Plasmas for Physical Vapor Deposition of nanostructured materials

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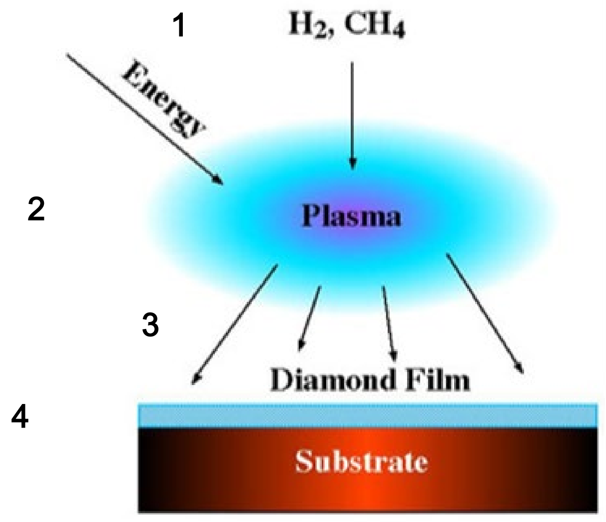
NanoLab

CIP 2026 1° Conferenza Italiana Plasmi

Plasmas for the synthesis of materials

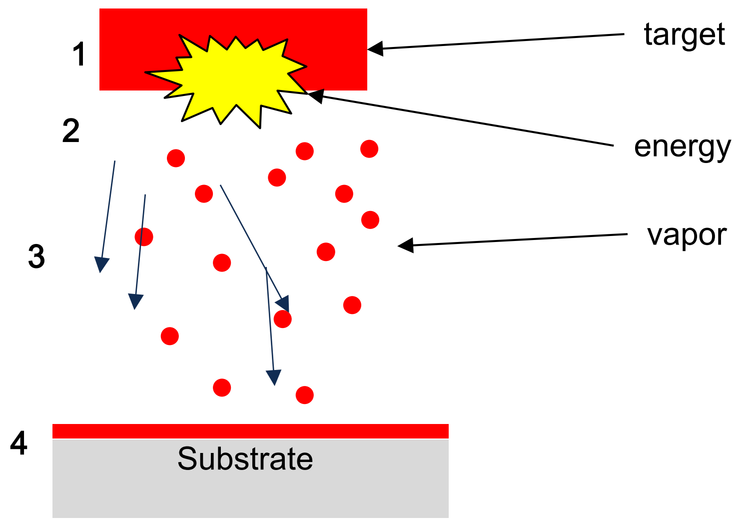
Plasma Assisted Chemical Vapour Deposition (CVD)

1. A fluid precursor (usually gas)
2. Chemical reactions due to plasma energy
3. “High energy” species diffusion
4. A solid layer is formed
5. A vacuum environment is needed



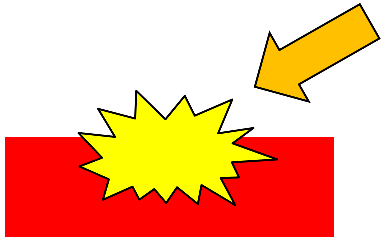
Physical Vapour Deposition (PVD)

1. Solid precursor (target)
2. Add Energy in a “physical” way
3. Vapor generated
4. Deposition on a substrate
5. A vacuum environment is needed



Plasmas for the synthesis of materials: PVD

1. In PVD **the way** in which the energy is delivered to the target defines the **deposition technique**



2. The **amount** of energy (per unit time) influences the features of the generated vapor (energy, atoms/ions)

3. The **features** of the vapor determine the **characteristics** of the growing film

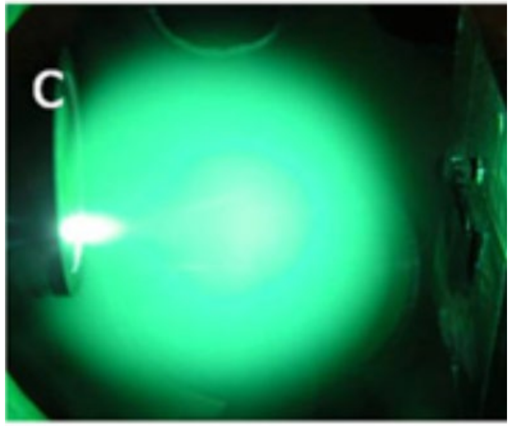
Which plasmas in PVD?

In some deposition techniques the energy is delivered by a plasma:

- Magnetron Sputtering (DC, RF, HiPIMS)
- Cathodic vacuum arc

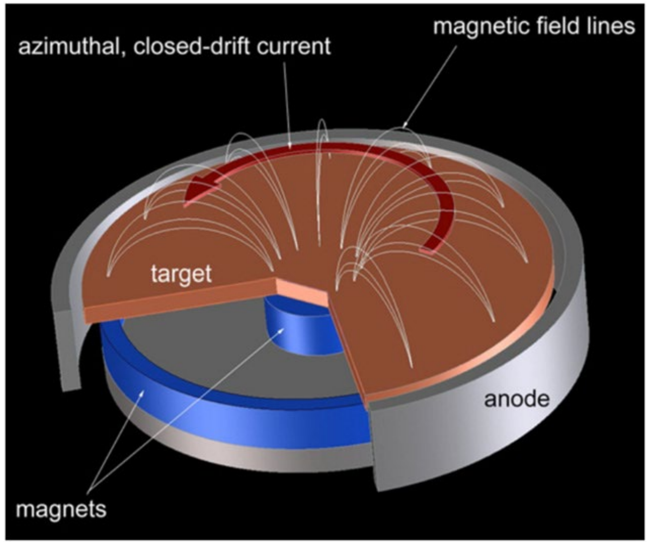
or a plasma is formed in the process:

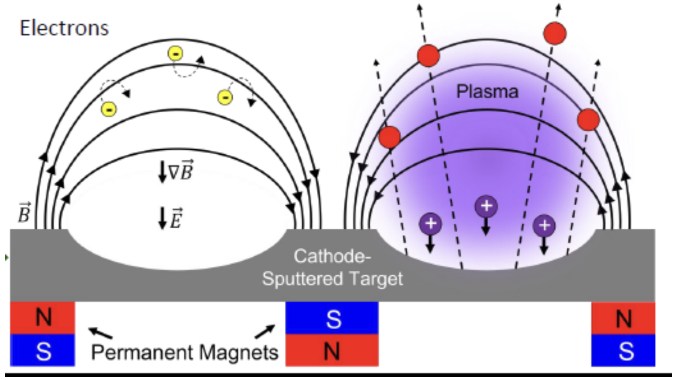
- Pulsed Laser Deposition (ns, fs)



DC Magnetron Plasma

1. Ar as working gas
2. Static magnetic field (mT)
3. A conductive target
4. Cathode powered with DC voltage of 100s V
5. Electrons, are trapped in the B field, E x B azimuthal motion
6. much higher probability of collision with Ar → more efficient ionization
7. Formation of a glow discharge plasma





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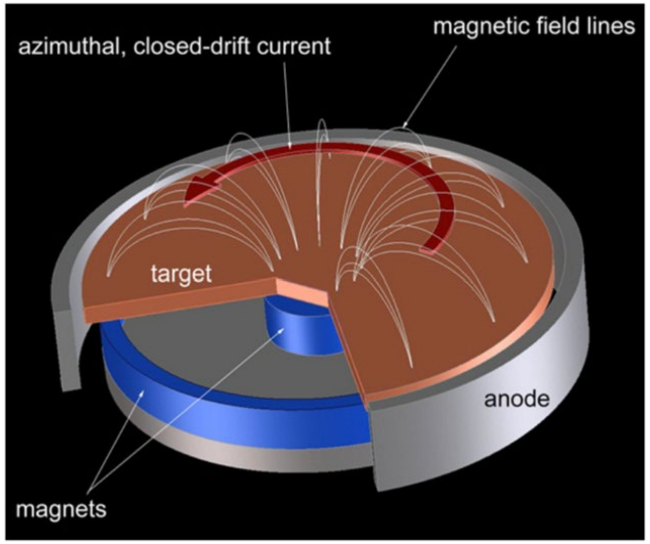
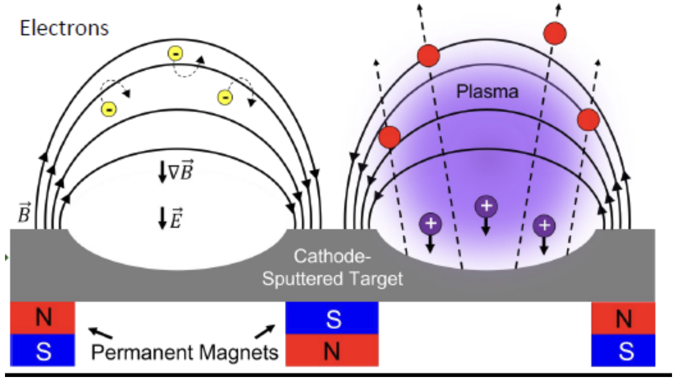
7. Formation of a glow discharge plasma
8. Due to cathode polarization ions impinge the cathode target 0.1 A/cm^2
9. Sputtered species are **neutrals** 1-10 eV
10. Plasma composition: 99% Ar, <<1% metal
11. Penning ionization $Ar^* + M \rightarrow Ar + M^+ + e^-$

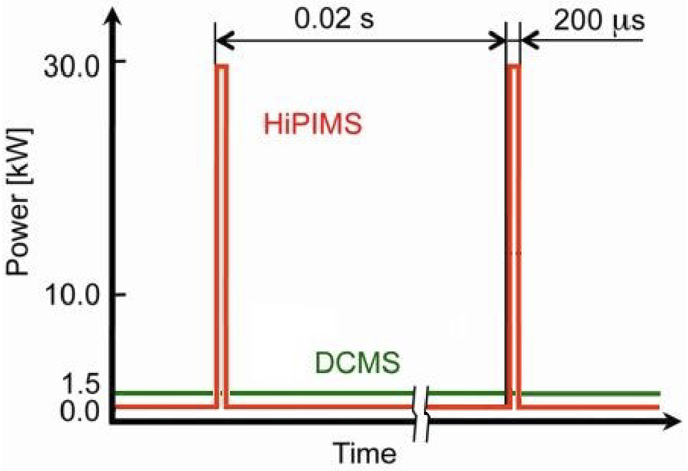




High Power Impulse Magnetron Sputtering Plasma

1. Same setup of DC Magnetron (cathode, B field, Ar, etc.)

2. Cathode powered with **pulsed voltage, width 25 – 100 μs,** of 100s V



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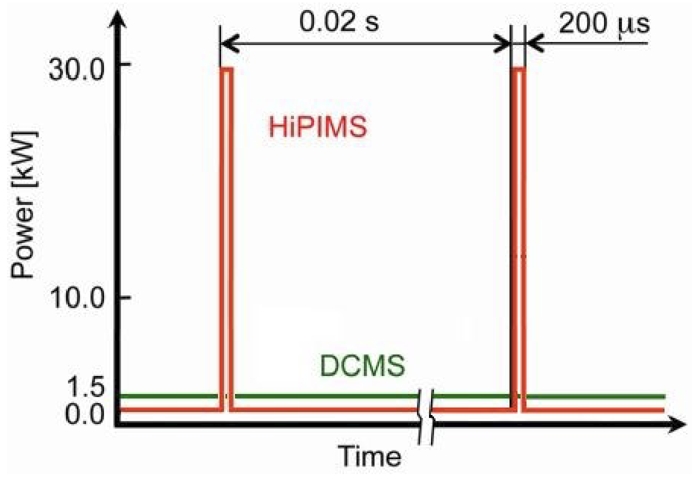
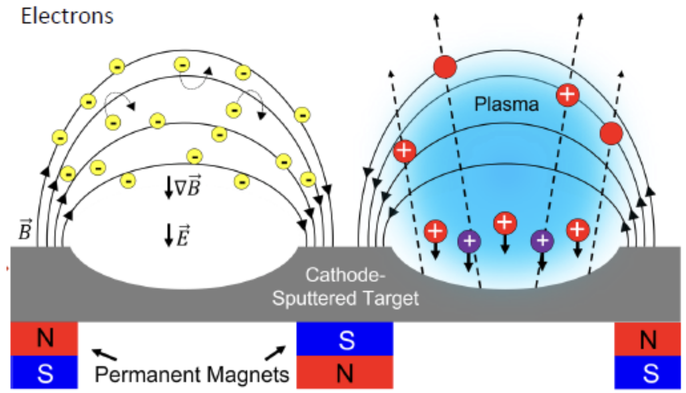
3. Much higher electron density → new physical phenomena occur
4. Direct electron impact ionization of sputtered species $e^- + M \rightarrow M^+ + 2e^-$
5. Plasma: Ar ions and metal ions (10%-70% of sputtered metal)
6. Metal ions are trapped close to the target.





