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High-Power Impulse Magnetron Sputtering (HiPIMS), From plasma analysis to thin film and nanoparticle synthesis

CHIPS
Chimie des Interactions Plasma Surfaces

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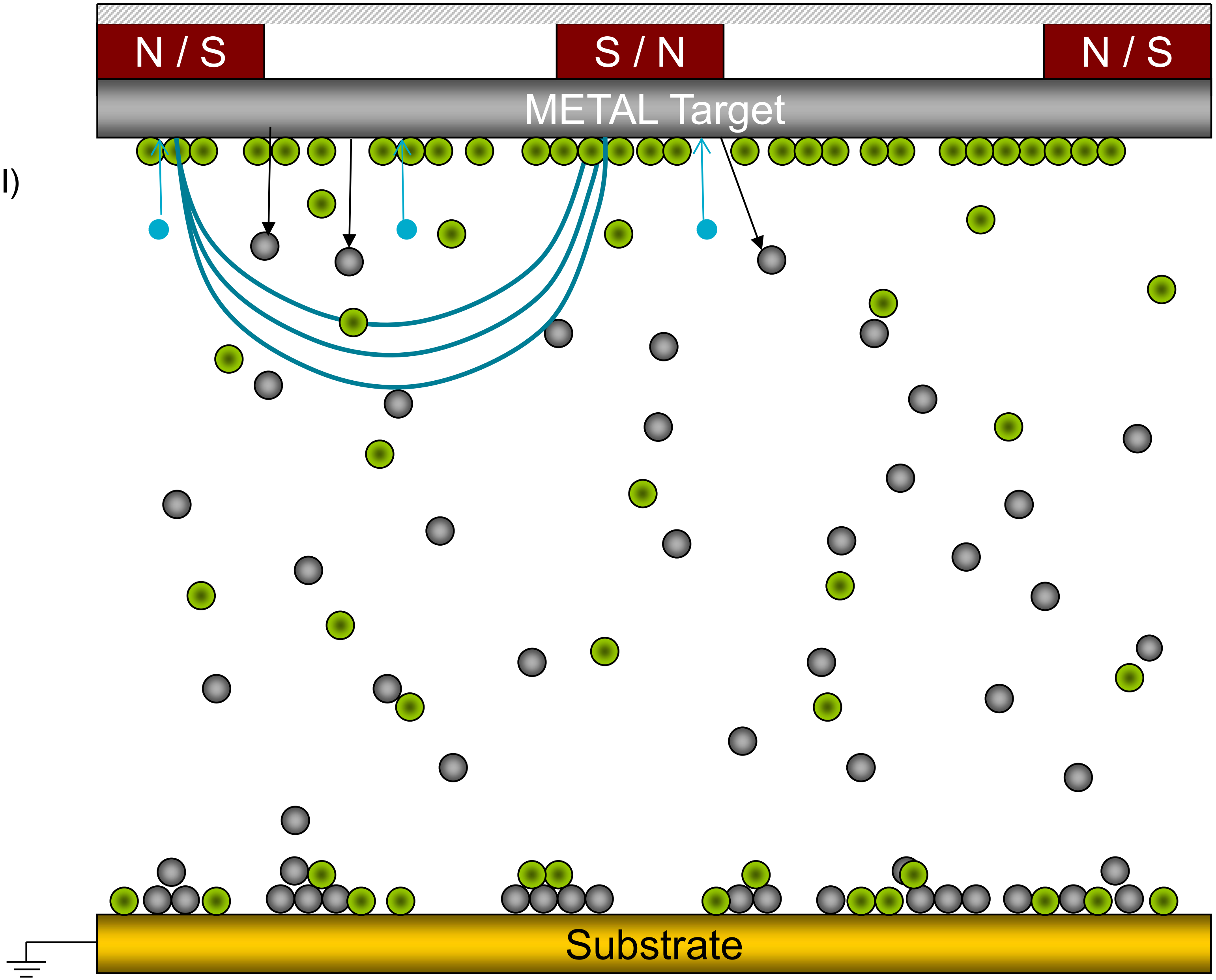
Conventional DC magnetron sputter deposition

CATHODE

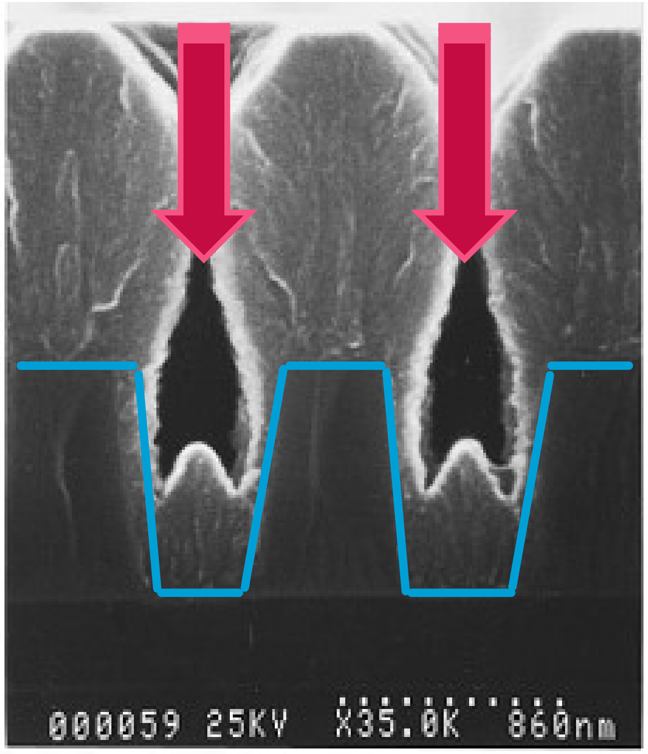
(Negative potential)



Magnetron sputtering in the (glass) industry

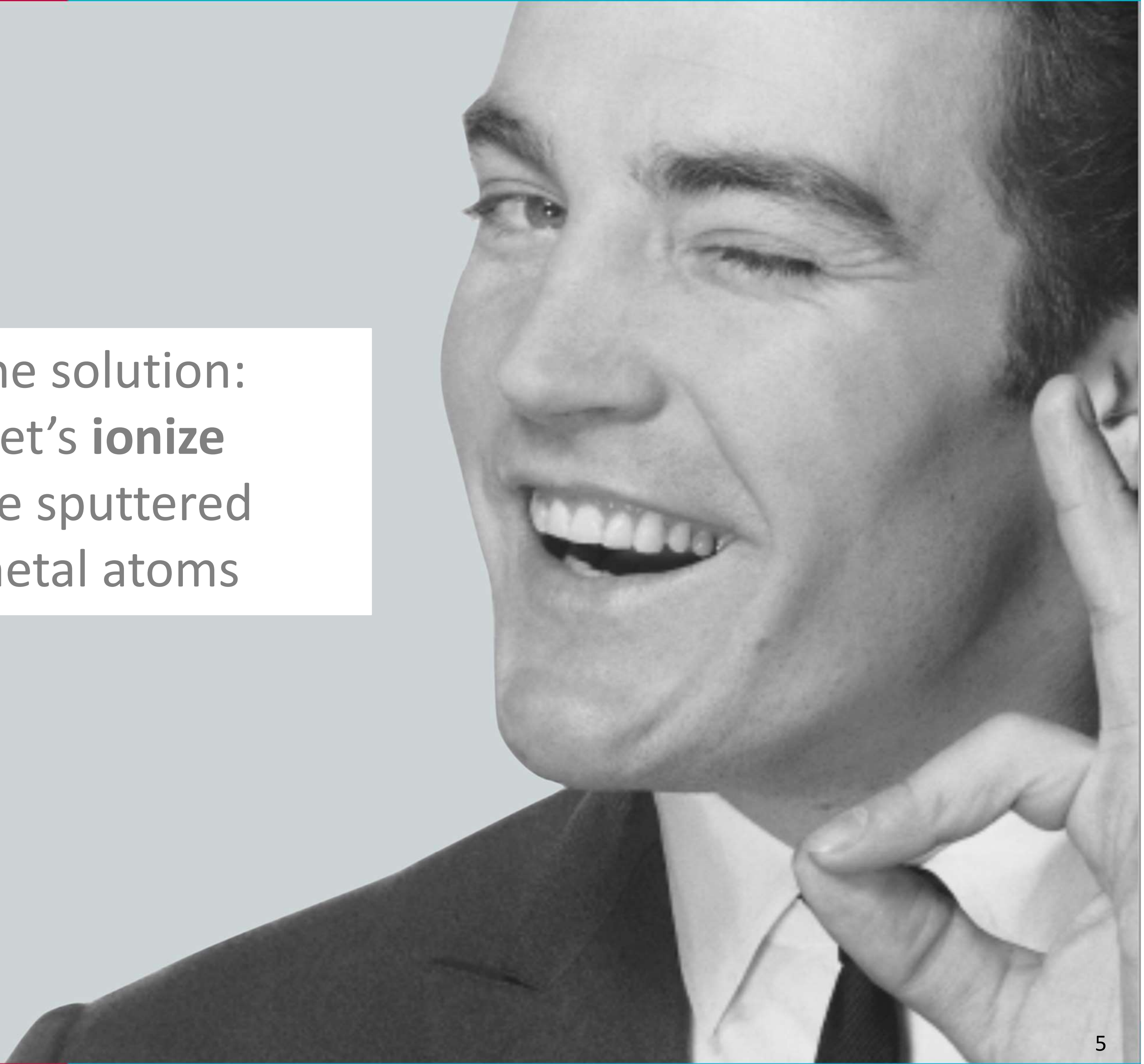
https://invest.dresden.de/

Filling trenches by magnetron sputtering



Hamaguchi and Rossnagel, J. Vac. Sci. Technol. (1995).

The solution:
Let’s **ionize**
the sputtered
metal atoms



Advantages brought by the ionization of the sputtered metal atoms

Metal ions (+ negative bias on the substrate) allows :

1. Controlling the **trajectory** of the film – forming species

– Conformal deposition

2. Controlling the **kinetic energy** of the film – forming species

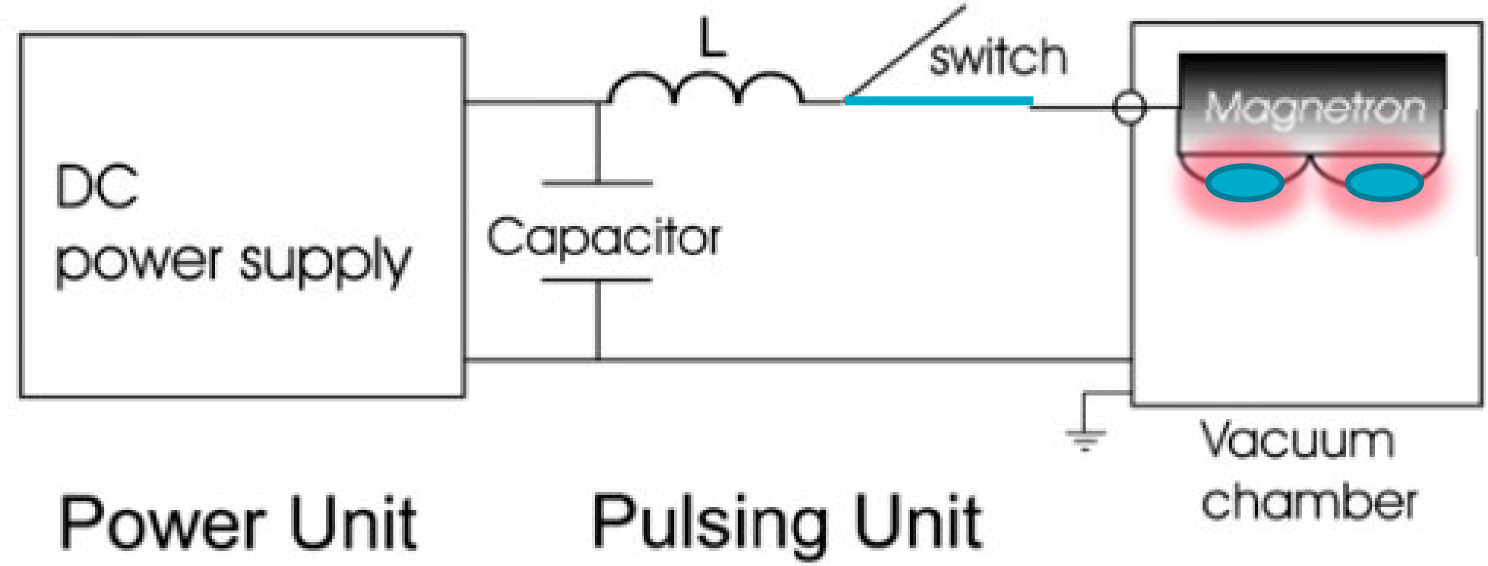
– Crystallinity, micro/nanostructure, roughness,... are modified

Sarakinos, Alami, Konstantinidis, Surf. Coat. Technol 2010

How can we do that ?

