HiPIMS Today

IUVSTA
1958-2018
60 years of the Union

UMONS
Université de Mons

On the synthesis of Titanium Dioxide, from DCMS to Bipolar HiPIMS

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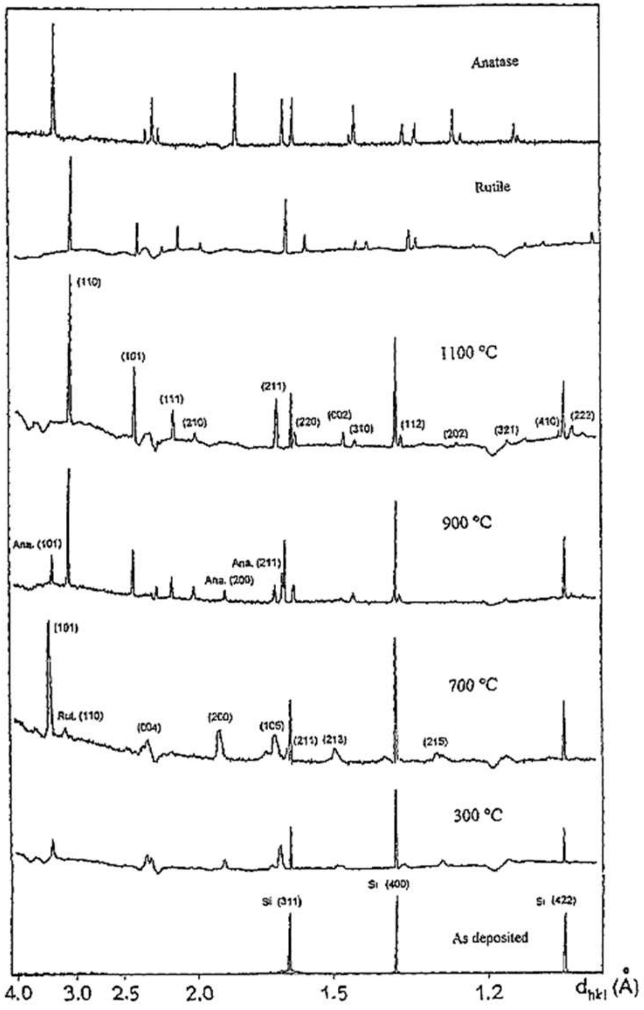
In the last century…

Annealing DC MS TiO_2 films

Rutile @ high temperature
Anatase @ « medium » temperature



← Rutile (1100°C)

← Anatase + Rutile (900°C)

← Anatase (300°C)

← Amorphous (25°C)

N. Martin et al, Thin Solid Films 300, **1997**, 113

YESTERDAY
Reactive HiPIMS of TiO_2 thin films

Growth of TiO_2 films, DCBPMS vs HiPIMS

HiPIMS discharge in Ar – O_2 (40% O_2) at 1 Pa (7mTorr)

Pulse characteristics :

- Duration : Short pulses of 7µs
- Voltage : 900V → peak current : 200A
- Repetition frequency : 1 – 3 kHz
- Average power : 1.5 – 2 kW
- 450 x 150 mm rectangular Ti target

DC Bipolar Pulsed Magnetron discharge (DCBPM):

- Frequency : 150 kHz
- Positive pulse duration : 2016 ns
- Same average power

Substrates : - Glass (4 mm thick)
- Steel foils (0.2 mm thick).

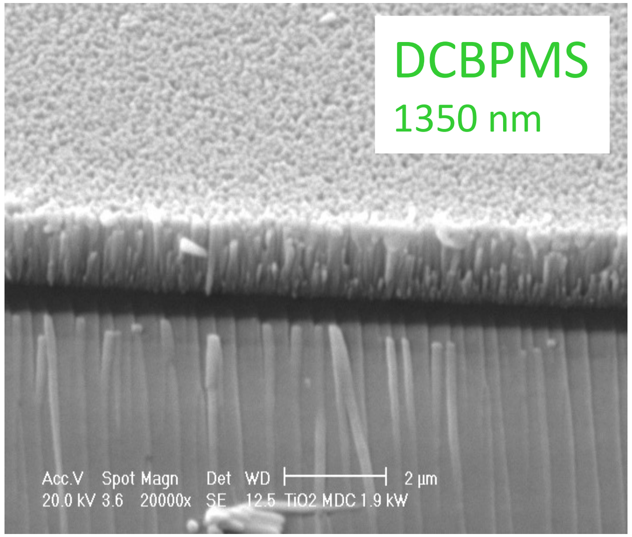
Konstantinidis et al, Thin Solid Films 515, **2006**, 1182.

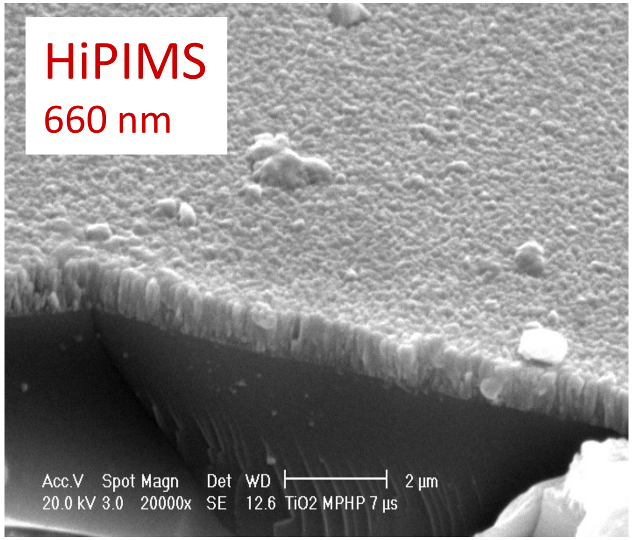
Thickness and morphology

Sputtering Technique	*Film Thickness* *(mechanical profilometer - Films on glass)*
DC-BPM	1350 nm
HiPIMS	660 nm

Films deposited (Power = 1.7 kW, 6 h duration)

