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

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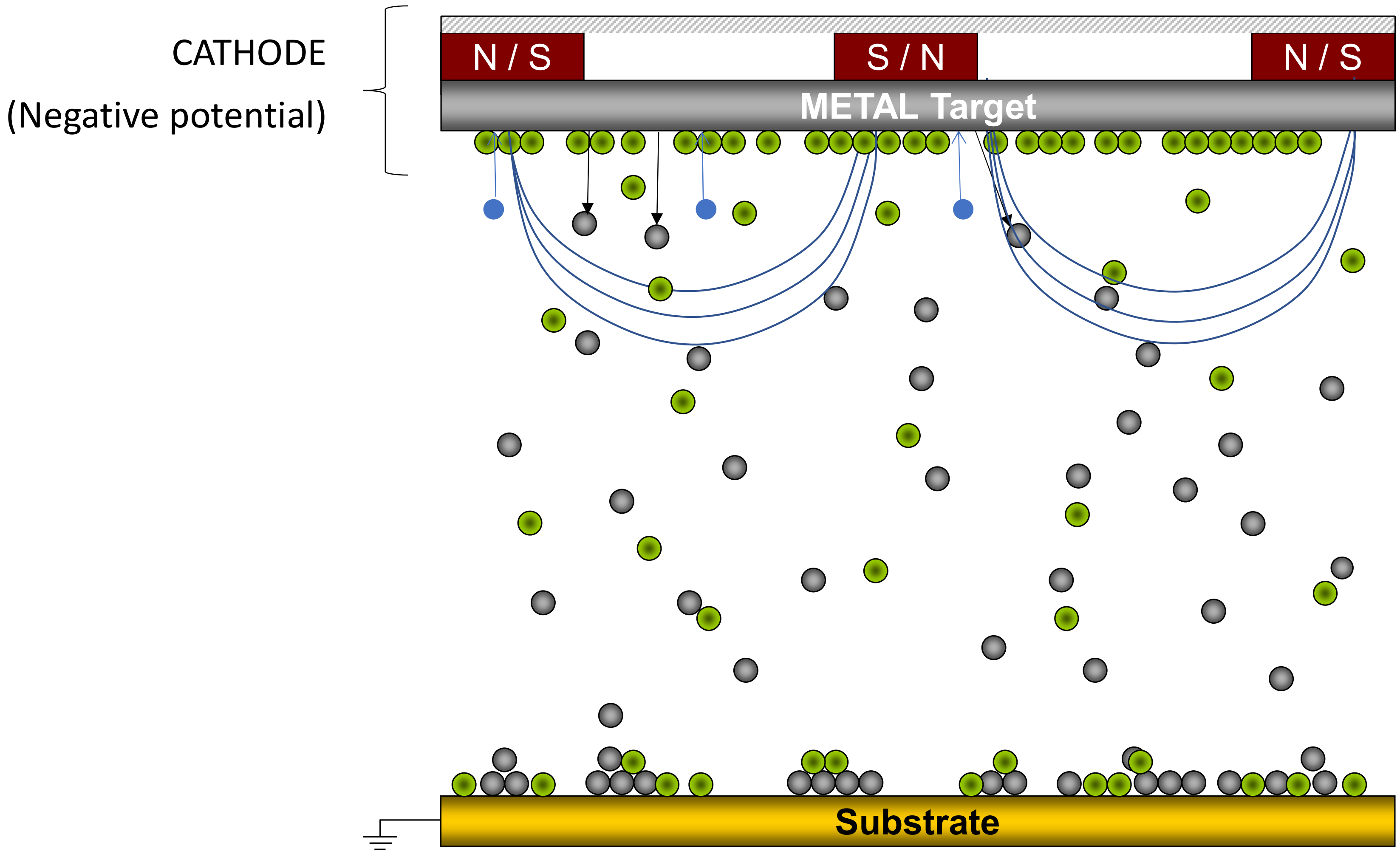
ISPlasma/IC-PLANTS

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

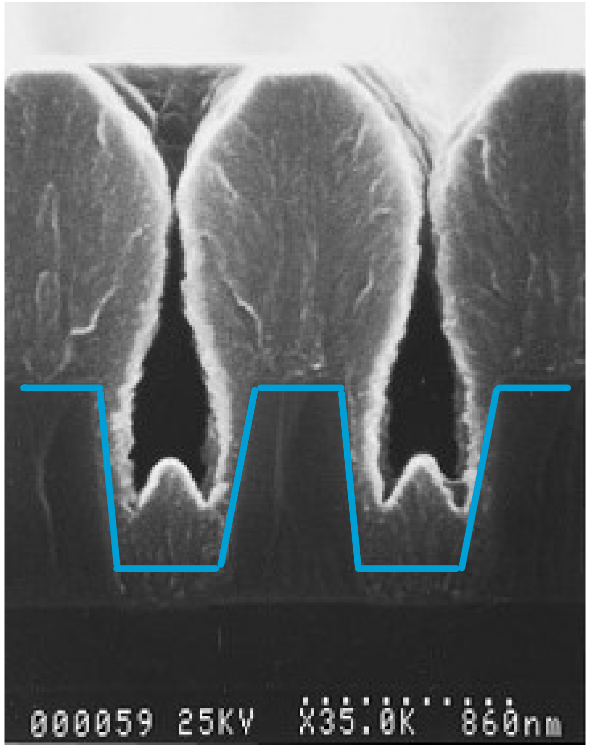
2. **What happens** if **we** implement HiPIMS for the synthesis of transition metal oxide thin films ?

Conventional DC magnetron sputter deposition



Magnetron sputtering in the Industry

Filling trenches 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

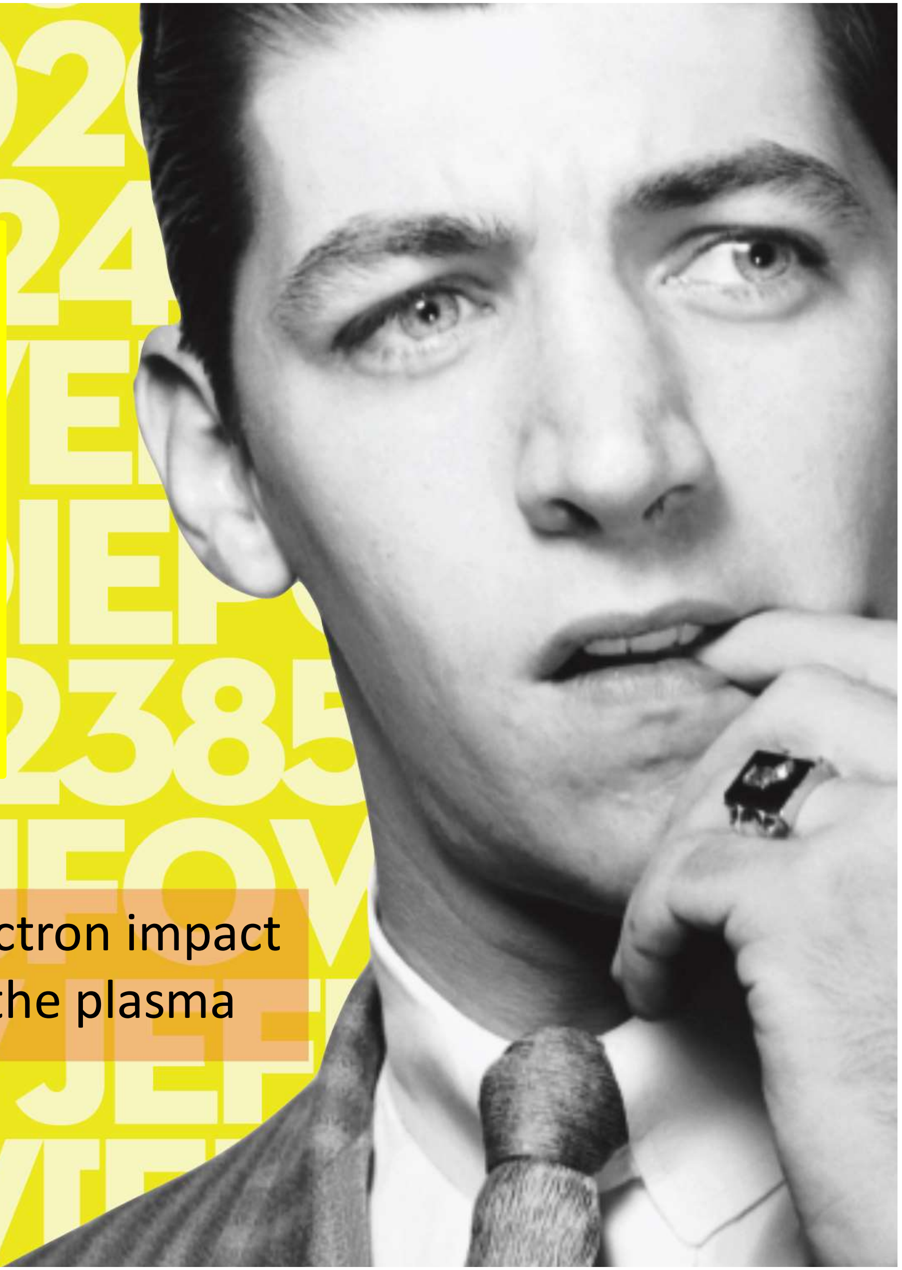
☛ Conformal deposition

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

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

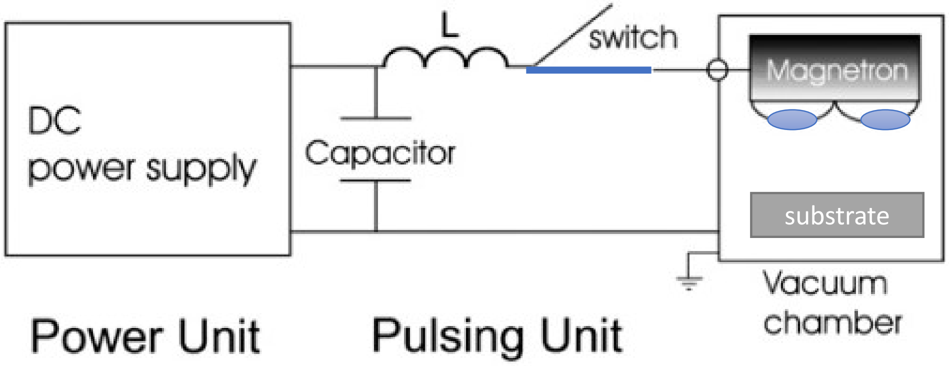
Sarakinos, Alami, Konstantinidis, Surf. Coat. Technol 2010

How can we do that?