- Promote ionization by electron impact
- « Heat » the electrons of the plasma

Architecture of a HiPIMS generator

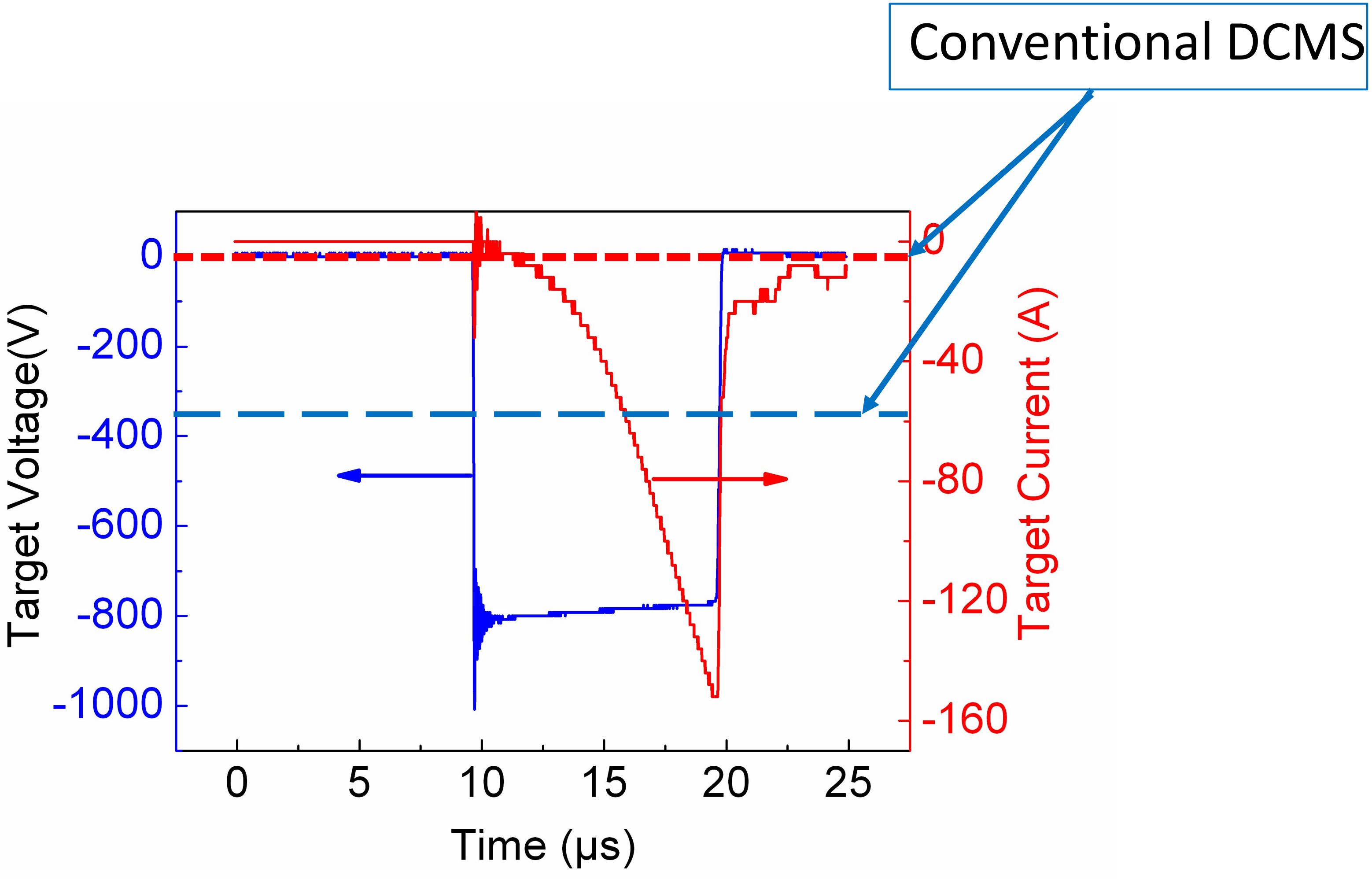


The power supply delivers:

- **Voltage up to 1 – 2 kV**
- Peak current in the range of 10-100 of Amps

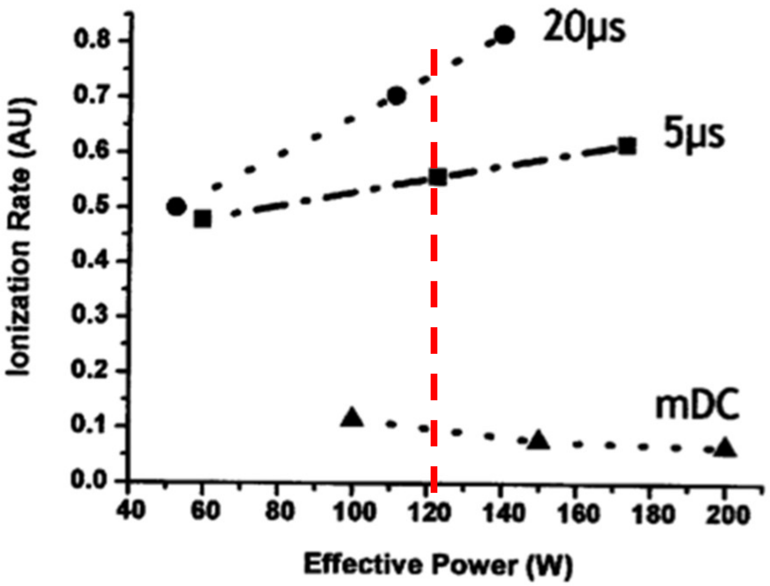
Pulsed discharge to avoid overheating the target/magnets

Typical Current-Voltage-Time waveforms

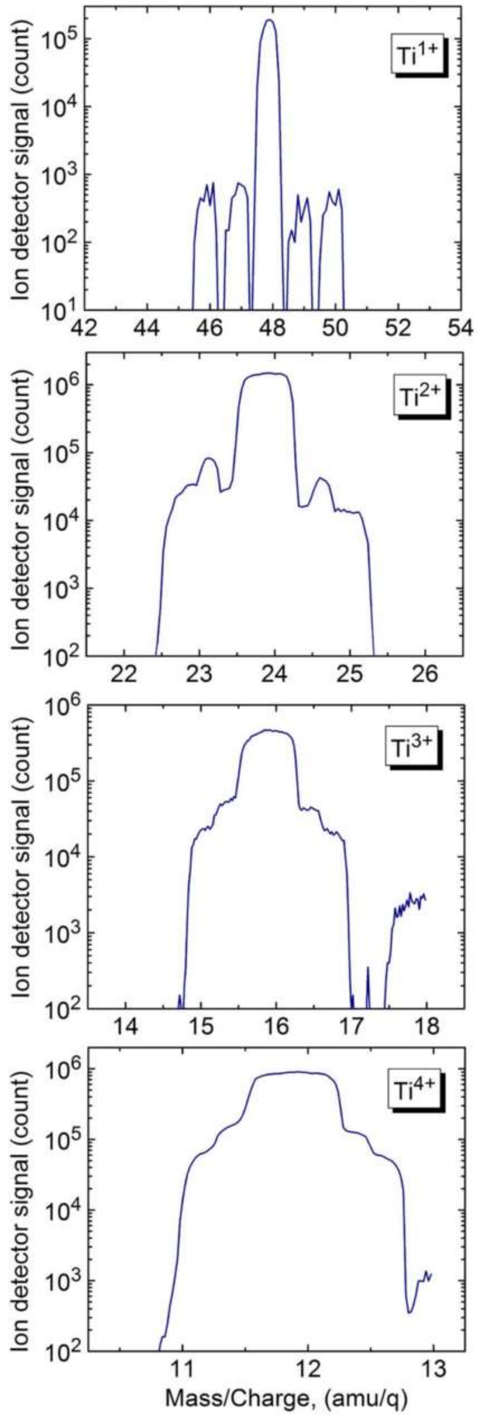


Evidences of the production of metal ionization

Metal ionization rate
from AAS measurements



Konstantinidis, J. Appl. Phys. (2006)



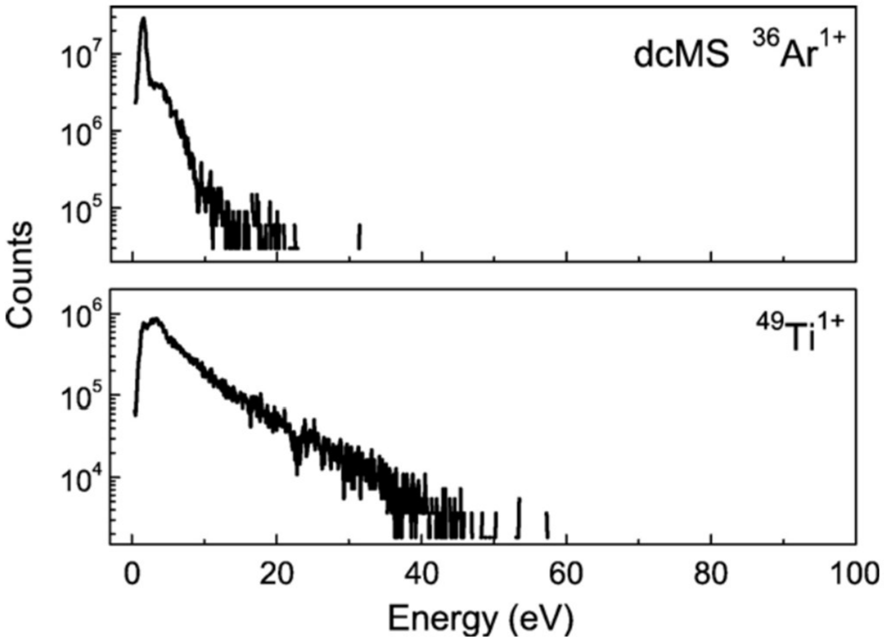
Mass Spec. data

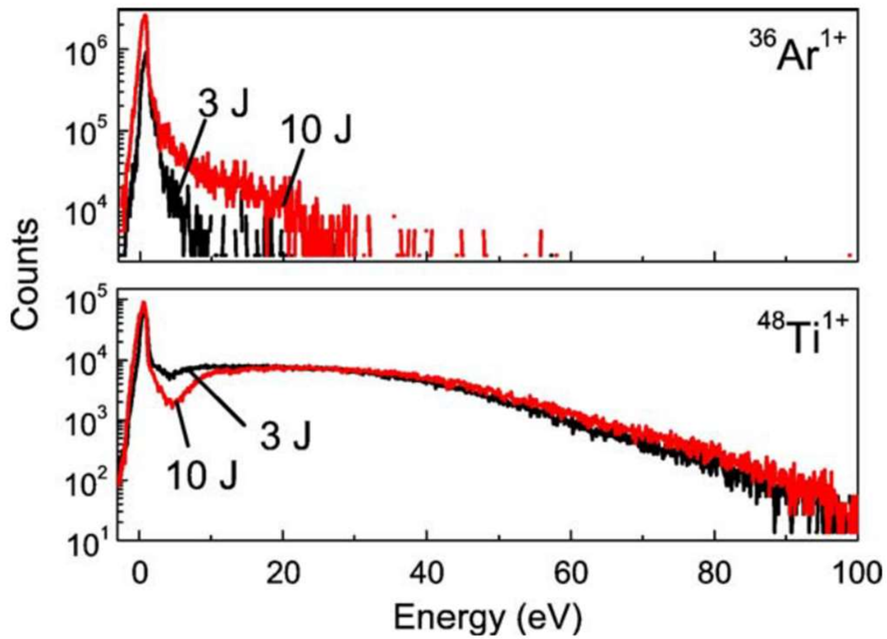
Andersson et al. Appl. Phys. Lett. (2008)

