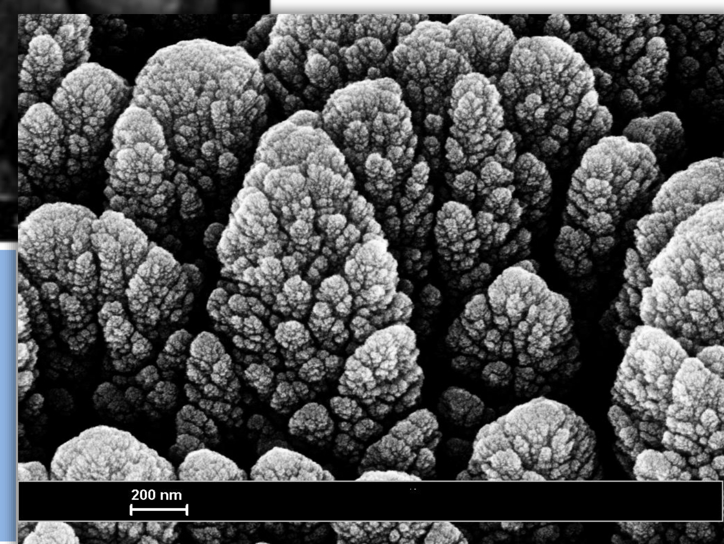


Substrate after the shock

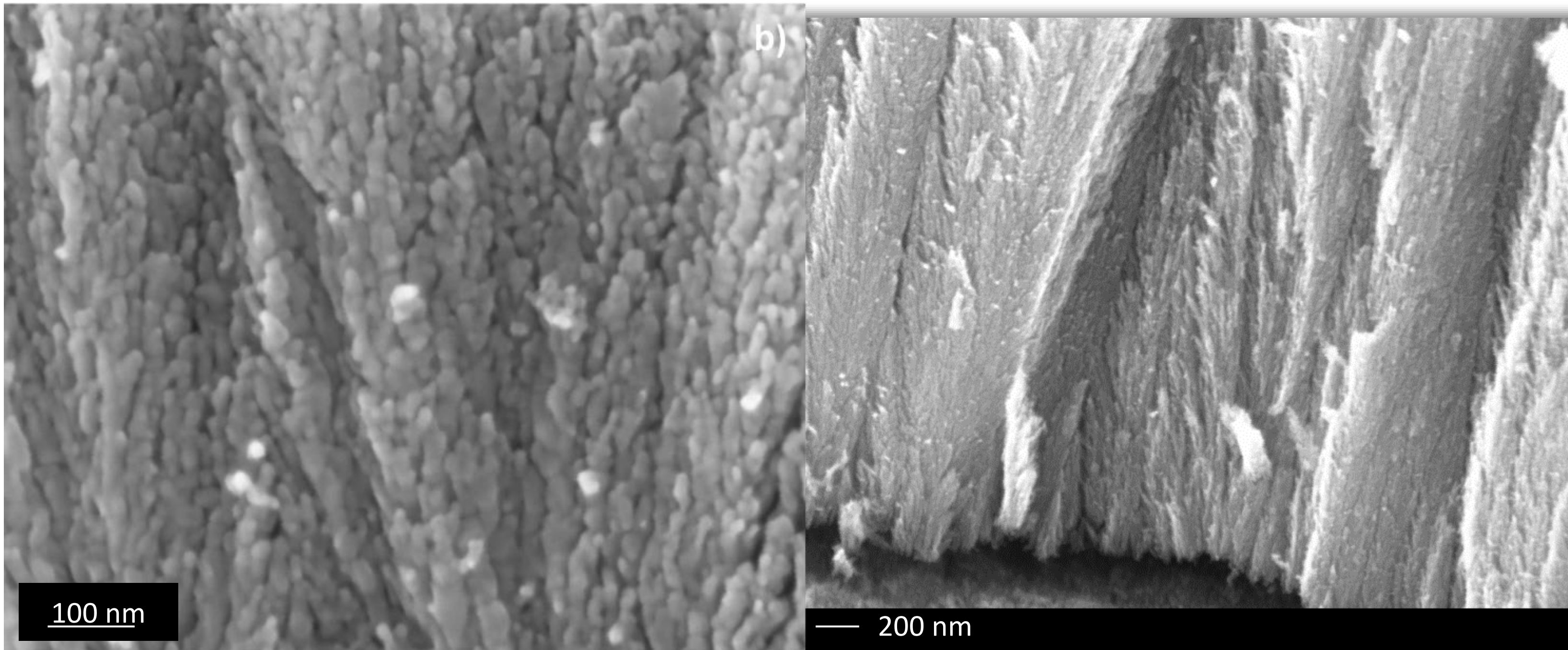
- Decreasing NP speed
- Losing directionality
- Collisions increase
- low deposition rates
- tree -like structures