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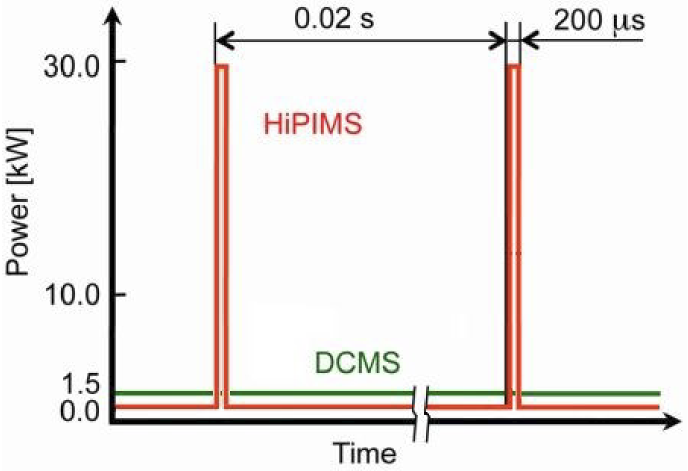
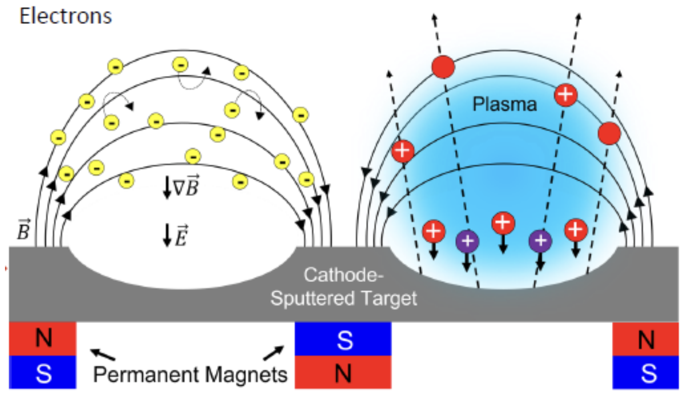
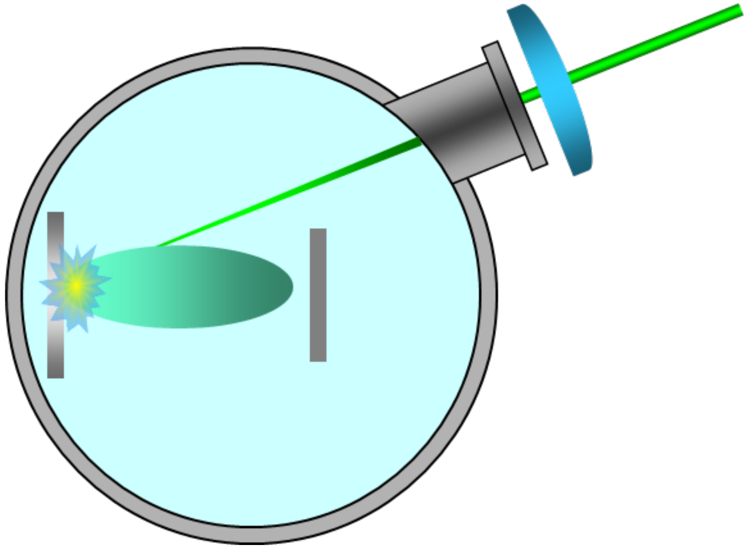
6. Metal ions are trapped close to the target.
7. Abnormal glow discharge plasma → plasma arc BUT stopped by pulse end.
8. Due to cathode polarization ions impinge the cathode target 1-10 A/cm^2 (during the pulse)



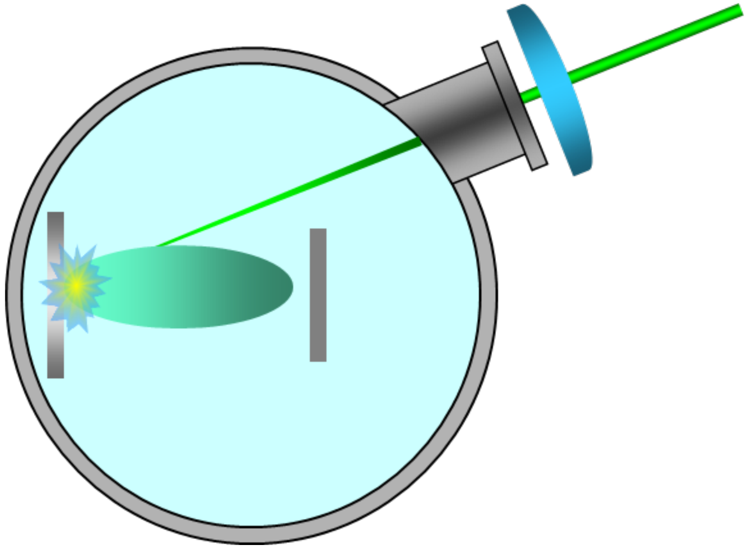


Pulsed Laser Deposition



1. Pulsed Laser focalized on solid target
2. Laser matter interaction
3. Plasma & neutrals expansion and thermalization
4. Deposition on substrate

Pulsed Laser Deposition



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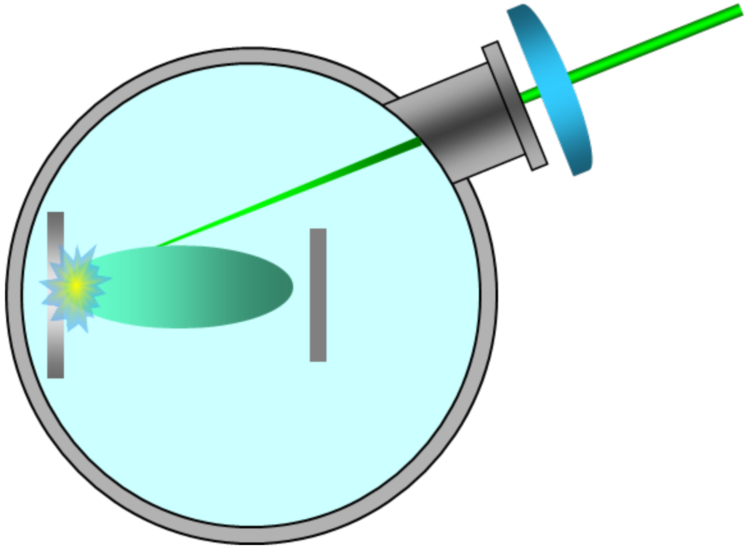
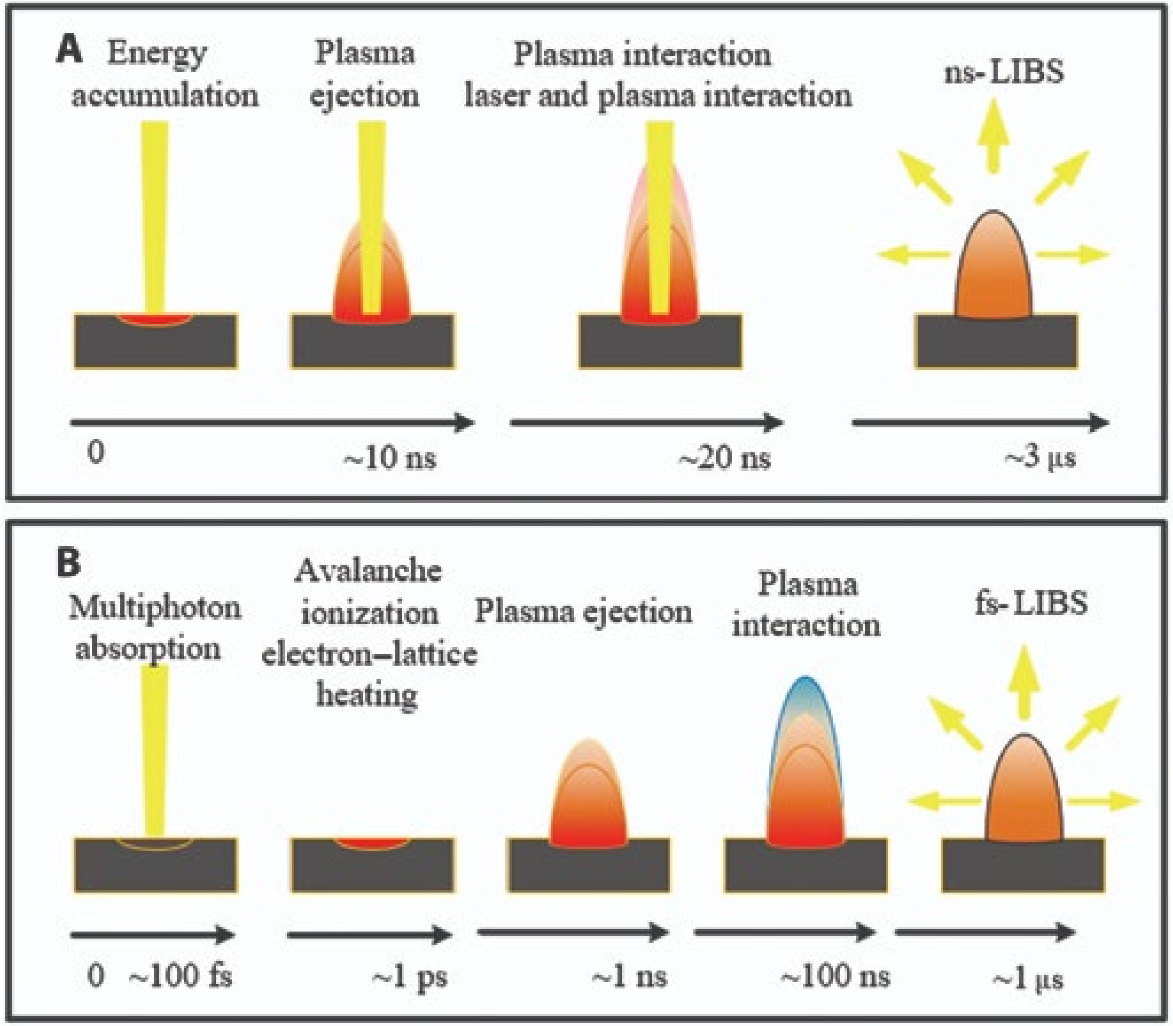
	λ [nm]	τ [s]	E [mJ]	Spot Area $[mm^2]$	F $[J/cm^2]$	I $[W/cm^2]$	RR [Hz]
ns (Nd:YAG)	532	$5\text{-}7 \cdot 10^{-9}$	730	10	8.8	$1.7 \cdot 10^9$	10
fs (Ti:Sapphire)	800	$80 \cdot 10^{-15}$	3.8	3.44	0.11	$1.38 \cdot 10^{12}$	10^3