Film – forming species with high kinetic energies

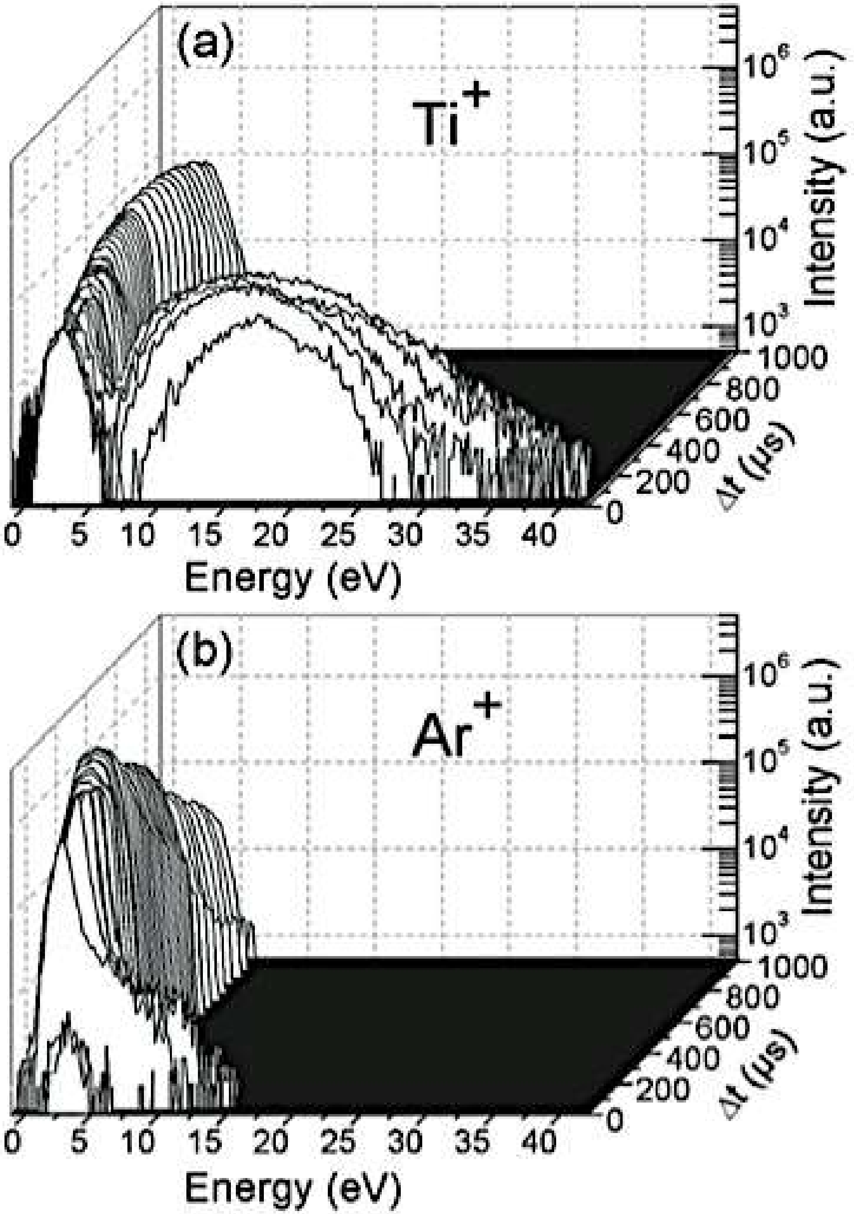
Time-averaged Energy-Resolved Mass spectrometry analysis

DC Magnetron	HiPIMS





Bohlmark et al, Thin Solid Films (2006).



Plasma dynamics

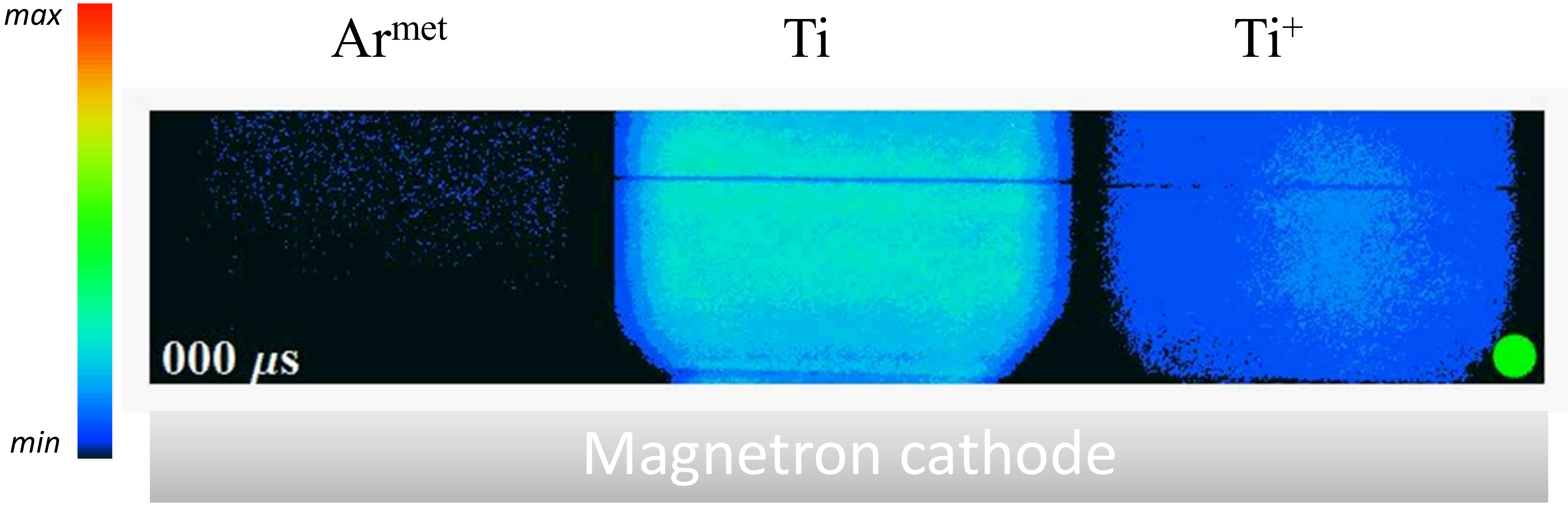
Time-Resolved Ion Energy Distribution Functions by Energy-Resolved Mass Spectrometry analysis

Palmucci et al, J. Phys. D: Appl. Phys. (2013)

Time & space – dependent plasma chemistry

Time-Resolved 2D mapping of plasma species by LASER induced Fluorescence

Pulse - 20 µs
Period - 1 ms
Pressure - 20 mTorr

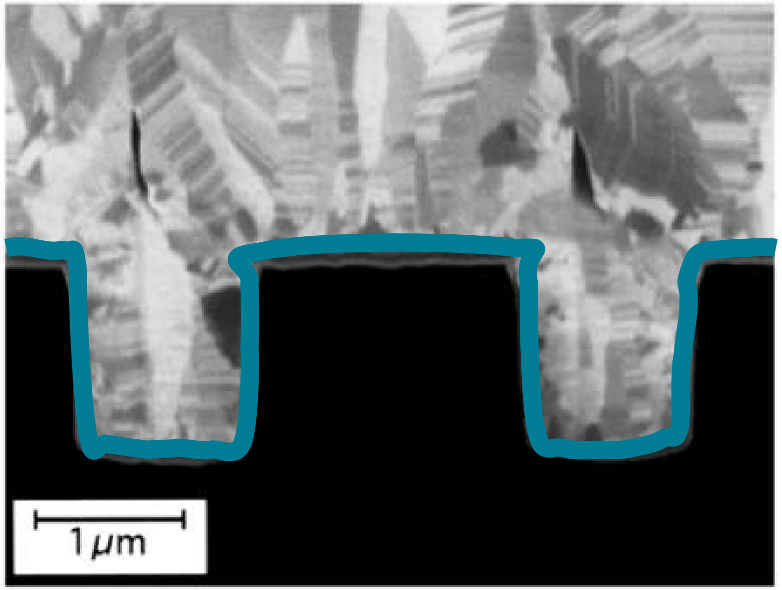


- ON-time
- OFF-time

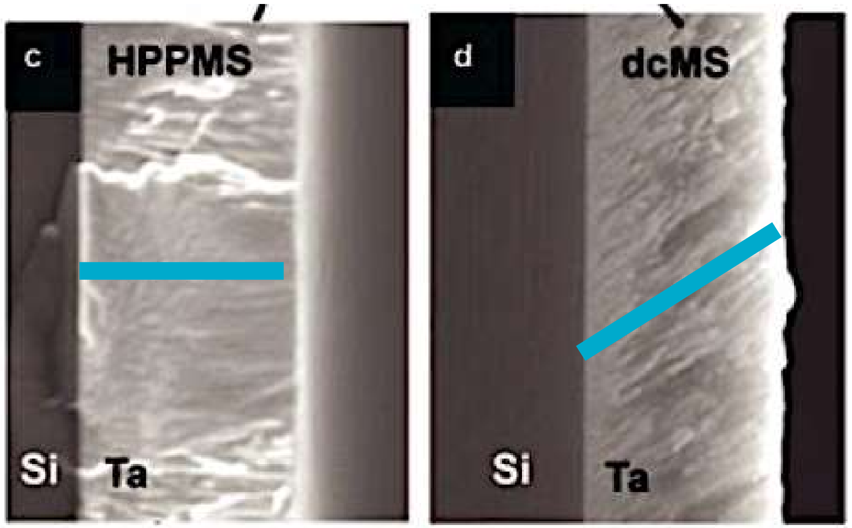
N. Britun et al, J. Appl. Phys. (2015).

Conformal deposition on complex-shape objects

Substrate surface tilted by 90° *vs*. target surface



Kouznetsov et al, Surf. Coat. Technol. (1999)



Alami et al, JVST A (2007)

Towards « a definition » of HiPIMS

1. Magnetron plasma
   – Glow discharge in ExB fields

2. Electric pulses
   – Duty cycle ≤ 1%

3. High power/peak current
   1. ~kW / A cm^{-2}
   2. $\Rightarrow N_e \sim 10^{12\text{-}13}\ cm^{-3}$

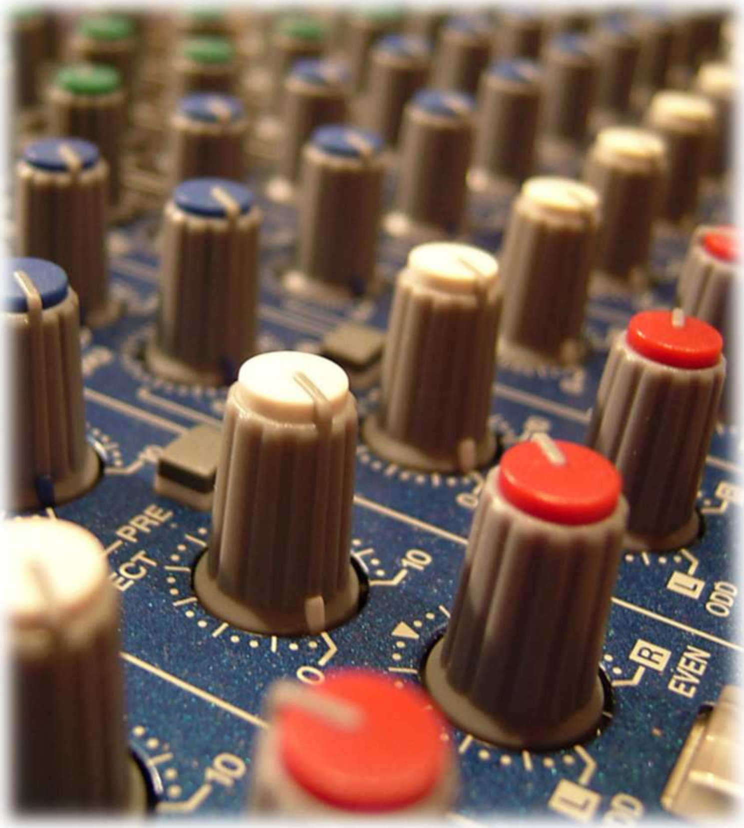
4. High ionization rate of the sputtered material

Sarakinos, Alami, Konstantinidis, Surf. Coat. Technol, 2010.