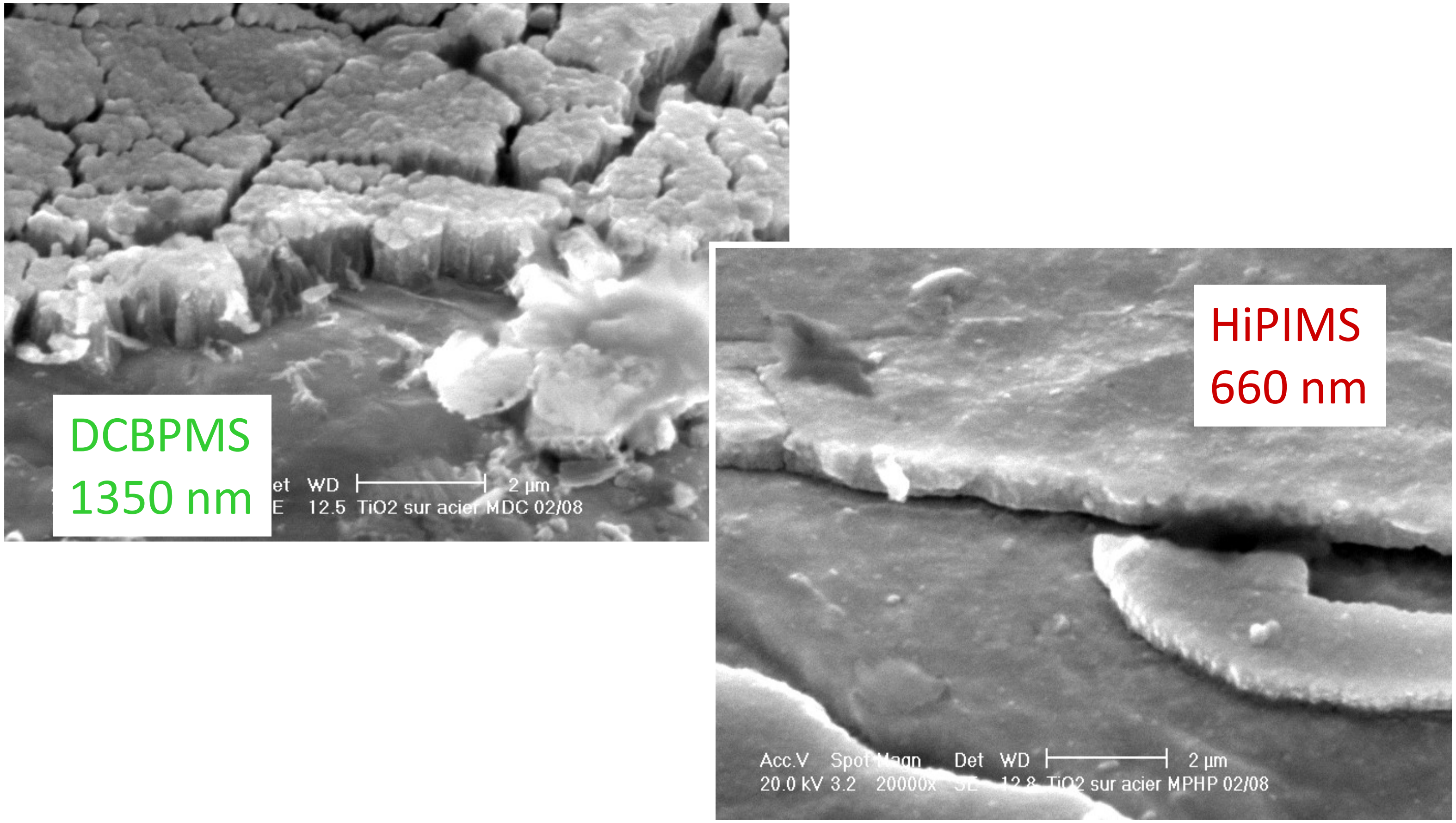
Morphology, HiPIMS deposited TiO_2 films on glass





X-ray Fluorescence measurements have shown
HiPIMS films are **denser** than DCBPMS ones (~20%)

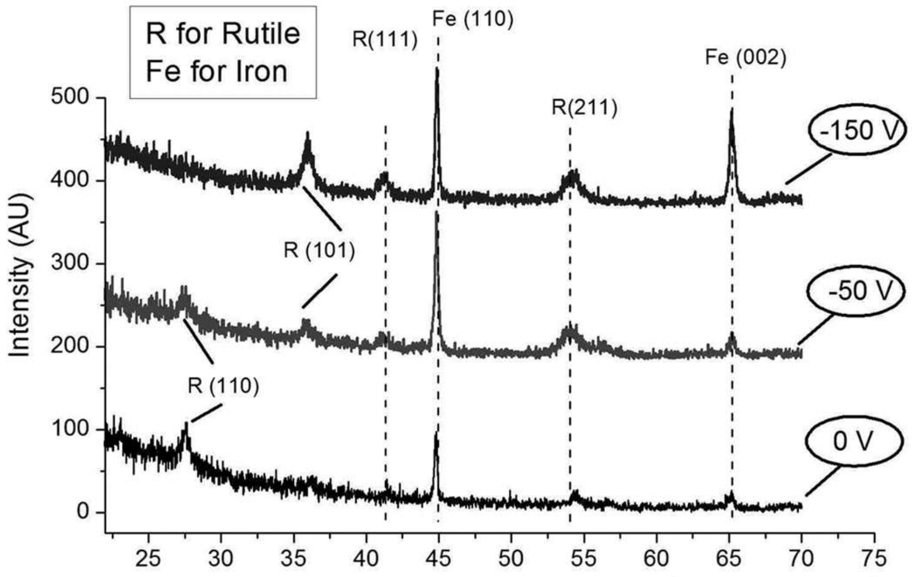
Morphology of TiO_2 films on steel substrates