Pulsed Laser Deposition



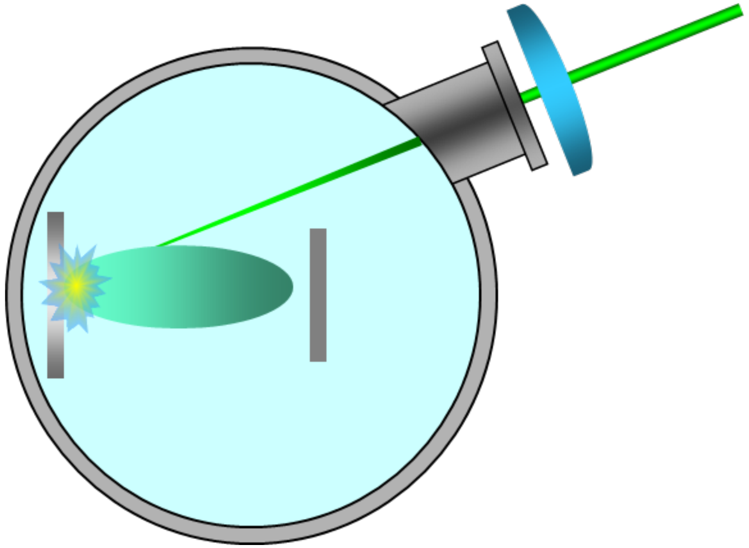


Mengyun Hu, e al. (2023)

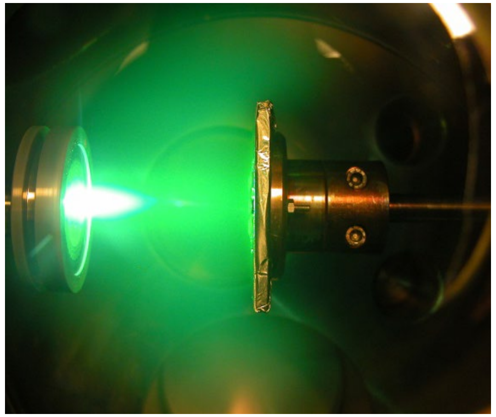
Different dynamics due to different pulse duration

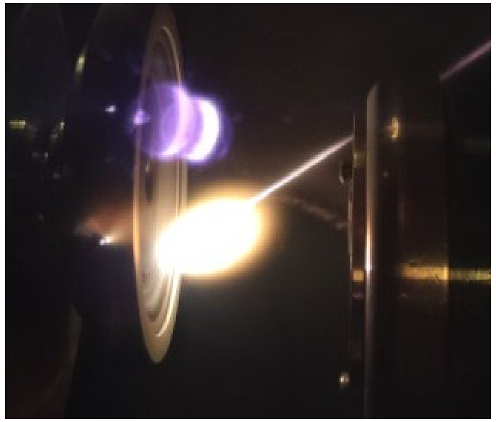
- ns-PLD → plasma generation during plume expansion (Inverse Bremsstrahlung)
- fs-PLD → all the pulse energy is absorbed → plasma generation

Pulsed Laser Deposition

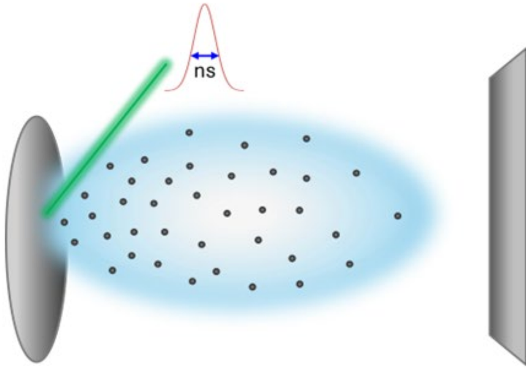


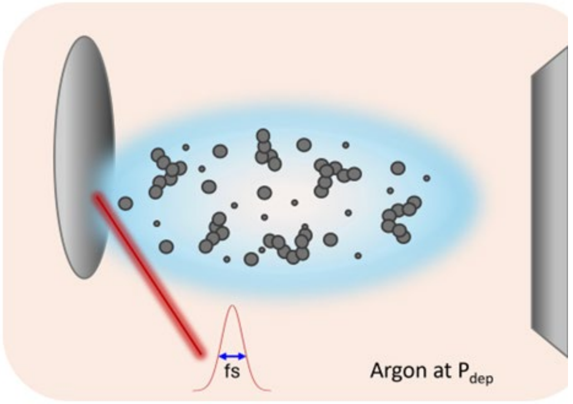
1. Energy: about 100s eV
2. In ns-PLD regime: ions and atoms
3. In fs-PLD: ions, atoms and nanoparticles due to phase explosion phenomena





• Atoms or ions





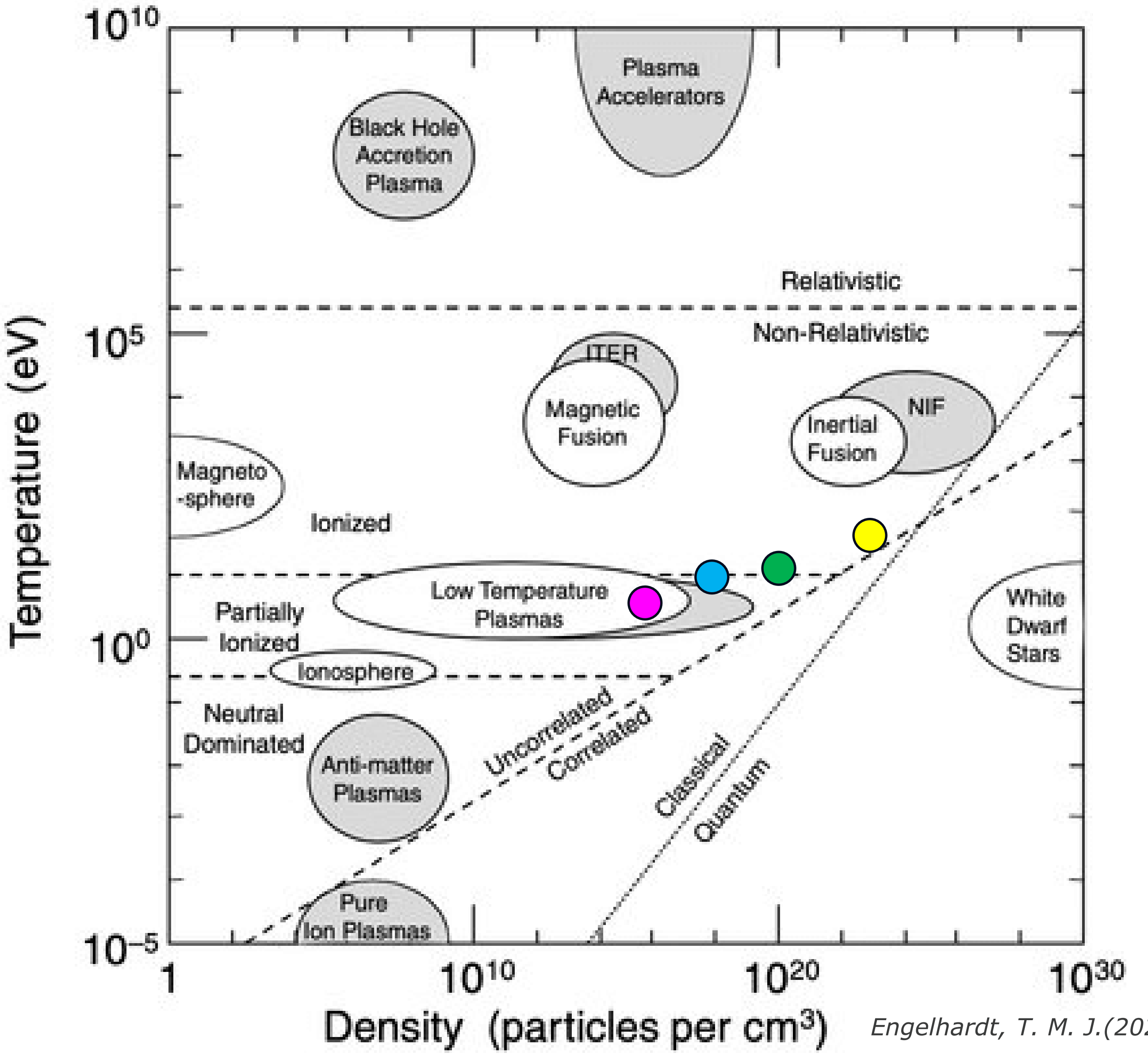
● Nanoparticles (NPs)

Clusters of NPs

You are here

	T_e (eV)	n_e (m^{-3})	% ioniz.
DC MS	$2-5$	$10^{15}-10^{17}$	<<1
HiPIMS (in the pulse)	$5-10$	$10^{18}-10^{19}$	10-70
ns-PLD (early plume)	$5-20$	$10^{20}-10^{22}$	10-100
fs-PLD (early plume)	$10-10^{2}$	$10^{21}-10^{23}$	30-100

Lieberman, M.A. (2005)
Anders, A. (2010)
Toftman , B. (2000)
Gattassv , R.R. (2008)