substrate on the border of the jet

- shadowing effects
- self-similar structures



Hierarchical structure employed for solar cells

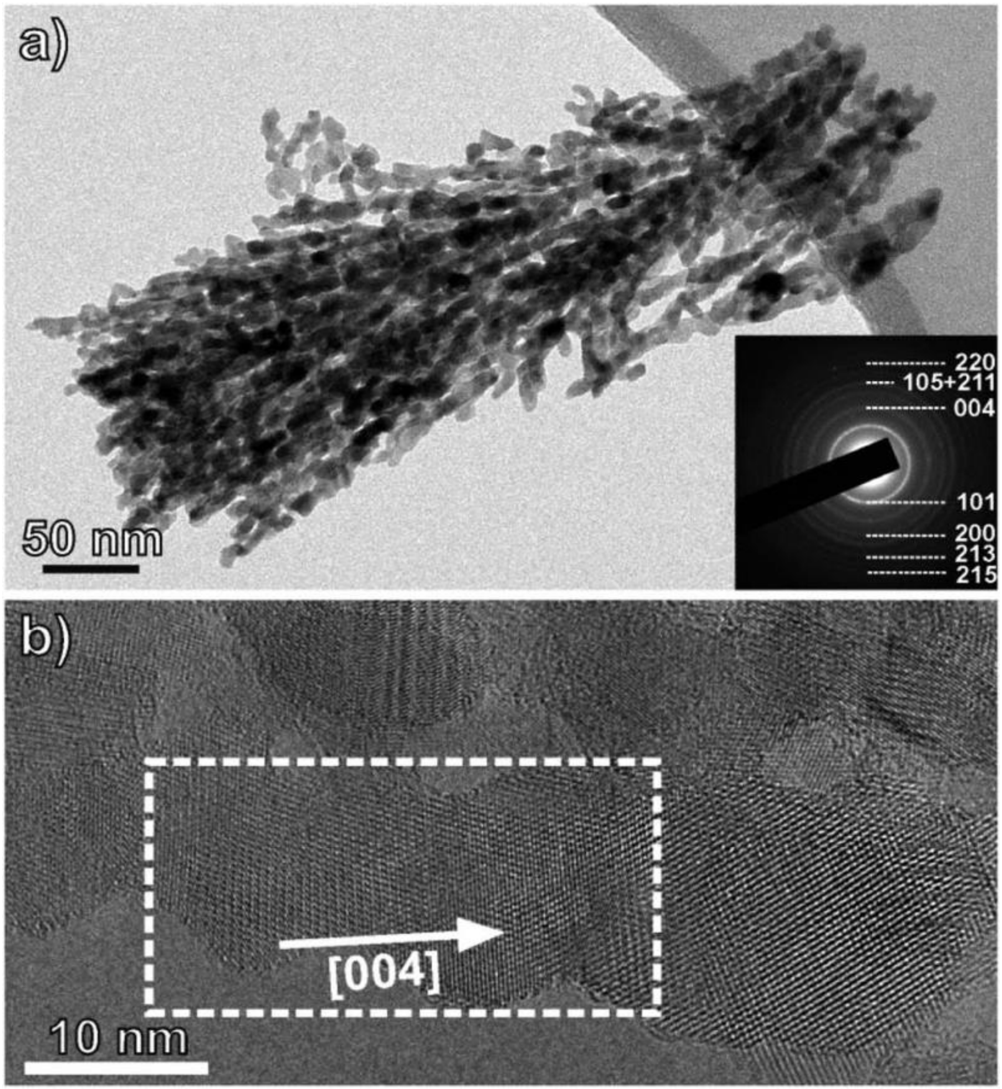


FE-SEM images of PA-SJD TiO_2 films

To the right: above a few tens of nanometres, tree-like structures are constrained to grow vertically due to mutual hindering.

To the left : higher magnification image showing the hierarchical structure from single nanometric grains (10 nm) to the tree-like mesoscale structure (100-500 nm)

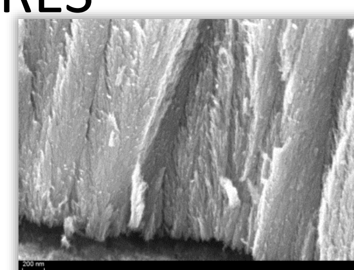
Hierarchical structures: TEM analysis



(a) bright-field TEM image of a typical tree-like structure, HIERARCHICALLY ORGANIZED STRUCTURES

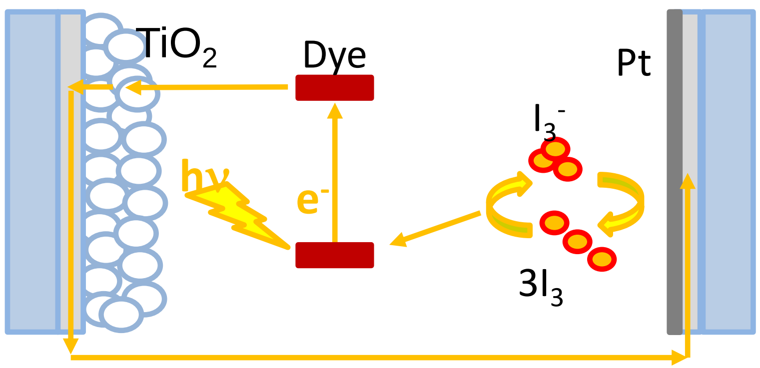
(b) HRTEM image of a zig-zag structure, formed by 10 nm sized single-crystalline domains (dashed box), ANATASE SINGLE CRYSTAL STRUCTURES

Trifiletti et al., *Journal of Materials Chemistry*, 2013
Piferi et al., *Nanomaterials*, 2022



Photovoltaics Applications

Dye Sensitized Solar Cells (DSSC)



- Nanostructures
- High porosity
- Chemical purity

Good efficiency!

Leandri, *Eur. J. Org. Chem*. 2013

Conclusions

A novel inductively coupled plasma source for hierarchically nanostructured thin film deposition

