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High-Power Impulse Magnetron Sputtering for the synthesis of functional metal oxide thin films

CHIPS
Chimie des Interactions Plasma Surfaces

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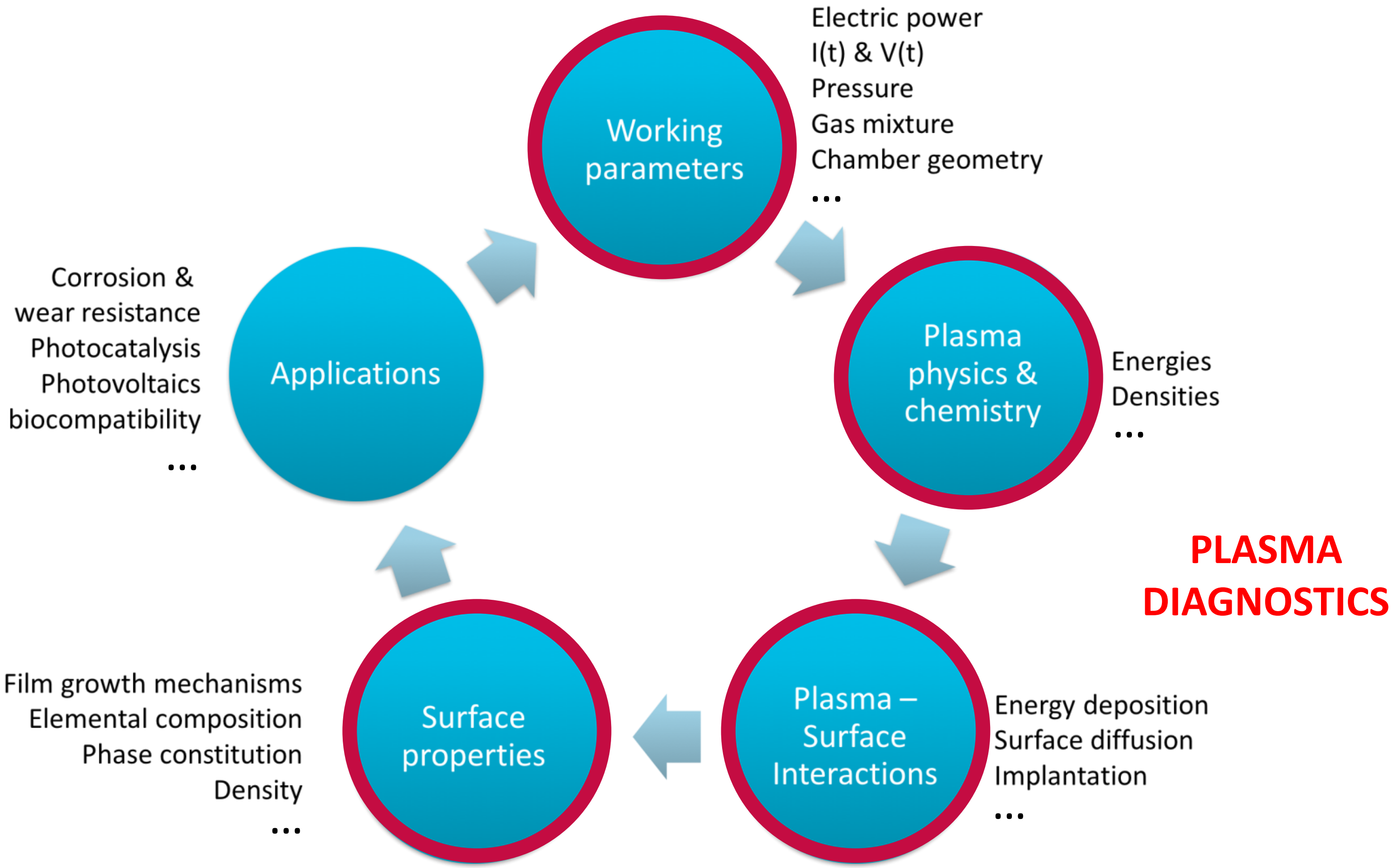
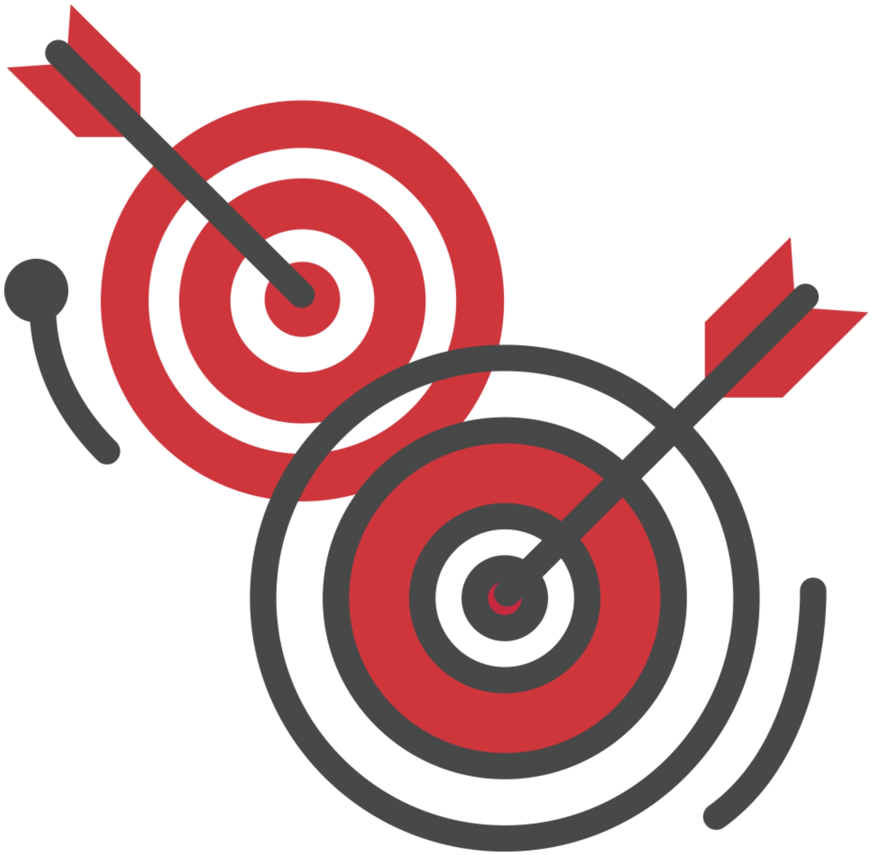
Our « philosophy »



1) High Power Impulse Magnetron Sputtering, **why and how** ?

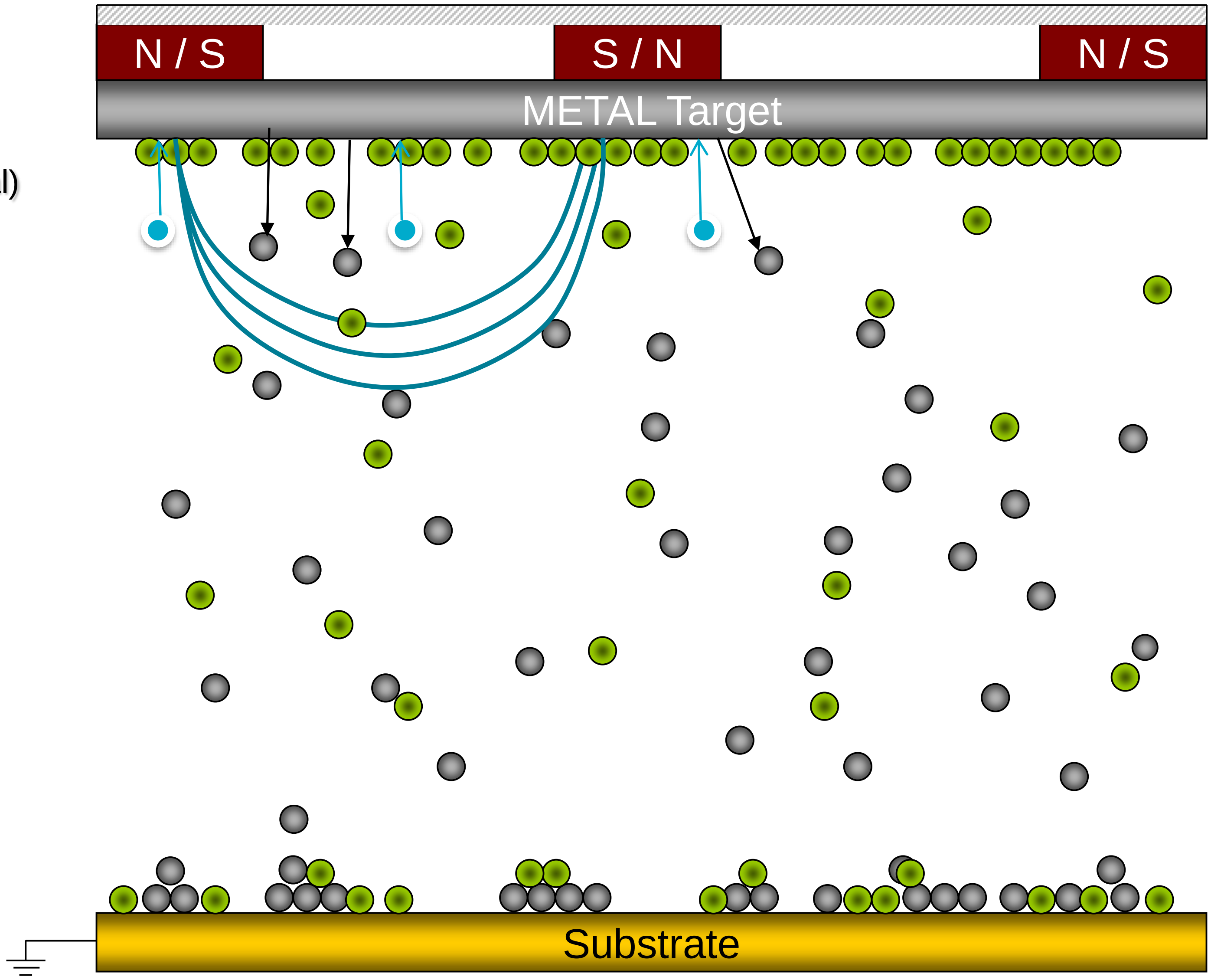


2) **What happens** if HiPIMS is used for the synthesis of transition metal oxide thin films ?

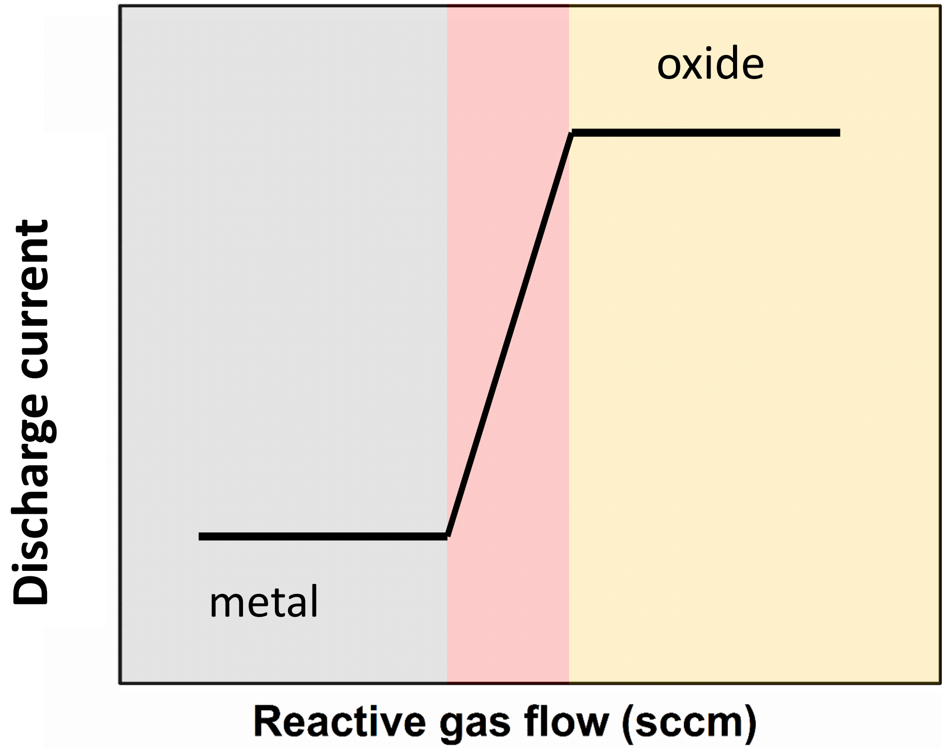
Conventional DC magnetron sputter deposition