DCBPMS
1350 nm

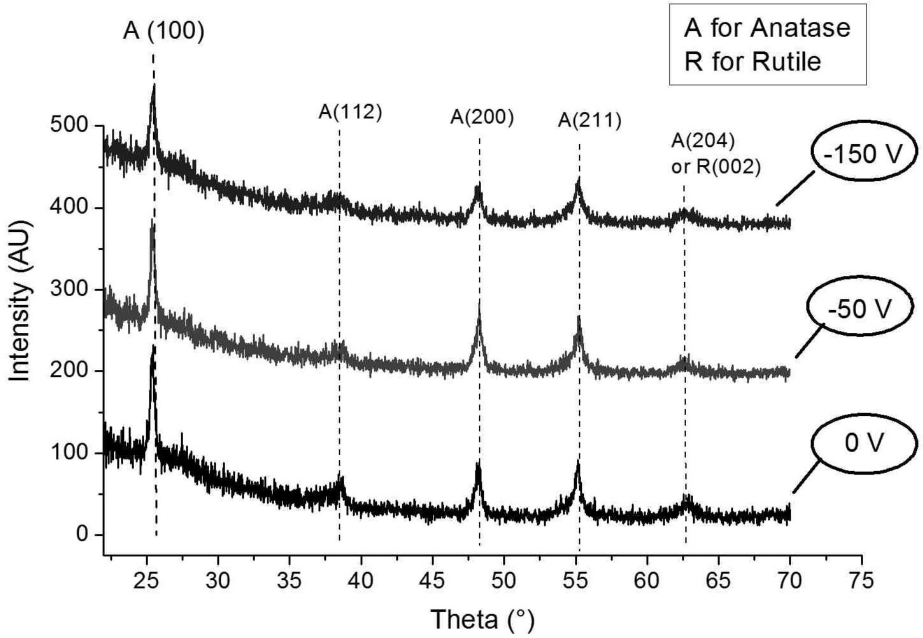
HiPIMS
660 nm

Crystalline structure of HiPIMS TiO_2 coatings



On **steel** foil

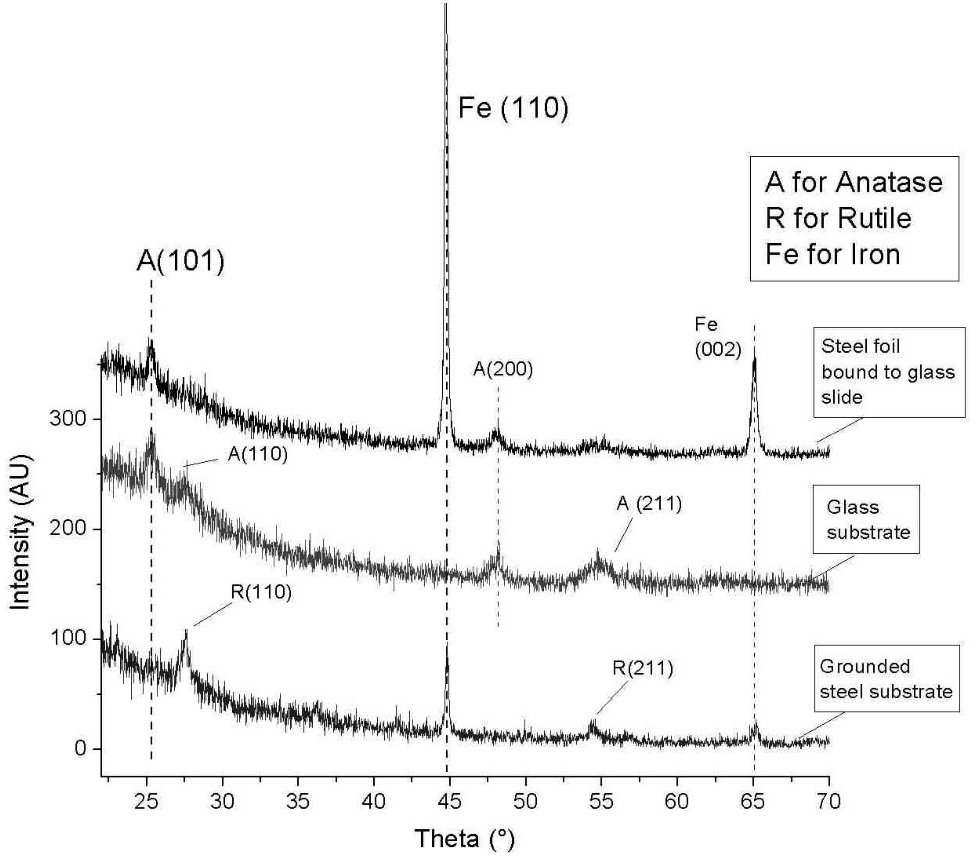
⇒ **RUTILE**, even without substrate bias



On **glass** plate

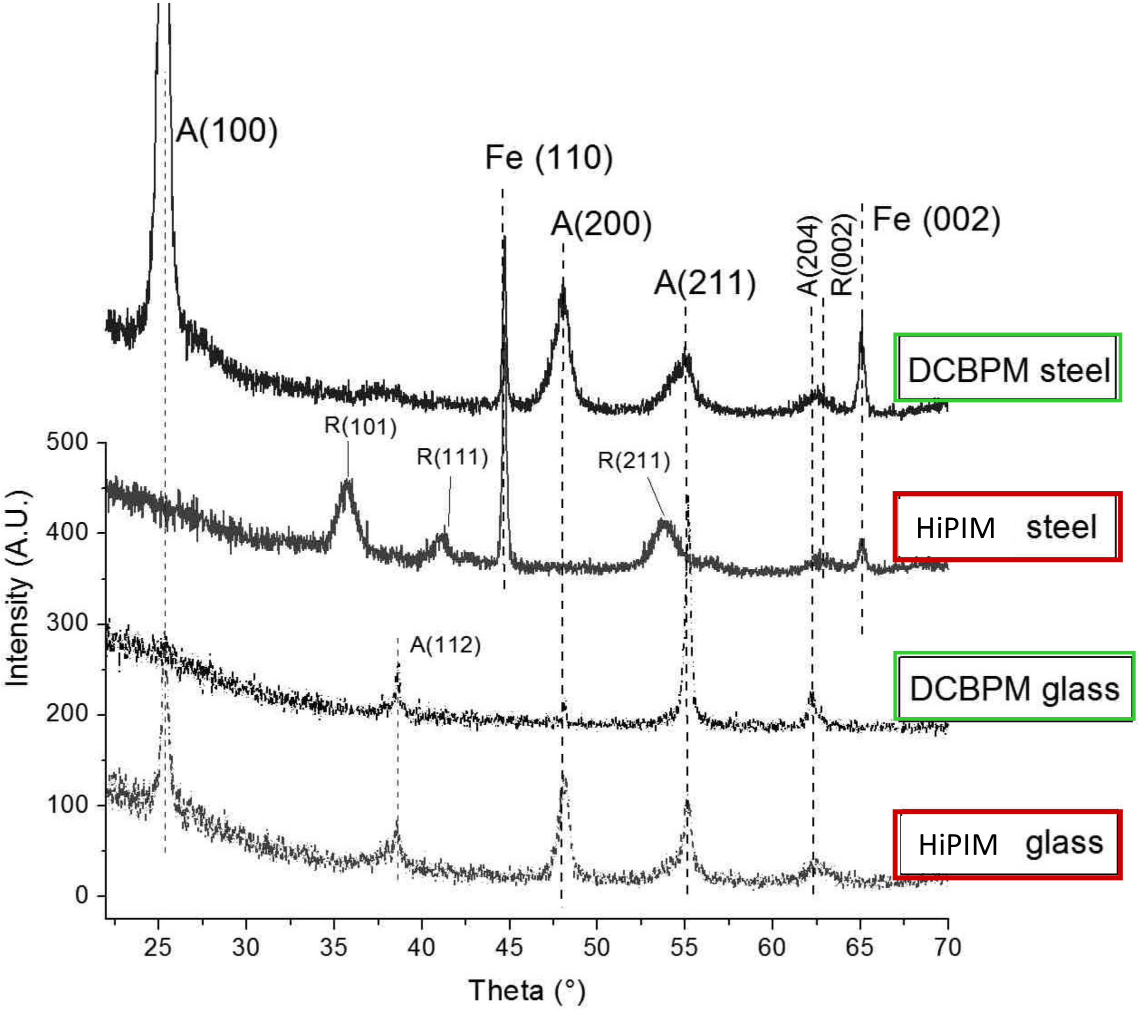
⇒ **ANATASE** structure

What if the steel substrate is floating ?