Some more knobs to tune film properties

- **Energy deposition**
  during film growth

- **More knobs for tuning the thin film properties**
  - Pressure & gas mixture
  - Magnetic & chamber geometry
  - Average power
  - Pulse duration & frequency
  - Pulse voltage

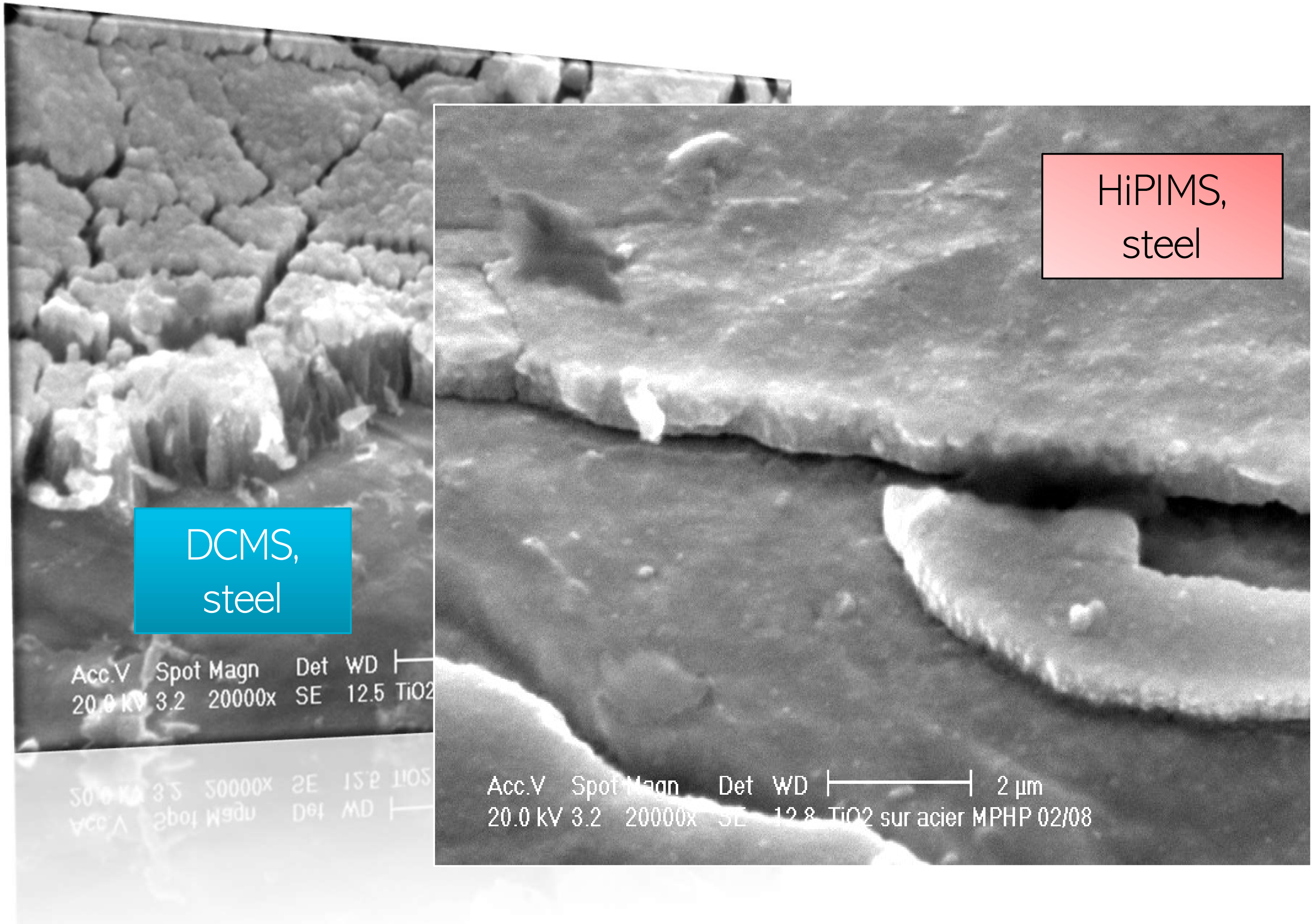


On the synthesis of metal oxide thin films by HiPIMS

1. Titanium dioxide
2. Aluminum-doped zinc oxide
3. Vanadium dioxide

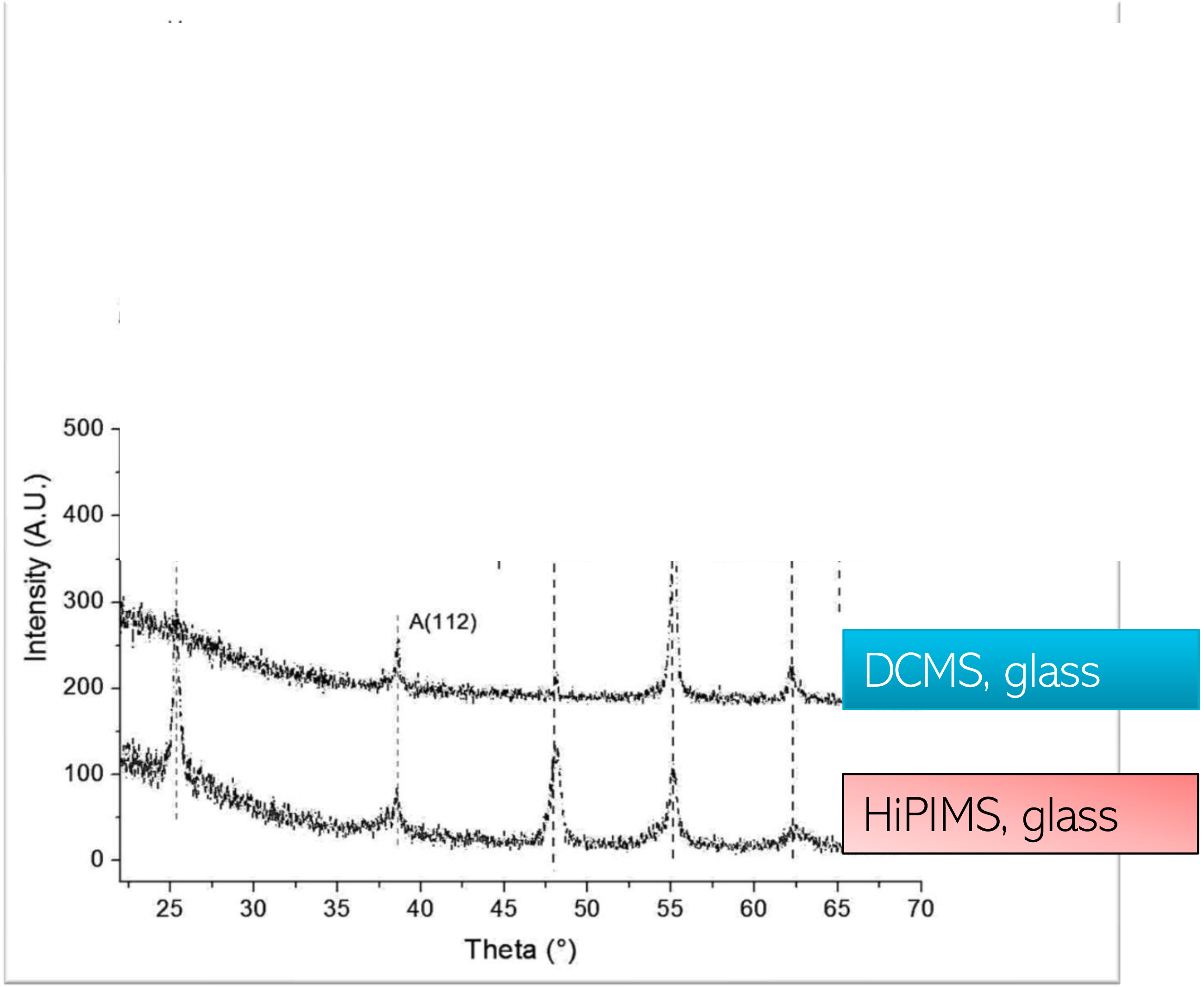
Titanium dioxide

Increased film compactness



Konstantinidis et al, Thin Solid Films (2006)

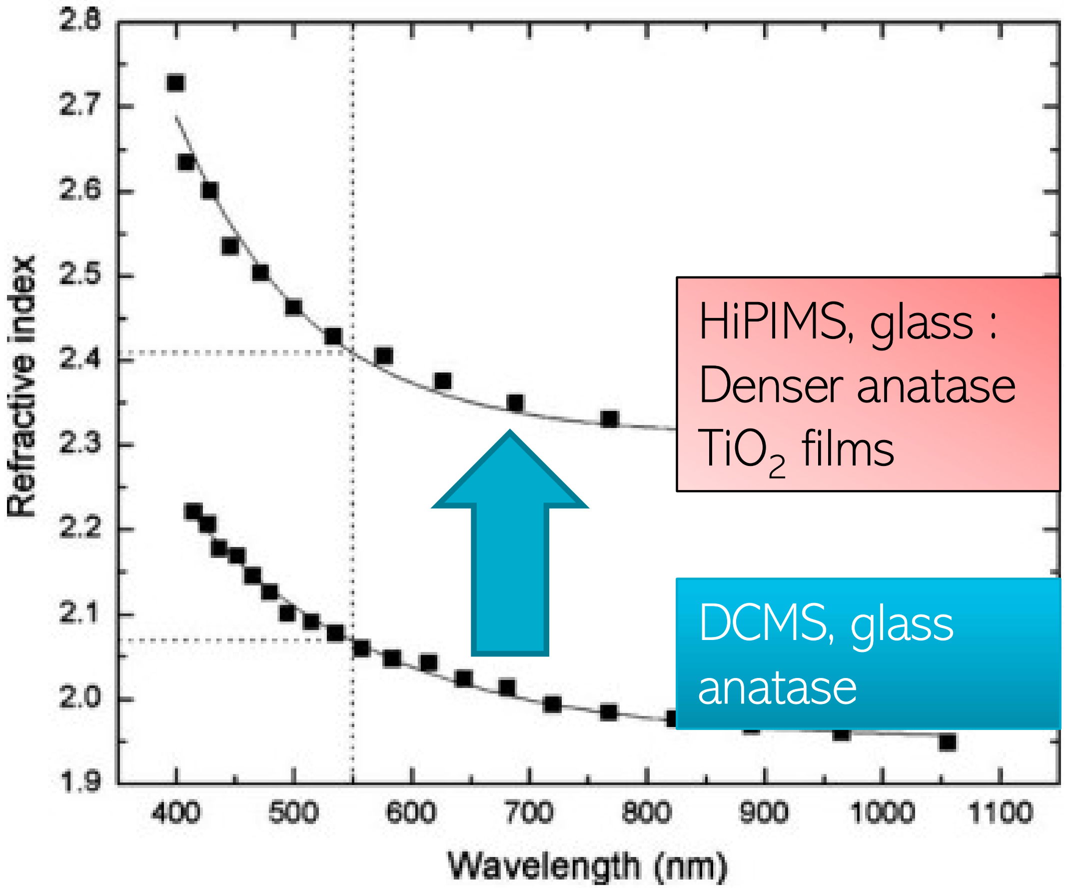
Growing high-temperature phase of TiO_2 by HiPIMS



Konstantinidis et al, Thin Solid Films (2006)

Increased refractive index of TiO_2 films

Anatase films deposited on glass



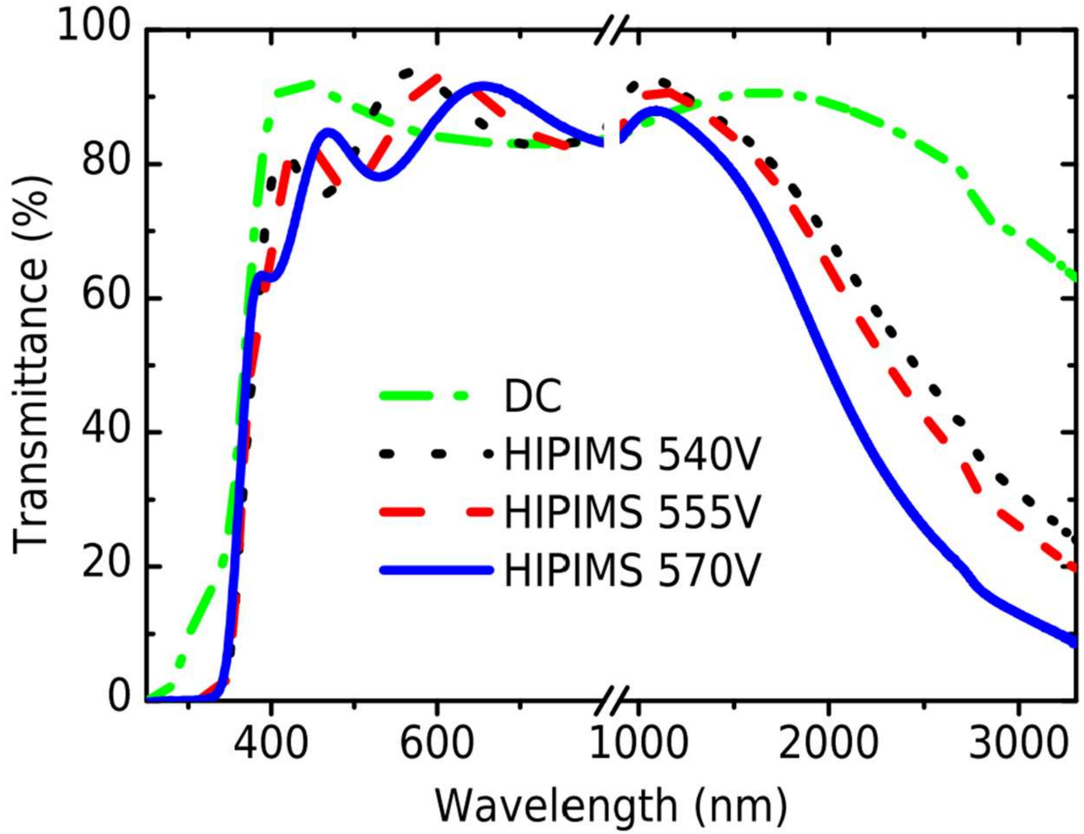
Konstantinidis et al, Thin Solid Films (2006)

Al-doped ZnO

Transmittance of Al-doped ZnO

Sputtering from
an **alloy target** (Zn+Al)
in Ar/O_2 atmosphere

Deposition
at **room temperature**



Mickan et al, Sol. Energy Mater. Sol. Cells (2016).

