HIPIMS 2021

11TH INTERNATIONAL CONFERENCE ON HIPIMS

POLITECNICO MILANO 1863

erc ERC-2014-CoG No. 647554
ENSURE

NanoLab
DIPARTIMENTO DI ENERGIA

Role of energetic ions in the growth of fcc and ω crystalline phases in Ti films deposited by HiPIMS

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Titanium films

22 3d^{2}4s^2
Ti
Titanium
47.867

- High mechanical strength,
- Excellent thermal stability
- Good corrosion resistance in harsh conditions
- Intrinsic biocompatibility

Interest in Ti films for:

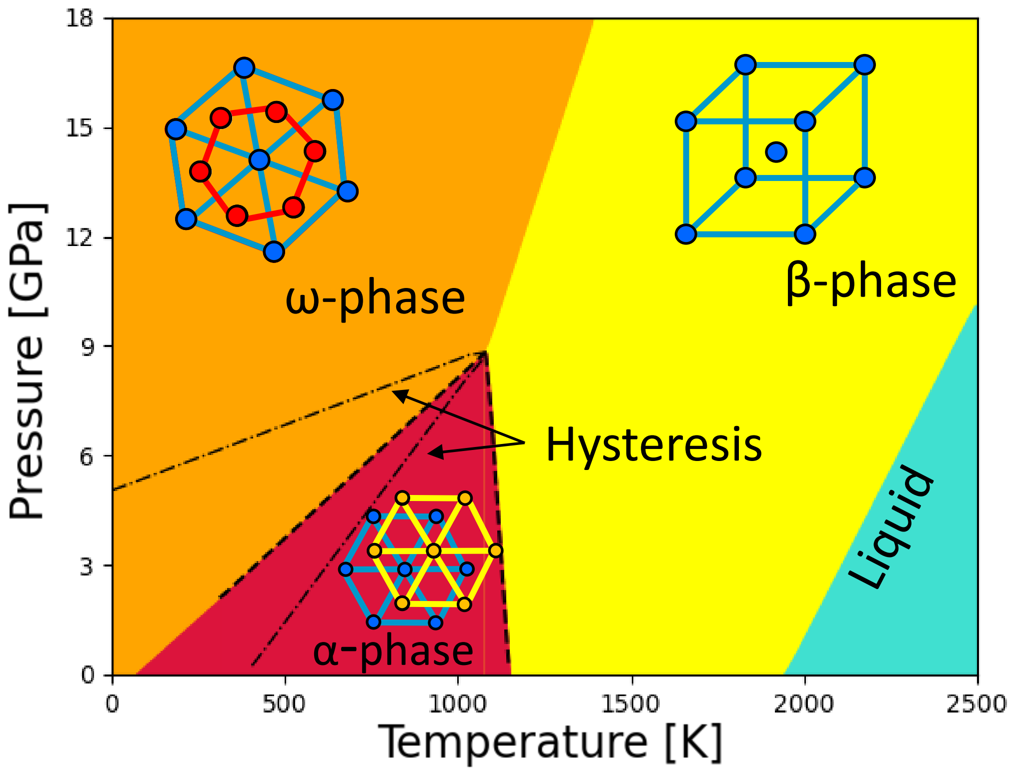
- **Industrial applications** (e.g. transistors, integration technology, MEMS, bolometers..)
- **Research applications** (e.g. targets in laser driven ion acceleration experiments)

Passoni M. et al., Plasma Phys. Control. Fusion 62, 014022, 2020

Properties of Ti films are related to the different crystal structures that Ti exhibits:

- **hcp** phase (**α-phase**)
- Denser **bcc** phase (named **β-phase**)
- **Hexagonal ω-phase**
- A new **face centered cubic (fcc) phase**, not predicted by the equilibrium phase diagram of Ti

Wawner F. E. et al., J. Vac. Sci.Technol. 6, 588–590, 1969



Influence of Ti phases

The tailoring of the crystalline phase of Ti films could be of interest in order to have different film properties:

- ω phase → improved **mechanical properties** (strength, hardness and fatigue resistance)

Lavrentiev V. et al., Scripta Materialia 44, 625-630, 2001

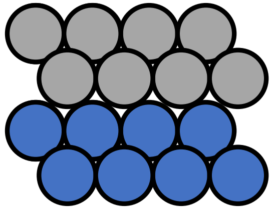
- fcc phase → influence on **electronic properties** (conductivity, specific heat, magnetic susceptibility)

Aguayo A., Phys. Rev. B 65, 092106, 2002

Considering thin films, the control of the crystalline phase using high temperatures or high pressures can present difficulties (e.g. compatibility with the substrate).