CATHODE

(Negative potential)



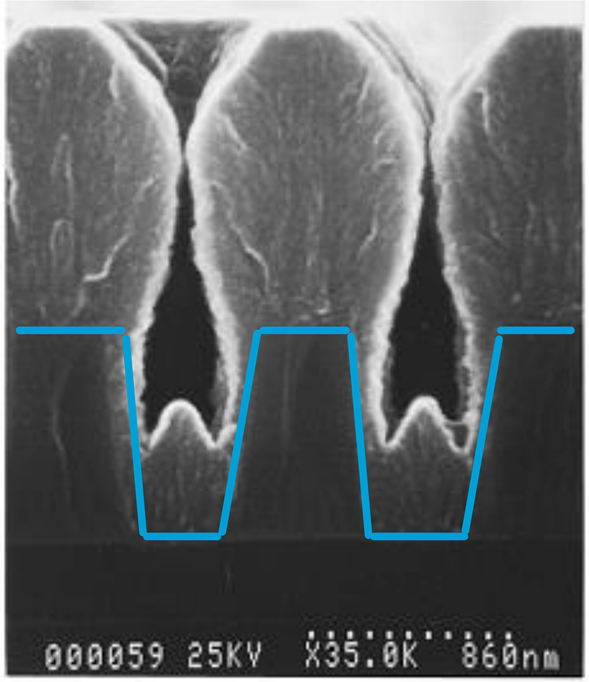
Target surface chemistry changes with O_2 partial pressure



Magnetron sputtering in the Industry

https://invest.dresden.de/

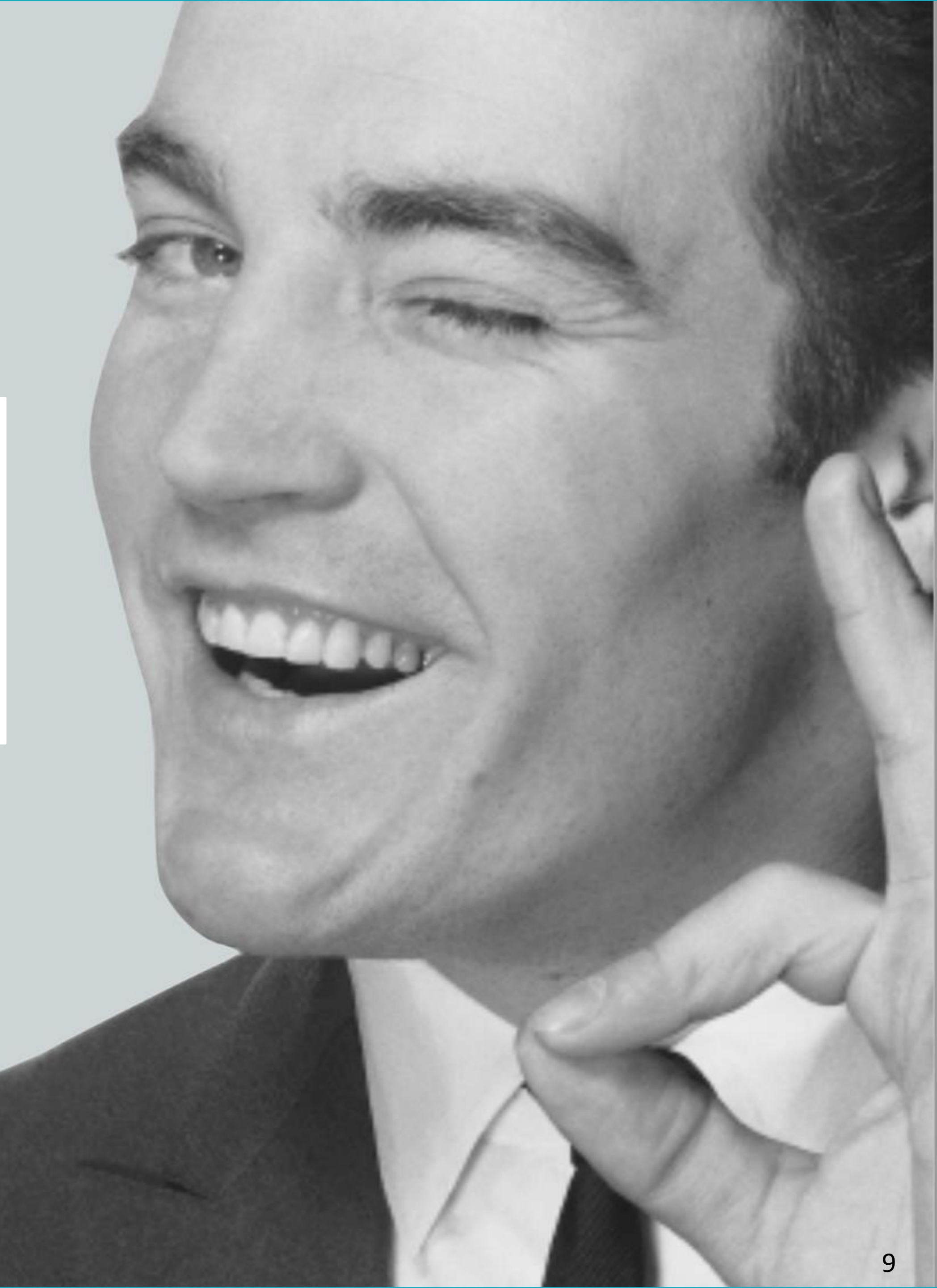
Filling holes by magnetron sputtering



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

…problem !

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

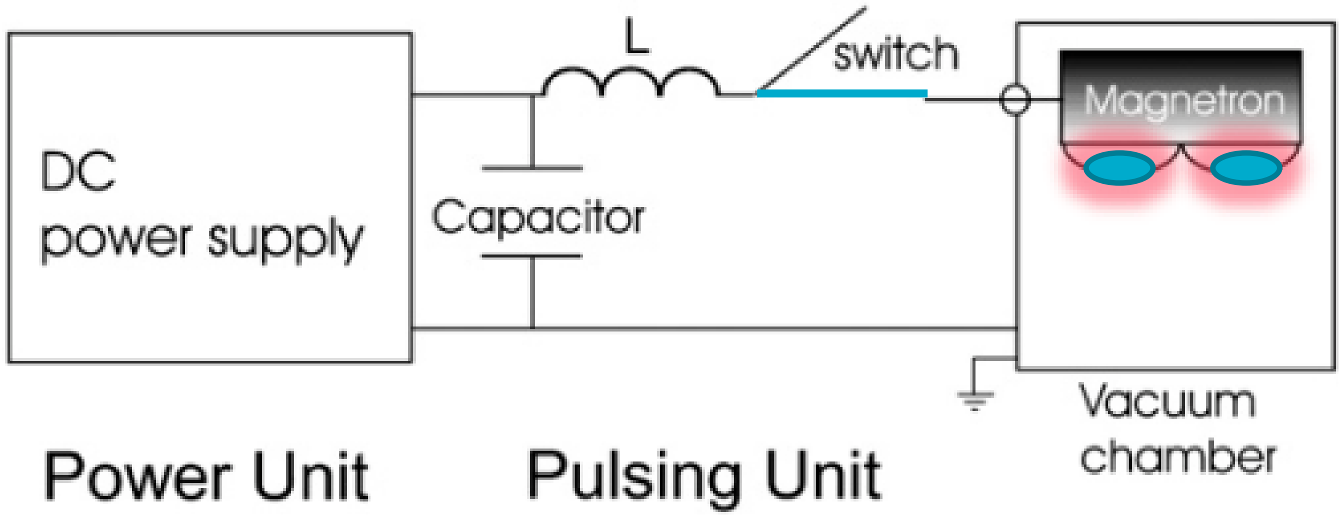
– Crystallinity, micro/nanostructure, roughness,... are modified

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 an HiPIMS generator



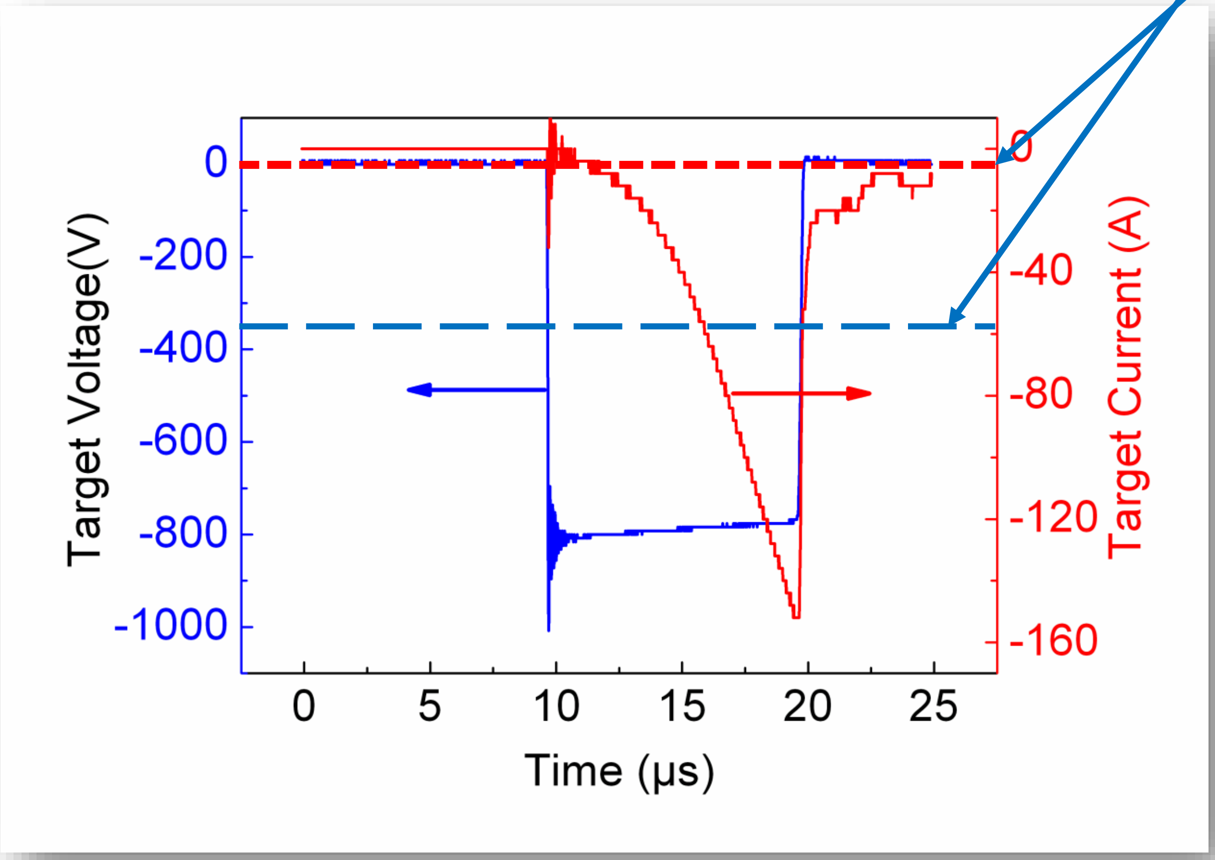
The power supply delivers:

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

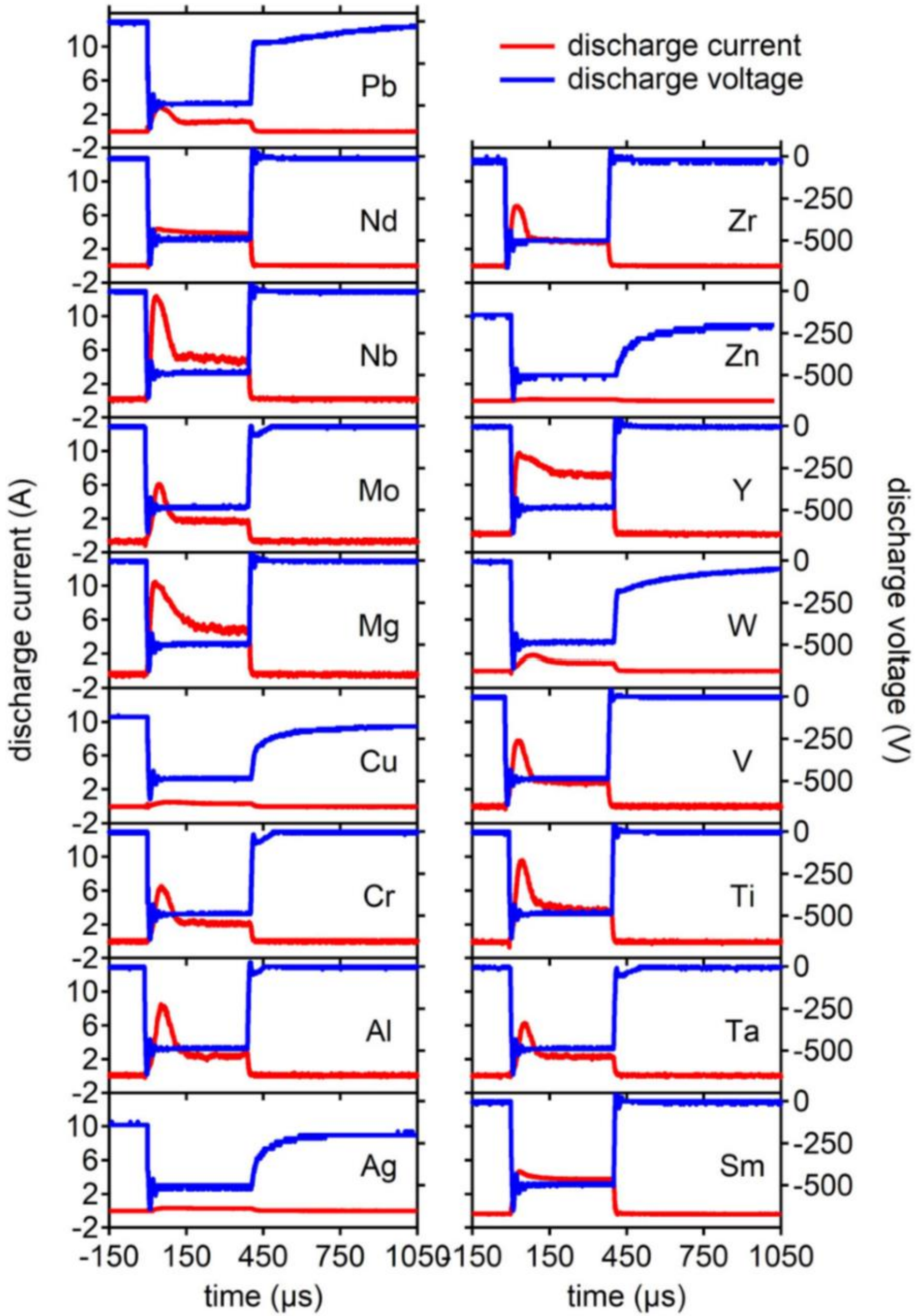
Pulsed discharge to avoid overheating the target/magnets

Typical Current-Voltage-Time waveforms

Conventional DCMS



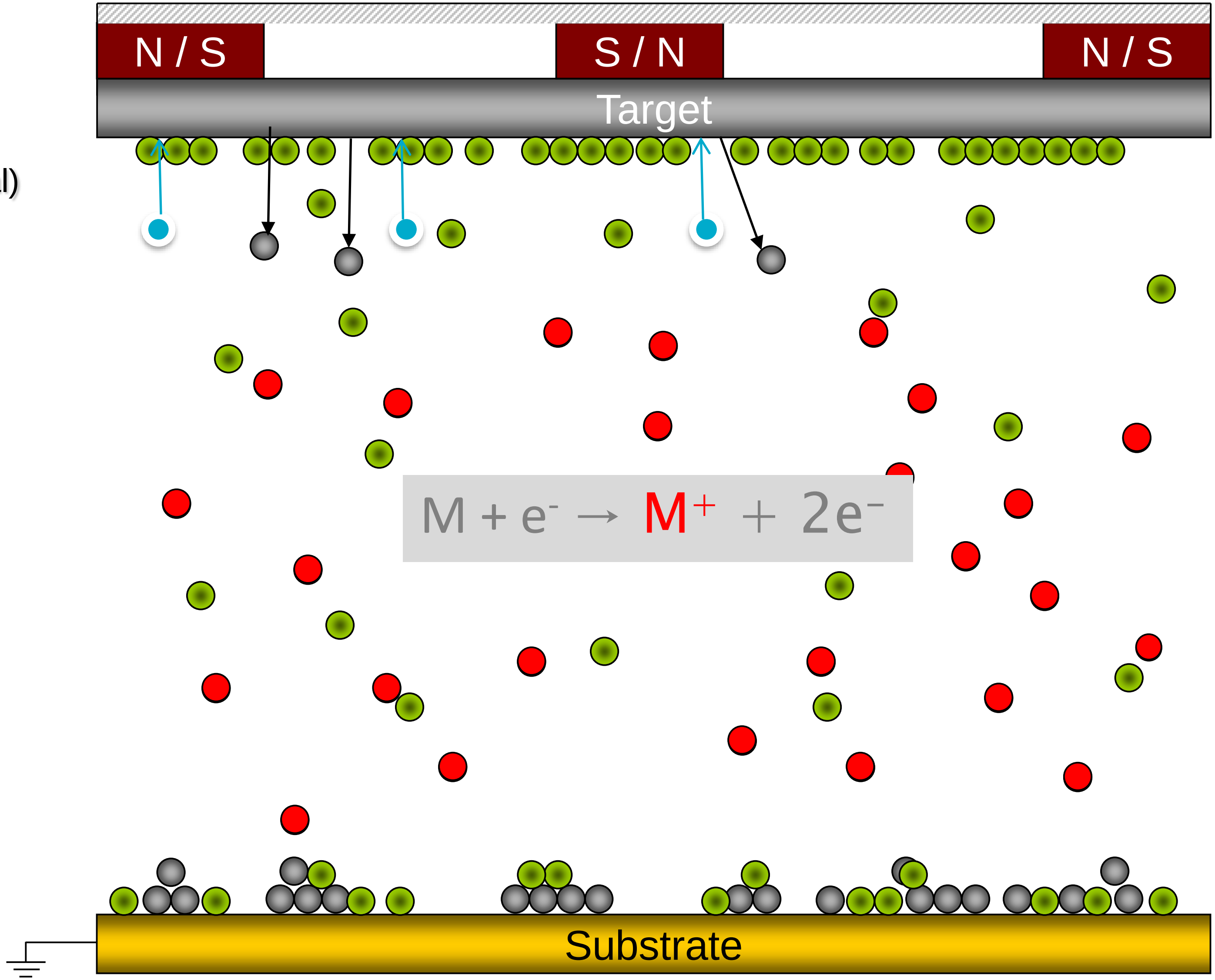
Current - Voltage - Time waveforms



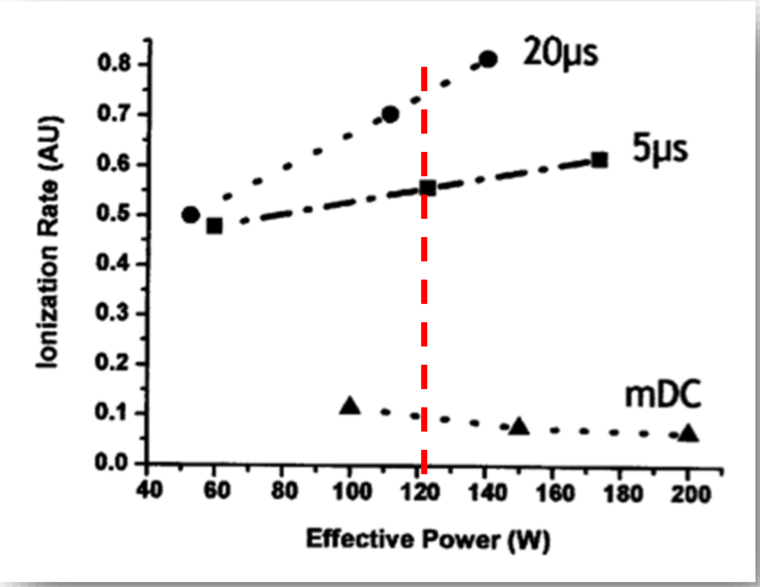
The HiPIMS plasma

CATHODE

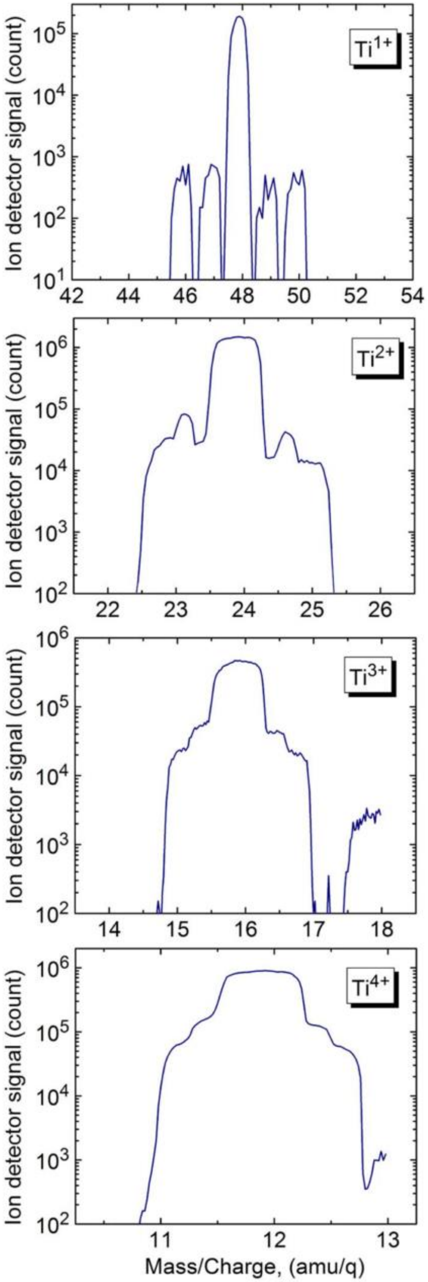
(Negative potential)



Production of ionized metal atoms



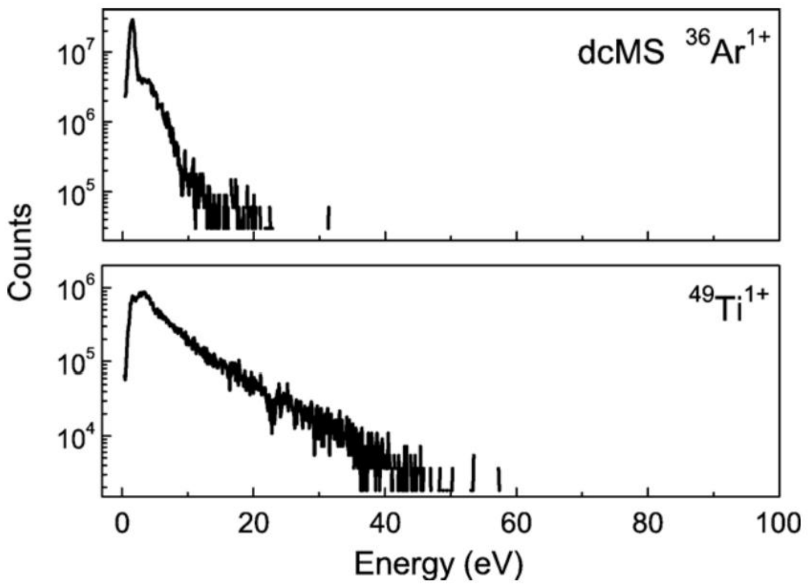
Konstantinidis, J.Appl. Phys. (2006)