Electric properties of ZnO:Al

HiPIMS leads to:

- Low resistivity (10^{-4} Ω cm)
- Spatial homogeneity

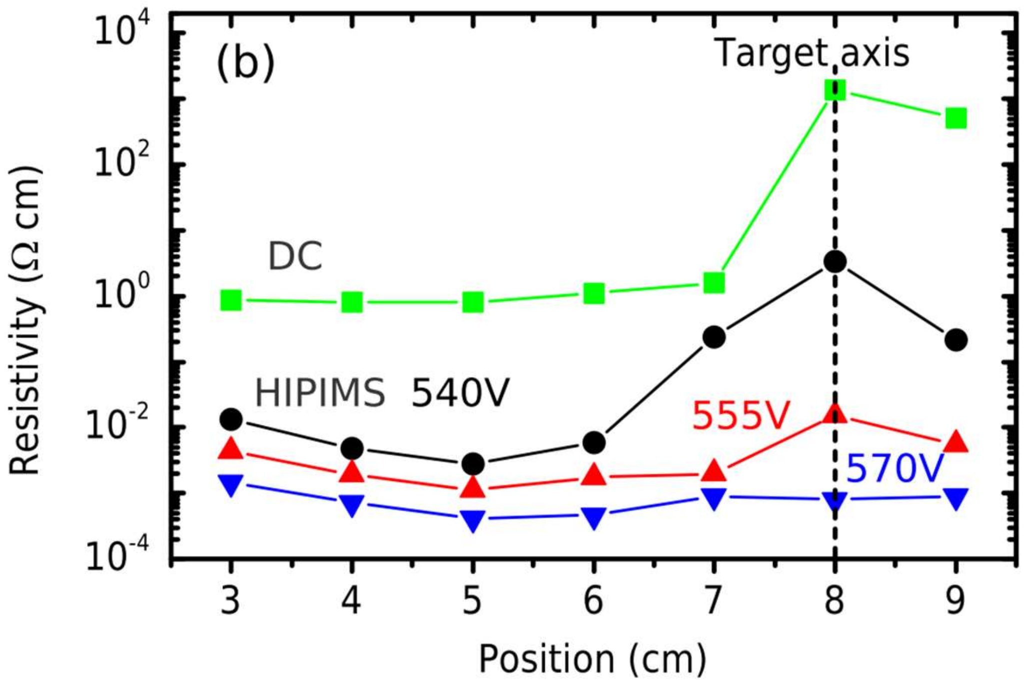


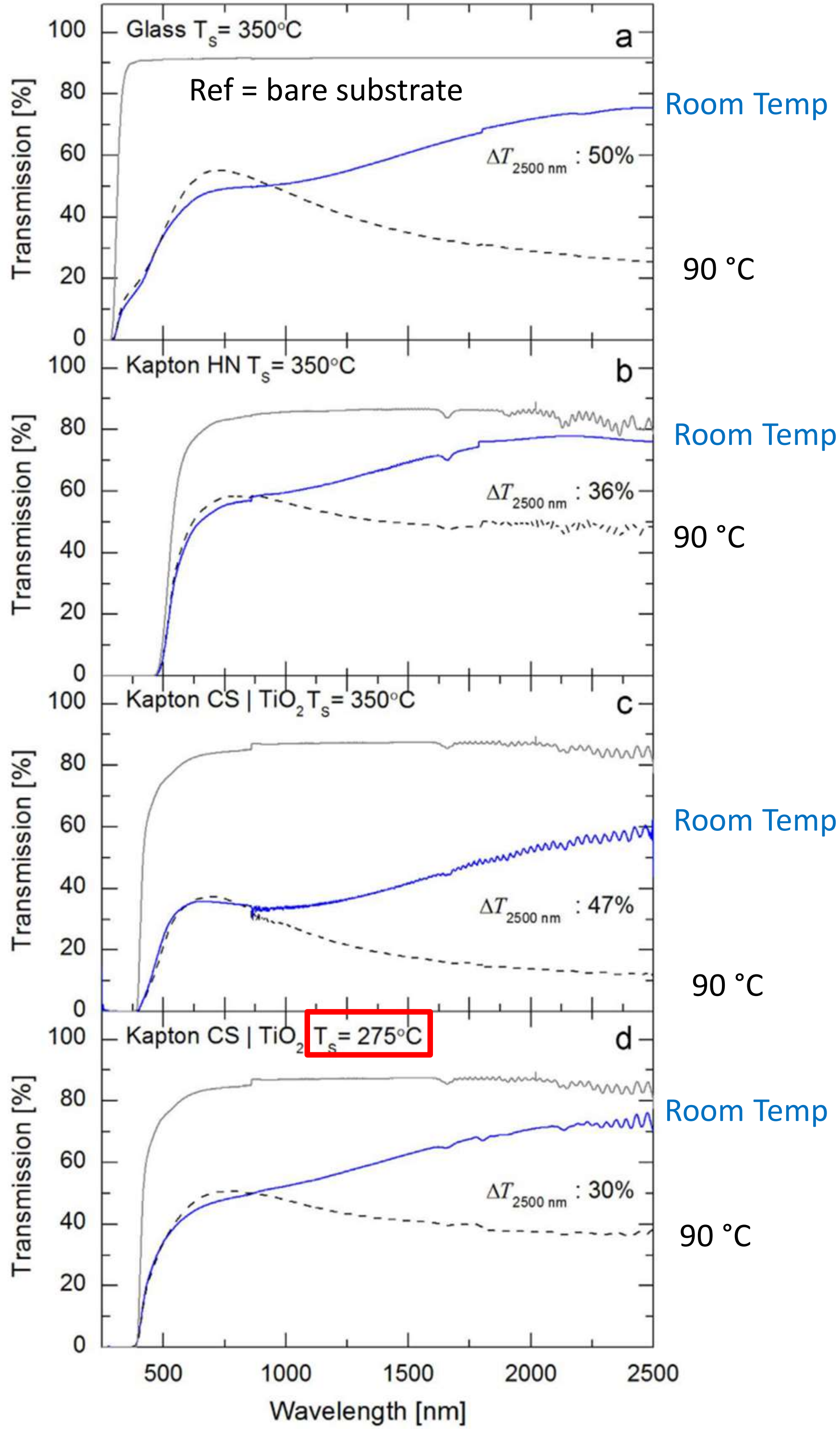
Table S2: Hall effect measurement results of the AZO film deposited using HiPIMS at 570 V

Position (cm)	Resistivity (Ωcm)	Mobility (cm^2/Vs)	Charge carrier concentration (cm^{-3})
3	2.05×10^{-3}	4.09	7.47×10^{20}
4	7.50×10^{-4}	7.38	1.13×10^{21}
5	7.21×10^{-4}	10.5	8.24×10^{20}
6	8.17×10^{-4}	7.07	1.09×10^{21}
7	1.23×10^{-3}	8.84	5.76×10^{20}

Mickan et al, Sol. En. Mater. Sol. Cells (2016).

Vanadium dioxide

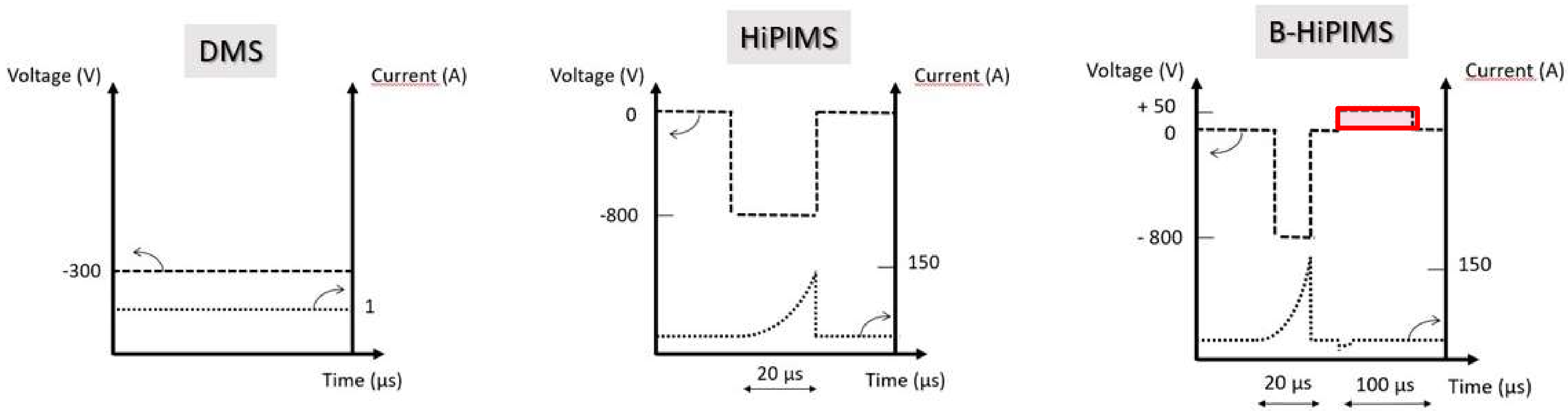
Synthesis of thermochromic VO_2 at lower temperature



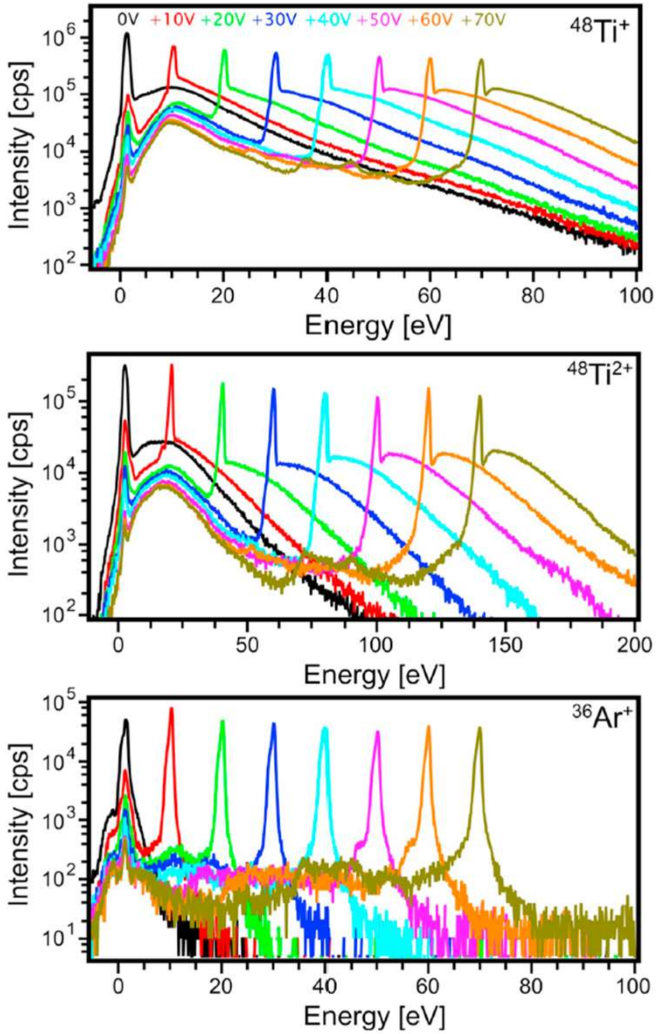
S. Loquai et al, Sol. Energy Mater. Sol. Cells (2016).

Similar results were obtained by
- A. Aijaz et al, Sol. Energy Mater. Sol. Cells (2016).
- J. Houska et al, Thin Solid Films (2018).