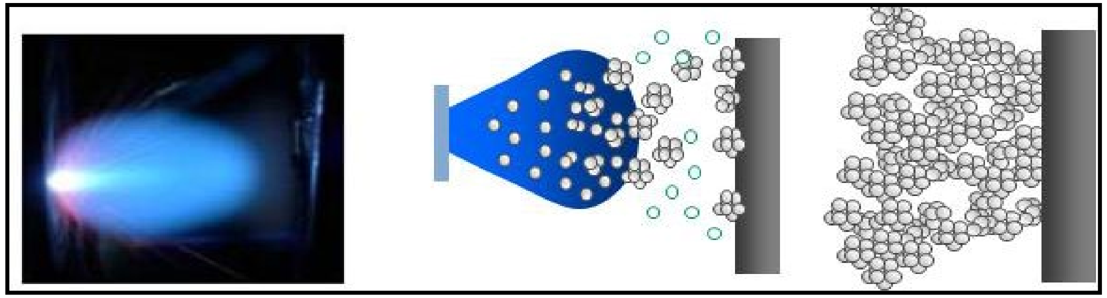


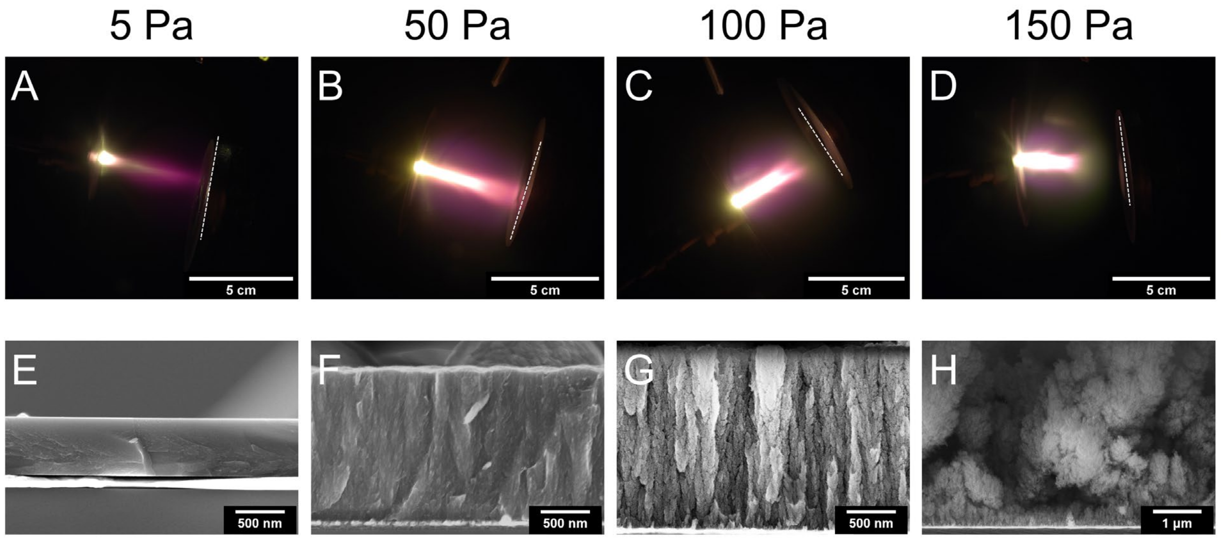
Engelhardt, T. M. J.(2021)

Some examples …

Nanostructured Si deposited by PLD for lithium on batteries

Need of porous Si film to allow formation of Li Silicide.





Background pressure

$Ar+H_2$ gas *Macrelli, A. (2026) under review*

1. The addition of a background pressure, allows to lower energy of the species
2. Nanoparticles are formed during ablation in a background atmosphere

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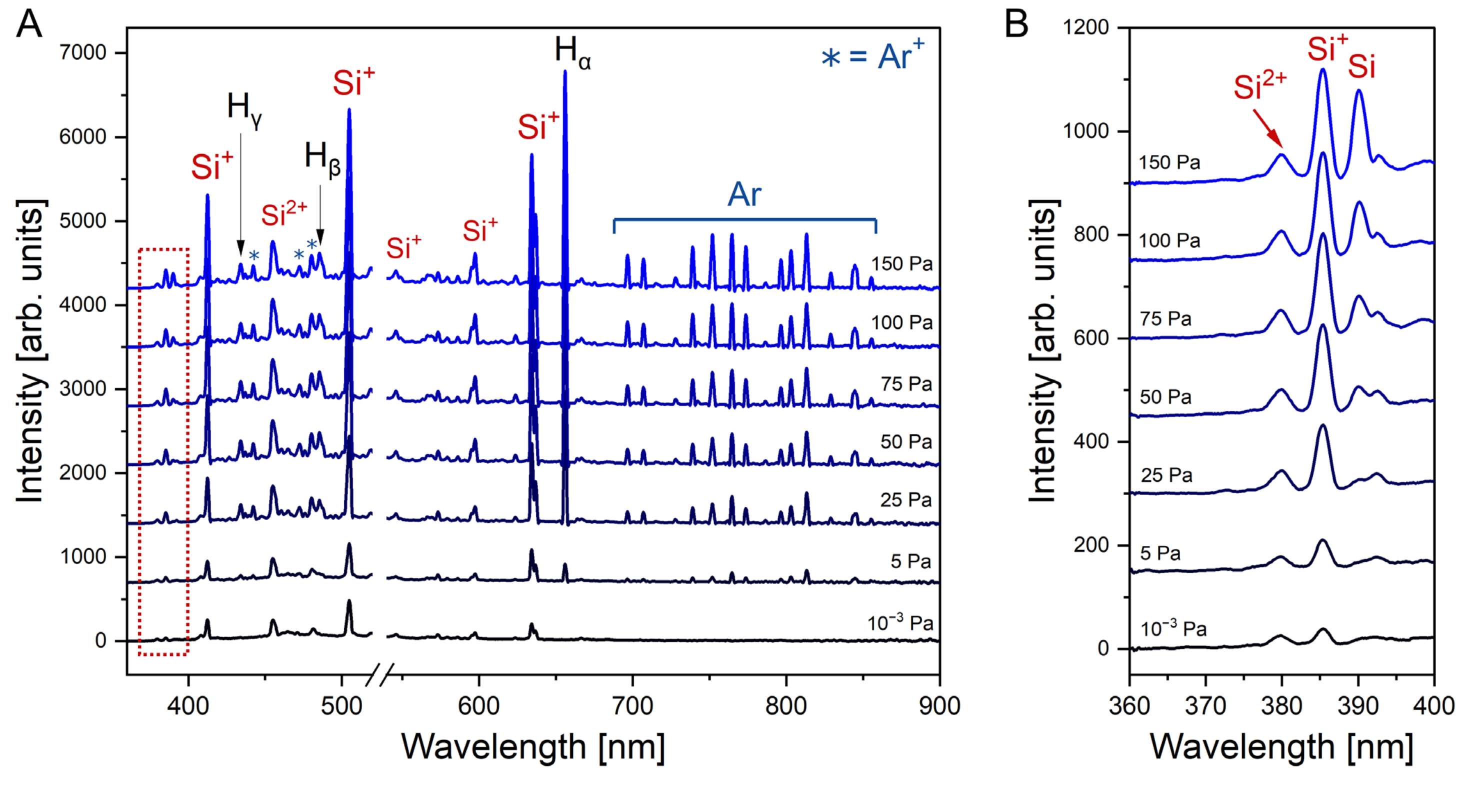

Macrelli, A. (2026) under review

1. Plasma plume analysed by Optical emission spectroscopy
2. Plume intensity grows increasing pressure
3. The appearance of Si neutral species is related to in plume nucleation of Si nanocrystals
4. Use of plasma state to tailor film properties

Ti films deposited by HiPIMS

Dellasega, D. (2021)

1. Ti films deposited by DC and HiPIMS

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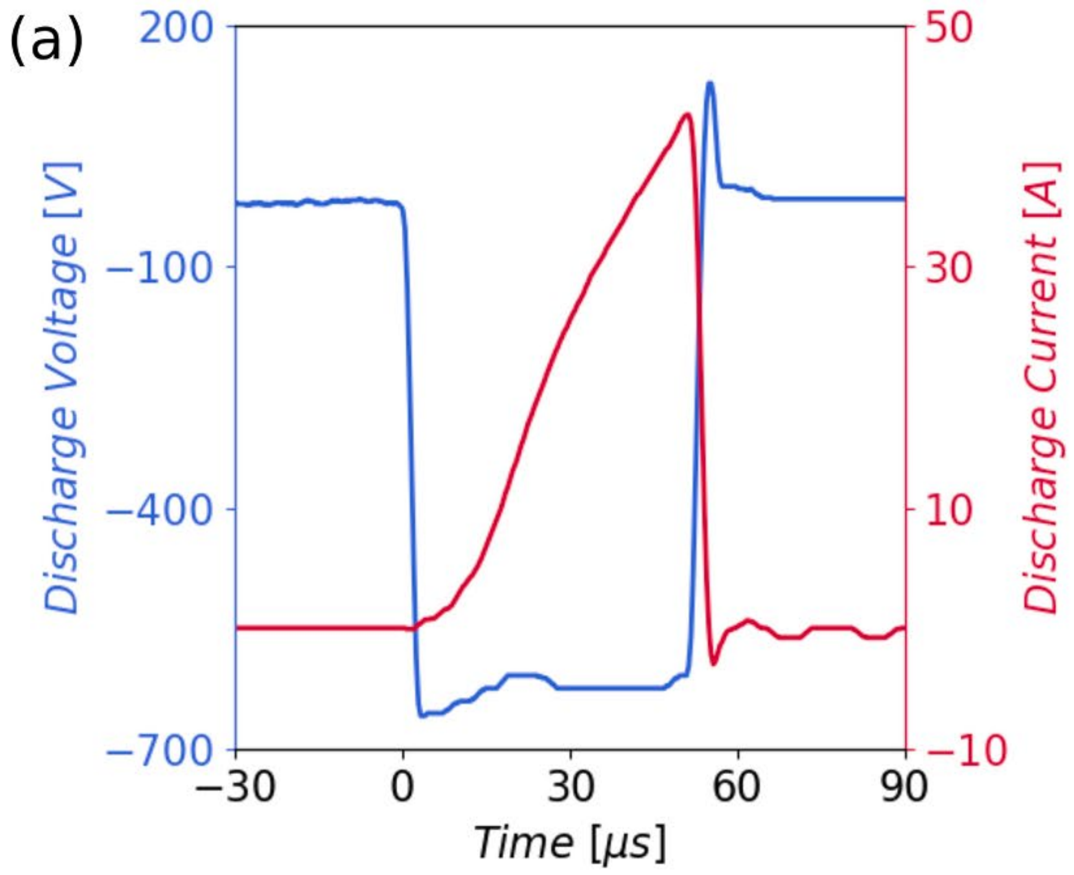
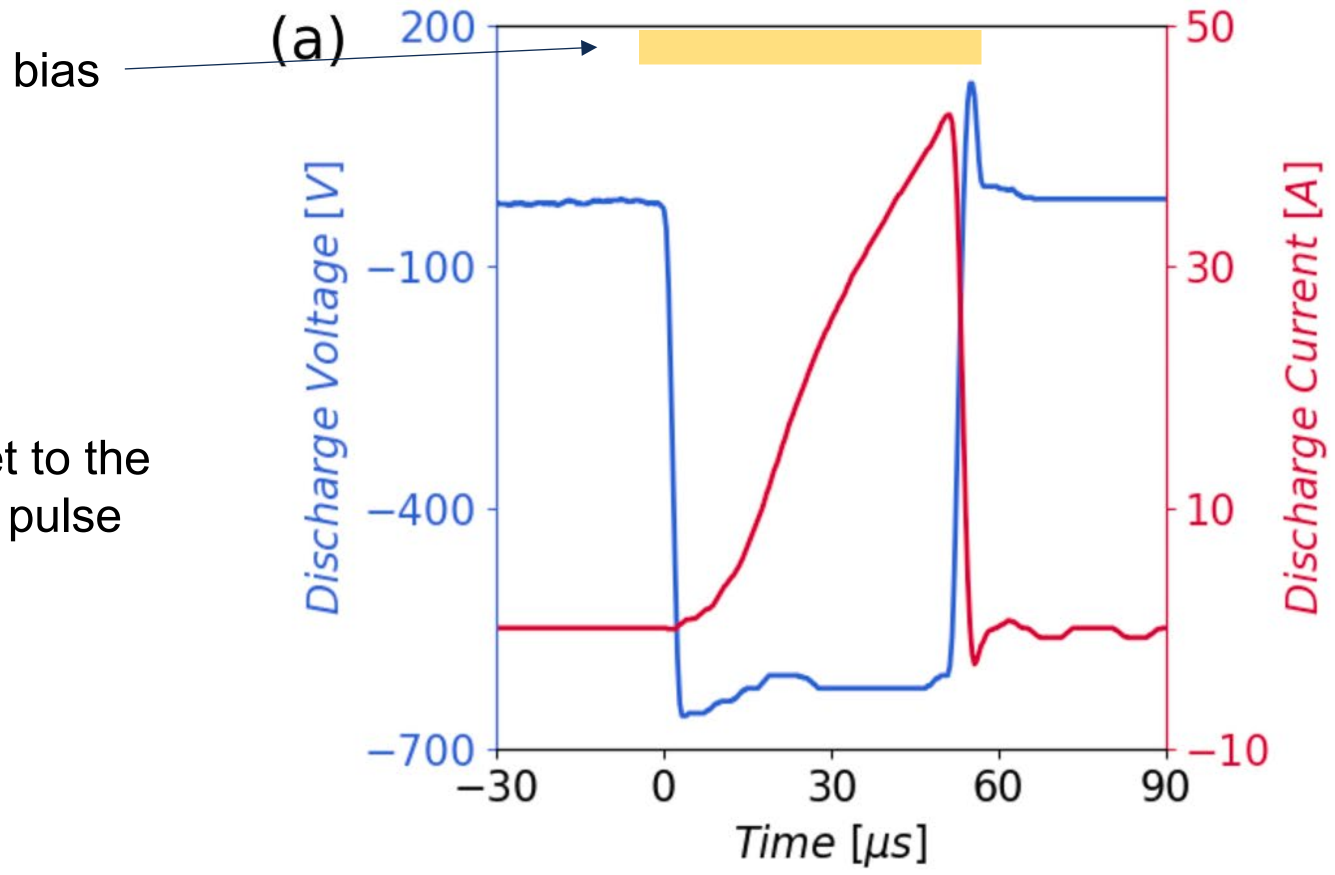