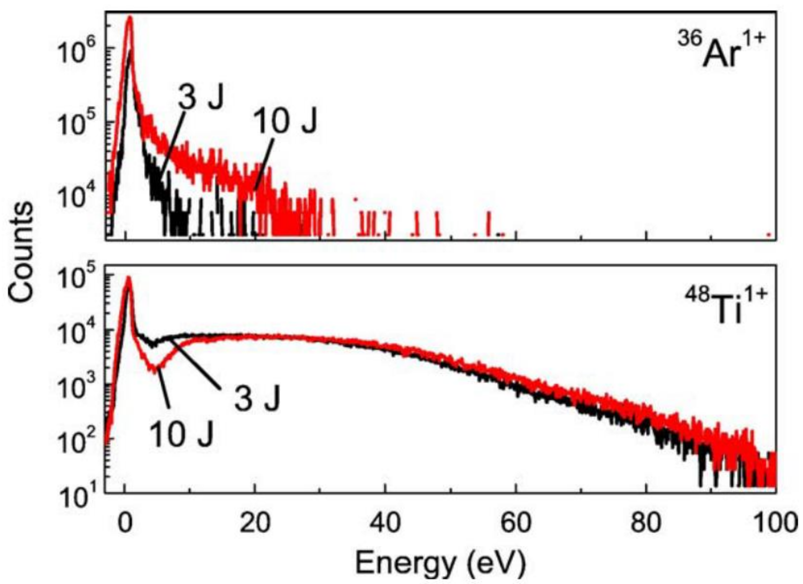
Andersson et al. Appl. Phys. Lett. (2008)

Film – forming species with high kinetic energies

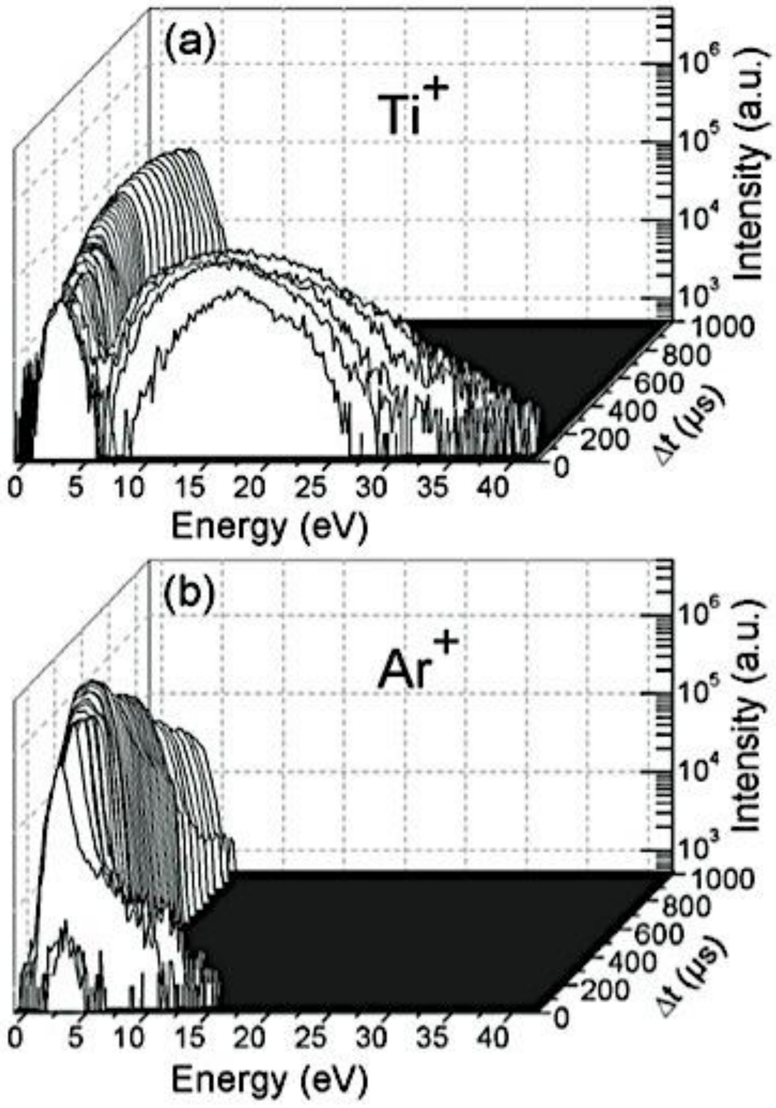
DC Magnetron



HiPIMS



Bohlmark et al, Thin Solid Films (2006).

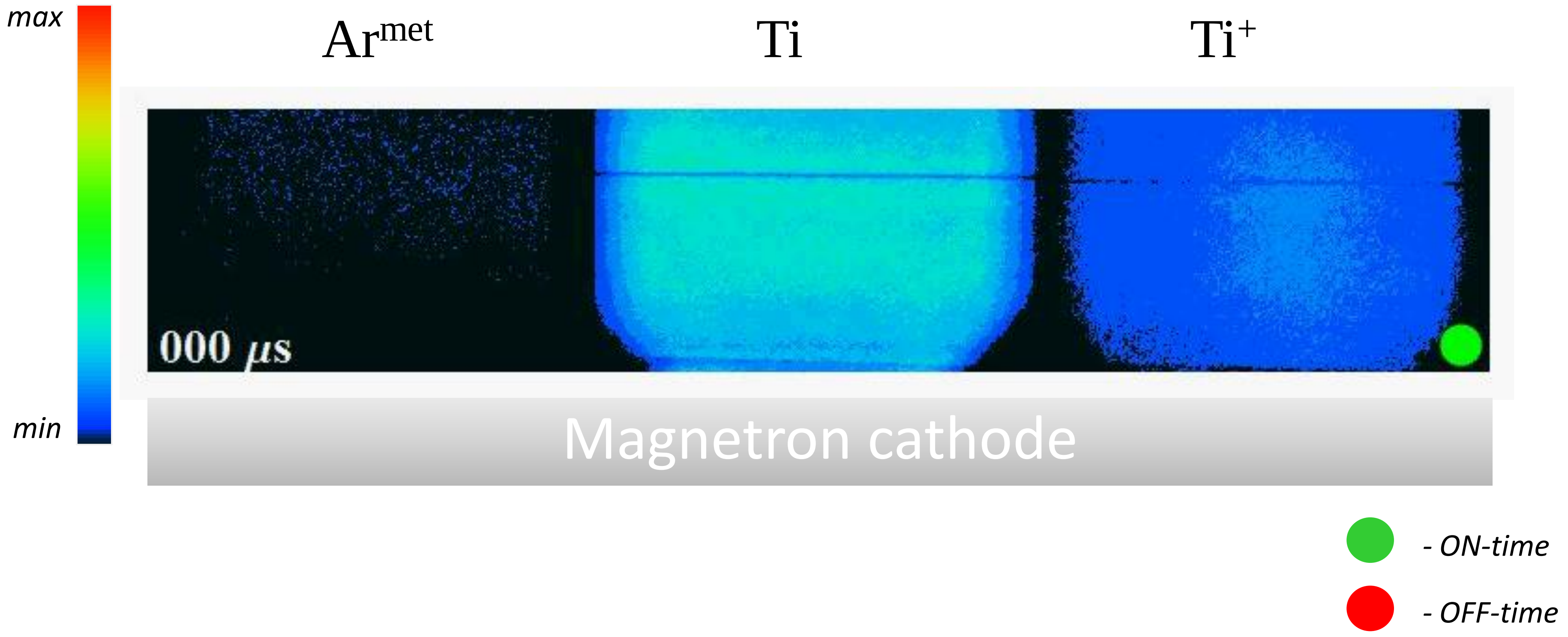


Plasma dynamics

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

Time & space – dependent plasma chemistry

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



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

Towards a definition of HiPIMS

1. Magnetron plasma
   – Glow discharge in ExB fields

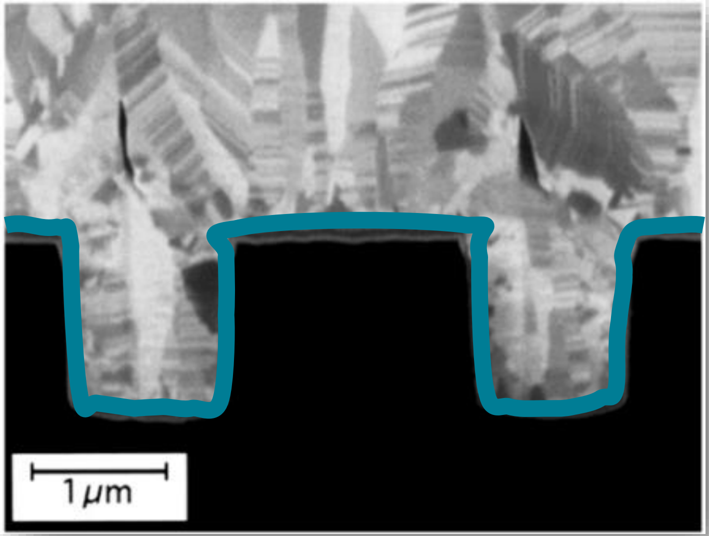
2. Electric pulses
   – Duty cycle ≤ 1%

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

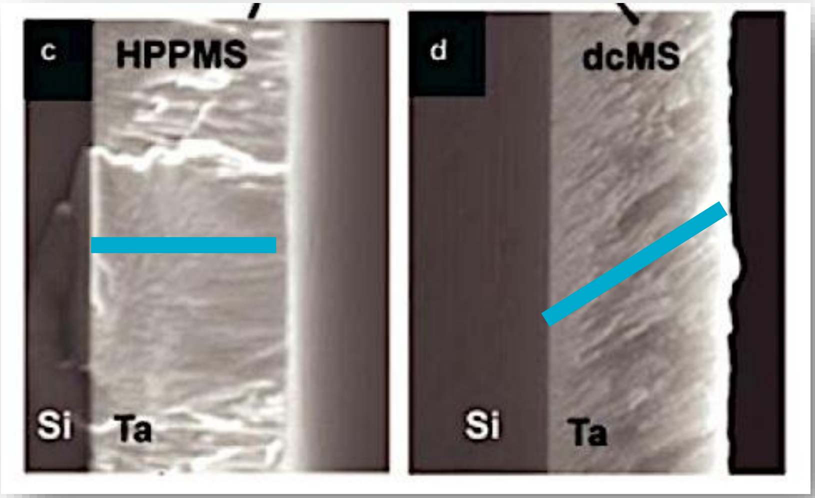
4. High ionization rate of the sputtered material

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

Conformal deposition on complex-shape objects



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



Alami et al, JVST A (2007)

Some more knobs to tune film properties

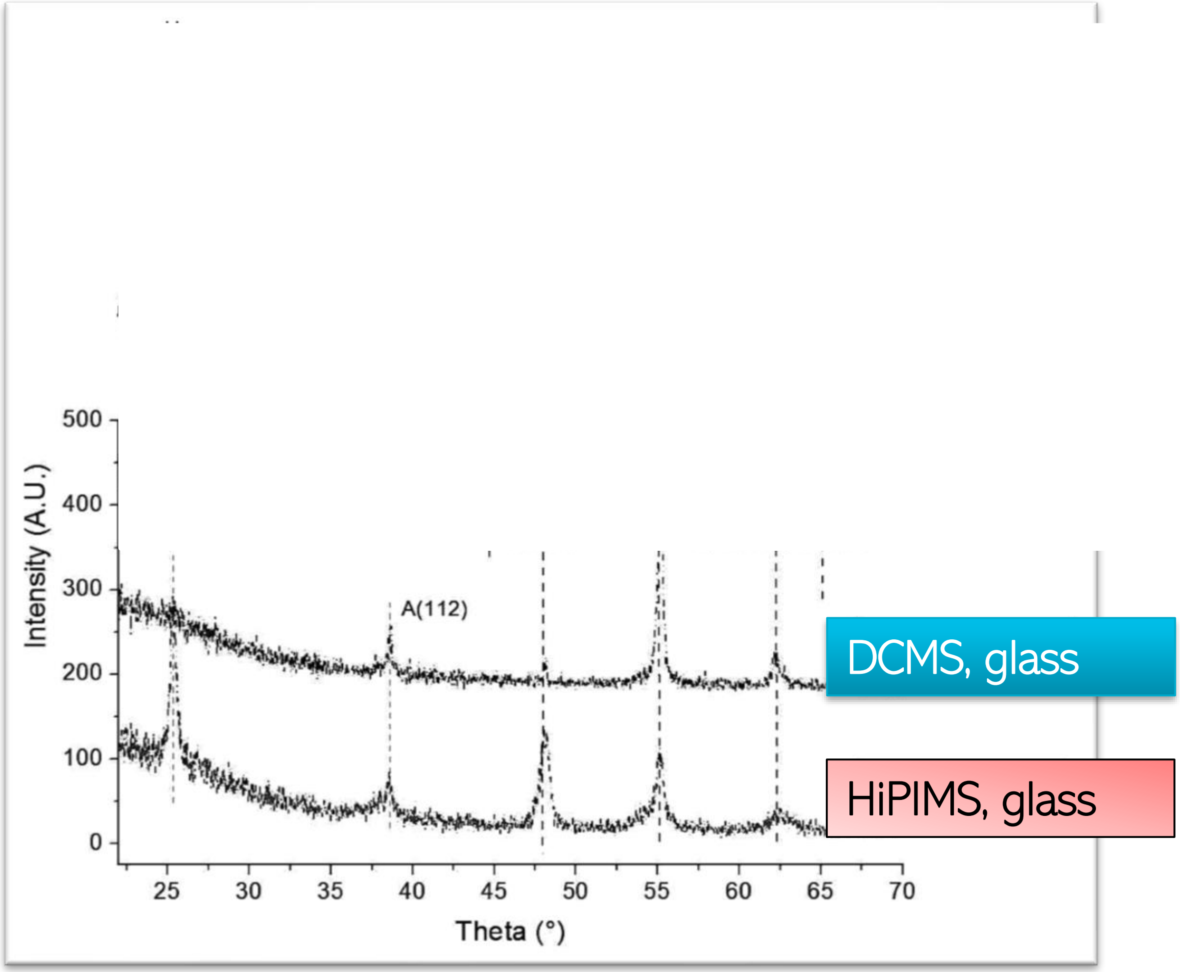
- **Energy deposition** during film growth
- **More knobs for tuning the thin film properties**
  - Pressure & gas mixture
  - Magnetic & chamber geometry
  - Average power
  - **Pulse duration & frequency**
  - **Pulse voltage**