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

Architecture of an HiPIMS generator

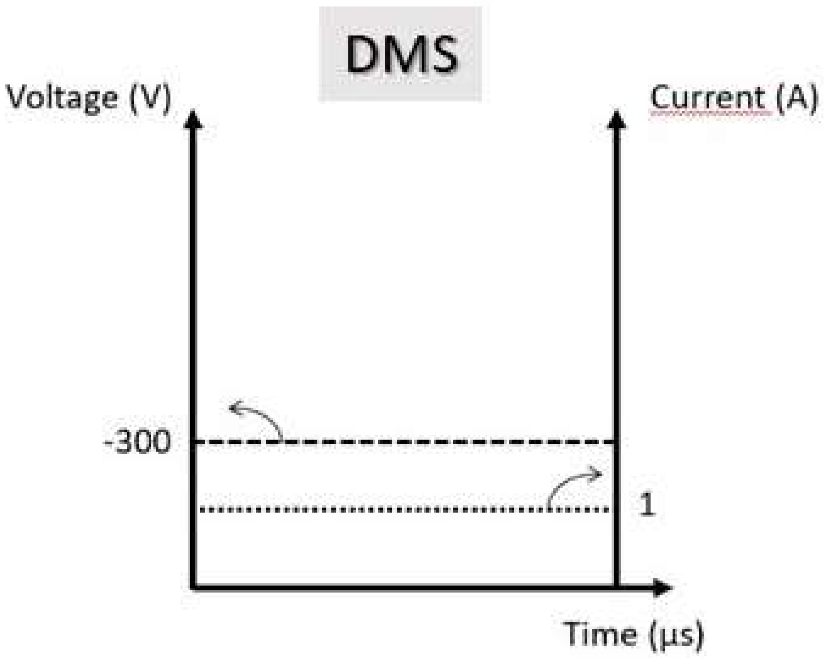


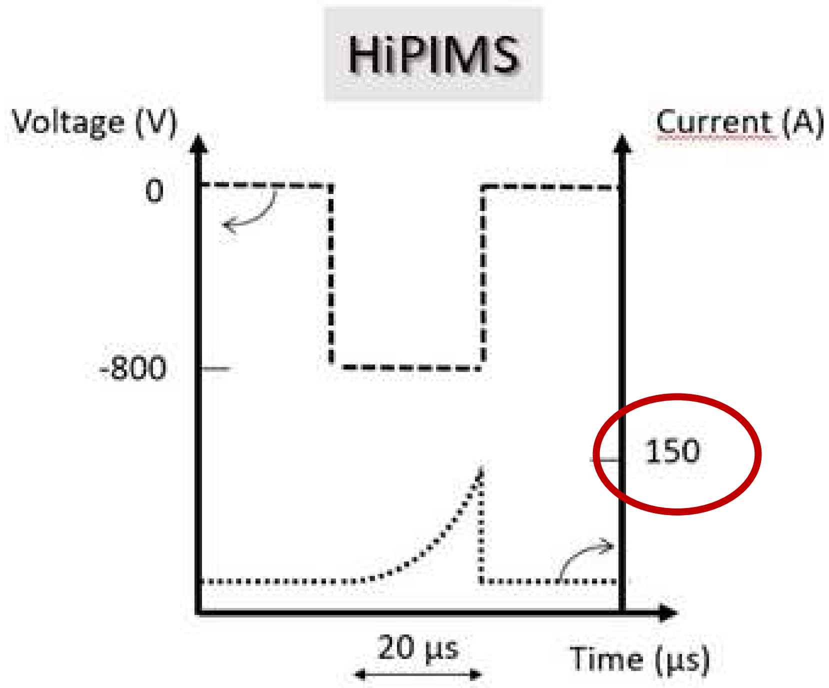
- The power supply delivers:
  - Voltage up to 1 – 2 kV
  - Peak current (power) equal to ~A/cm^2 (~kW/cm^2)

- Pulsed discharge to avoid overheating the target/magnets

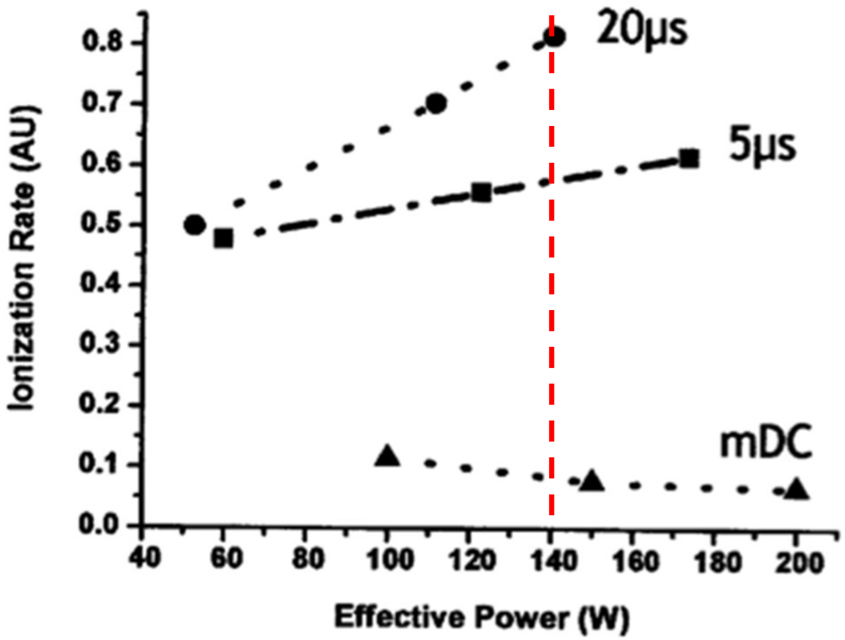
Current-Voltage-Time waveforms

Average sputter power 300W / 1.3 Pa / 5 cm in diam. Ti target

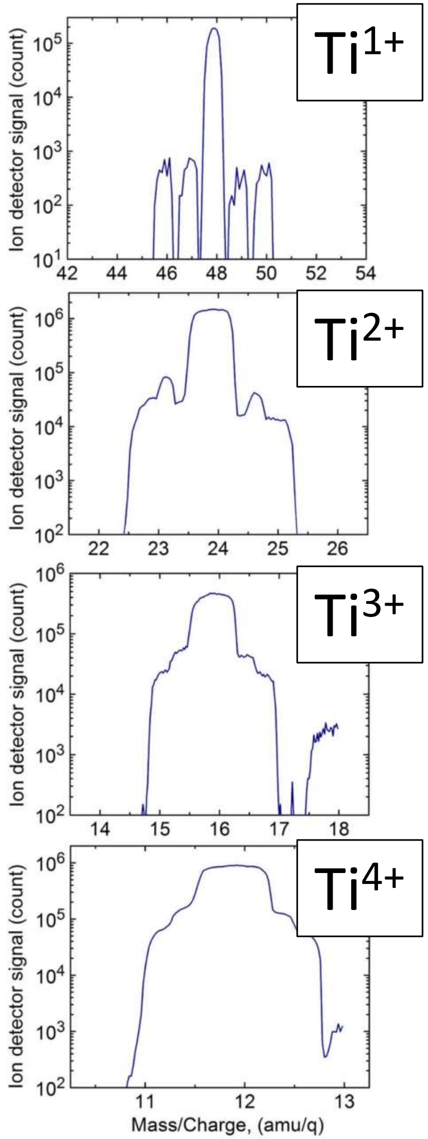




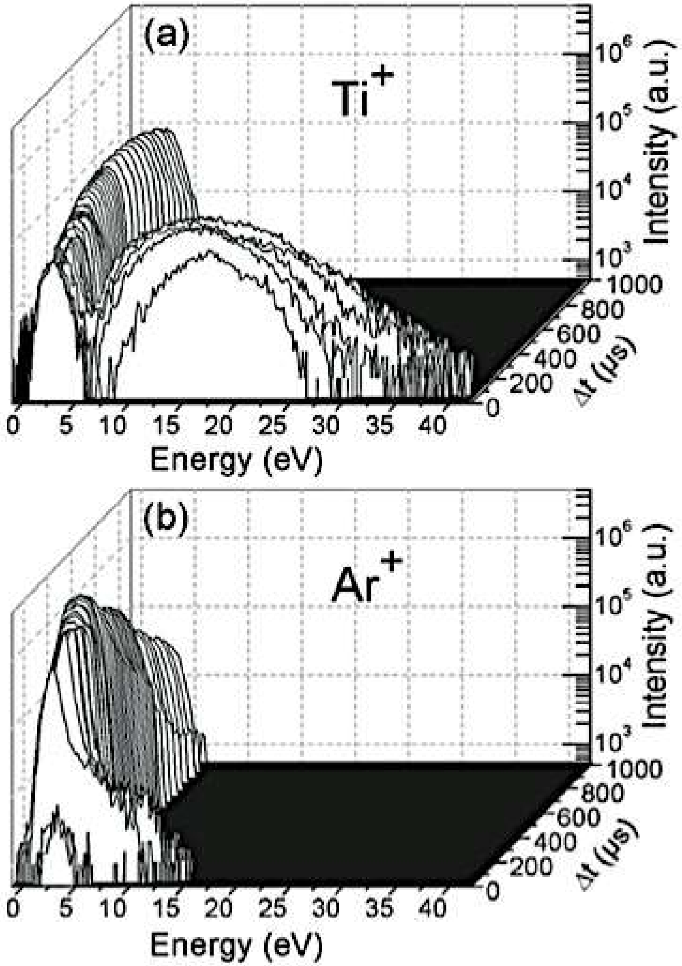
Towards the production of ionized metal atoms



Konstantinidis, J.Appl. Phys. (2006)