HiPIMS Pulse and current

Ti films deposited by HiPIMS

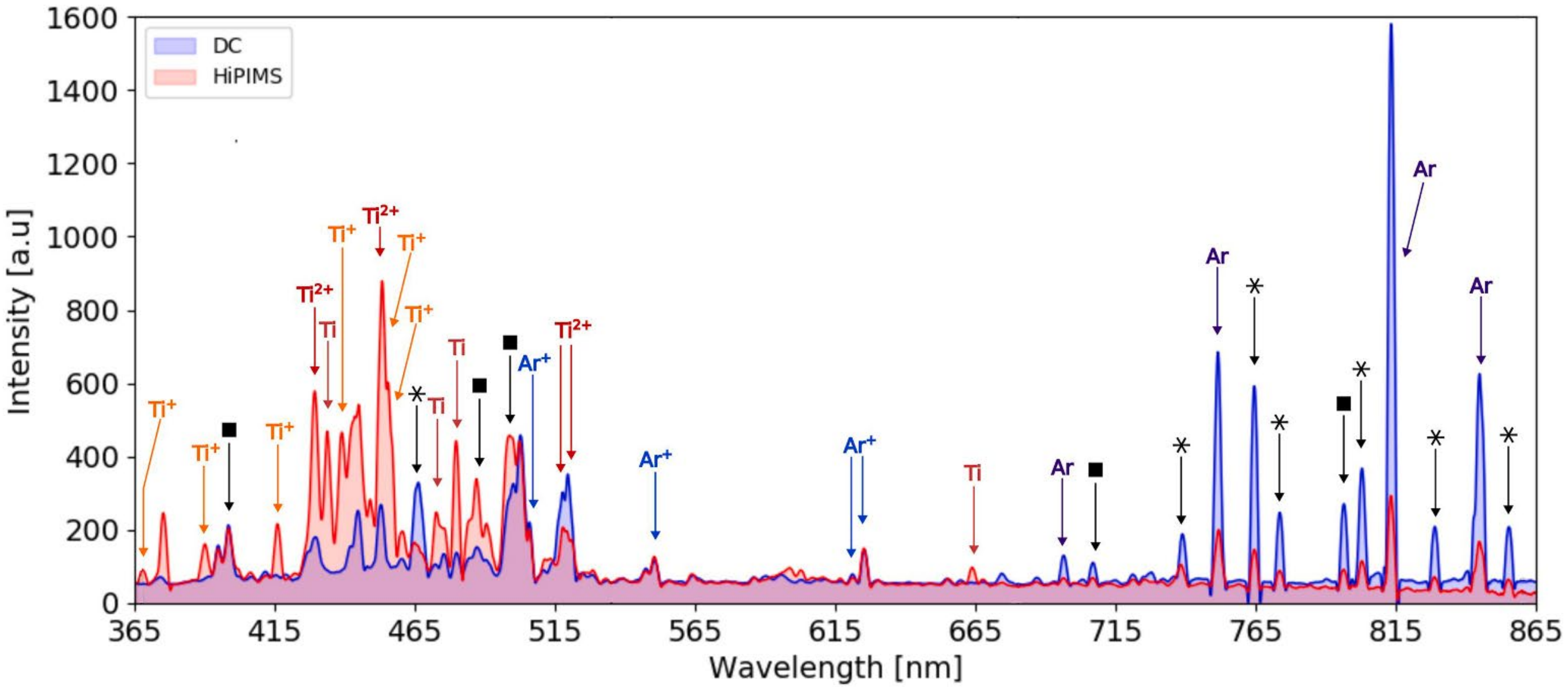
Dellasega, D. (2021)

1. Ti films deposited by DC and HiPIMS
2. Use Ti ions to modify growth of the film
3. A proper bias (0 V, 300 V, 500 V) was set to the substrate synchronized with the HiPIMS pulse



HiPIMS Pulse and current

HiPIMS vs DC plasma



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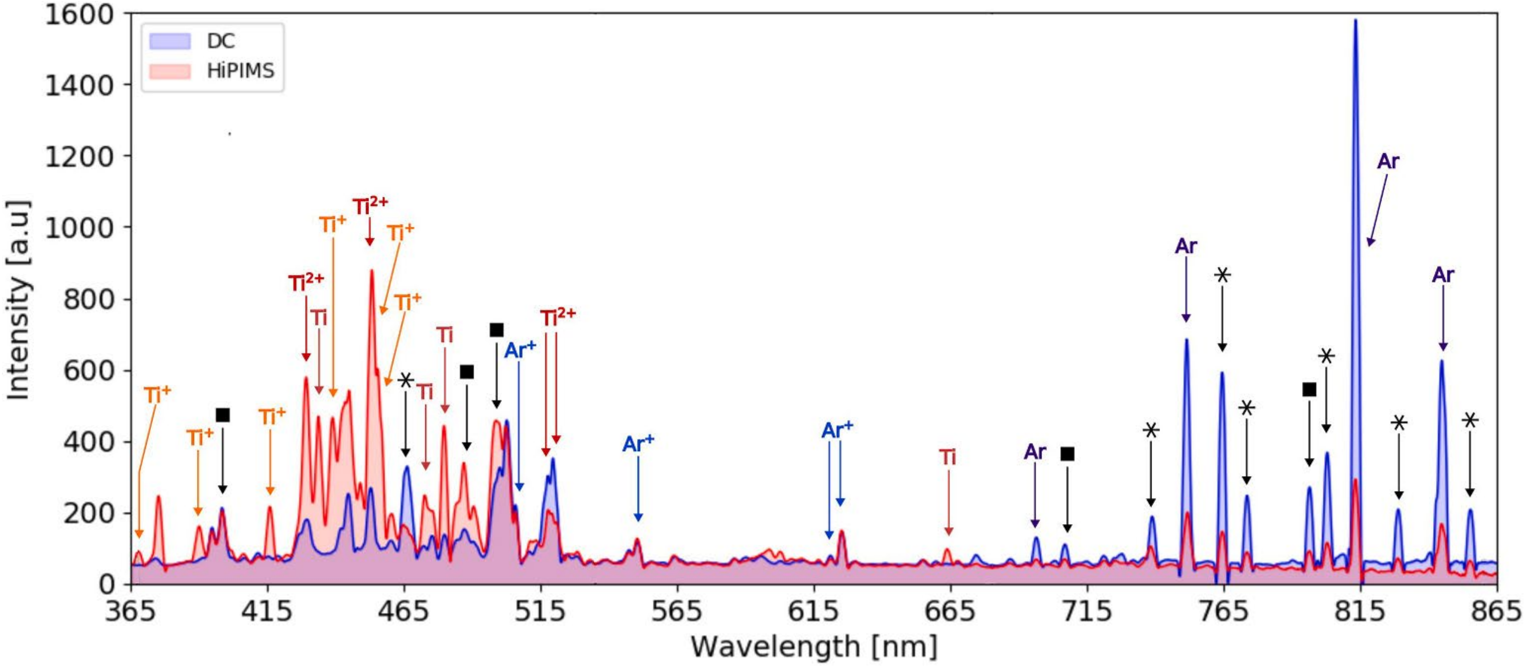
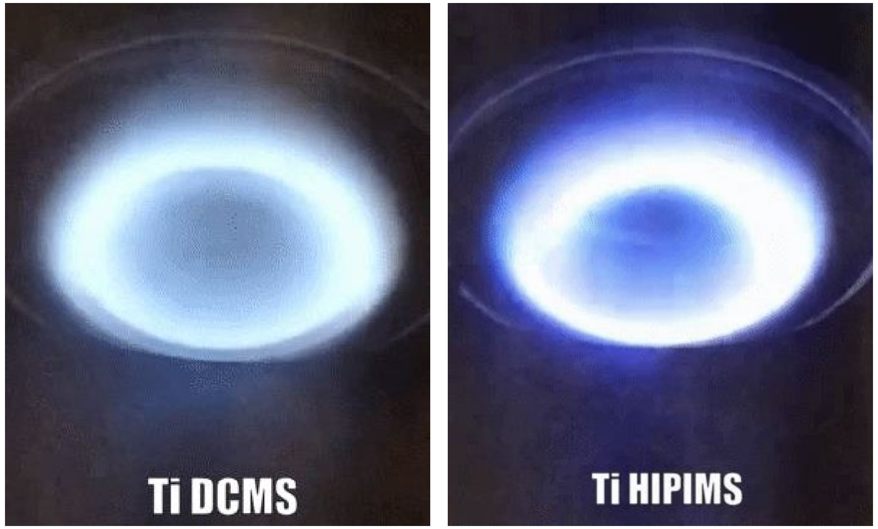
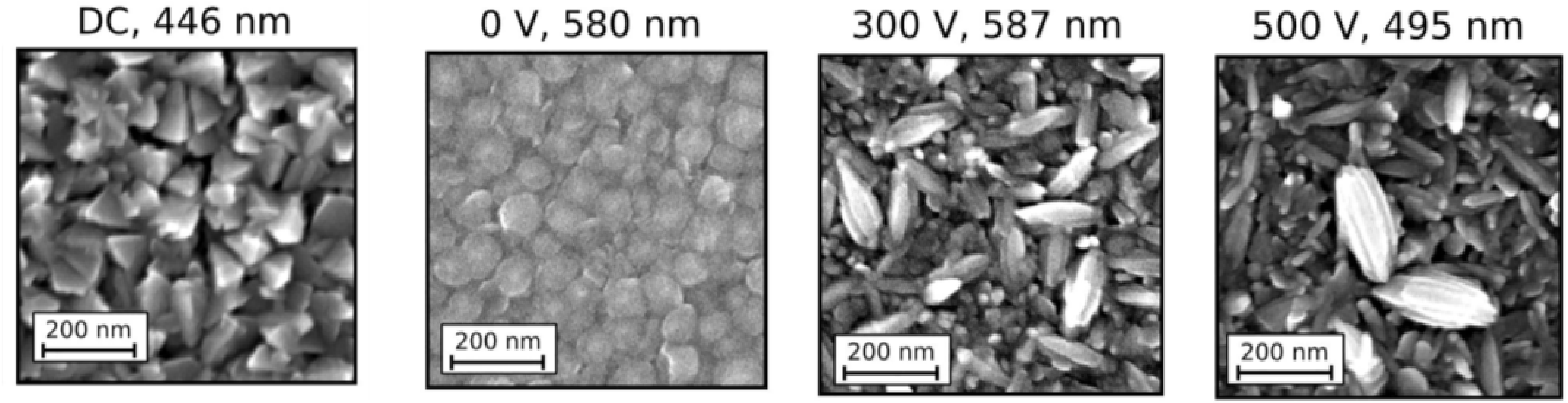