On the synthesis of metal oxide thin films by HiPIMS

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

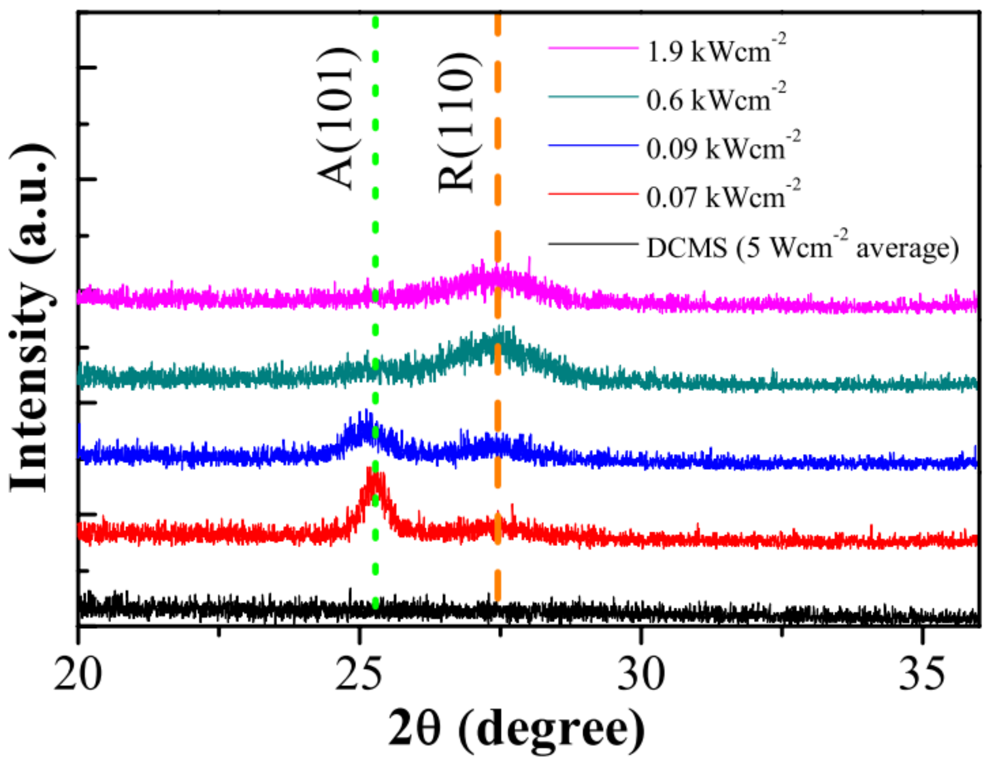
Titanium dioxide

Growing high-temperature phase of TiO_2 by HiPIMS



Konstantinidis et al, Thin Solid Films (2006)

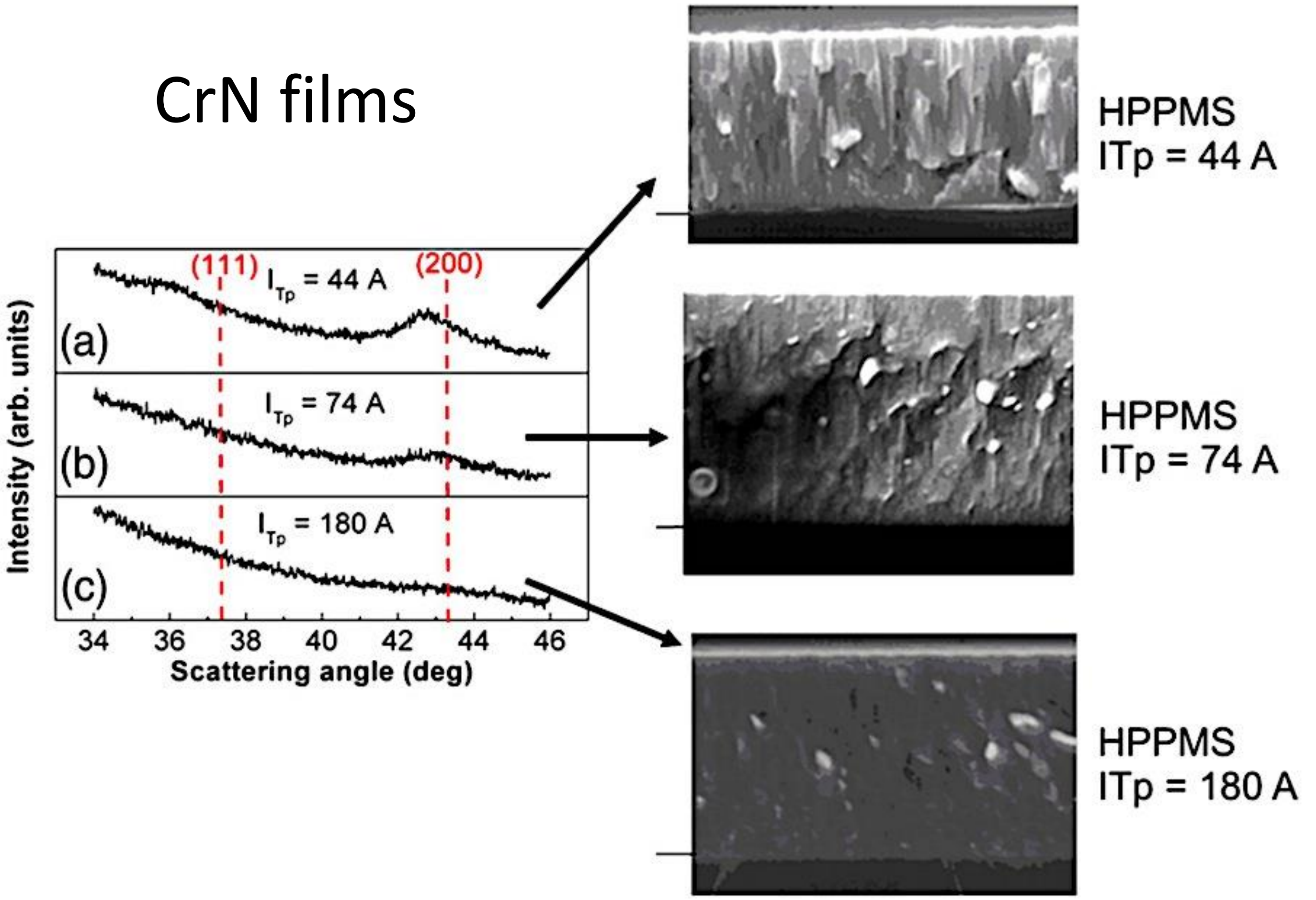
Modulating the phase constitution through peak power



Aiempanakit et al, Surf. Coat. Technol. (2011)