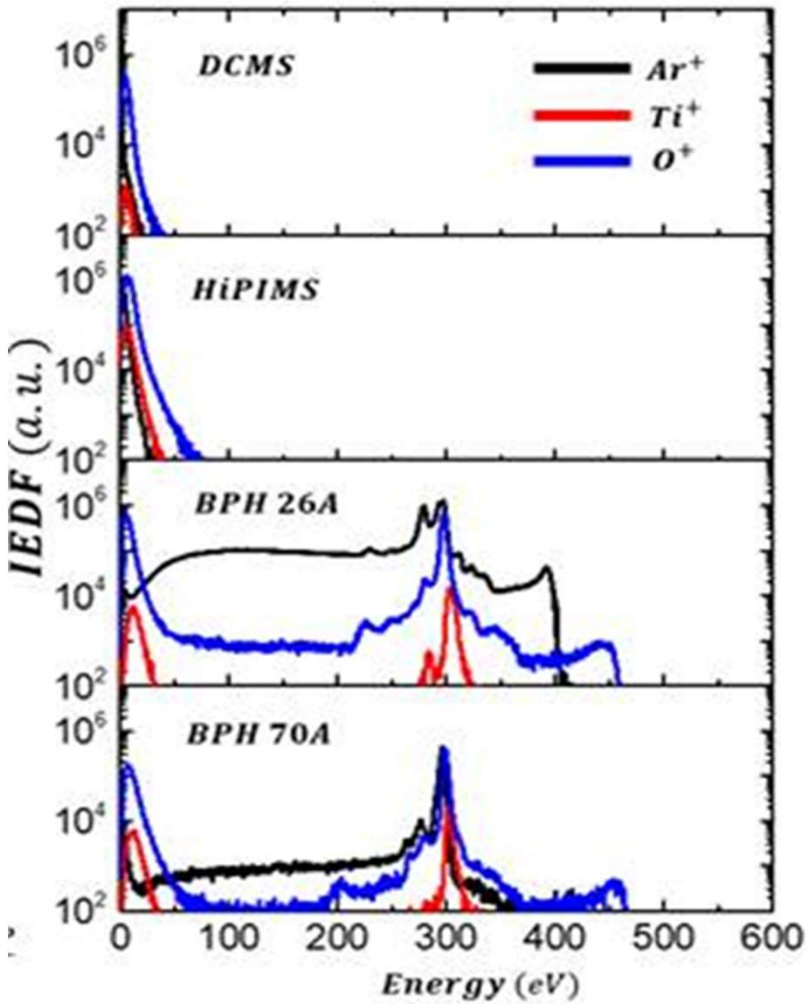
Recent development in HiPIMS technology: Bipolar HiPIMS



Ion energy is controlled by the positive voltage



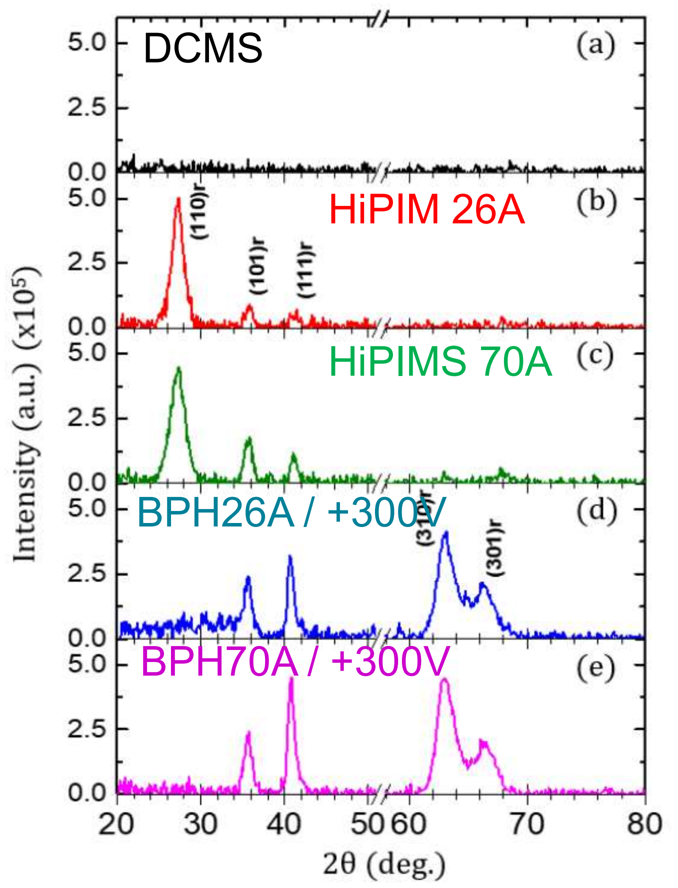
Keraudy et al Surf. Coat. Technol. 2018



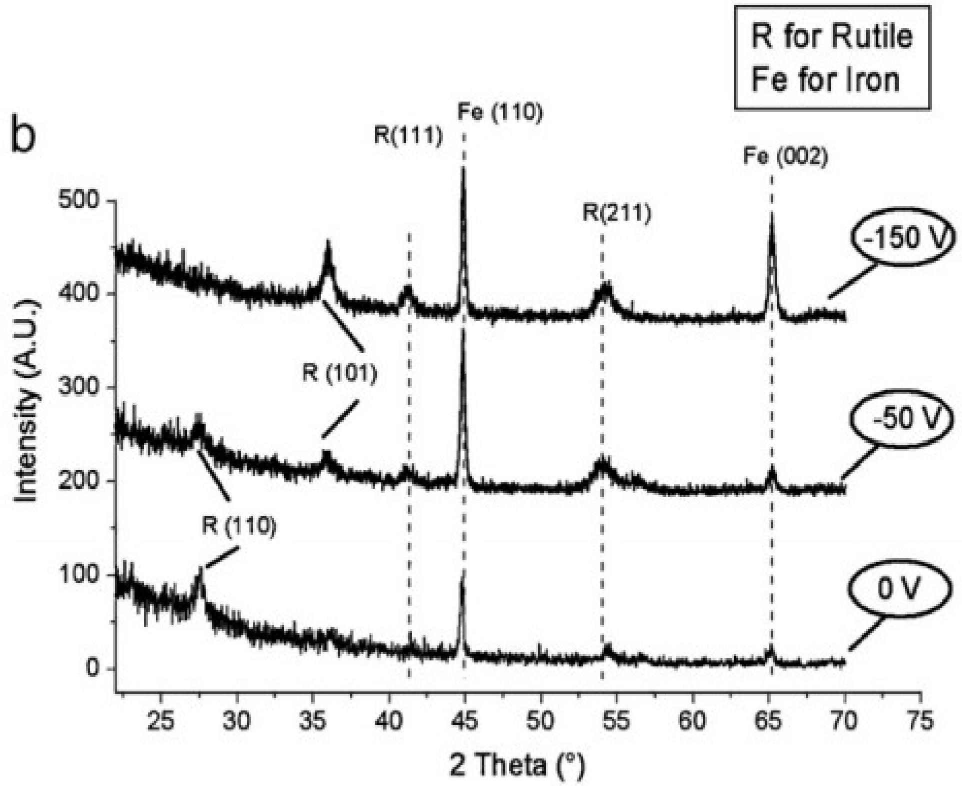
Michiels et al, J. Phys. D. Appl. Phys. 2021

Comparison of the XRD data

Positive pulse on cathode has the same effect as applying a negative bias on the substrate



Michiels et al, J. Phys. D. Appl. Phys. 2021

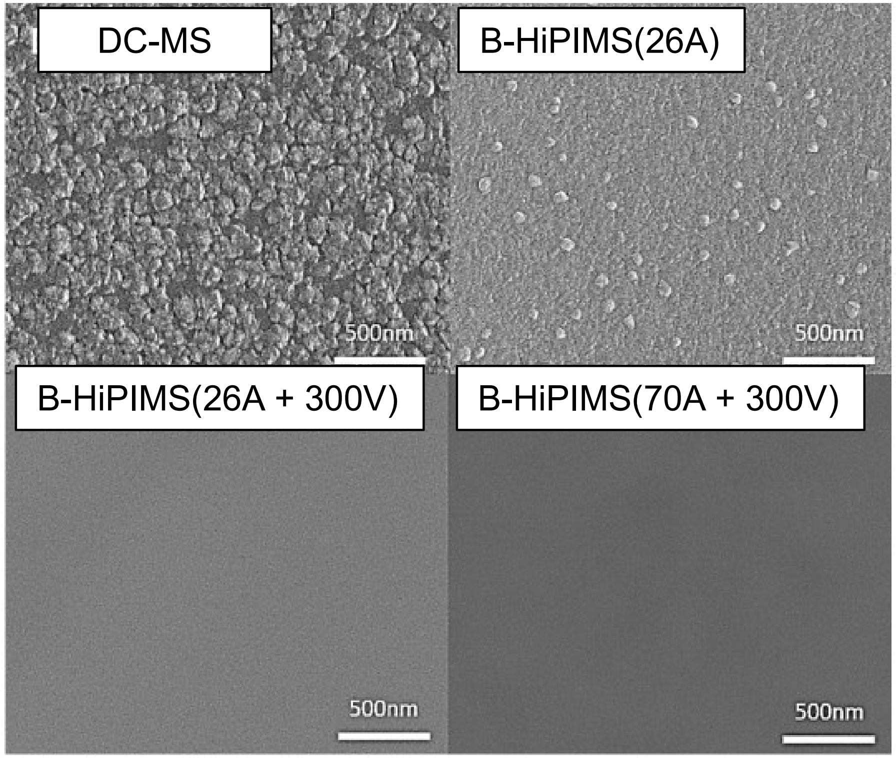


Konstantinidis et al, Thin Solid Films (2006)