Able to control
nanostructure size
porosity
chemical purity

TiO_2 films tested for Photovoltaics Application

Dye Sensitized Solar Cells

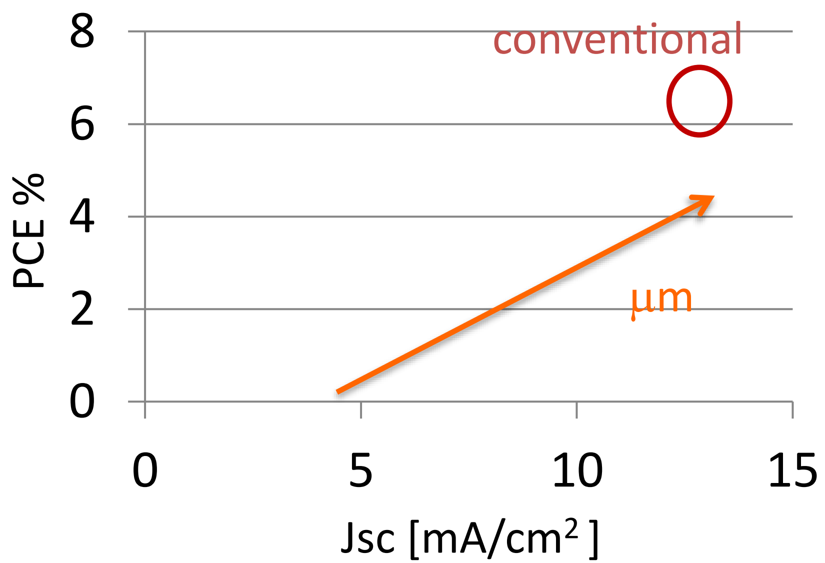
TiO2 film	Dye adsorbed [10^{-8} mol/cm^2]	Jsc [mA/cm^2]	Voc [mV]	FF [%]	PCE [%]
PA-SJD-0.8 μm	2.9	3.2	793	67	1.7
PA-SJD-1.2 μm	1.5	5.6	739	68	2.8
PA-SJD-1.6 μm	1.6	6.6	737	65	3.2
PA-SJD-2.2 μm	2.2	10.1	742	68	5.1
PA-SJD-3.6 μm	3.6	11.4	738	61	5.1
PA-SJD-4.7 μm	4.7	11.8	755	66	5.9
*Conventional-9 μm	9.0	13.0	749	69	6.7

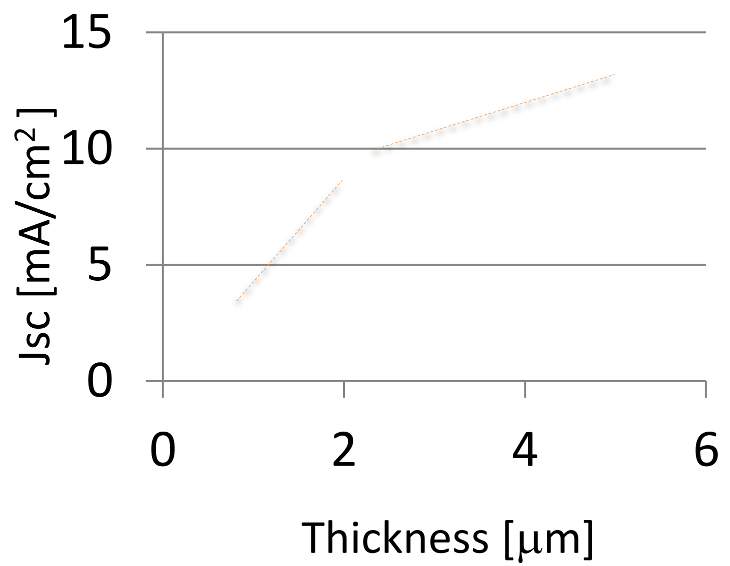
*a conventional TiO_2 photoanode prepared via screen-printing from a commercial paste while keeping all of the other fabrication conditions unchanged