Too high ion flux may lead to amorphization

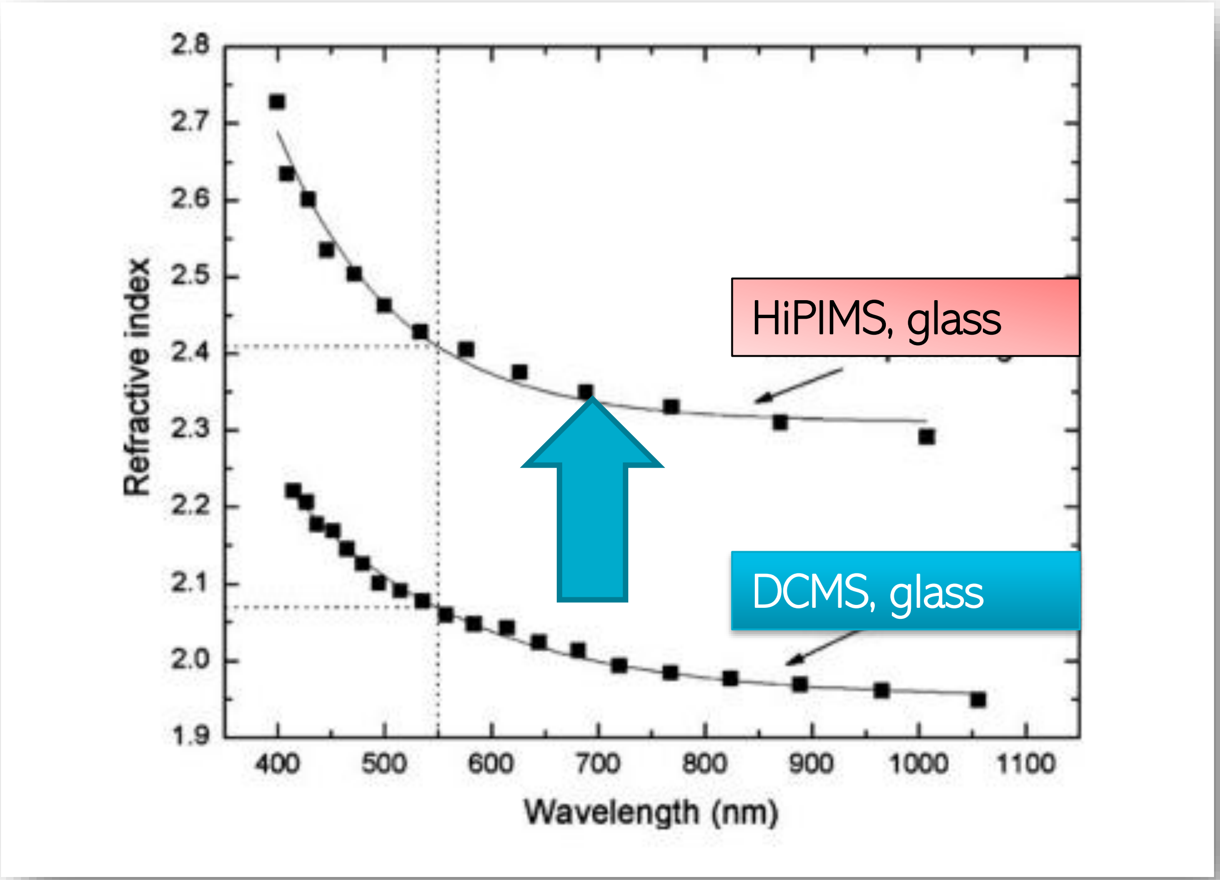
CrN films



Alami et al, J. Phys. D: Appl. Phys. 2009

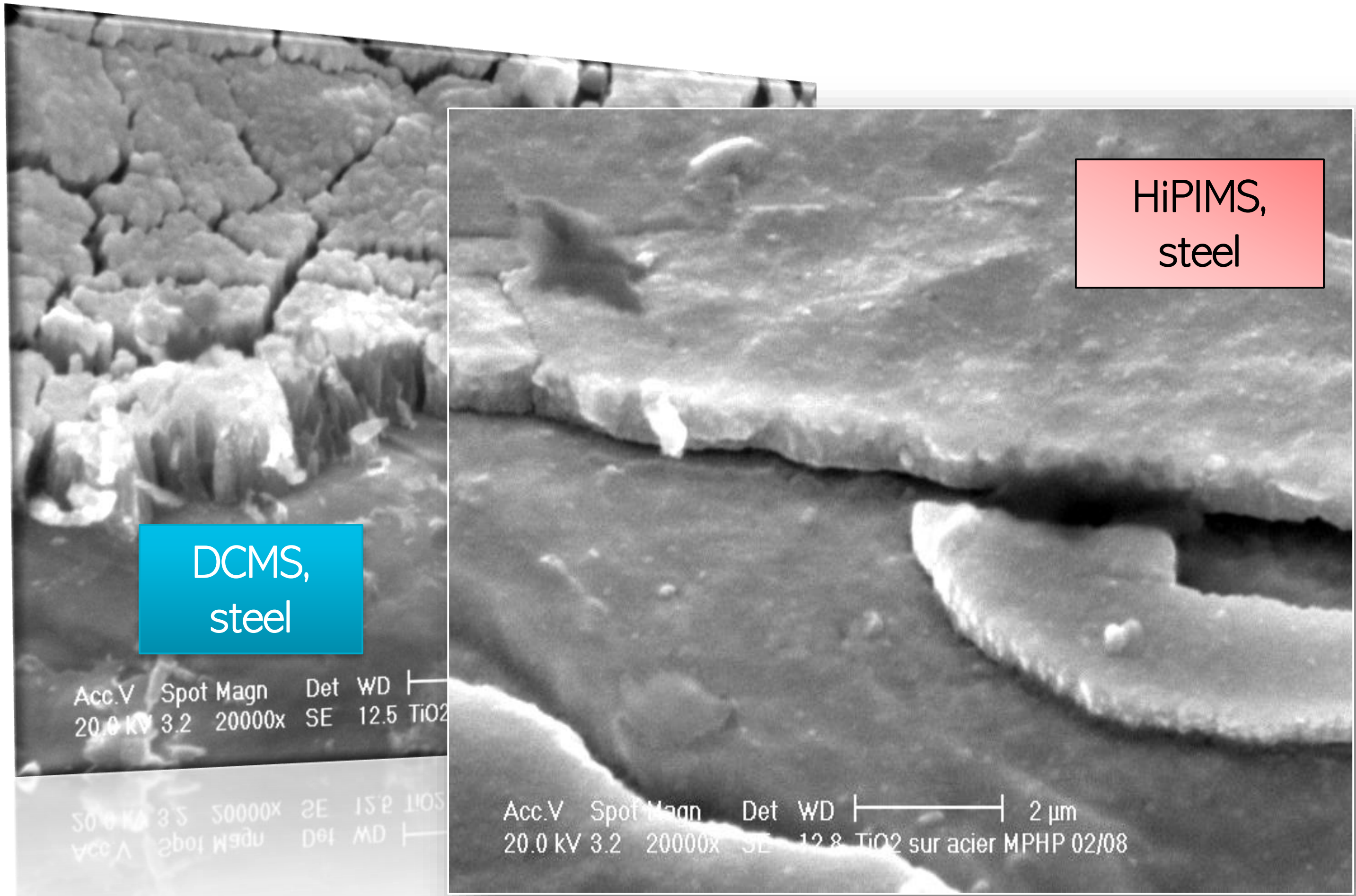
Increased refractive index of TiO_2 films

Anatase films deposited on glass



Konstantinidis et al, Thin Solid Films (2006)

Increased compactness



Konstantinidis et al, Thin Solid Films (2006)

Deposition of photocatalytic TiO_2 onto polymers

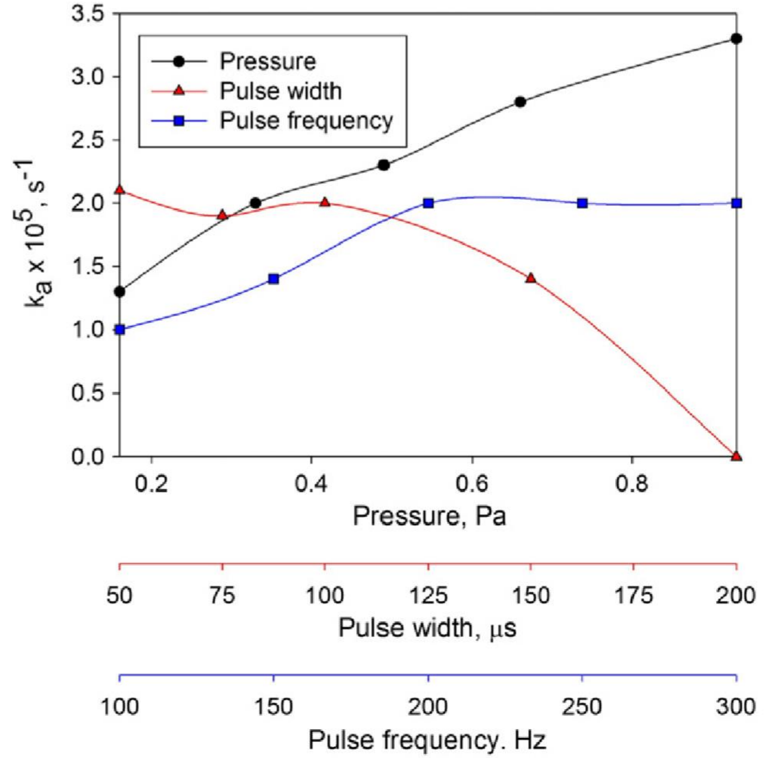


Fig. 5. First rate order constant value for the process of photodegradation of MB as a function of sputtering parameters (pressure, pulse width, pulse frequency).

100 nm thick films

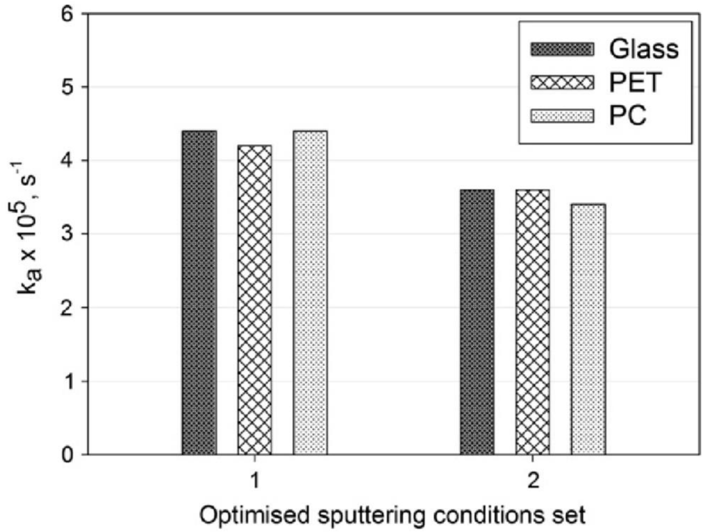


Fig. 7. First rate order constant value for the process of photodegradation of MB of the coatings deposited onto various substrate types under optimised conditions.

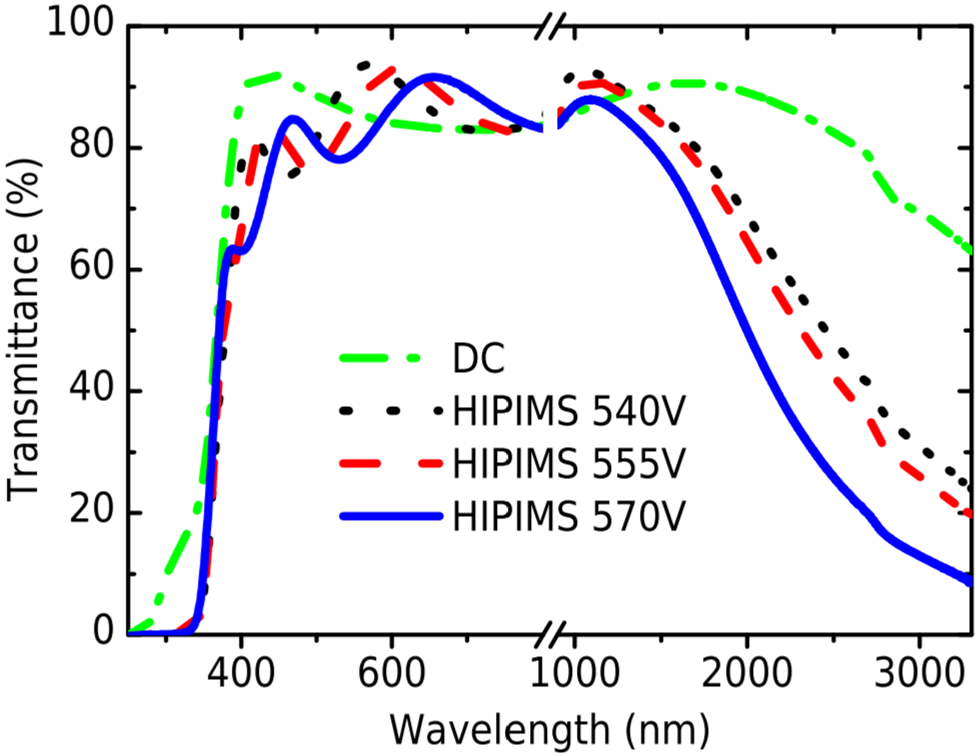
Ratova et al, Surf. Coatings Technol. (2014).