Cathodes

Morphology and structure of deposited Ti



1. Different morphology varying amount and energy of impinging ions
2. New nanostructure form at 300 and 500 V!

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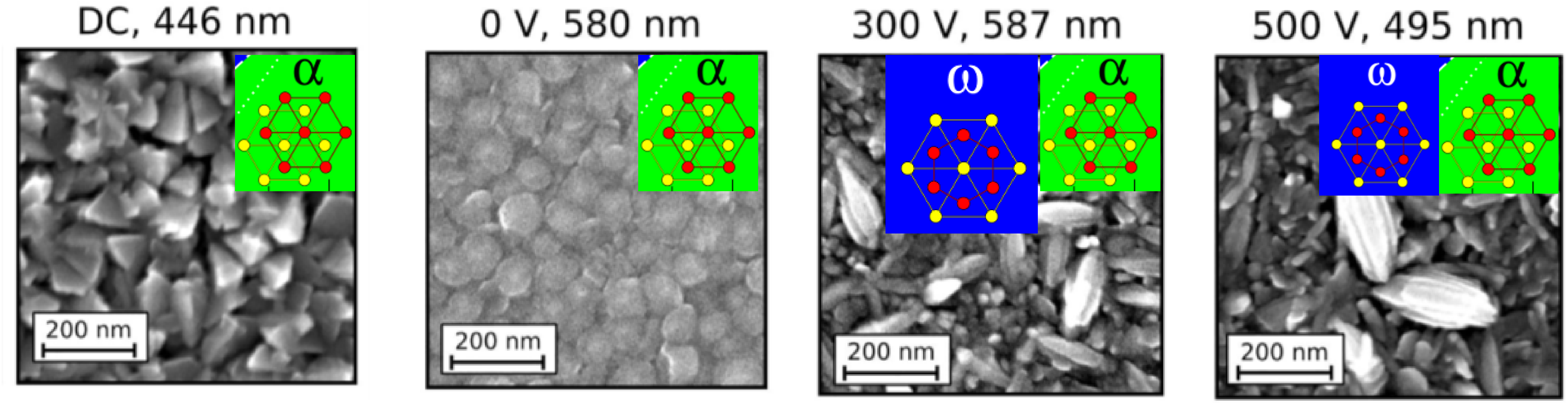


1. Different morphology varying amount and energy of impinging ions
2. New nanostructure form at 300 and 500 V!

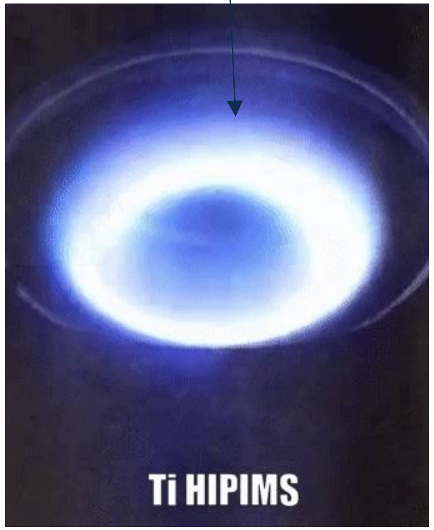
3. New crystalline phase is present in the film! From α hcp → ω hex

Modelling HiPIMS plasma: IRM model

Offer a deeper insight into complex HiPIMS physics + role of process parameters.

Ionization Region Model (IRM) *Gudmundsson, J.T. (2008)* *Raadu, M.A. (2011)*

Ionization Region



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Averaged volume global time-dependent plasma chemical model.
Semi-empirical model: set of ordinary differential equations (electrons, ions, neutrals, metastable species etc.)
+
process parameters (e.g. pressure, config., I(t))

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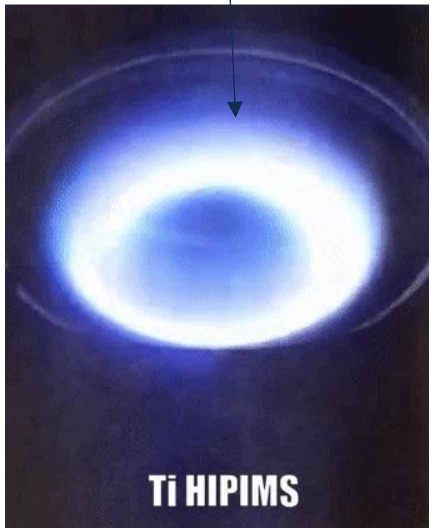

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temporal evolution of the plasma species, during and after the pulse

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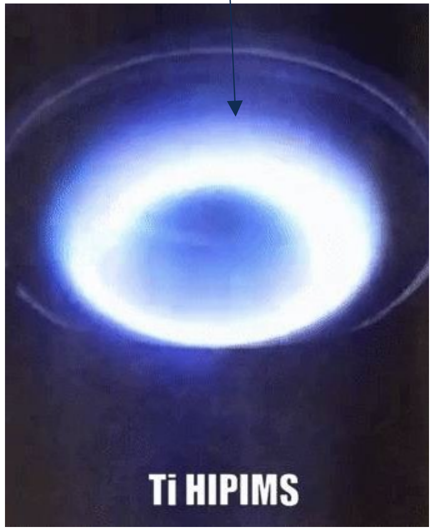

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For details on IRM model and recent applications:

Poster session 2, **P. 41**
D. Vavassori,

"Plasma modelling of non-reactive and reactive HiPIMS discharges for tungsten deposition"

Other example of 0D model:

Poster session 2, **P. 22**
M.Lauriola,

"Numerical investigation of the Microwave Electrothermal Thruster cavity and plasma at Politecnico di Milano"

Modelling HiPIMS plasma: simulating plasma current

Depositions of W films for Plasma Wall Interaction studies. Need of a compact W with properties of bulk W.

IRM model applied to Ar+W HiPIMS plasma to obtain the best process parameters

Modelling HiPIMS plasma: simulating plasma current

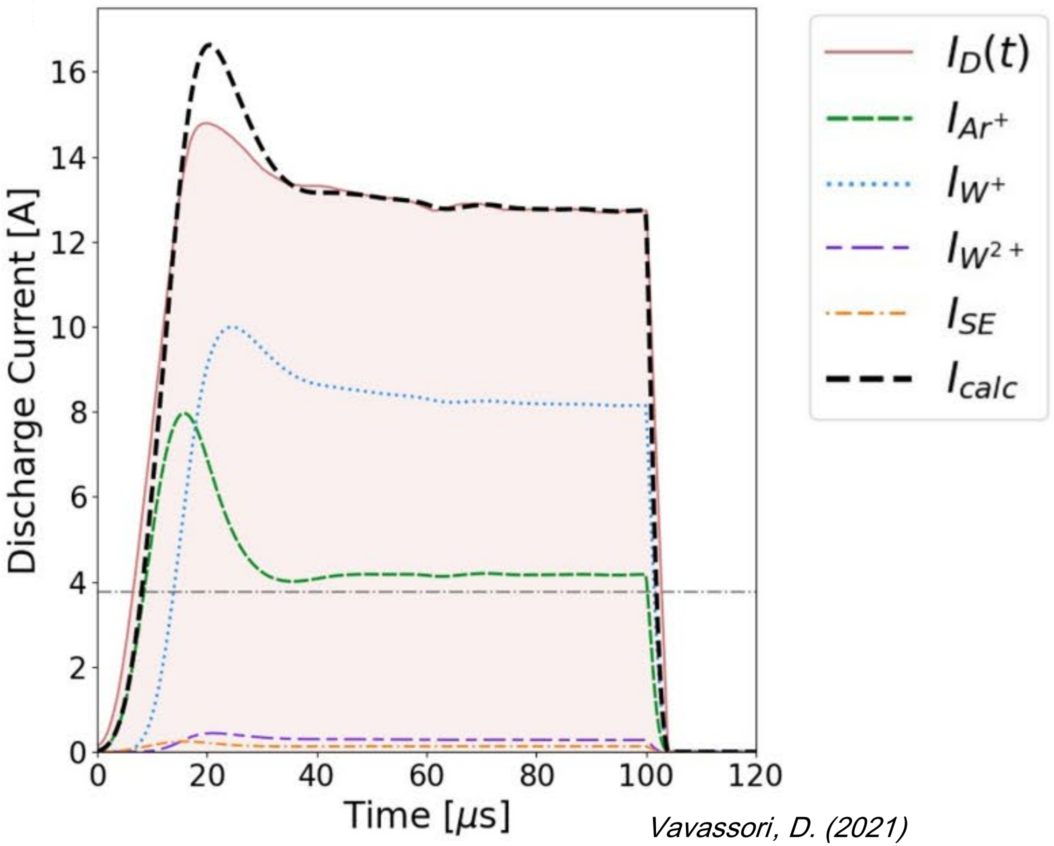
Depositions of W films for Plasma Wall Interaction studies. Need of a compact W with properties of bulk W.