Trifiletti et al., *Journal of Materials Chemistry*, 2013

Dye Sensitized Solar Cells

Charge transport properties

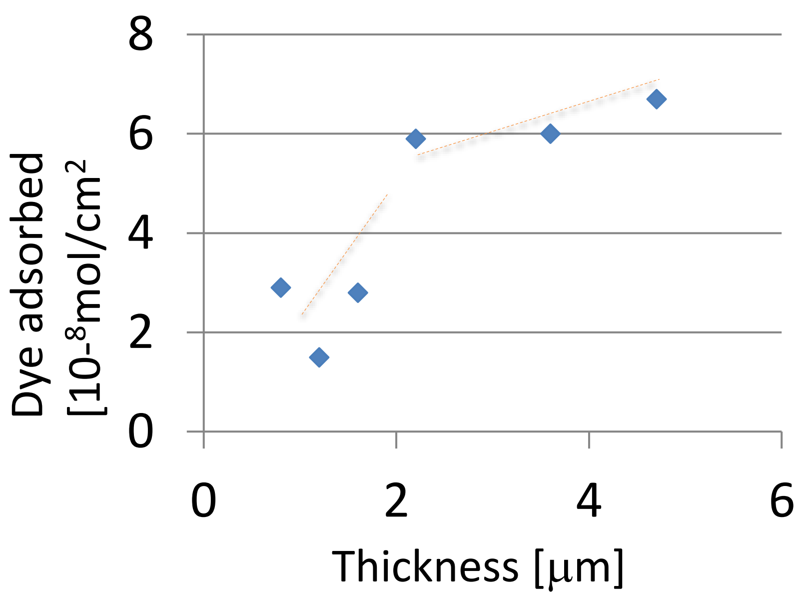




- Efficiency PCE = J_{sc} x V_{oc} x FF is proportional to the current density
- Current density strongly increases with thickness up to 2.2 μm then linear dependence is weaker