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



Plasma dynamics

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

Towards a « definition » of HiPIMS

1. Magnetron plasma
   - Glow discharge in ExB fields, at low pressure (~Pa range)

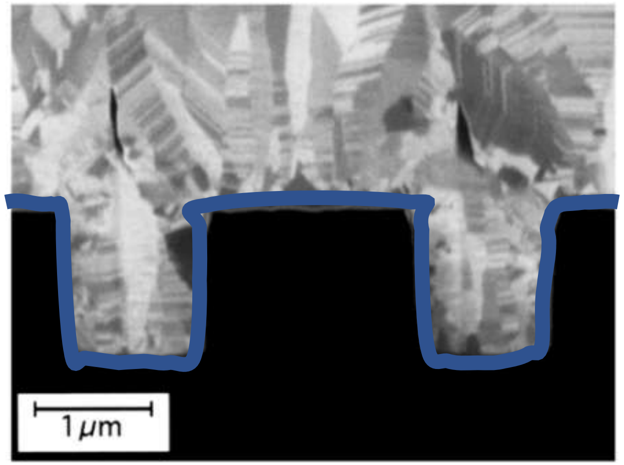
2. Electric pulses
   - Duty cycle ≤ 1%

3. High power/peak current
   - ~kW / A cm^{-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.

Enabling conformal deposition on complex-shape objects …



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

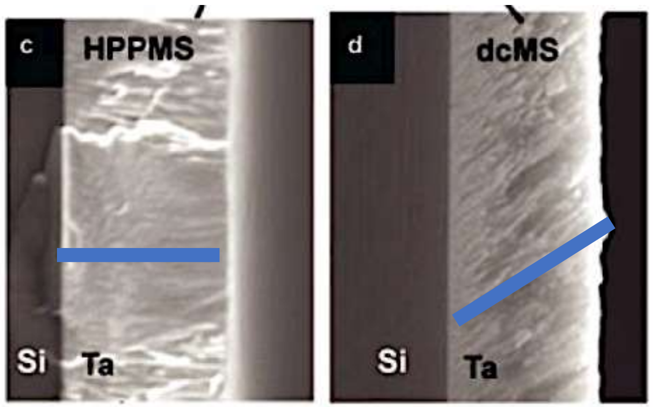
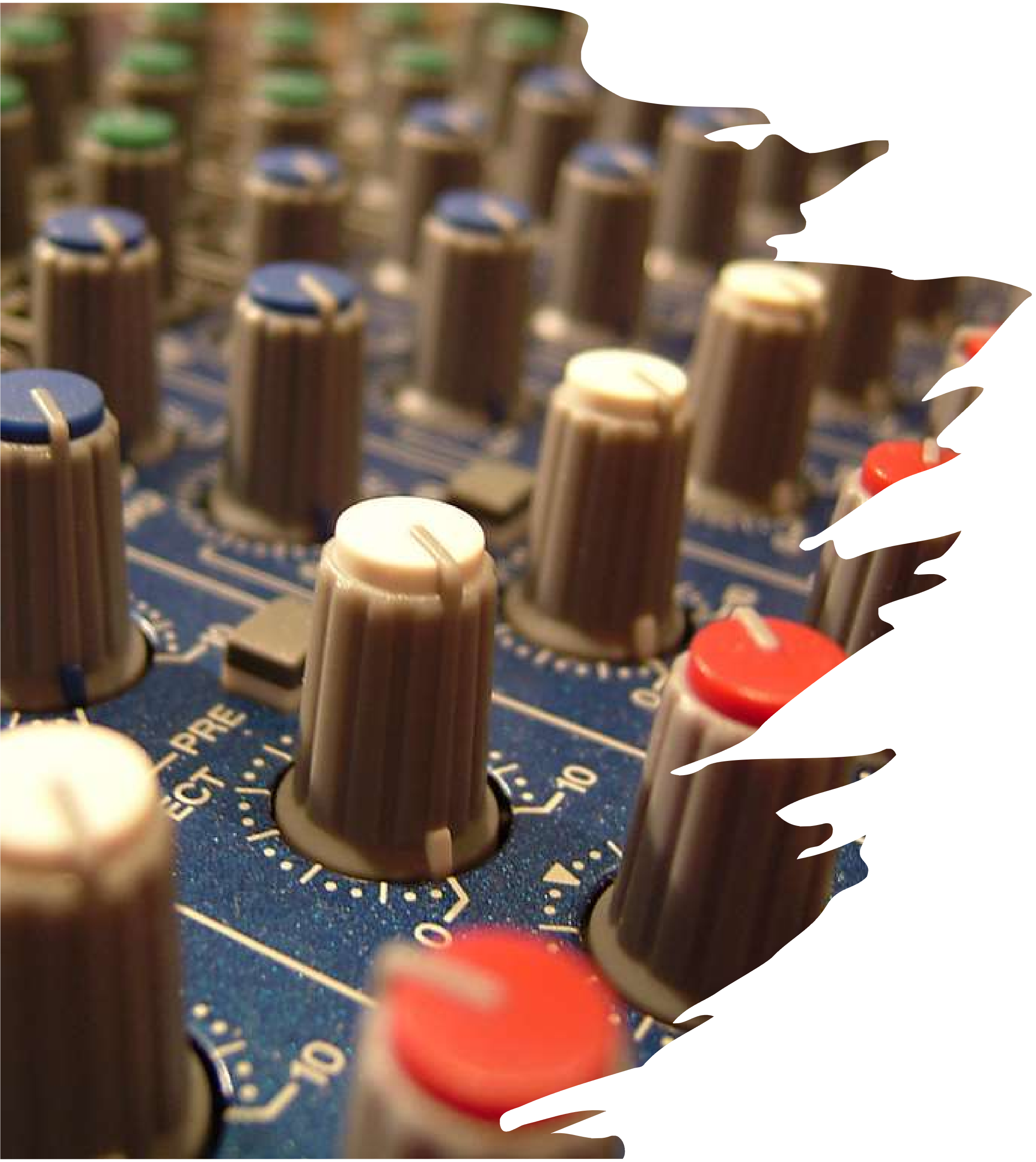


FIG. 1. SEM images of Ta films grown by HPPMS sputtering and dcMS near the opening of the trench (a) and (b), and approximately half way along the wall of the trench (c) and (d). Both films were grown at room temperature with a substrate bias of −50 V.

Alami et al, JVST A (2007)



... and providing 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**

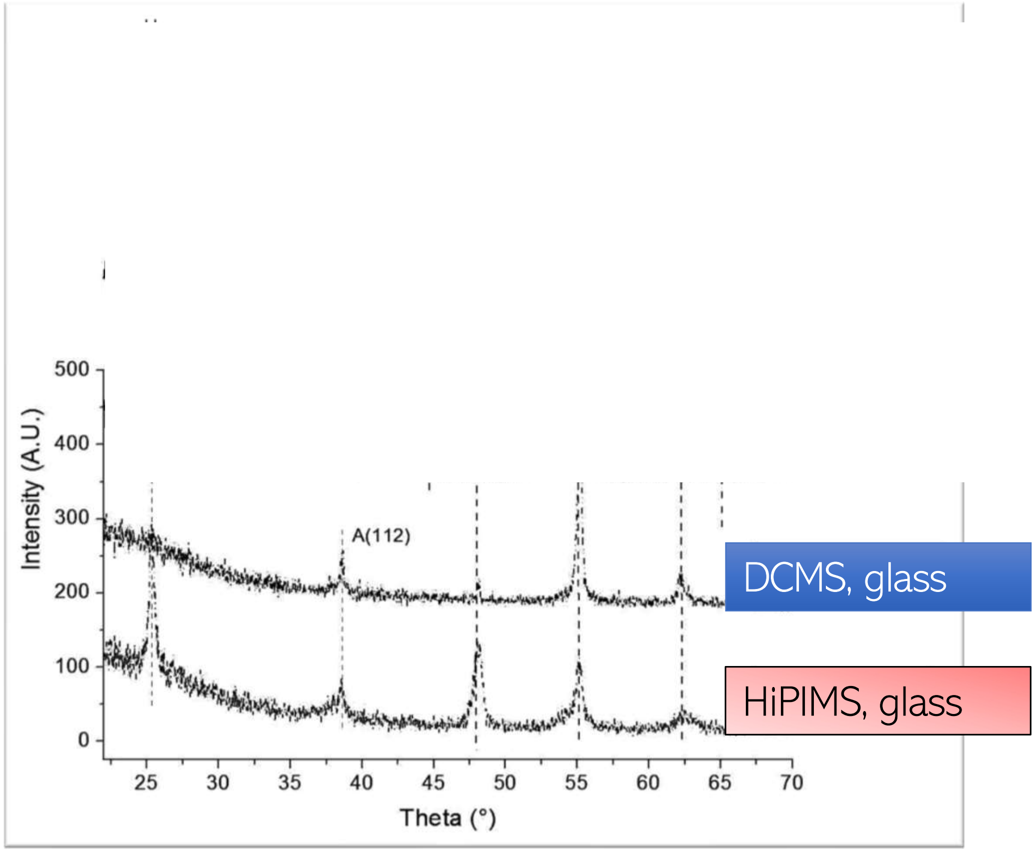
On the synthesis of functional metal oxide thin films by HiPIMS

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

Titanium dioxide

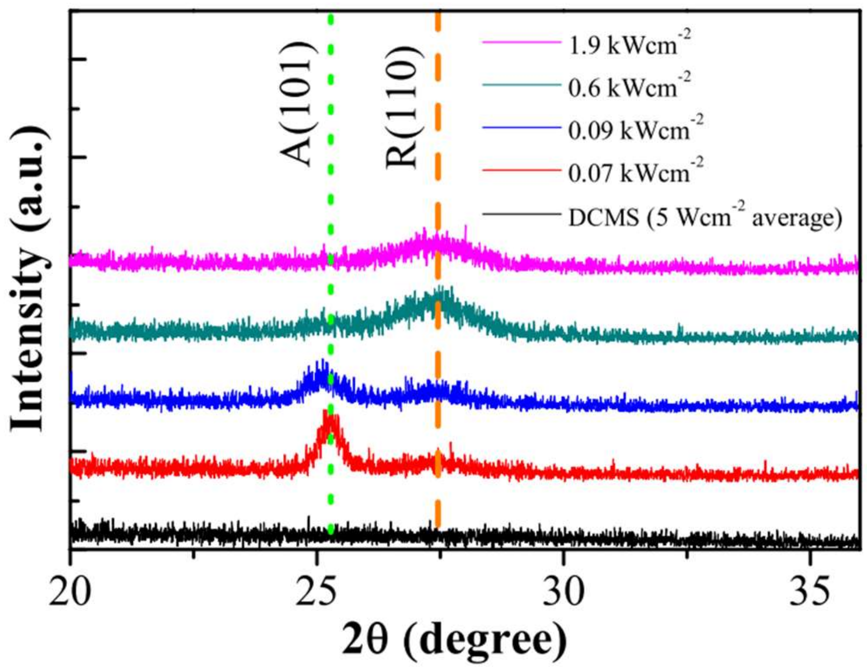
Applications in optics, catalysis

Growing high-temperature phase of TiO_2 by HiPIMS



Konstantinidis et al, Thin Solid Films (2006)