IRM model applied to Ar+W HiPIMS plasma to obtain the best process parameters

Temporal evolution and contribution of the different plasma species to the total current

1. From Ar → W

2. Evolution of the two contributions



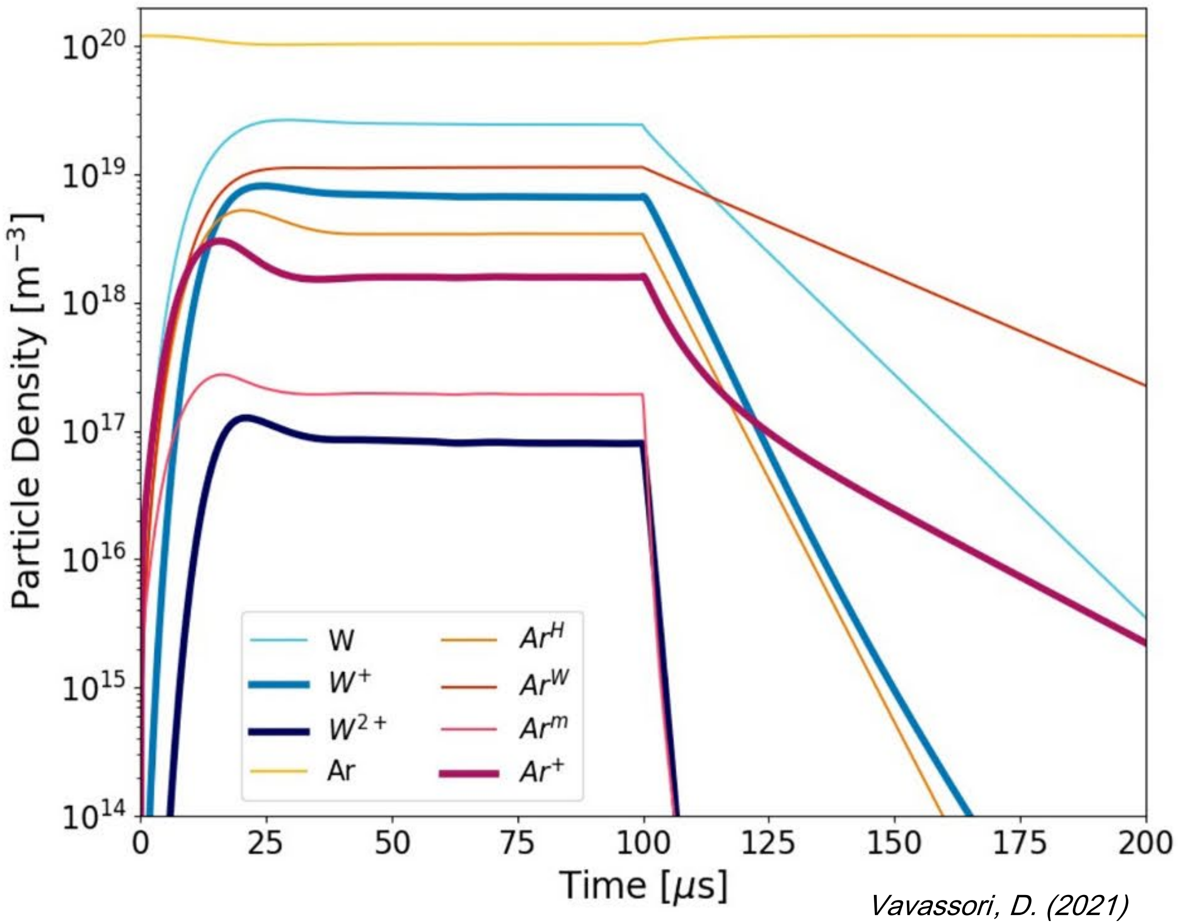
Vavassori, D. (2021)

Modelling HiPIMS plasma: particle density profile

Depositions of W films for PWI studies
Target: W
Temporal evolution of particle density profile during and after the pulse:

1. Ion families don’t disappear after pulse end

2. Different decay times



Vavassori, D. (2021)

Modelling HiPIMS plasma: ion fluxes

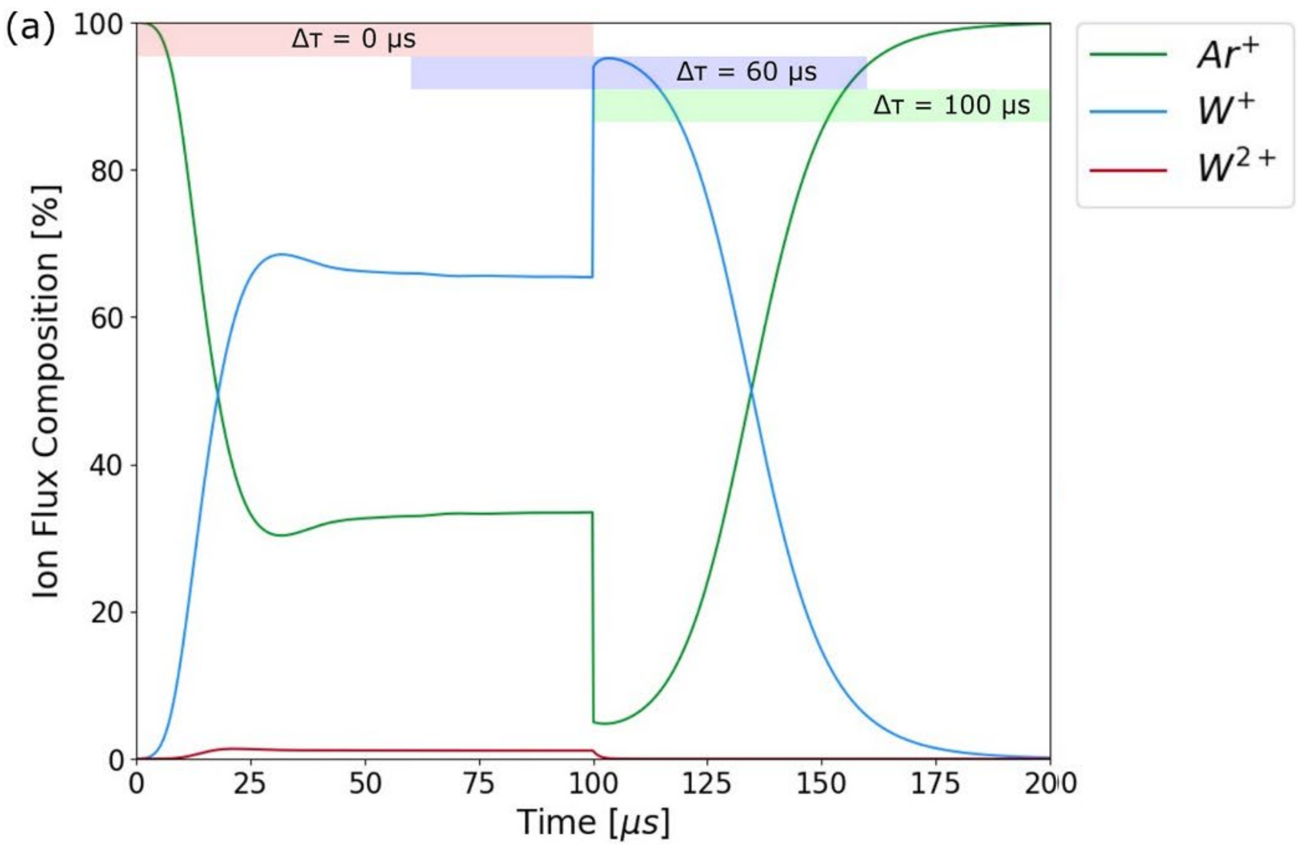
Depositions of W films for PWI studies
Target: W
Temporal evolution of ion flux composition during and after the pulse:

1. During the pulse high amount of W but low flux due to back attraction

2. Just after the pulse only W and high flux

3. At longer times high flux but predominance of Ar

4. Important to set properly the delay time between main pulse and bias pulse!!

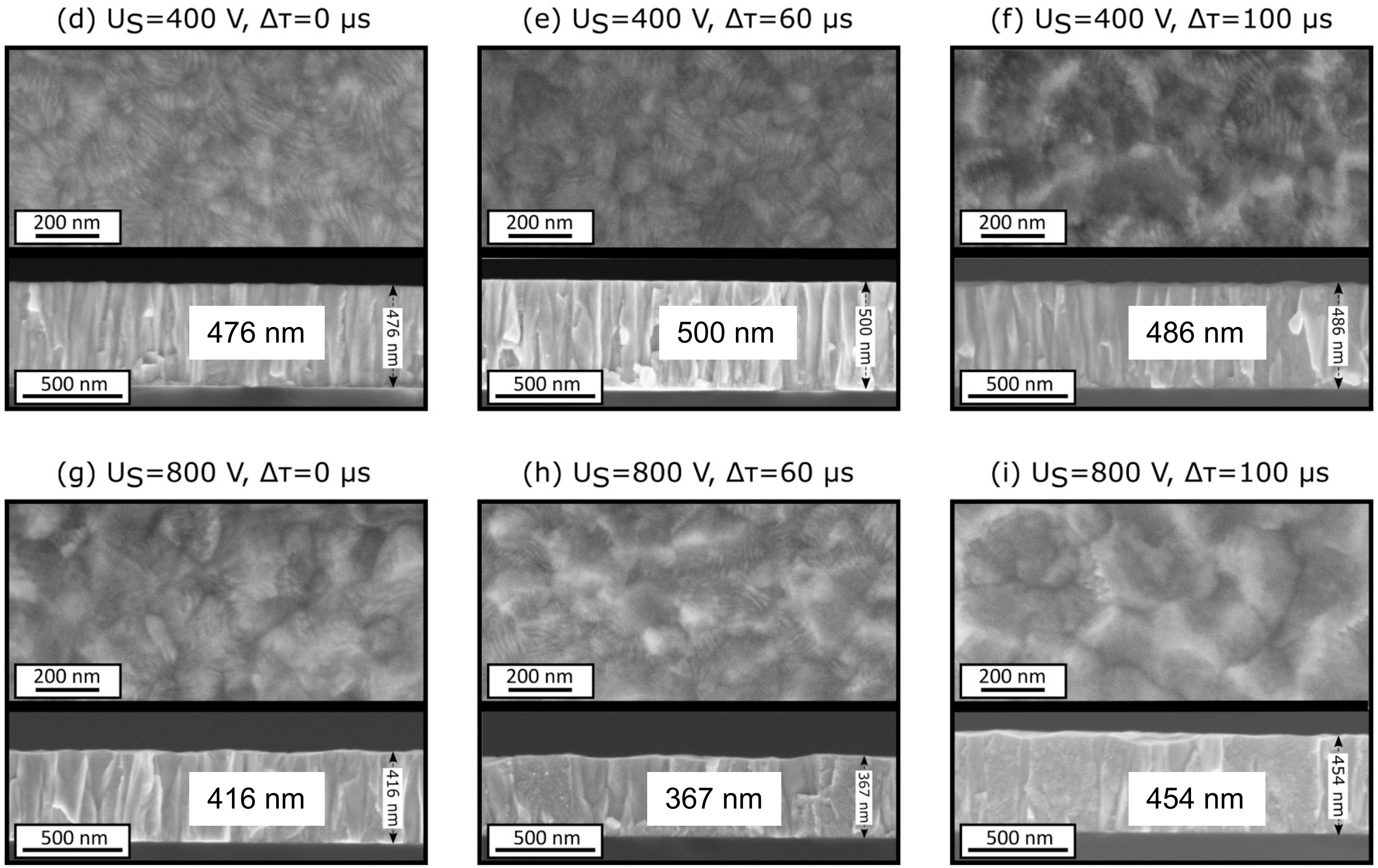


From modelling to experiment

Depositions of W films for PWI studies
Target: W
Voltage: 200 V, 400 V, 800 V
Bias delay: 0, 60, 100 μs