Dye Sensitized Solar Cells

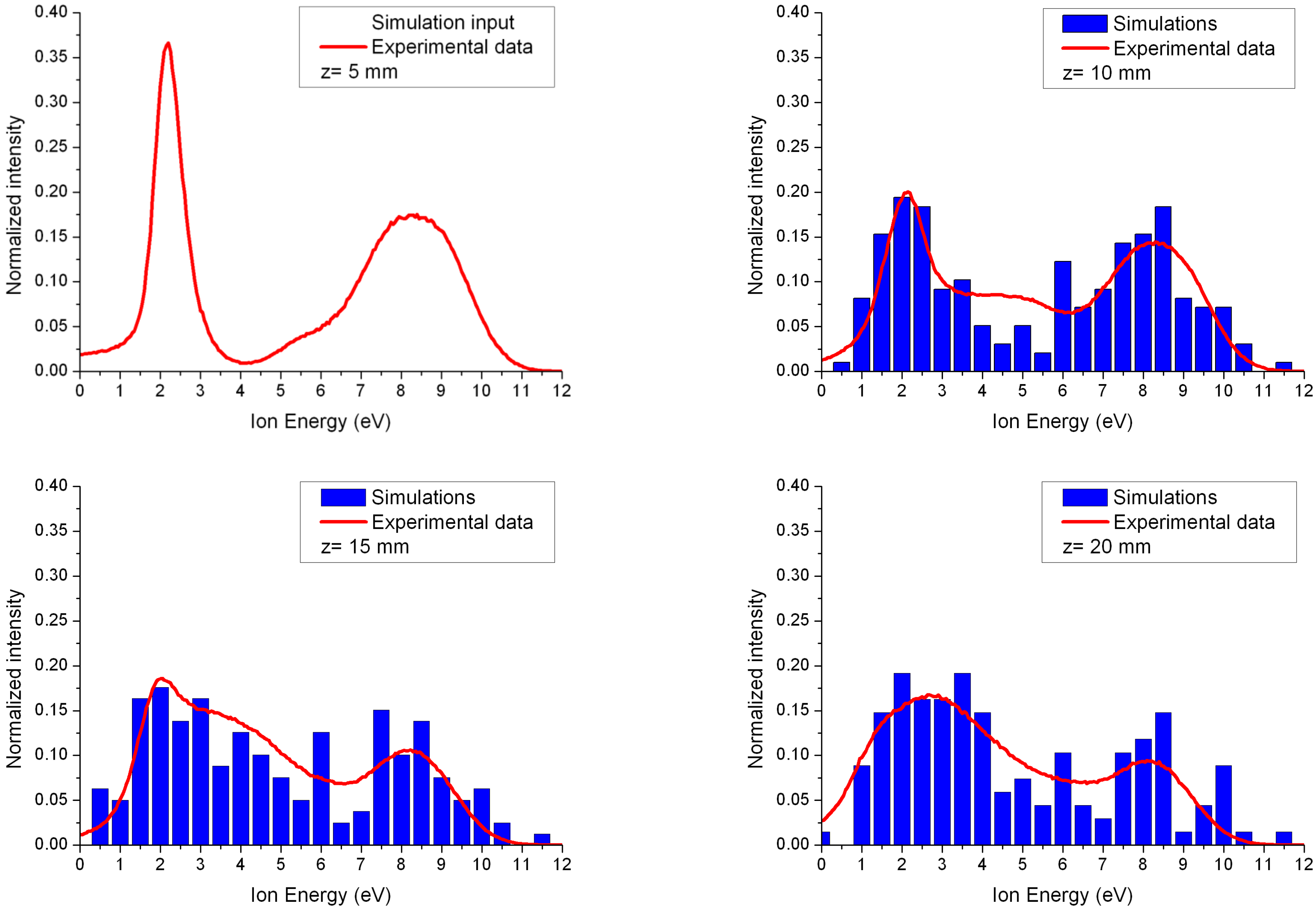
Dye adsorption properties



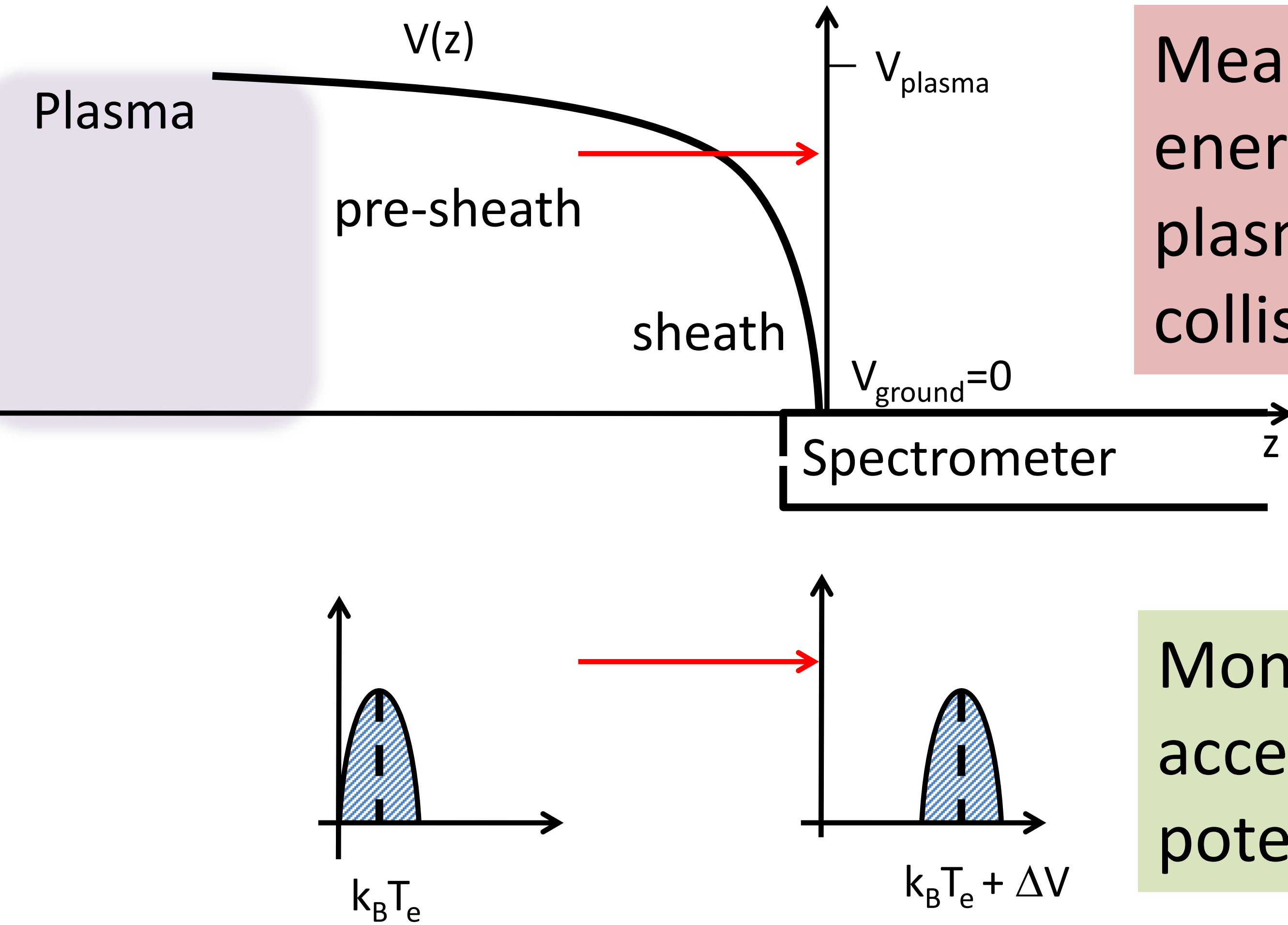
TiO2 film	Dye adsorbed [10-8 mol/cm²μm-1]
PA-SJD-0.8 μm	3.7
PA-SJD-1.2 μm	1.3
PA-SJD-1.6 μm	1.8
PA-SJD-2.2 μm	2.7
PA-SJD-3.6 μm	1.7
PA-SJD-4.7 μm	1.4
*Conventional-9 μm	1.0