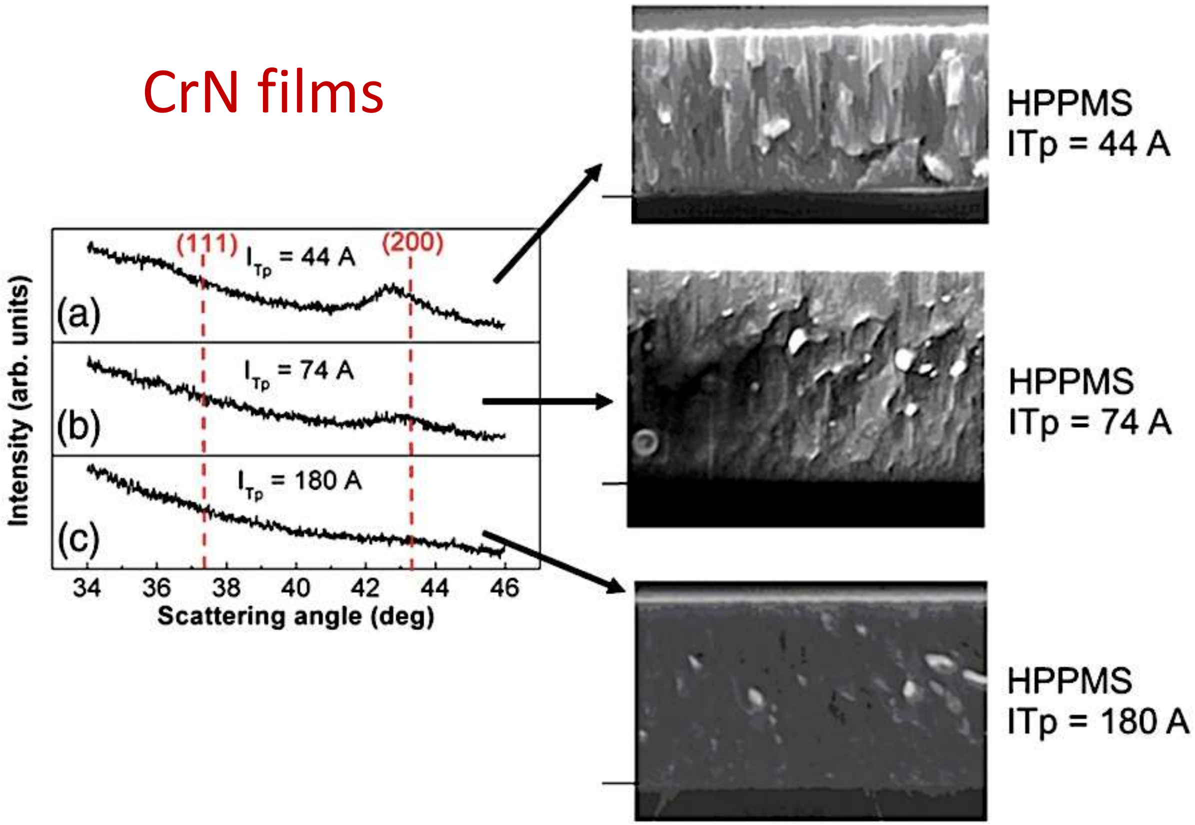
Modulating the phase constitution through peak power



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

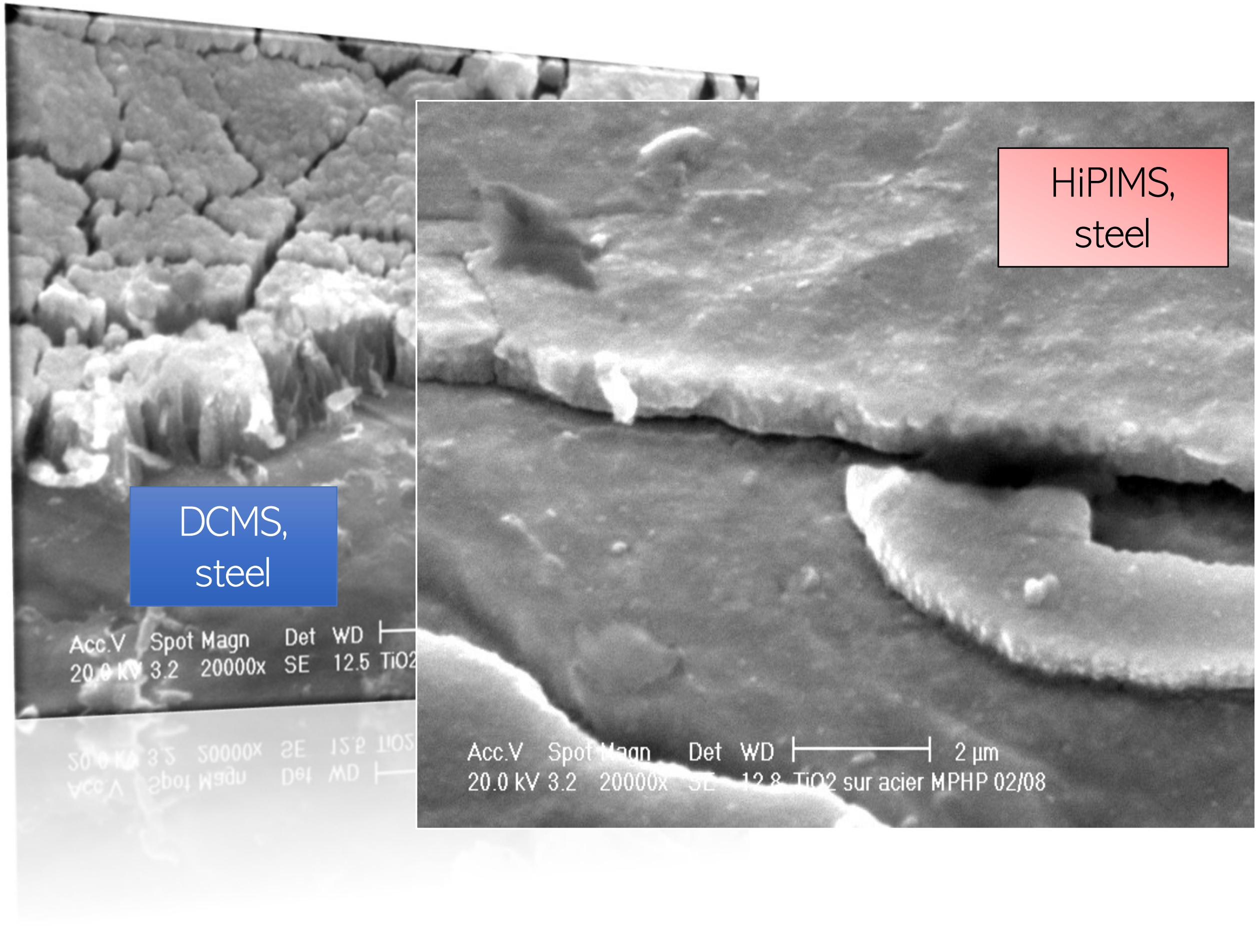
A too large ion flux may lead to amorphization

CrN films



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

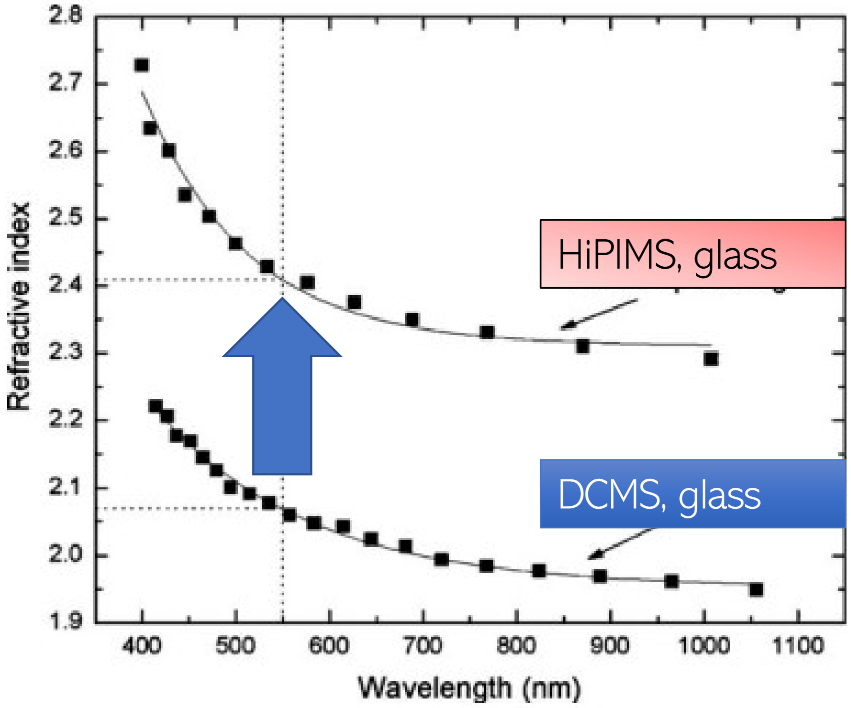
Increased compactness thanks to HiPIMS



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)

Efficiency of photocatalytic TiO_2 films deposited on polymers

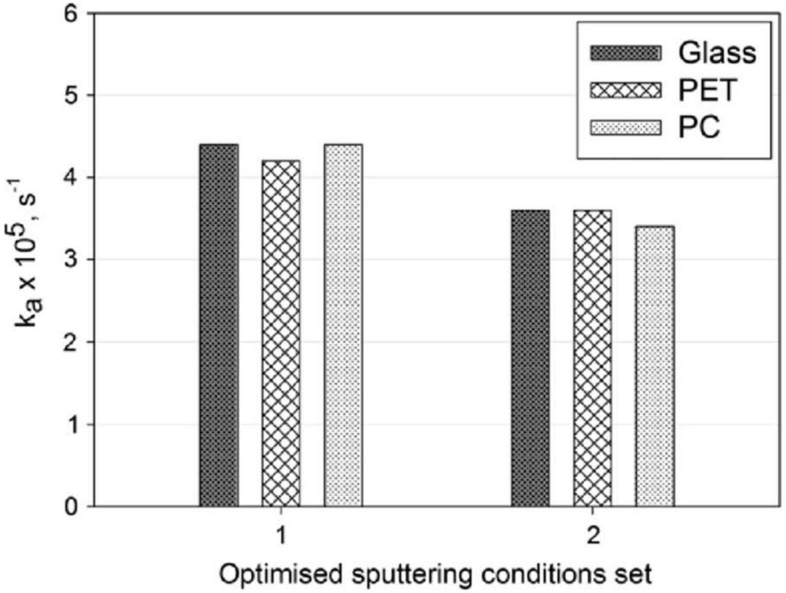


Fig. 7. First rate order constant value for the process of photodegradation of MB of the coatings deposited onto various substrate types under optimised conditions.