Steel foil at **FLOATING** potential → **ANATASE** structure like on glass

Comparing DC-BPMS and HiPIMS sputtering



- On glass :

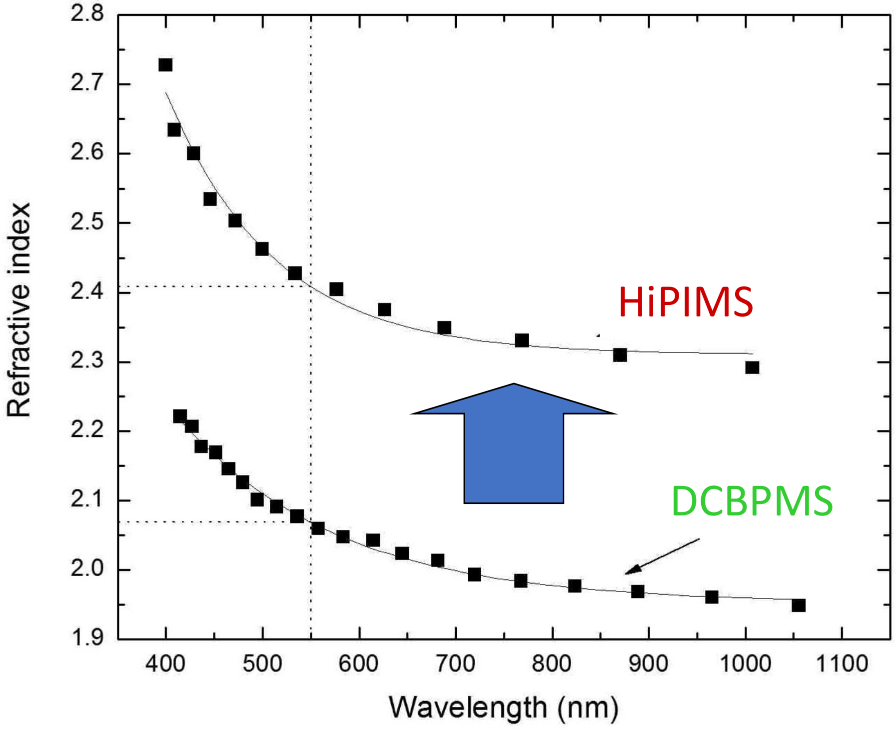
ANATASE, different textures

- On steel :

HiPIMS : RUTILE

DCBPMS : ANATASE

Refractive index, TiO_2 on glass



On glass, both films are anatase.
→ Higher index could be attributed to film **densification by HiPIMS**

Influence of substrate, summary

TiO_2 films deposited by HiPIMS

- are denser
- have a different crystalline structure (RUTILE on steel)
- have a higher refractive index

Ionization degree induced by short pulse is enough to modify film properties

Capacitance of substrate is an influential factor regarding the energy deposition during film growth

Energy flux measurements during TiO_2 deposition

Various contributions
to the energy flux at the substrate

surface

$$P_E = \int J_{in} \bullet dS = \int (J_i + J_e + J_n + J_{rad} + J_{film}) \bullet dS$$

Total input power

Energy delivered
per unit time and area

ions

electrons

neutrals

radiations

condensation of film forming species,
chemical reactions, ...

A. Thomann, Surf. Coat. Technol. 377, 124887 (2019).

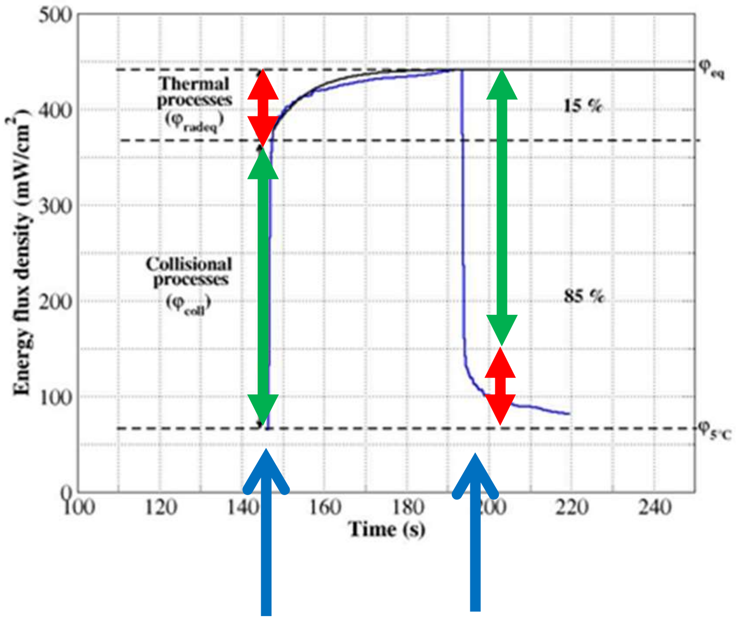
The energy flux at the substrate

Thermopile – based probe

→ Allows to distinguish:

1. Rapid processes
    - Plasma related contributions
2. Slow processes
    - IR emitted by slowly heated body
        → **Target** bombarded by plasma ions.