Topography and cross-section

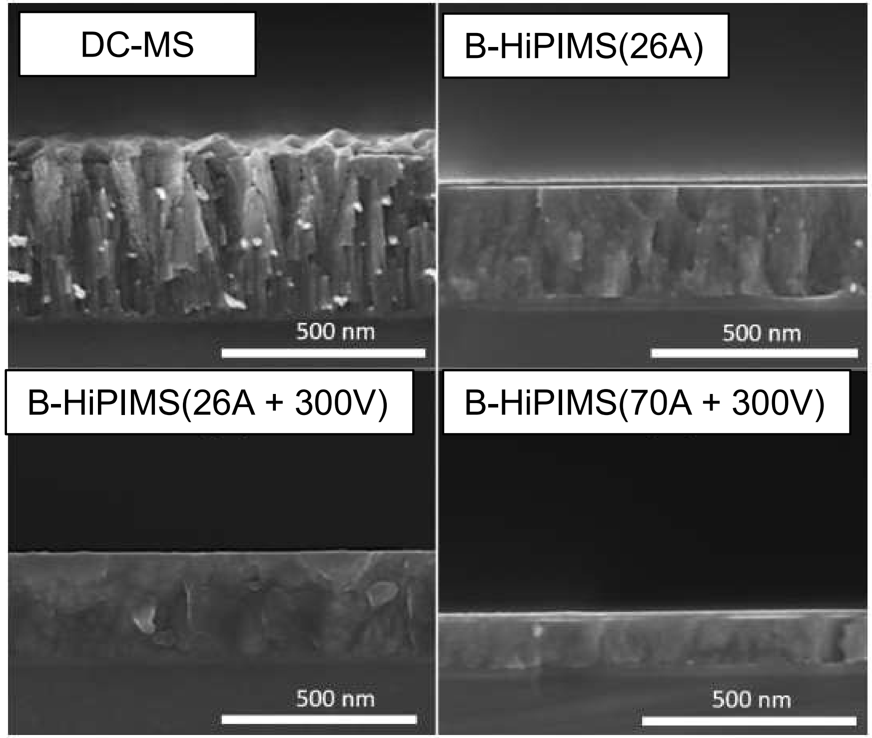
Ar/Ti+O ~ 0,04%

Ar/Ti+O ~ 0,4%



Ar/Ti+O ~ 2,5%

Ar/Ti+O ~ 2,5%

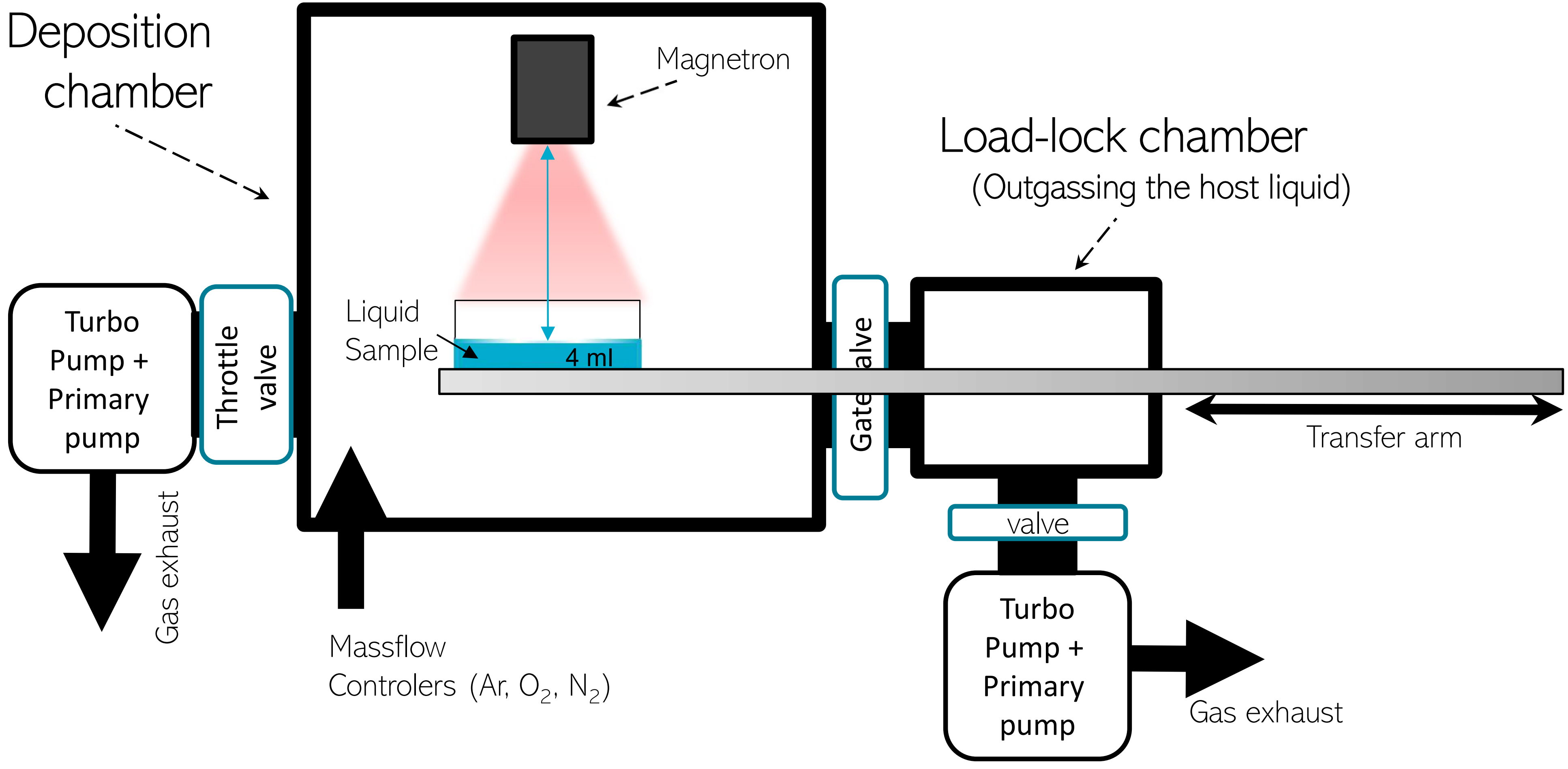


Low resistivity Si substrates

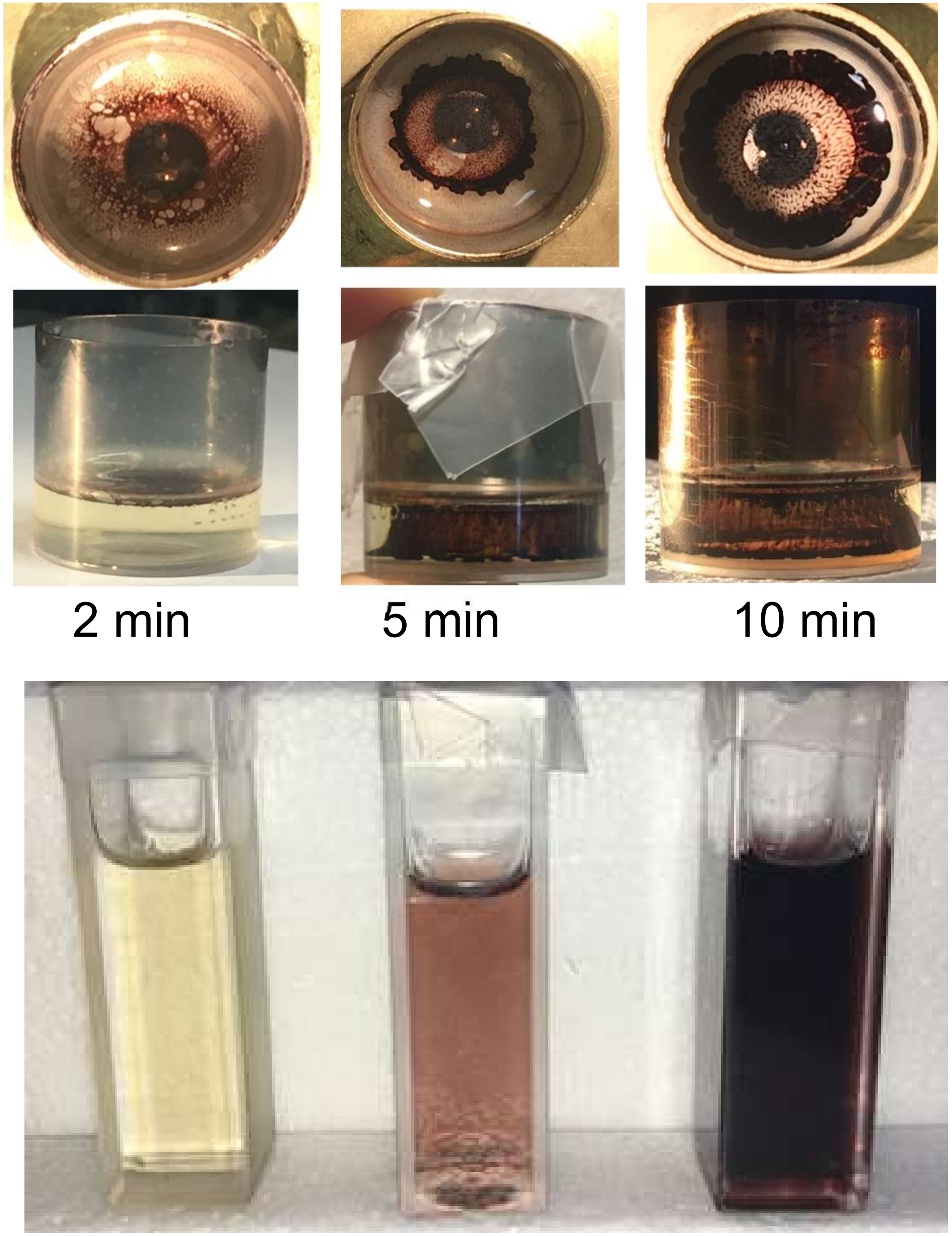
Michiels et al, J. Phys. D. Appl. Phys. 2021

Sputtering onto liquid substrates for the synthesis of nanoparticles

Experimental set-up

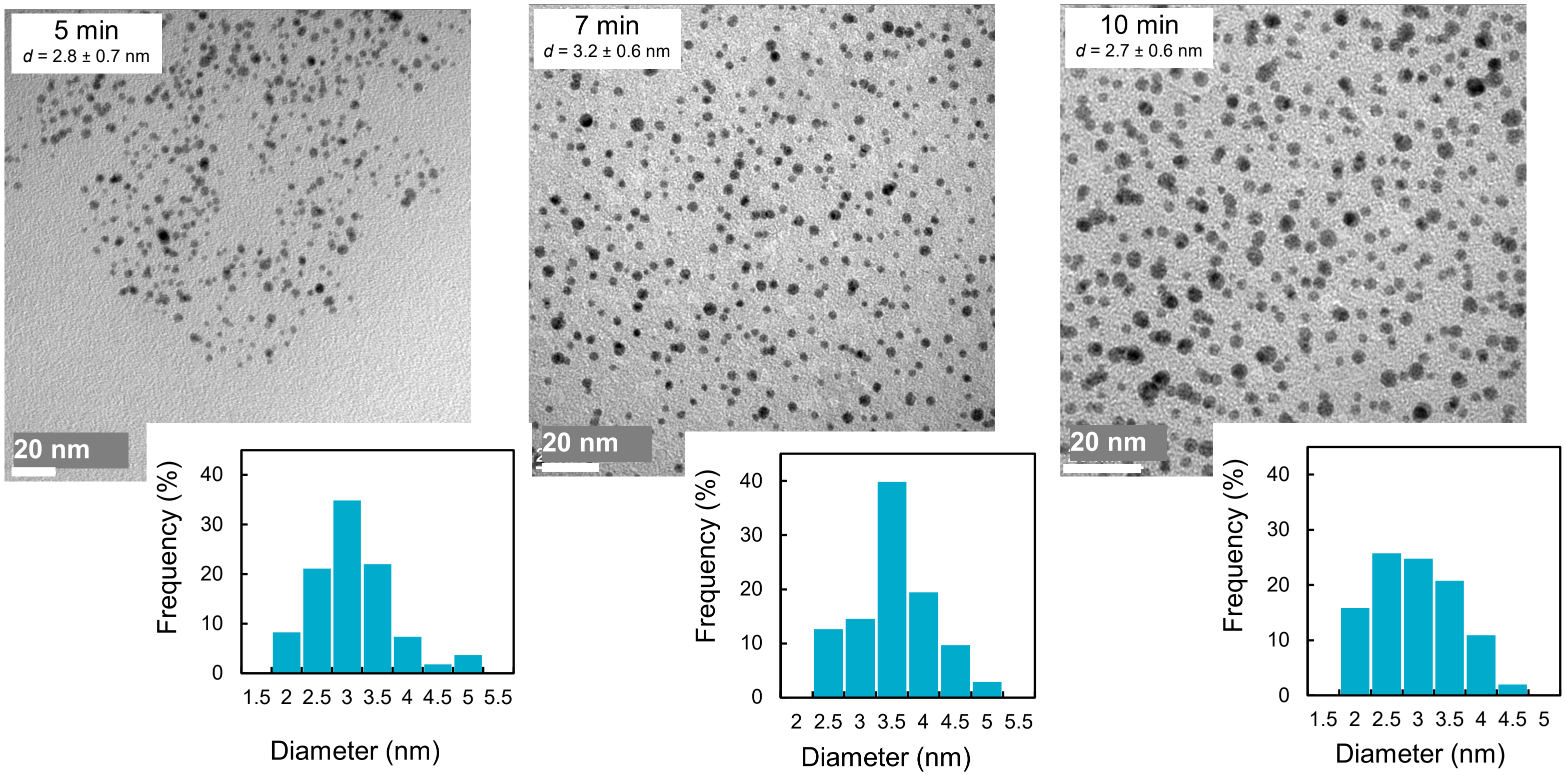


DC - Sputtering of Gold on castor oil : Effect of sputter time



Sergievskaya et al, Front. Nanotechnol. 3, (2021).