100 nm thick films

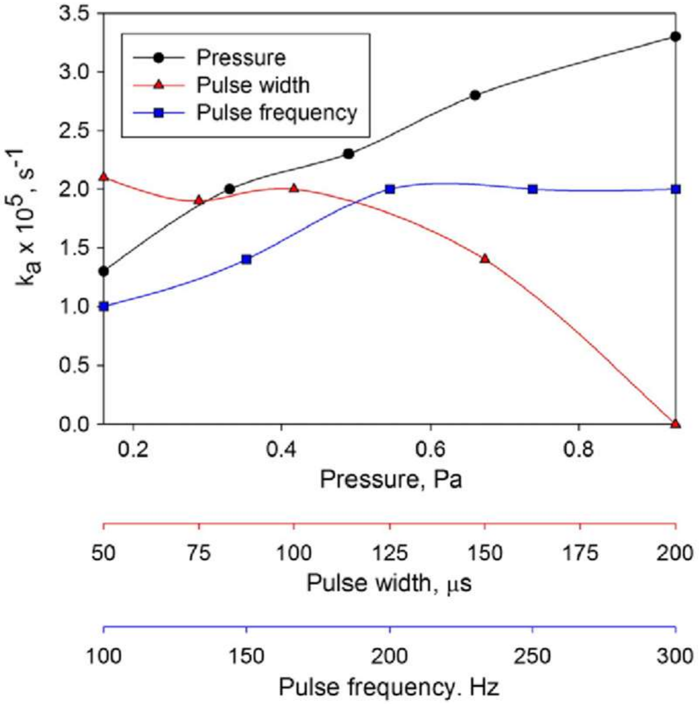


Fig. 5. First rate order constant value for the process of photodegradation of MB as a function of sputtering parameters (pressure, pulse width, pulse frequency).

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

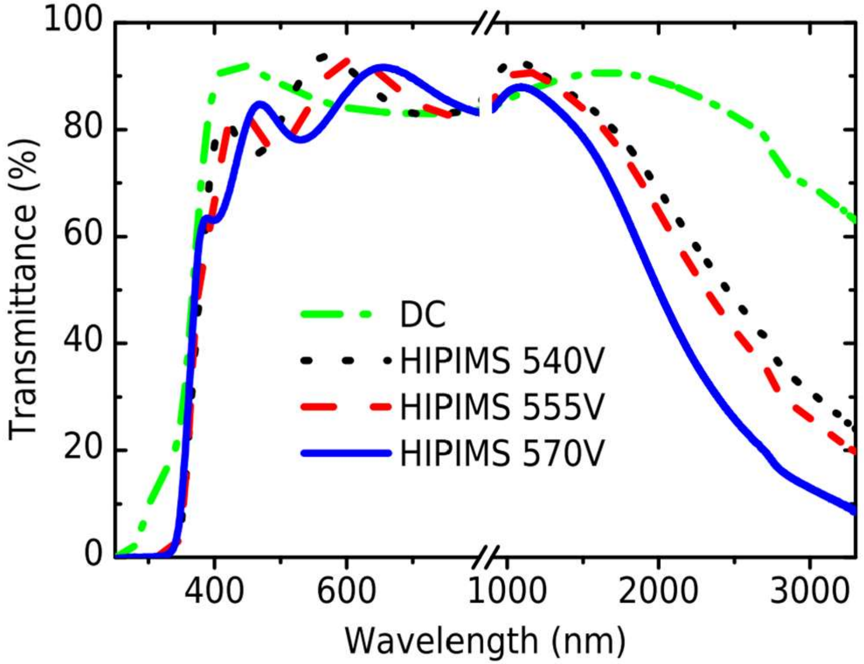
Al-doped ZnO

Transparent Conducting Oxide

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).

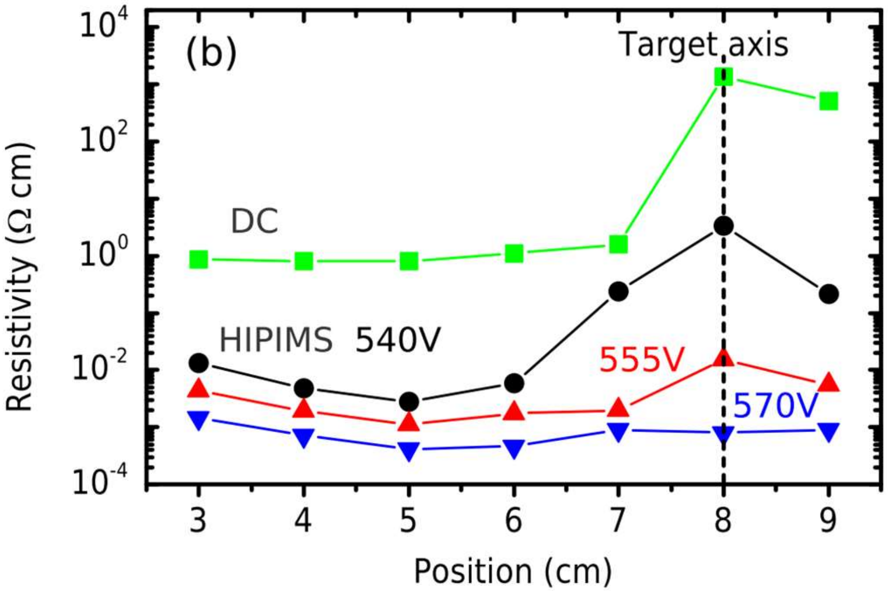


Table S2: Hall effect measurement results of the AZO film deposited using HiPIMS at 570 V

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).

Enhanced conductivity of ZnO:Al

- HiPIMS leads to:
  - Lower resistivity (10^{-4} Ω cm)
  - Improved spatial homogeneity

Vanadium dioxide

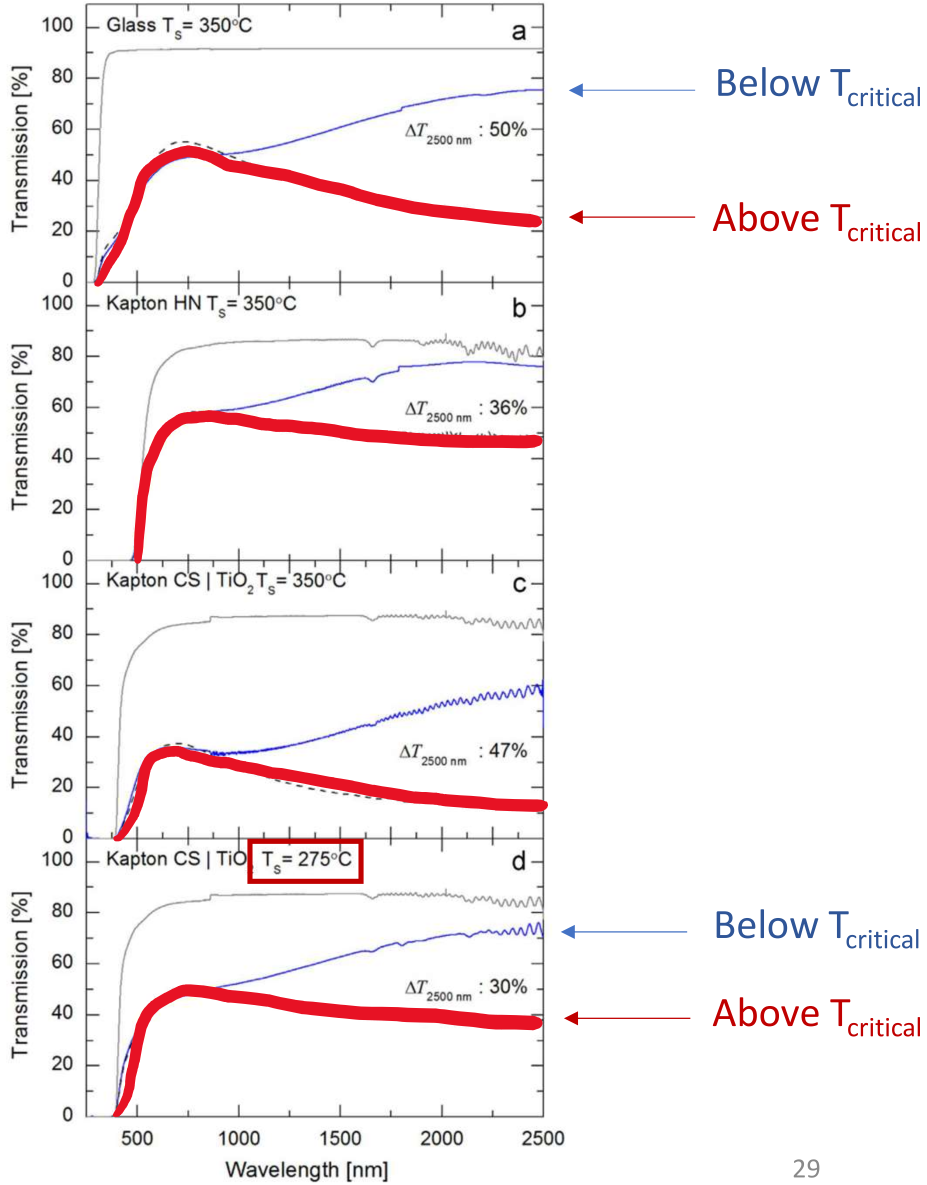
Thermochromism e.g., for smart window applications

Synthesis of thermochromic VO_2 at low temperature

$T_{critical}$ ~68°C

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).