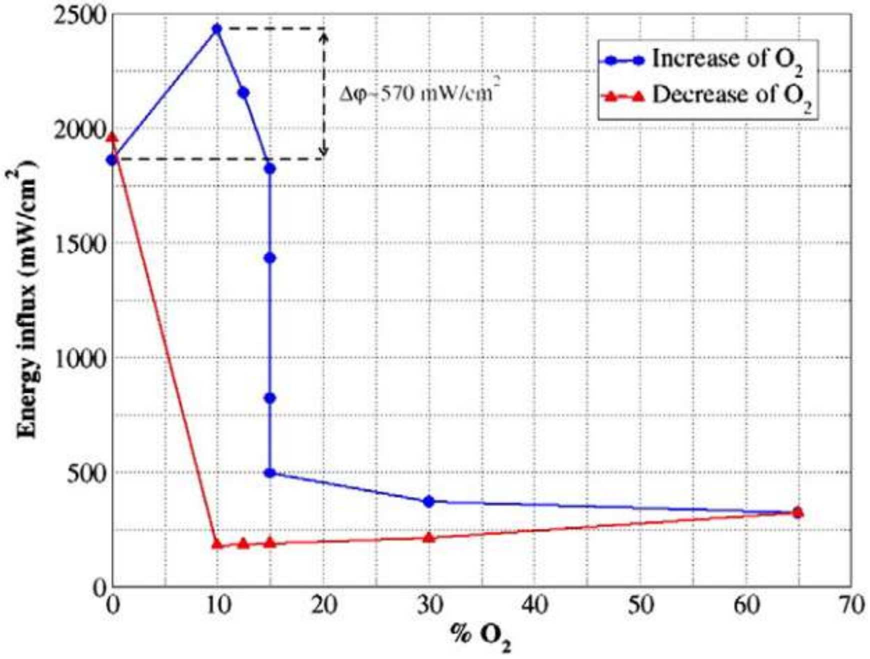
Energy Flux vs time

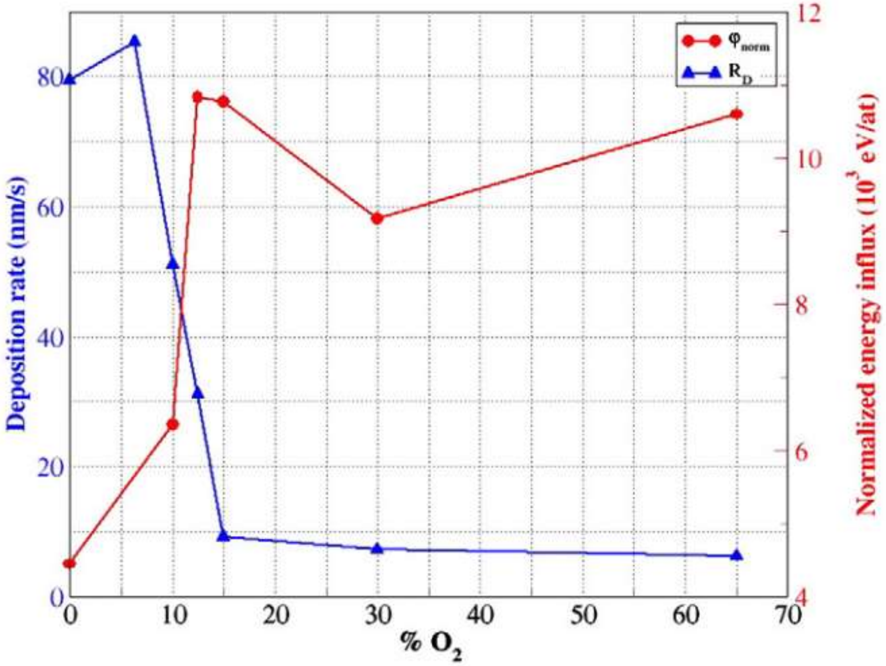


Plasma ON   Plasma OFF

1. P.-A. Cormier et al, J. Appl. Phys. 113, 013305 (2013).
2. P.-A. Cormier et al, Thin Solid Films 545, 44 (2013).
3. A. Thomann, Surf. Coat. Technol. 377, 124887 (2019).

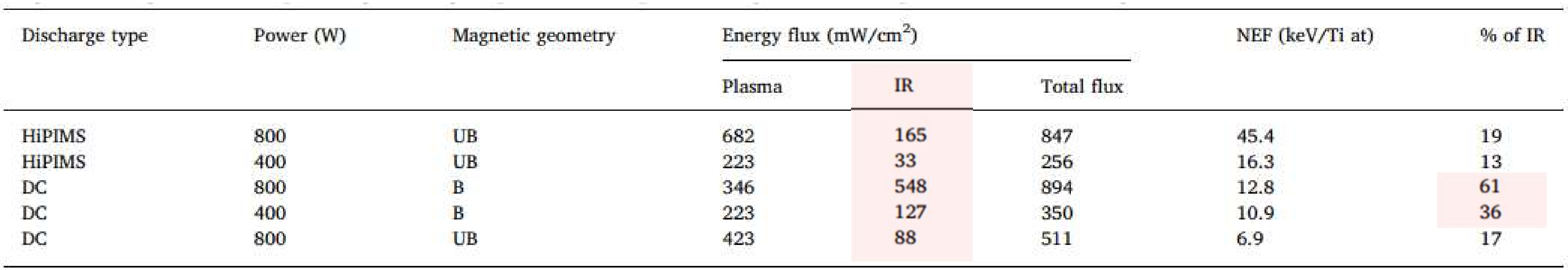
Energy flux at the substrate surface, metallic vs oxide modes





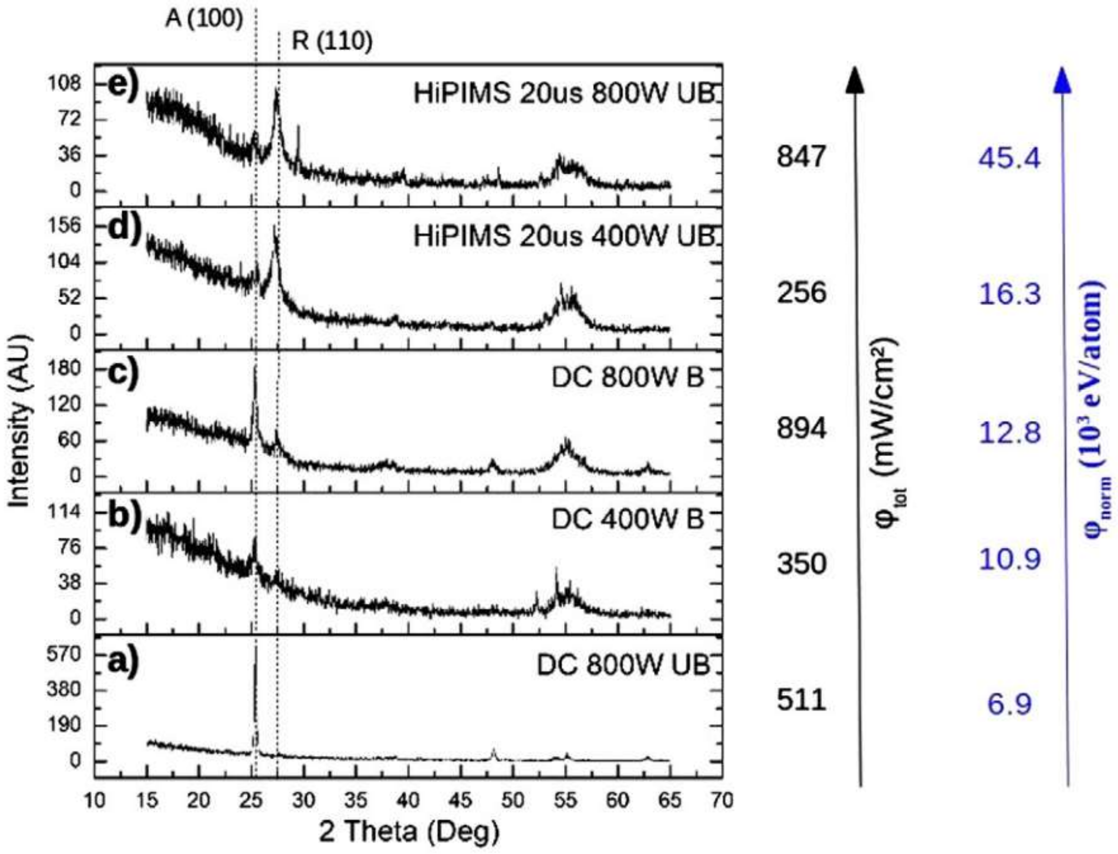
- Increased energy deposition comes from high energy O^- negative ions