1. With 400 V and delay 0 or 60 μs best properties in terms of crystallinity, density and internal stress.

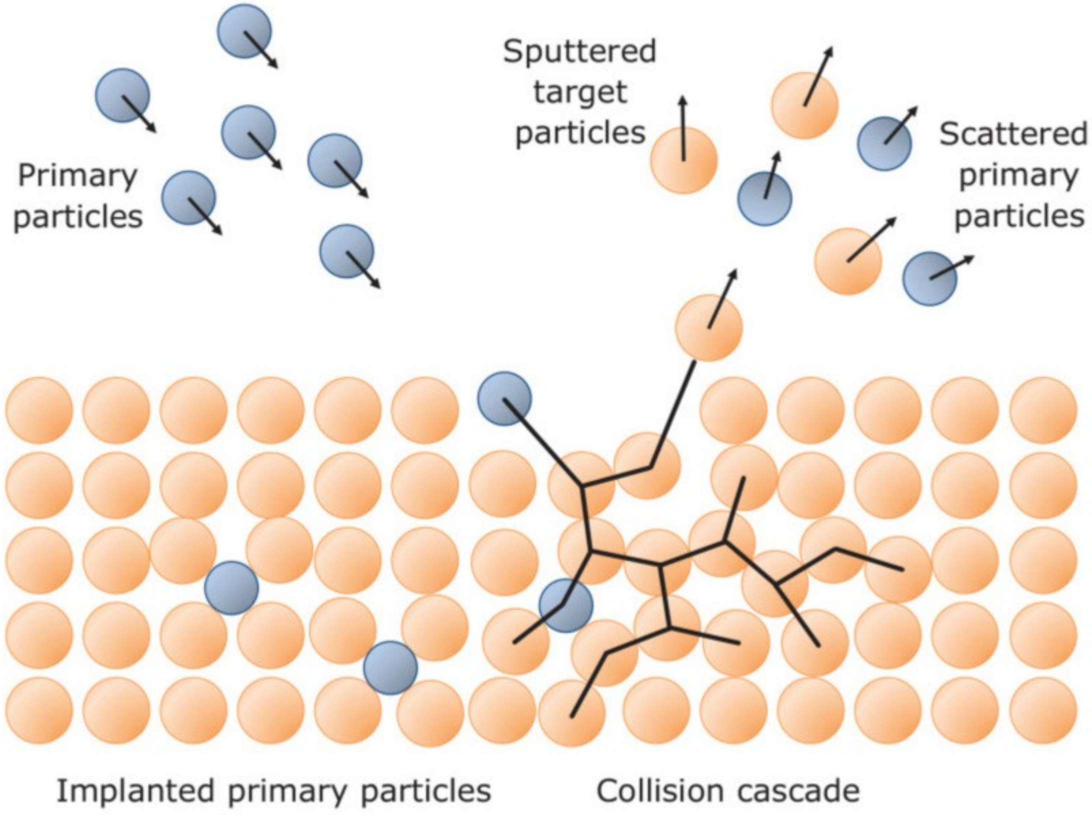
2. At 800 V resputtering of the film! Sputtered thickness related to delay (i.e. type of impinging ion)



Thanks a lot for your kind attention!

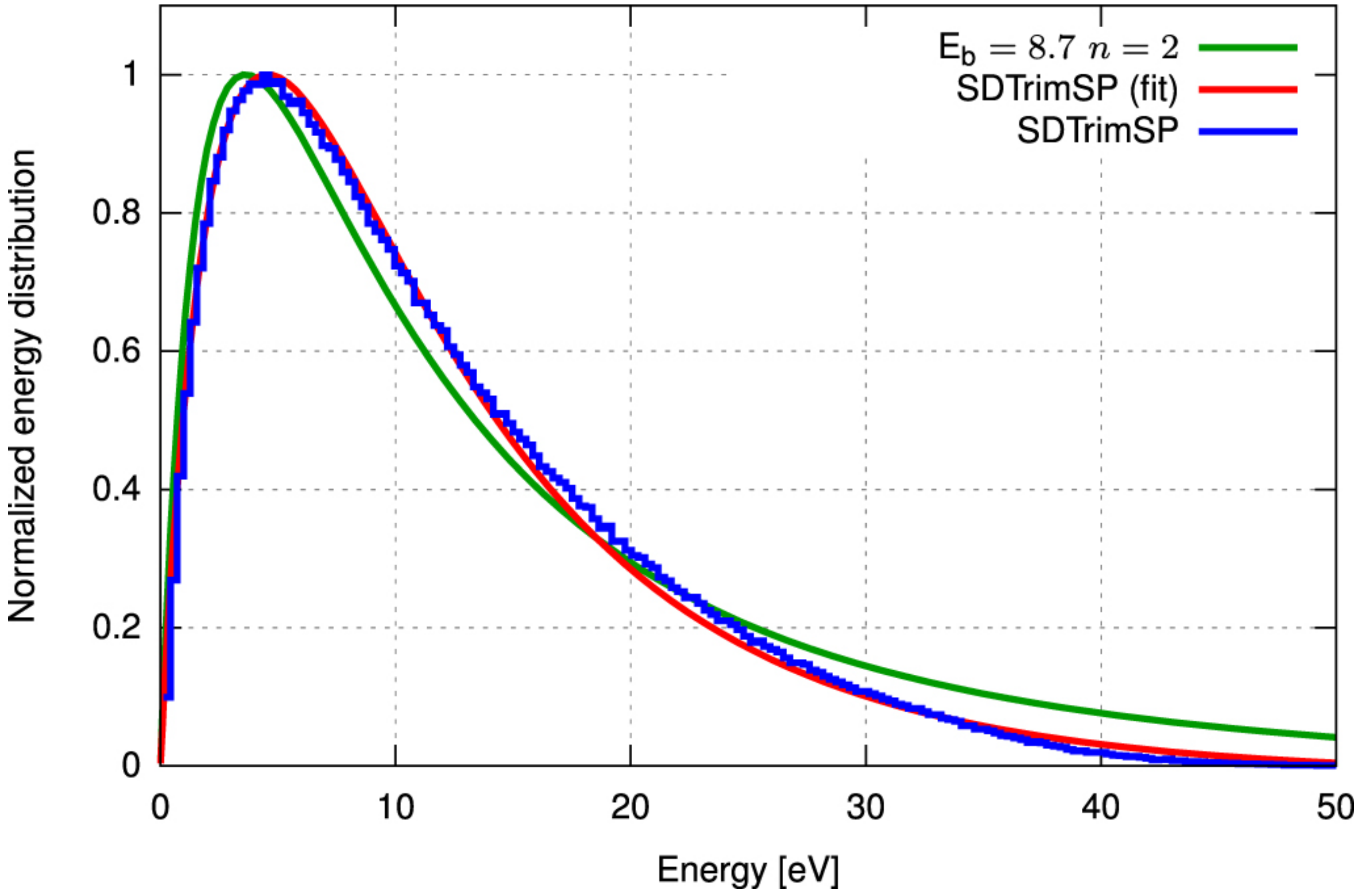
Physical sputtering

1. high - energy ions hit the target surface,
2. collision cascade, transferring kinetic energy to surface atoms,
3. Target atoms exceed their surface binding energy and escape.

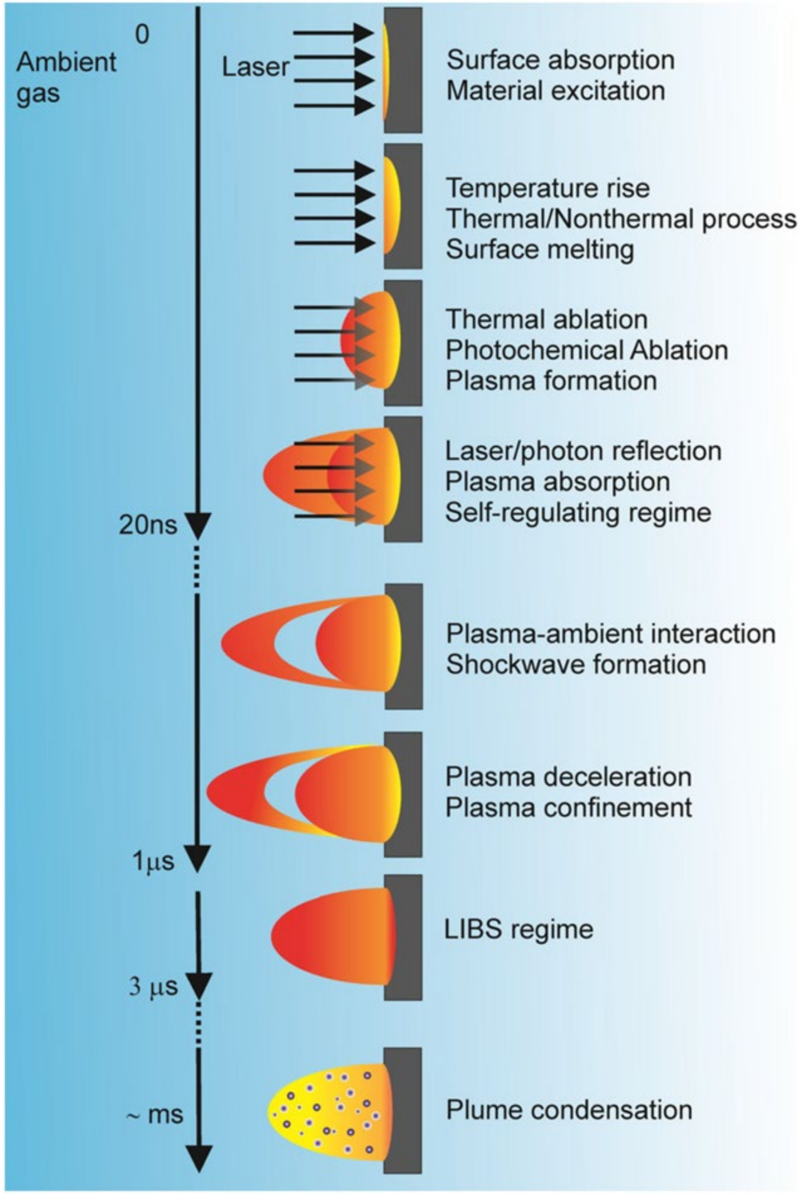


Physical sputtering

Energy distribution function of W atoms at Ar^+ ions impact of 150 eV from SDTrimSPand Thompson. The SDTrimSPdata is shown using blue color .



Ns-PLD


0
Ambient gas
Laser
Surface absorption
Material excitation
Temperature rise
Thermal/Nonthermal process
Surface melting
Thermal ablation
Photochemical Ablation
Plasma formation
Laser/photon reflection
Plasma absorption
Self-regulating regime
20ns
Plasma-ambient interaction
Shockwave formation
Plasma deceleration
Plasma confinement
1μs
LIBS regime
3 μs
~ ms
Plume condensation