- The dye adsorption increase with thickness is similar to the density current one suggesting a strong relationship between the two quantities.
- The amount of adsorption dye for thickness unit is higher than the conventional one Dye adsorption is related to the presence of the nanostructures.

Simulation results along the jet



Ion Energy Distribution in a ICP

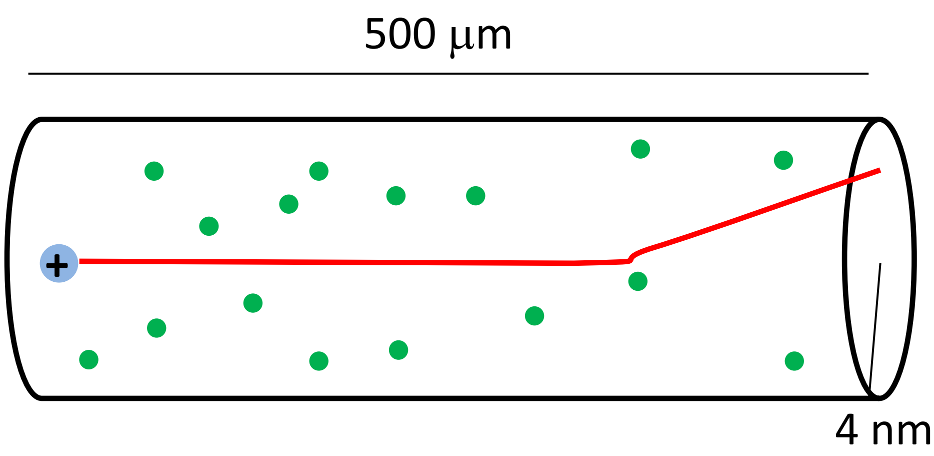


Measuring the ion energy from the plasma across a collisionless sheath

Monoenergetic IED, accelerated by potential difference

Ion Energy is simply: $E= k_BT_e + q(V_{plasma} – V(z))$

First principle calculation model



Assumptions:

- Electrons do not influence IEDF
- Neutral density in each simulation cell is obtained from isentropic expansion equations
- Ions are accelerated by the potential gaps between V_{plasma} and V_{jet} then V_{jet} and 0