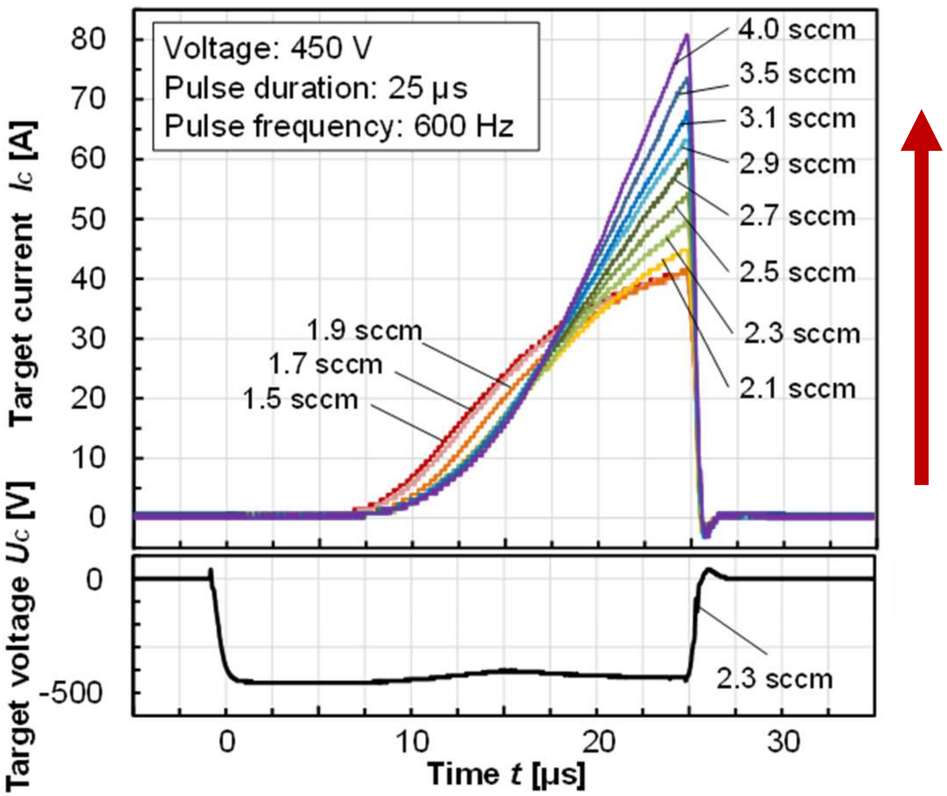


Recent developments in HiPIMS technology

- Peak curent controlled reactive HiPIMS
- Bipolar HiPIMS

Peak curent controlled Reactive HiPIMS

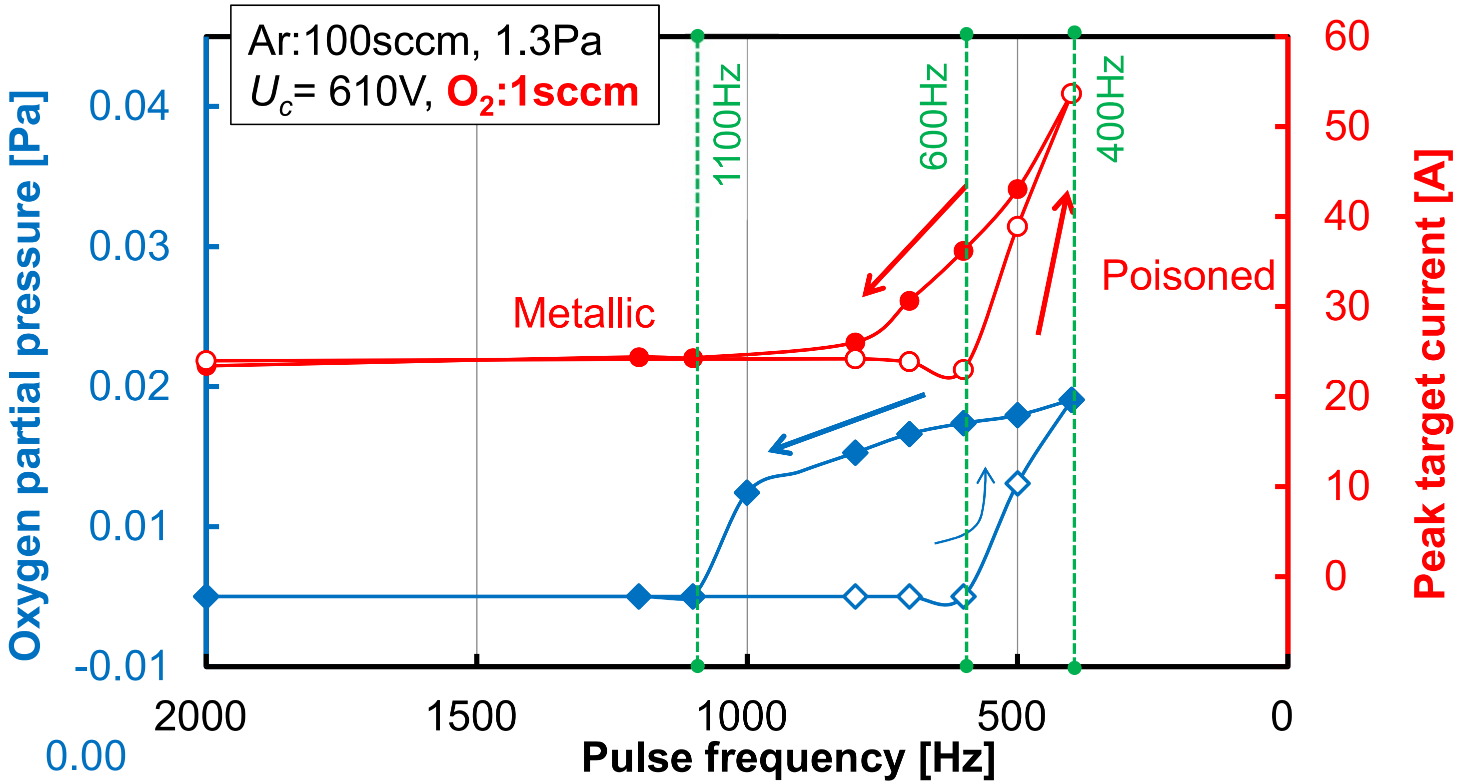
The peak curent increases as the reactive gas pressure increases



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

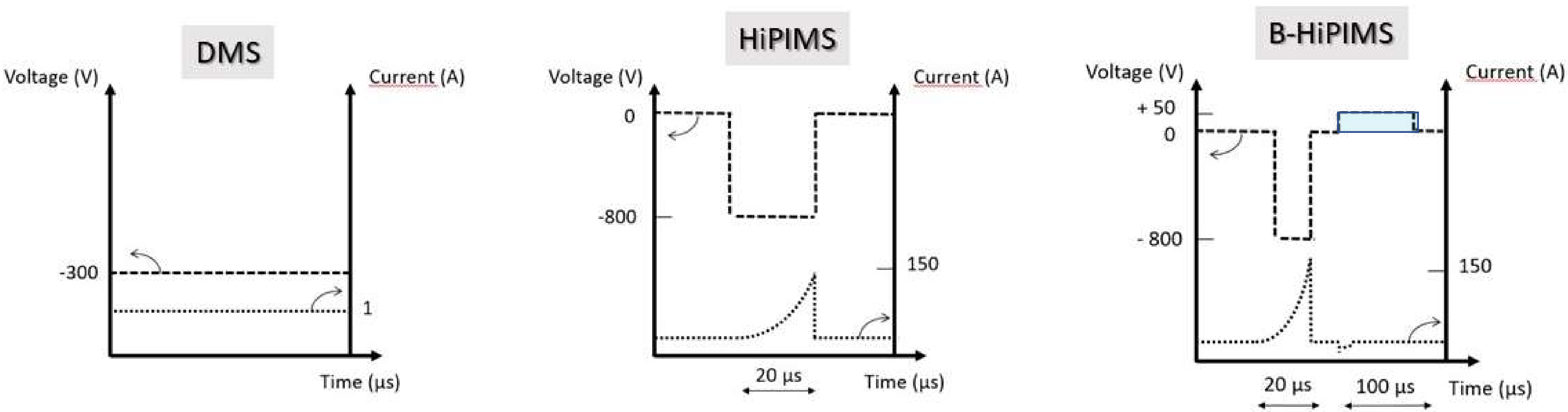
Hafnium nitride deposition

Controlling discharge conditions, working inside the unstable transition zone



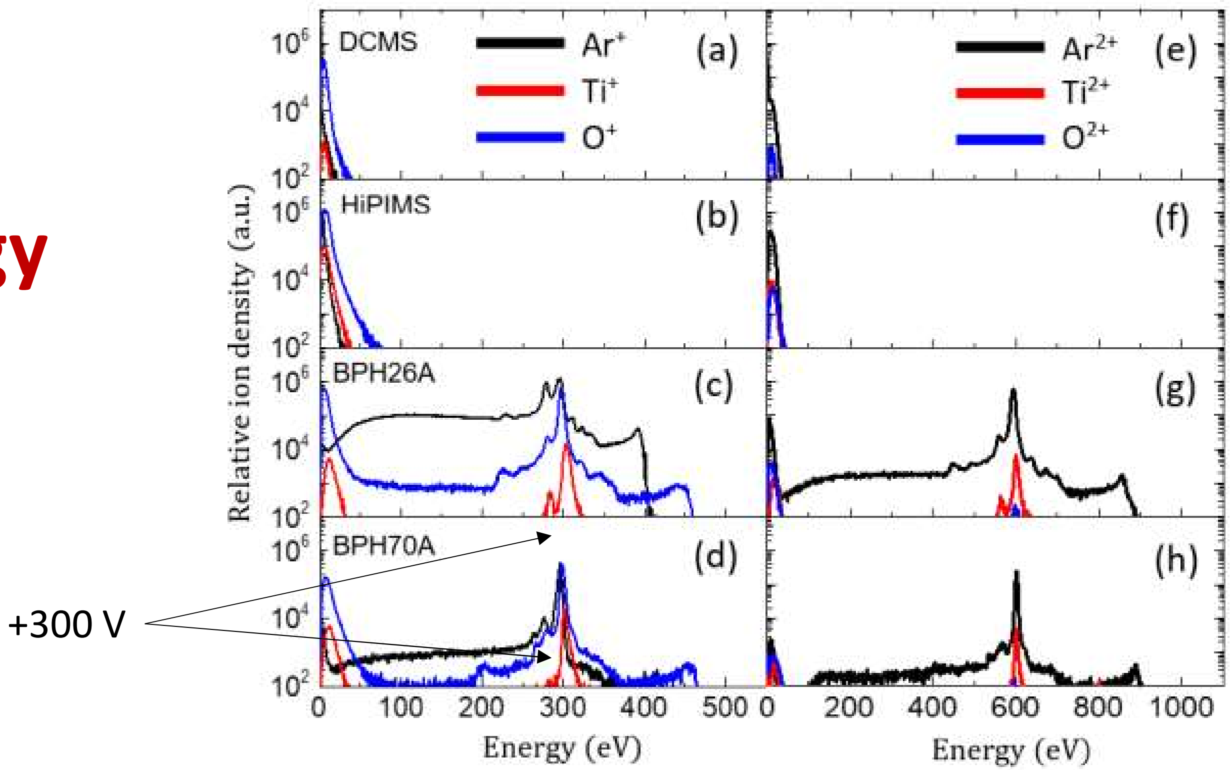
Shimizu et al., Intern. Conference on Reactive Sputter Deposition, Gent (Belgium), 2018.

How can we control the metal ion energy *without substrate bias* ?



Konstantinidis et al, J. Appl. Phys (2006)
Britun et al, Appl. Phys. Lett. (2018).