IR emission from a heated sputter target



Discharge type	Power (W)	Magnetic geometry	Energy flux (mW/cm^2)			NEF (keV/Ti at)	% of IR
			Plasma	IR	Total flux		
HiPIMS	800	UB	682	165	847	45.4	19
HiPIMS	400	UB	223	33	256	16.3	13
DC	800	B	346	548	894	12.8	61
DC	400	B	223	127	350	10.9	36
DC	800	UB	423	88	511	6.9	17

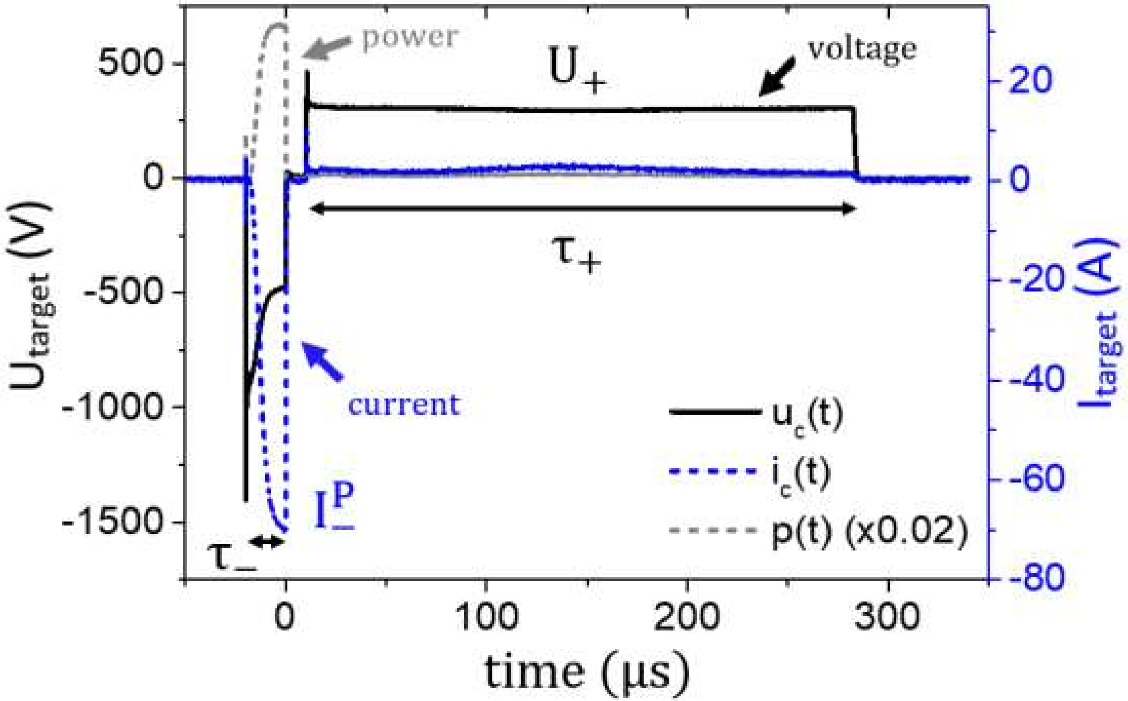
XRD vs Energy per adparticle



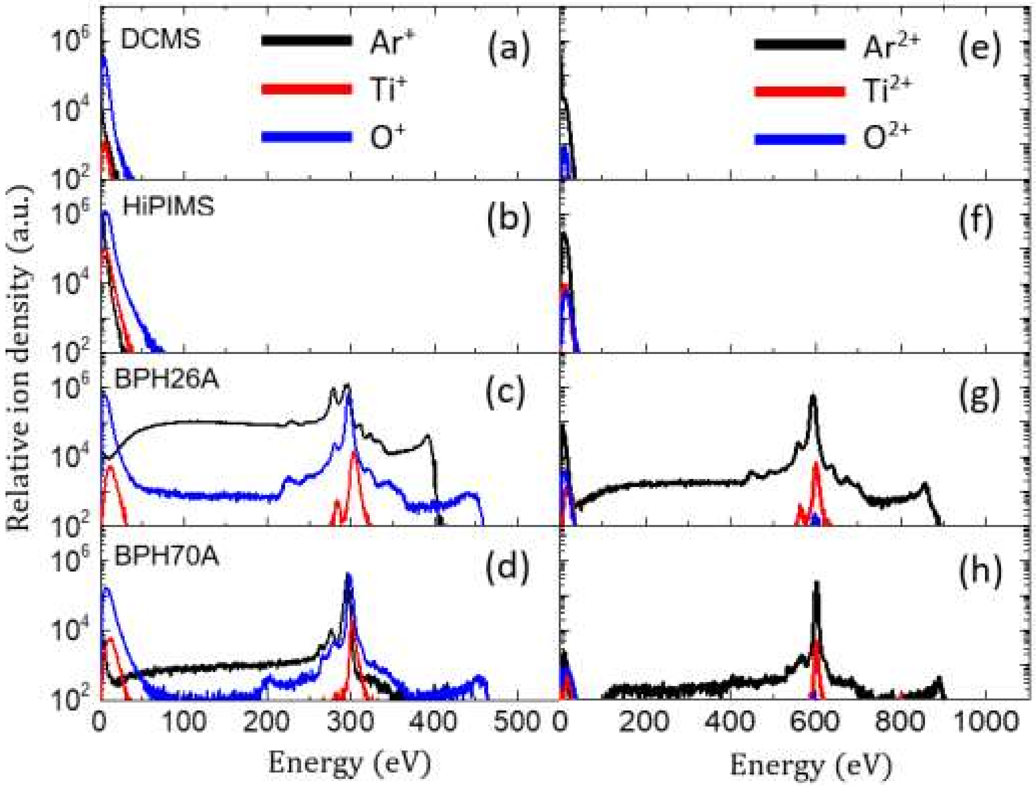
TODAY
Reactive bipolar HiPIMS of TiO_2 thin films