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

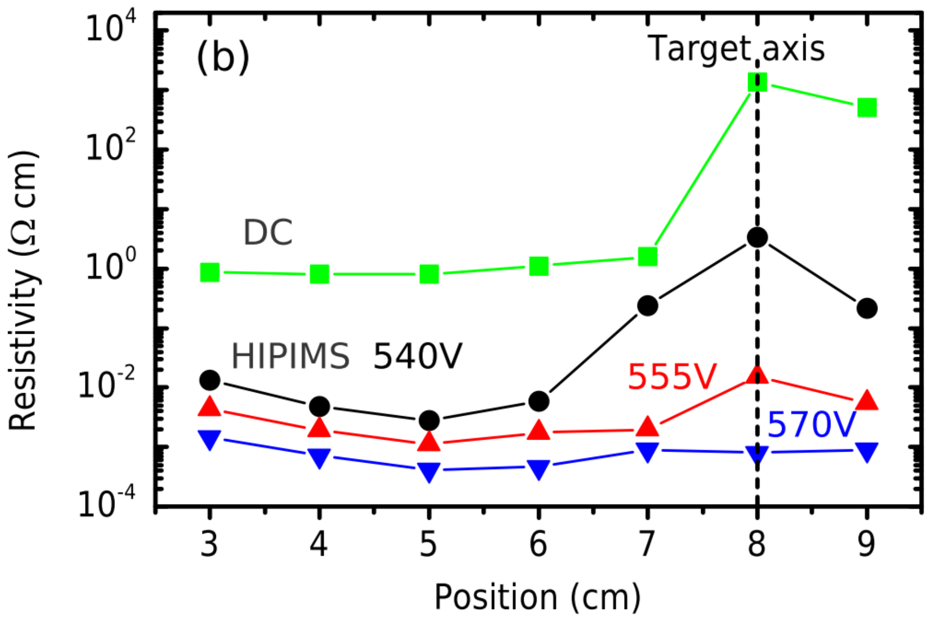


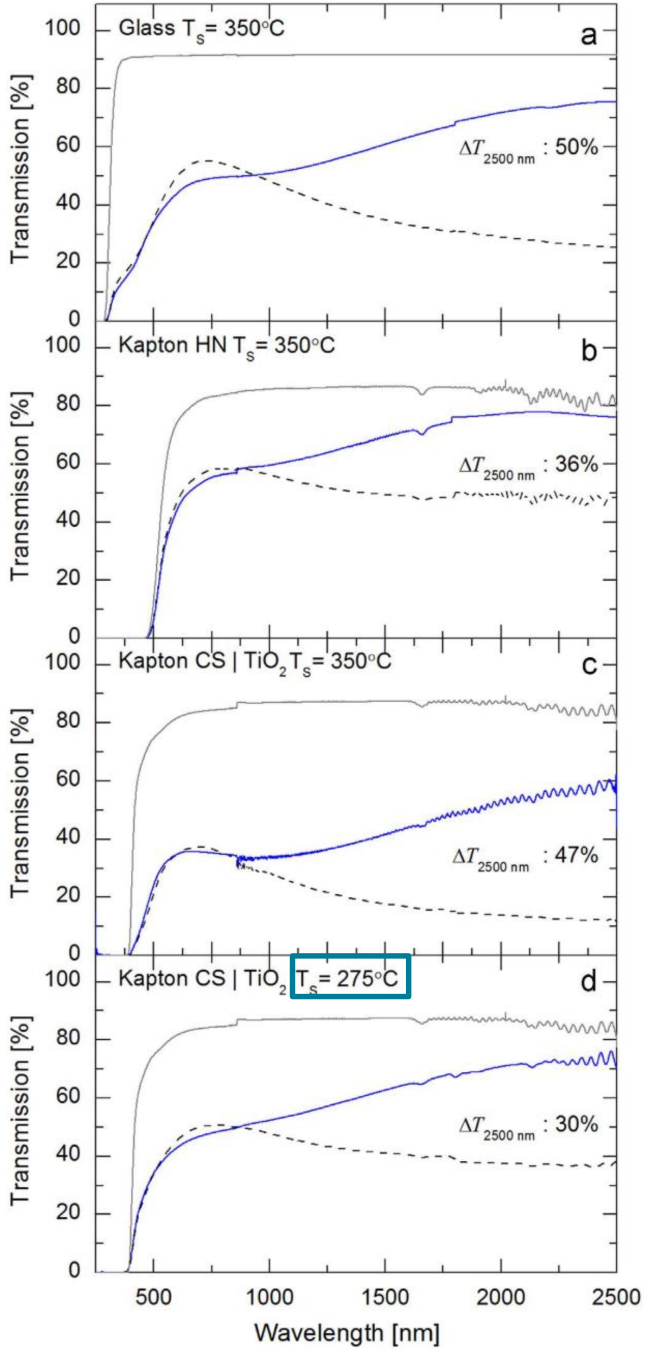
Table S2: Hall effect measurement results of the AZO film deposited using HiPIMS at 570 V

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 low temperature



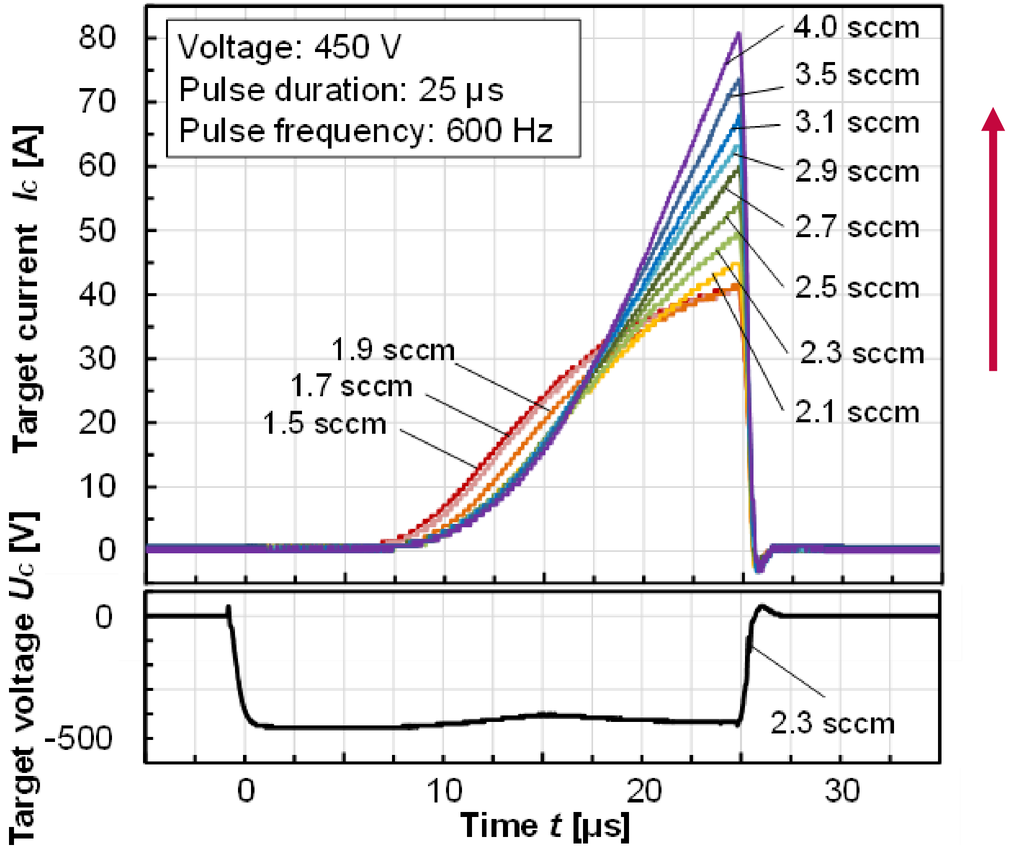
S. Loquai et al, Sol. Energy Mater. Sol. Cells (2016).

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

Recent developments in HiPIMS technology

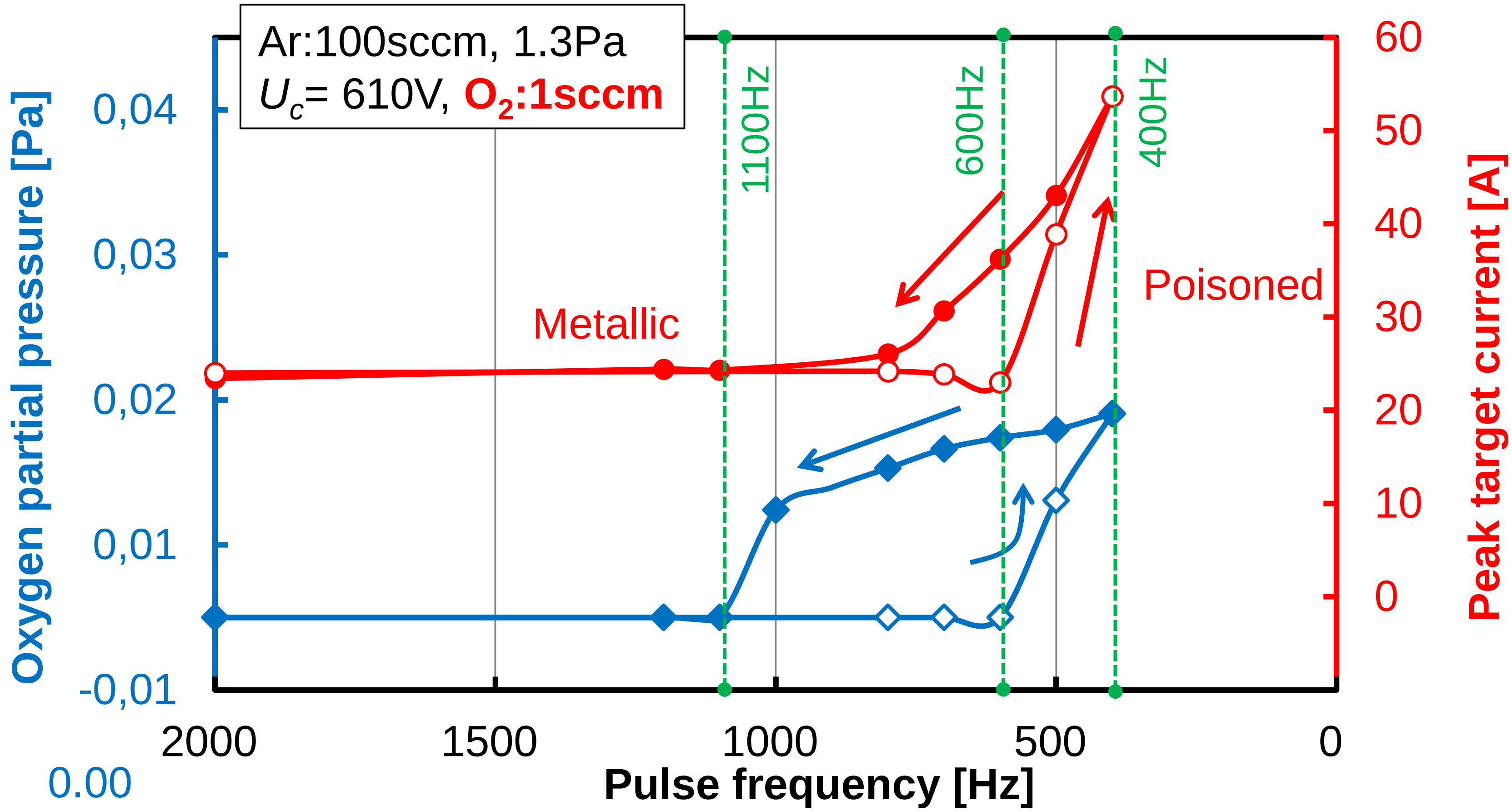
1. Peak curent controlled reactive HiPIMS
2. Bipolar HiPIMS