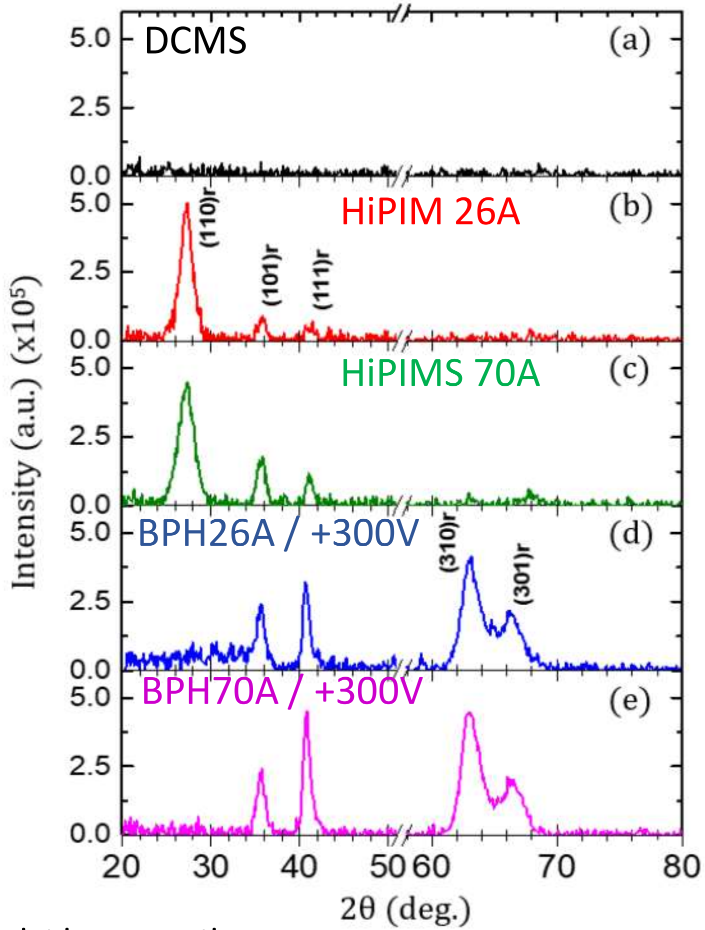
Controling the ion energy by the + voltage applied on the cathode



Michiels et al, manuscript in preparation

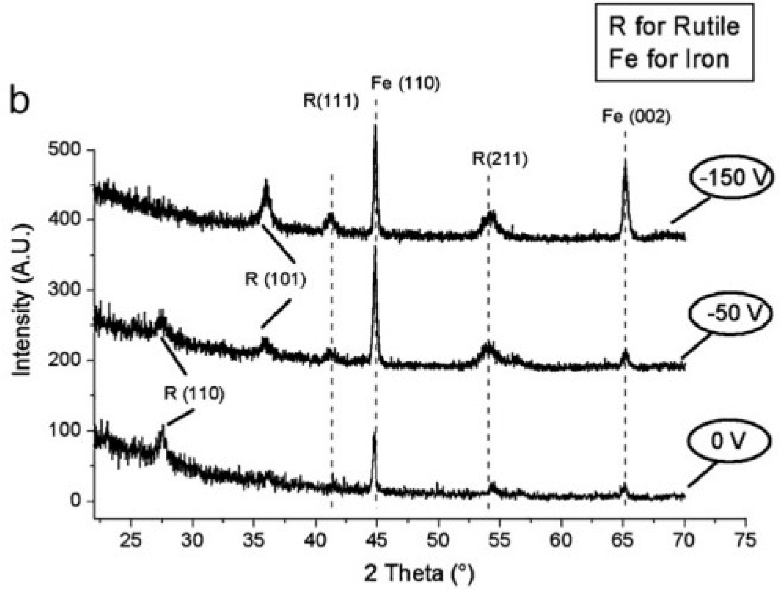
Comparison of the XRD data

Low resistivity Si substrates



Michiels et al, manuscript in preparation

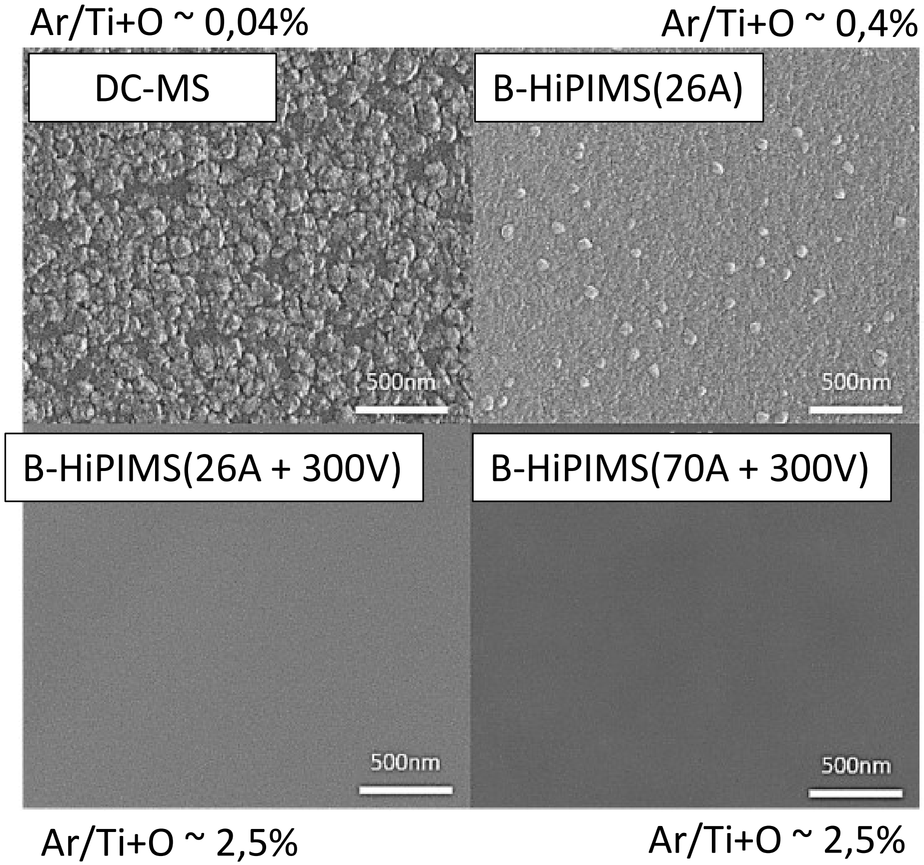
Positive pulse on cathode as the same effect as applying a negative bias on the substrate

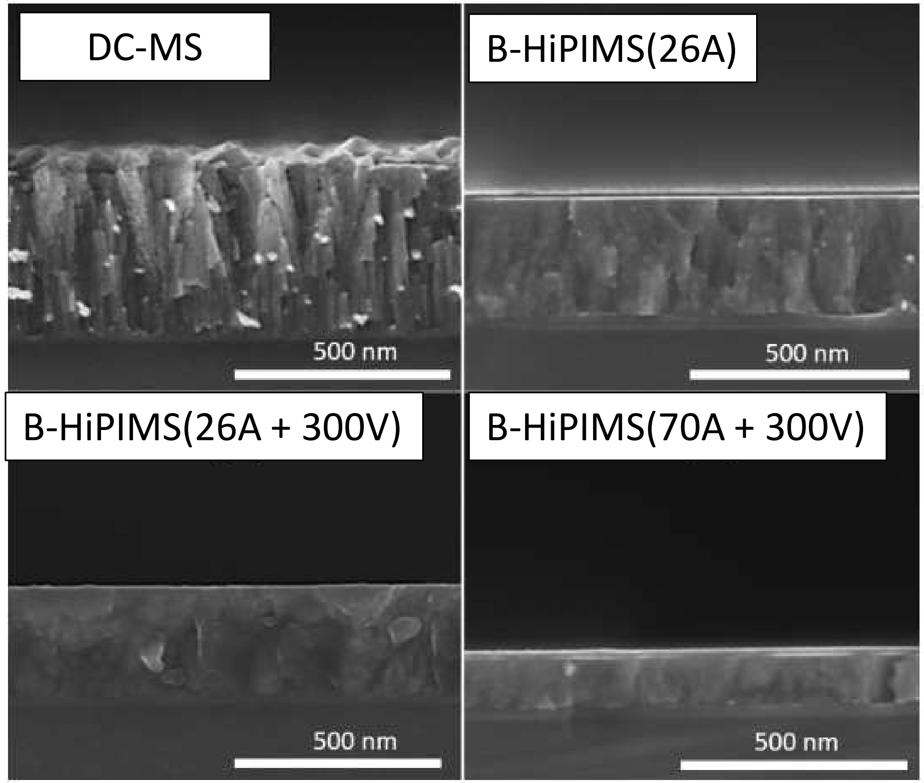


Konstantinidis et al, Thin Solid Films (2006)