Michiels et al, manuscript in preparation

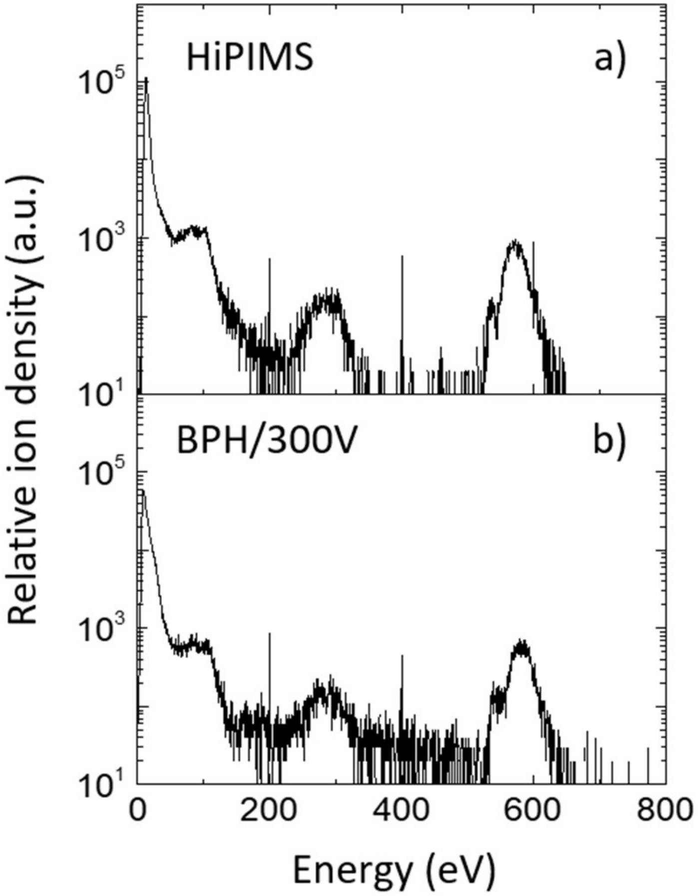
I & V waveforms



Ion Energy Distribution Functions, $U_+ = 300V$

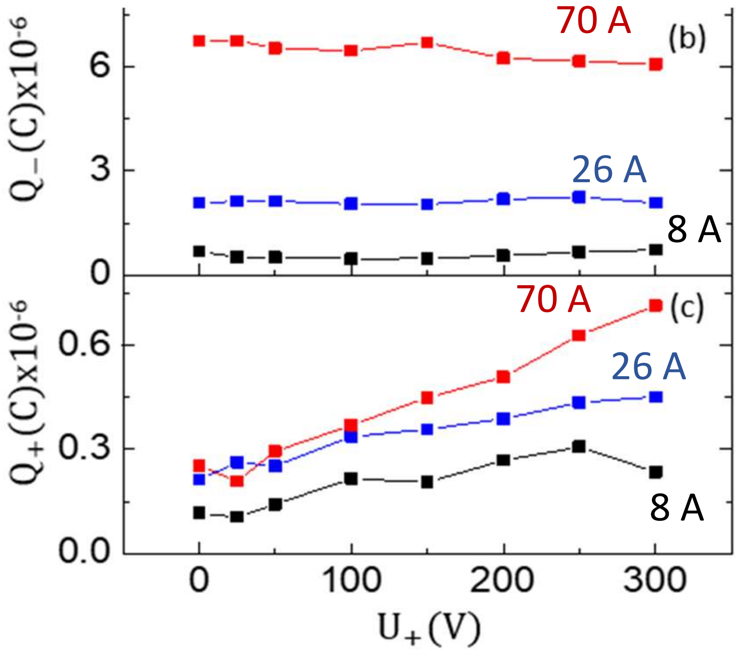


IEDFs for O^- ions, HiPIMS vs B-HiPIMS

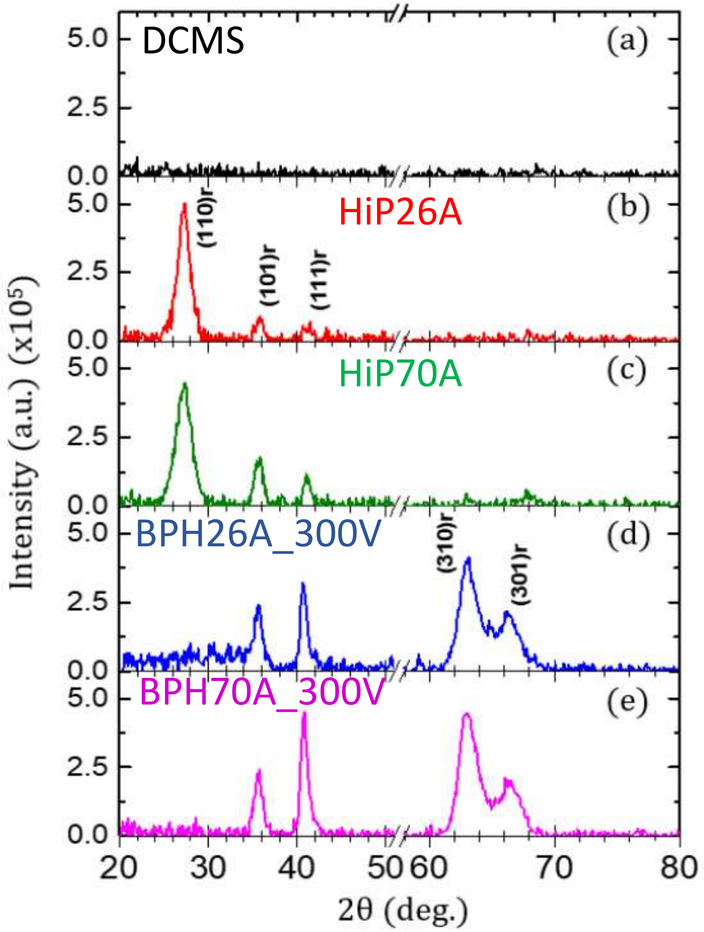


Cathode voltage = 600V

Charge collection at the substrate



Comparison of the XRD data

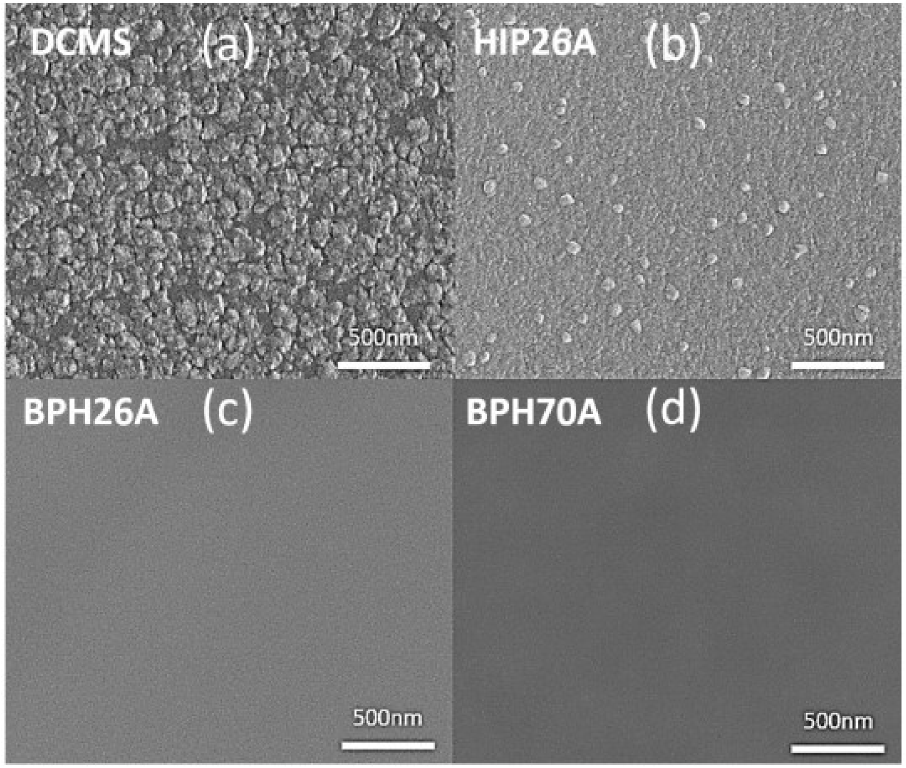


Low resistivity Si substrates

Topography and cross-section SEM images

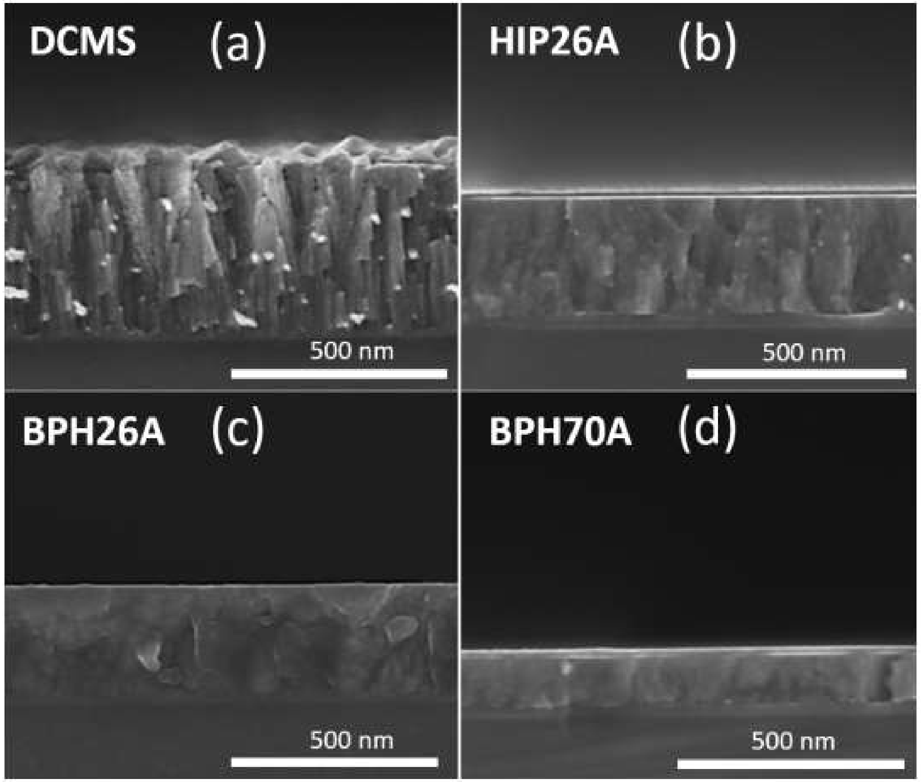
Ar/Ti+O ~ 0,04%

Ar/Ti+O ~ 0,4%



Ar/Ti+O ~ 2,5%

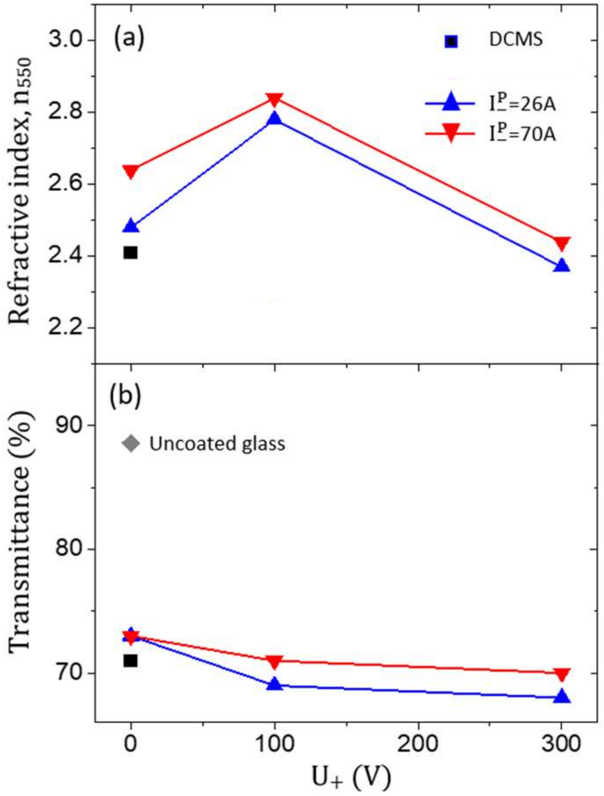
Ar/Ti+O ~ 2,5%



Refractive index

Process	Density (g/cm^3)	Crystallinity	n (Ellipsometry)
DCMS	3,6	Amorphous	2,41
HiPIMS_26Amp	3,9	rutile	2,53
BPH_26_300V	3,4	rutile	2,49
BPH_70_300V	3,5	rutile	2,60

Bipolar HiPIMS of TiO_2 on glass



Summary

1. Energy deposition is increased when running a HiPIMS plasma
    - Pay attention to the substrate electric connection (floating vs grounded) espescially for classic HiPIMS
    - Optimization of the magnetic field is necessary to allow ions to do their job otherwise (balanced field) the target surface may become a radiator and the film is annealed in situ.
2. HiPIMS films are usually found to be well crystallized while DCMS films are amorphous or contain anatase nanocrystals
3. Refractive index is higher in HiPIMS based deposition processes
4. During Bipolar HiPIMS, the positive pulse controls the energy and the amounts of positive ions collected at the substrate
    - Argon is incoporated in the film

5. HiPIMS was tested sucessfully on a (small scale) rotating magnetron

W.P. Leroy et al, J. Phys. D. Appl. Phys. **44**, 115201 (2011).

What about HiPIMS tomorrow ?

Acknowledgements

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