Peak curent controlled R-HiPIMS

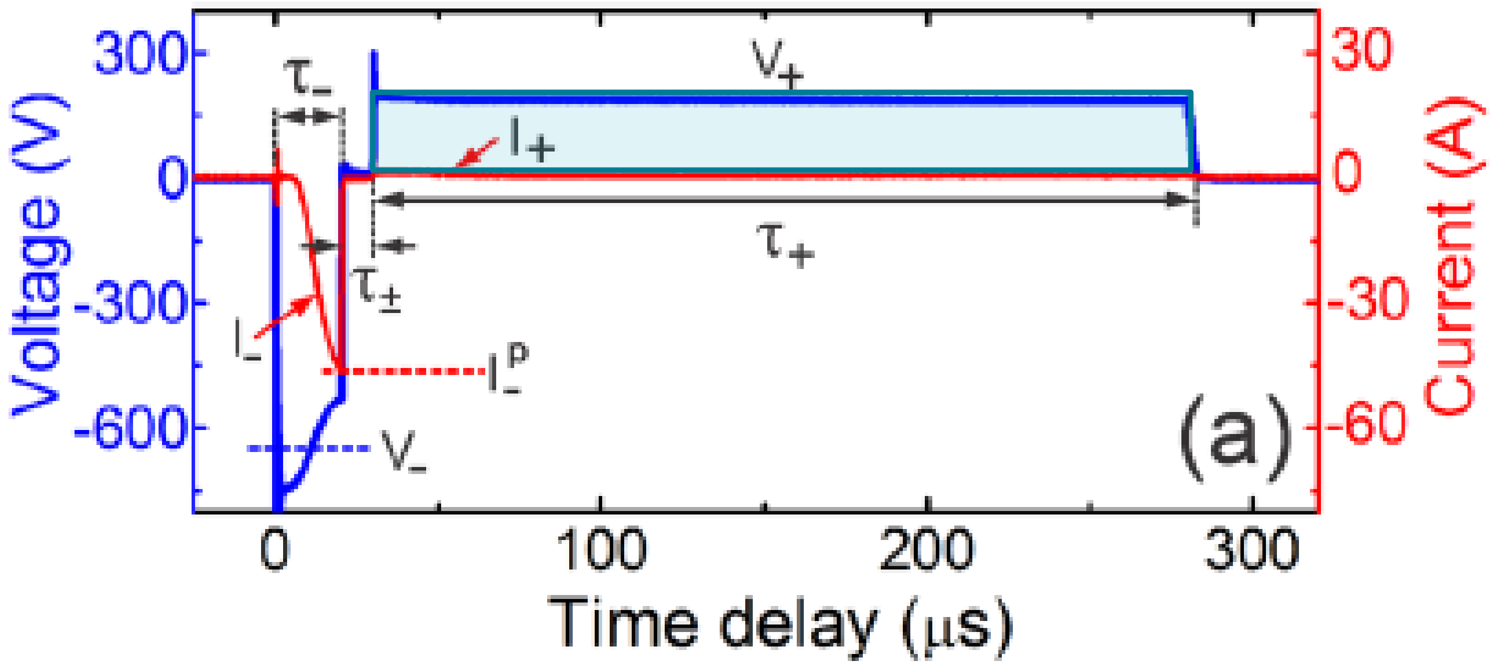


T. Shimizu et al., J. Phy. D (2016)

Controlling discharge conditions, working inside the unstable transition zone

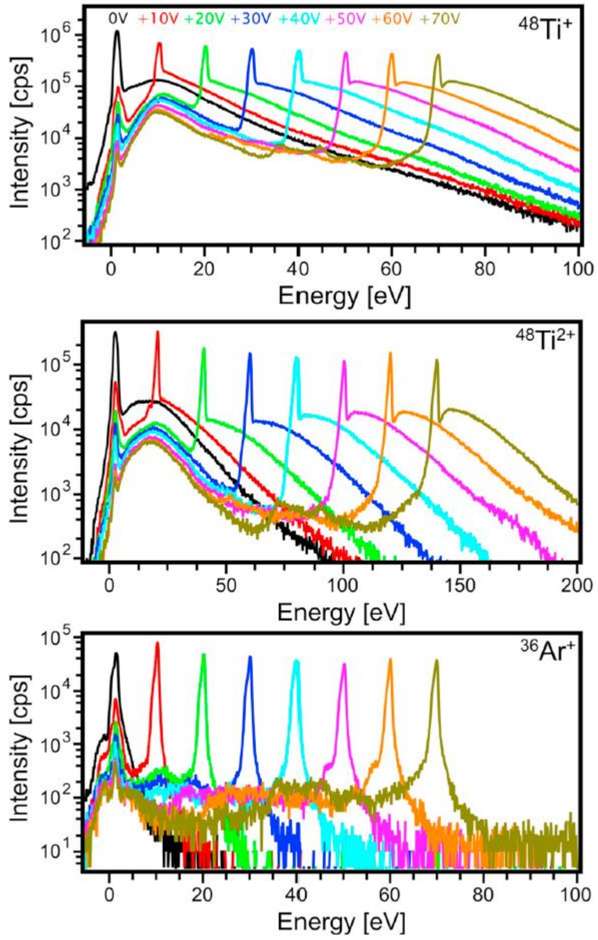


Bipolar HiPIMS controlling ion energy without the need of a substrate bias

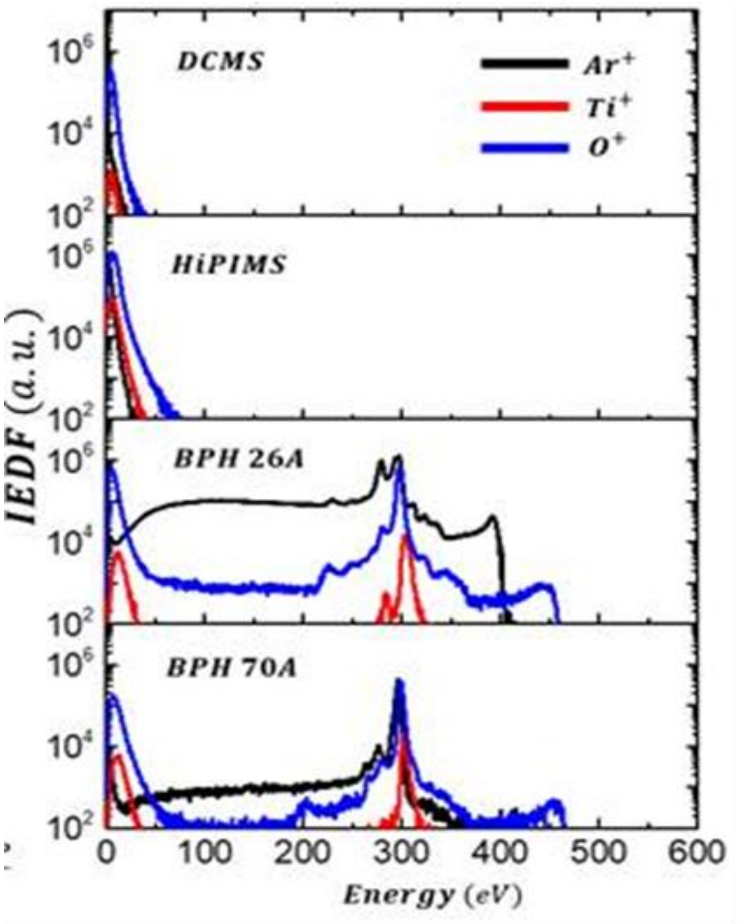


Britun et al, Appl. Phys. Lett. (2018).

Ion energy is controlled by the positive voltage

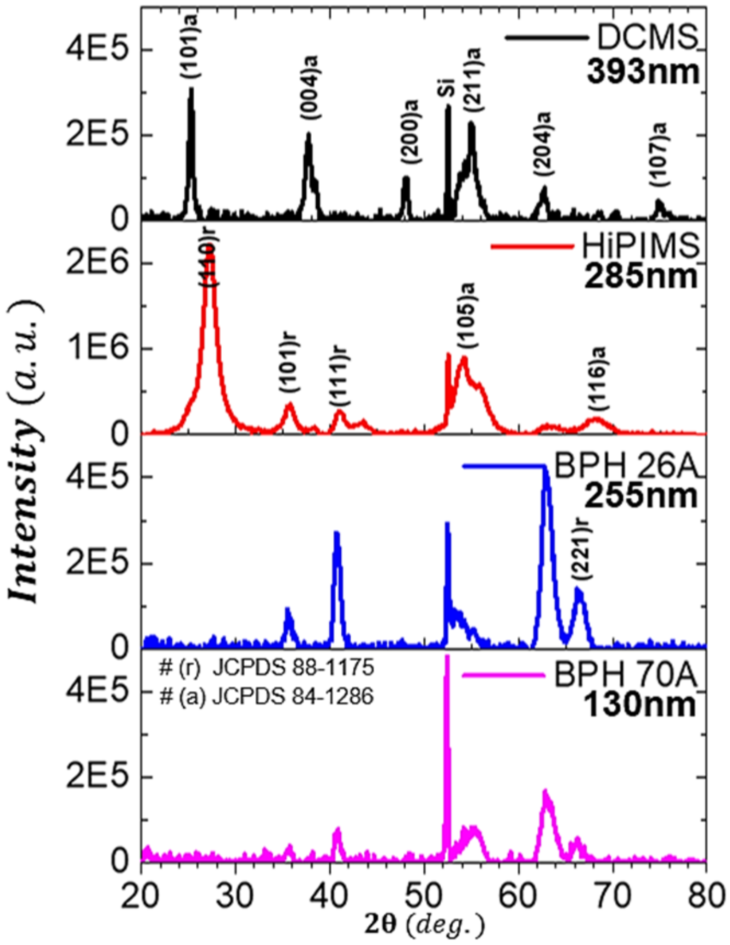


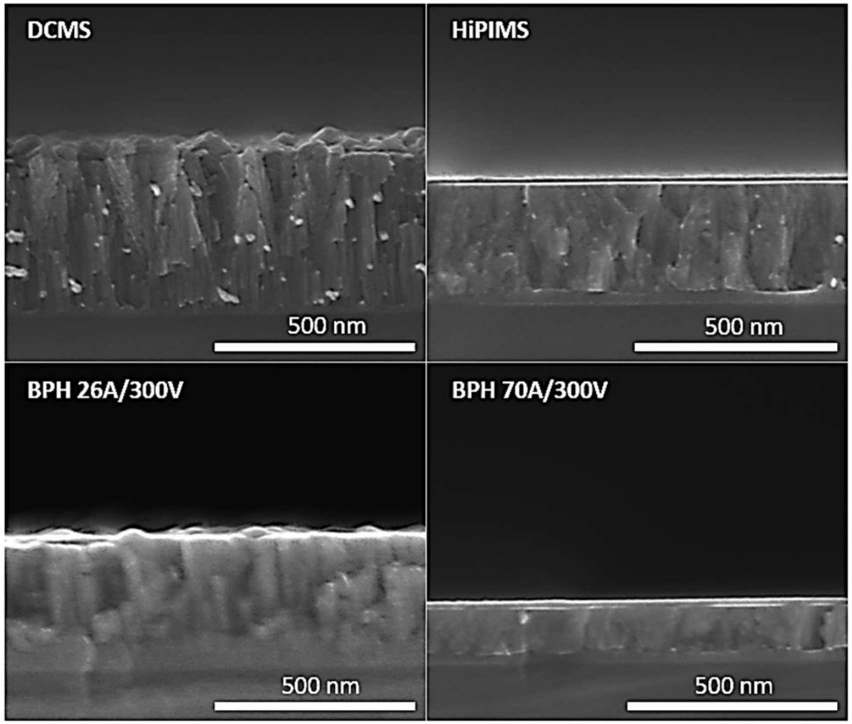
Keraudy et al Surf. Coat. Technol. 2018



M. Michiels et al, manuscript in preparation

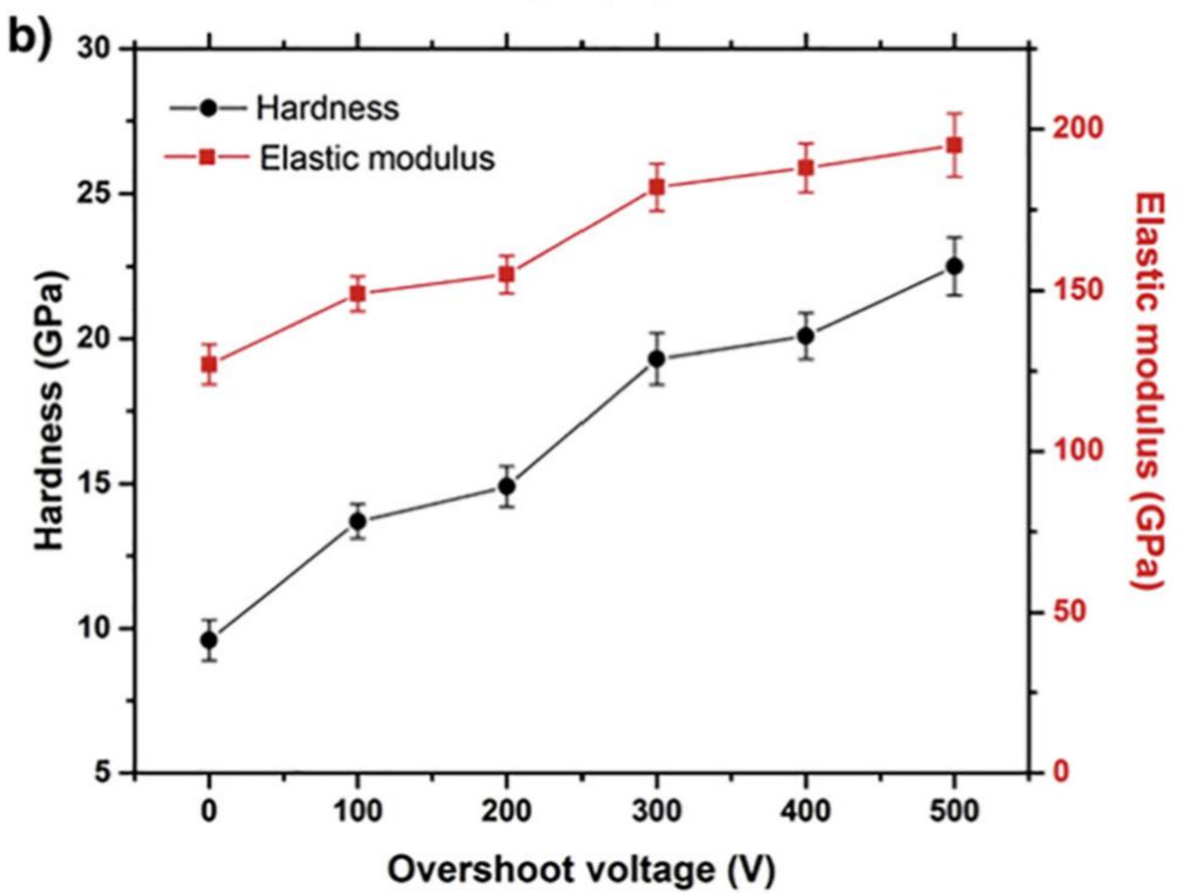
TiO_2 by Bipolar HiPIMS on glass substrates





M. Michiels et al, manuscript in preparation

Influence of positive voltage on the properties of DLC coatings



Santiago et al, Surf. Coatings Technol. (2019).

Summary

1. HiPIMS promotes intense ion bombardment during deposition which 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 oxides onto temperature sensitive materials like polymers

3. Recent developments aim at providing even more control on the film growth process

In Mons, we don't have dears but we have a dragon