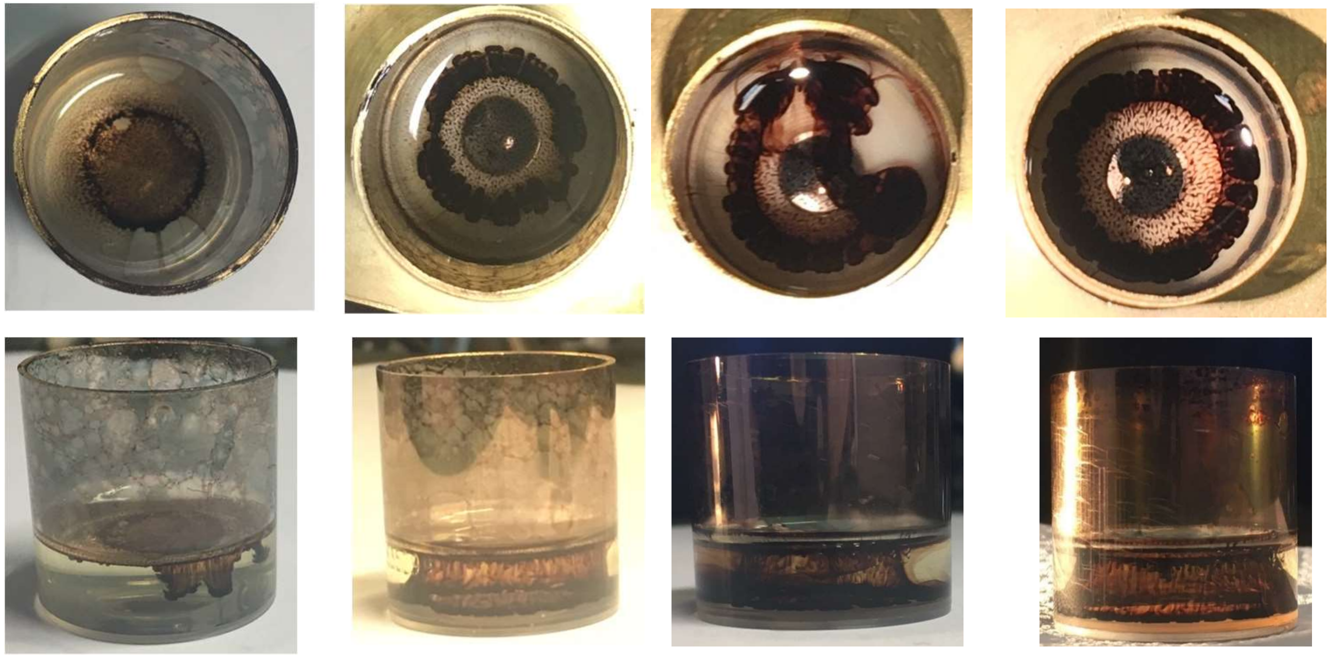
TEM observation of the NP



NP size ~2.7 – 3.2 ± 0.6 nm

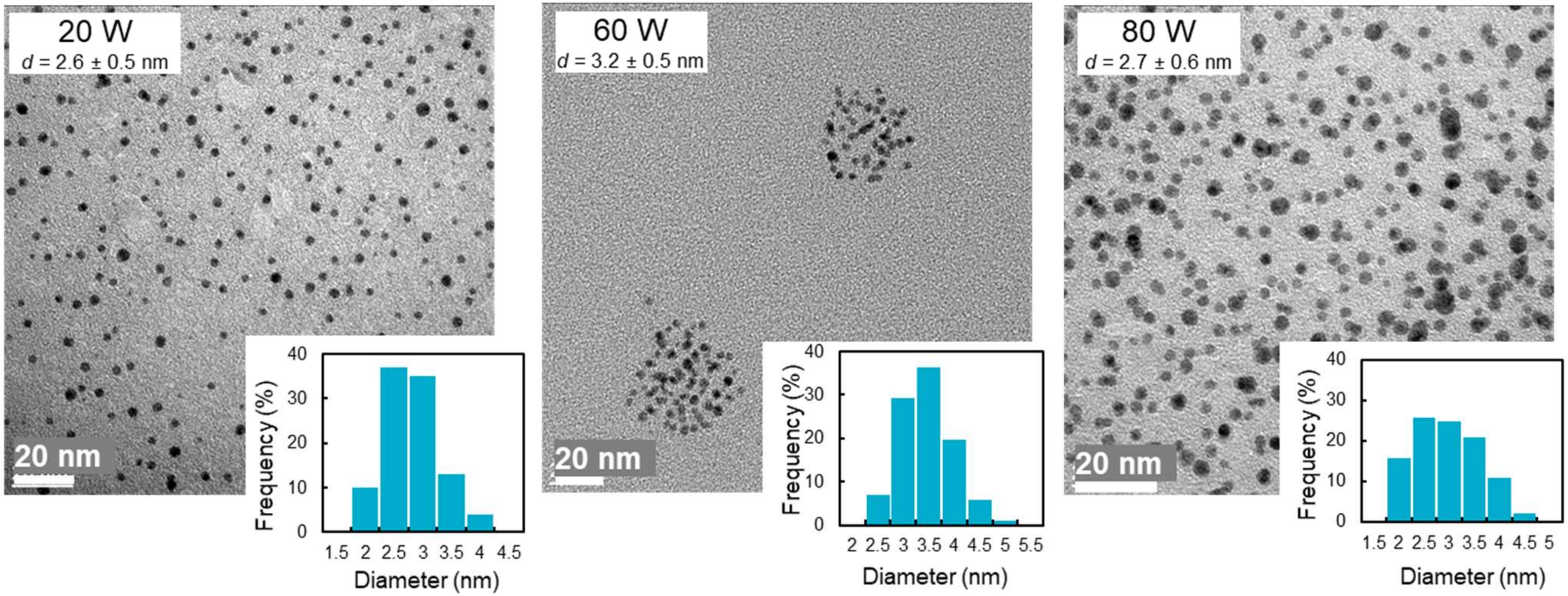
Effect of DC sputter power

Sputter time: 10 min



20 W   40W   60W   80W

TEM observation of the NP



NP size ~2.7 – 3.2 ± 0.5 nm

DC-MS *vs.* (unipolar) HiPIMS

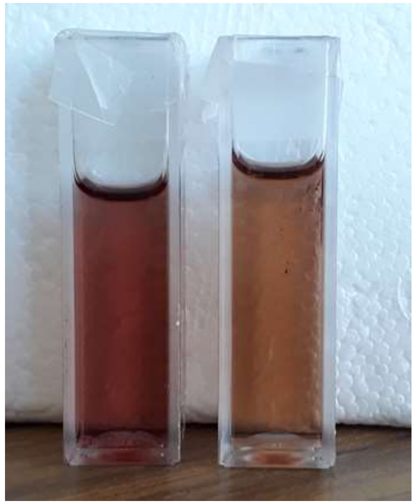
P_{Ar} = 5 mTorr, 80 W, 10 min

DC-MS:
Φ = $(1.8 \pm 0.2) \cdot 10^{-7}$ moles/cm$^2 \cdot$min

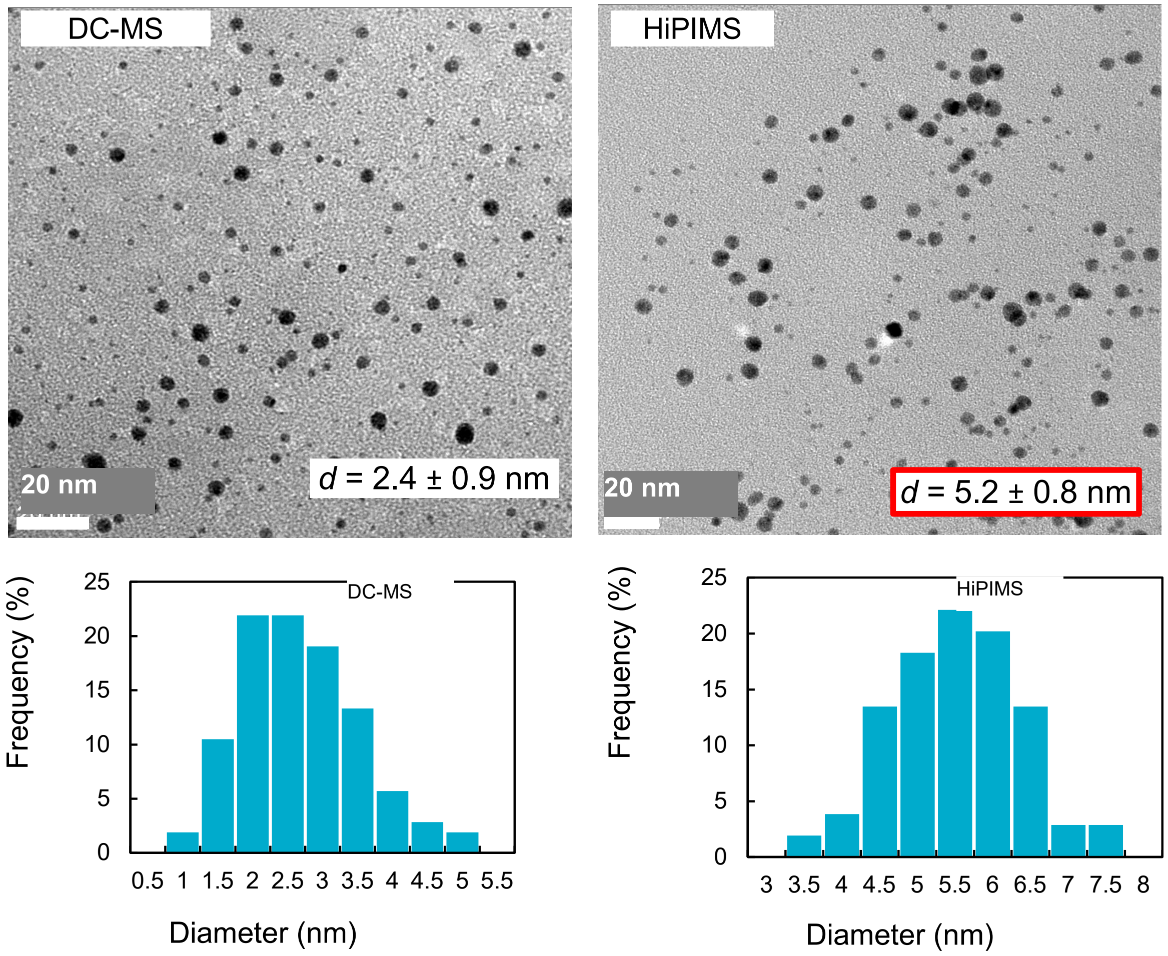
HiPIMS:
T_{on} = 20 µs, I_{pk} = 0.3 A/cm^2, f = 800 Hz,
Φ = $(0.9 \pm 0.1) \cdot 10^{-7}$ moles/cm^2 min

DC-MS HiPIMS

DC-MS HiPIMS



TEM analysis of the NP



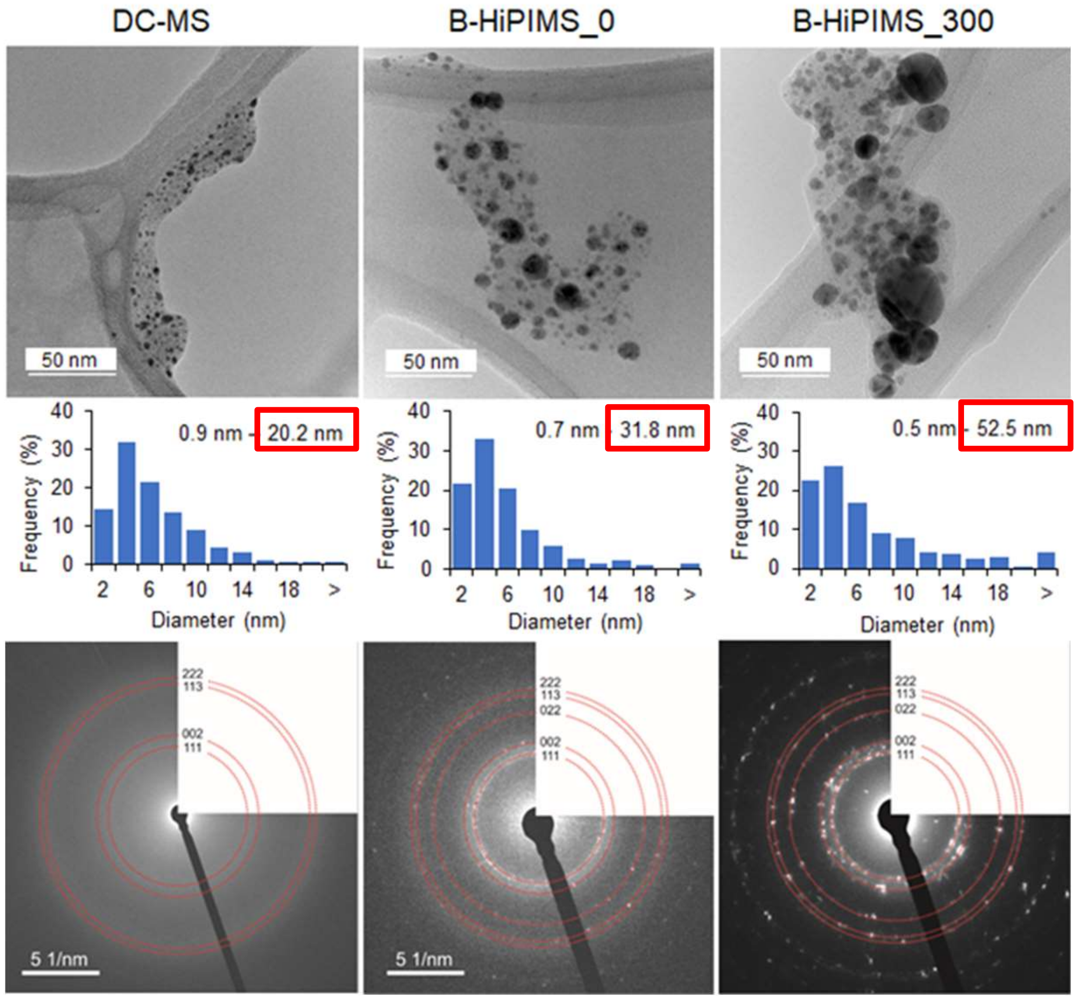
NP size is increased when produced by HiPIMS plasma

Silver onto castor oil :
DC-MS *vs.* Unipolar & Bipolar HiPIMS

P_{Ar} = 5 mTorr, 80 W, 10 min
Flux DC-MS: (1.8 ± 0.2)·10^{-7} moles/cm^2 min

Flux HiPIMS: (0.9 ± 0.1)·10^{-7} moles/cm^2 min
f = 800 Hz, $T_{ON,-}$ = 20 µs, I_{pk} = 0.3 A/cm^2

Flux B-HiPIMS: (0.2 ± 0.1)·10^{-7} moles/cm^2 min
f = 800 Hz, $T_{ON,-}$ = 20 µs, I_{pk} = 0.3 A/cm^2
V_+ = +300V, $T_{ON,+}$ = 250 µs, $T_{+/-}$ = 10µs



Number of particles larger than 20 nm
- 0.1% for DC-MS,
- 1.3 % for HiPIMS (B-HiPIMS_0)
- 4.2 % for bipolar HiPIMS (BHiPIMS_300)

Sergievskaya et al, Colloids Surf. A **615**, 126286 (2021).

Summary

1. HiPIMS modifies the growth process and film properties
   - Increased density
   - Modified crystallinity (high-temp. phase, texture, crystallite size)
   - Lower roughness
2. HiPIMS may facilitate the deposition of functional films onto temperature sensitive materials like polymers
3. Recent developments e.g., bipolar HiPIMS, aim at providing even more control on the film growth process
4. Sputtering can be carried out onto selected liquids to produce colloidal solutions.
   - HiPIMS mimics *in situ* annealing procedure of the NPs