Ar^+ ions collide with Ar neutrals losing their energy by elastic collisions

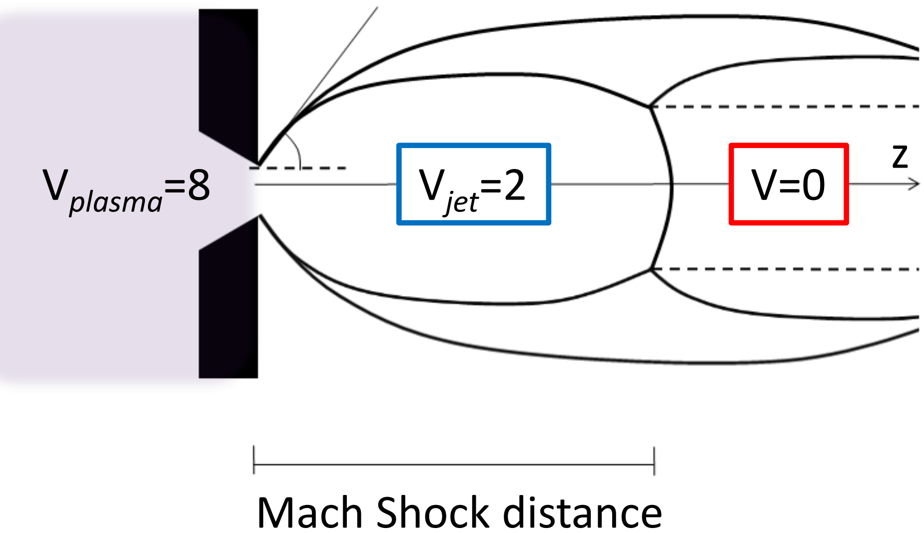
We can simulate Ar^+ IEDF numerically evolving their dynamics from 5 to 20 mm and solving the equation of motion

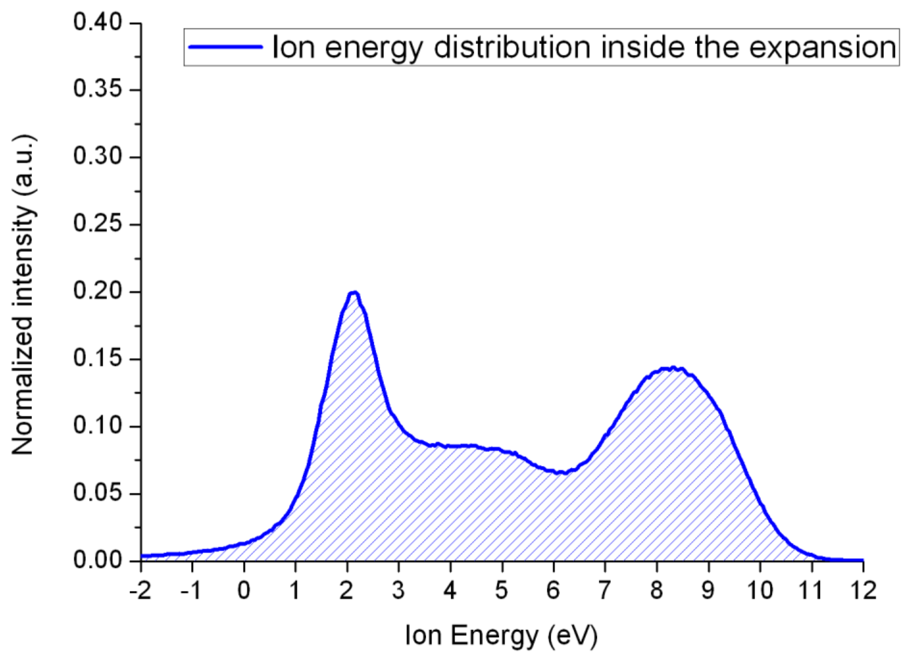
Ar^+ - Ar interactions are modelled with a 12-4 L-J potential (no charge exchange)

$$e\varphi(\mathrm{r}) = 4\epsilon\left(\frac{A}{\mathrm{r}^{12}} - \frac{B}{\mathrm{r}^{4}}\right)$$

Measuring IEDF

We have collisions across the jet





We have two potential gaps, thus two peaks in our IEDF

Energy is evolving through collisions