Topography and cross-section SEM images

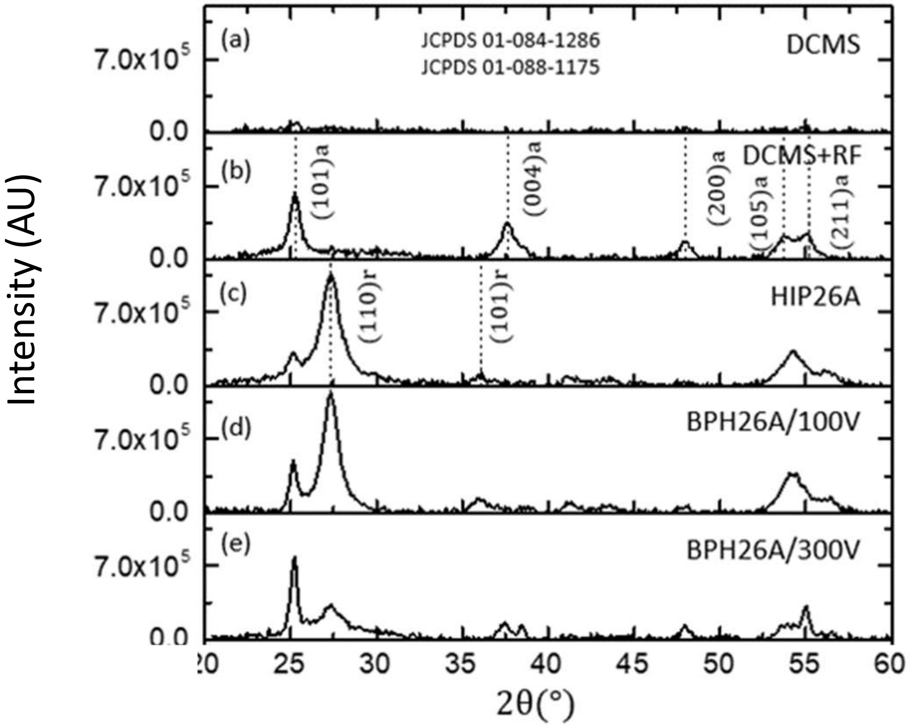
Low resistivity Si substrates

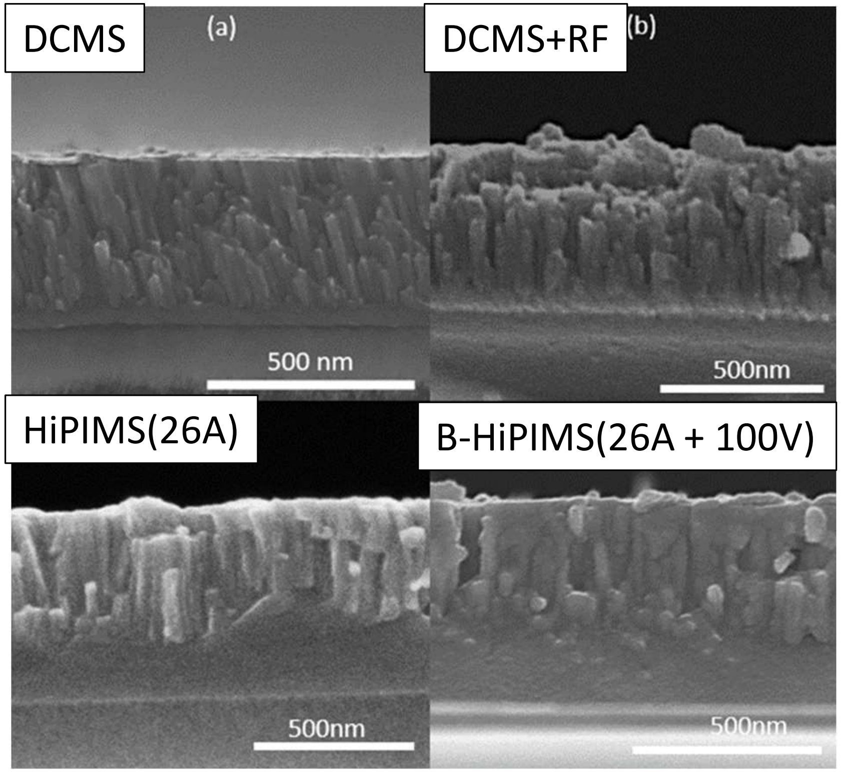




Michiels et al, manuscript in preparation

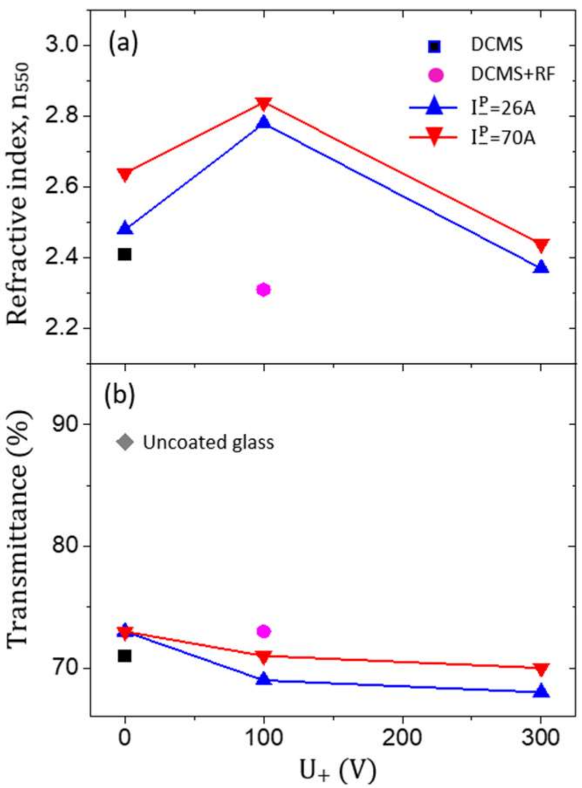
Microstructure of TiO_2 films deposited by B-HiPIMS on glass

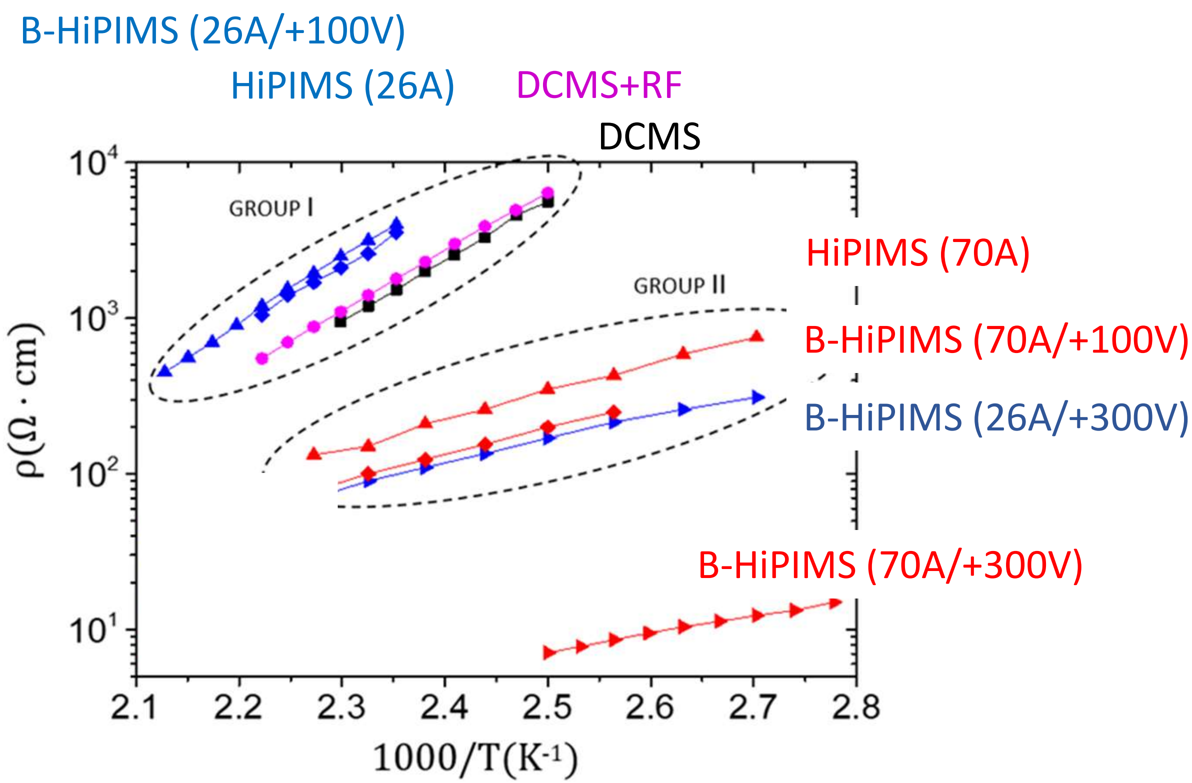




Michiels et al, manuscript in preparation

Michiels et al, manuscript in preparation





Optimization of the properties of TiO_2 films on glass

Summary

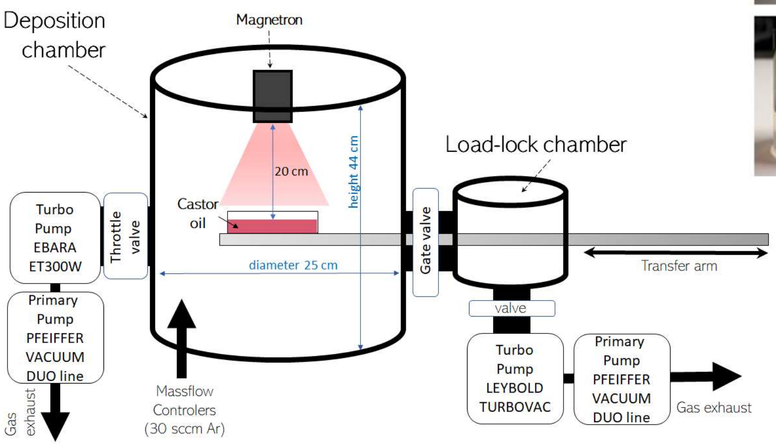
1. HiPIMS enables coating complex objects

2. 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

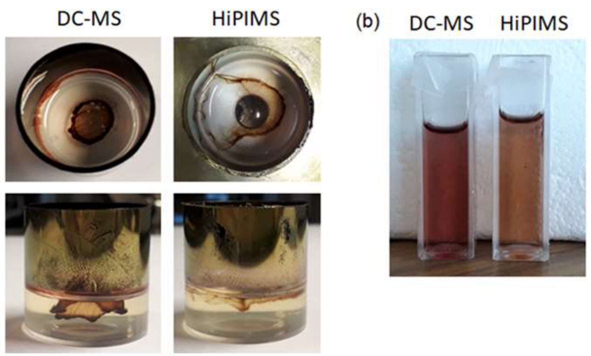
3. HiPIMS may facilitate the deposition of functional oxides onto temperature sensitive materials like polymers

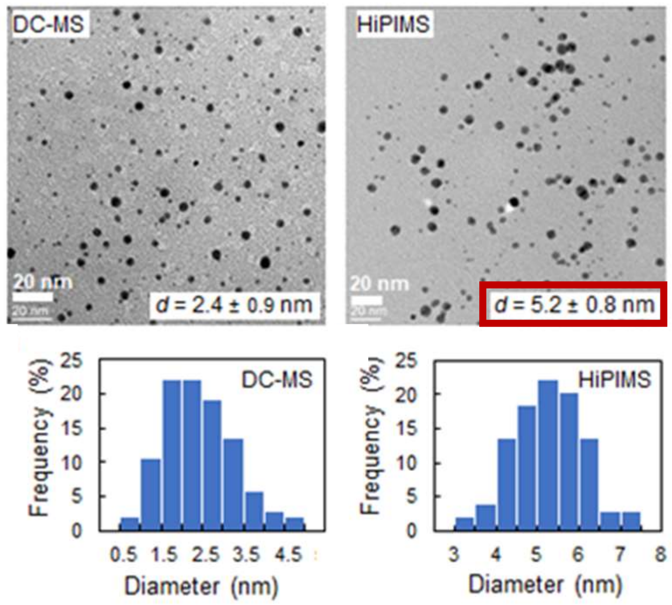
4. Recent developments aim at providing even more control on the film growth process

Sputtering onto liquid substrates for the synthesis of nanoparticles, the role of HiPIMS



Gold sputtered onto castor oil





A. Sergievskaya et al., Coll. Surf. A Physicochem. Eng. Asp. **615** (2021).
A. Segievskaya et al., manuscript in preparation