As an alternative to this, what strategies can be used?

Phase tailoring of Ti film



→ Affinity with the substrate inducing an epitaxial growth.

- Epitaxy leads to grow crystalline phases different from the α-phase
- Both fcc and ω-phase have been observed → films thicknesses **10s of nm**

Kim S. K. et al., J. Phys.: Condens. Matter 8, 25, 1996
Sugawara Y. et al., J. Mat. Res. 15, 2121-2124, 2000

→ Addition of an energetic ion flux to the neutral flux of atoms during the deposition.

- **Energy, flux and type** of the involved **species** affect both **microstructure and phase composition** of the growing film
- Role of **argon ions** on the phase of the Ti films has been investigated.
- Mixture of fcc and α-phase has been observed → **films thickness ≈ 100÷200 nm**

Chakraborty J. et al., Acta Materialia 59, 7,2011
Fazio M. et al., Thin Solid Films 593, 110-115, 2015

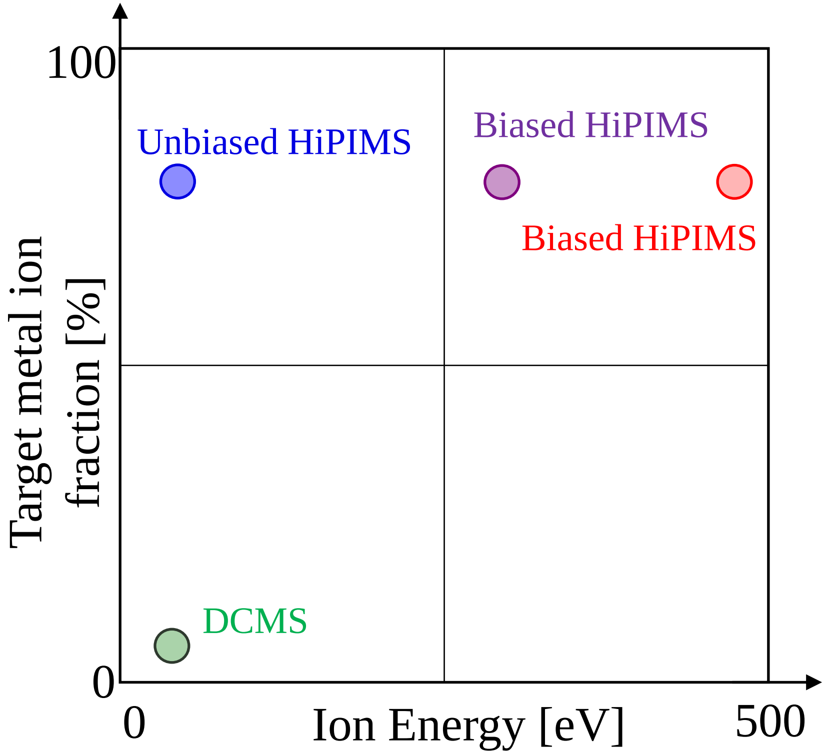
It could be of extreme interest to address the role of the ion environment (energy and type) in determining the synthesis of such phases

Phase tailoring of Ti film by HiPIMS

The HiPIMS could be an ideal tool:

- High plasma density and **high ionization fraction**
- **Ion and neutral** of the **same element** contribute to the growth of the films
- **Energy** can be **controlled** by electric fields (i.e. a bias voltage to the substrate)

Possibility to precisely set the energy of the ions showing the effect of the energy of the species.



→ Optimize the deposition parameters with the aim of **maximizing the ion/neutral ratio**

→ Compare Ti films grown with different "ion conditions":

- Direct Current Magnetron Sputtering (**low ion fraction** and **low ion energy** environment)
- Unbiased HiPIMS (**high ion fraction** and **low ion energy** environment)
- Biased HiPIMS (**high ion fraction** and **high ion energy** environment)

HiPIMS deposition parameters

Fixed parameters

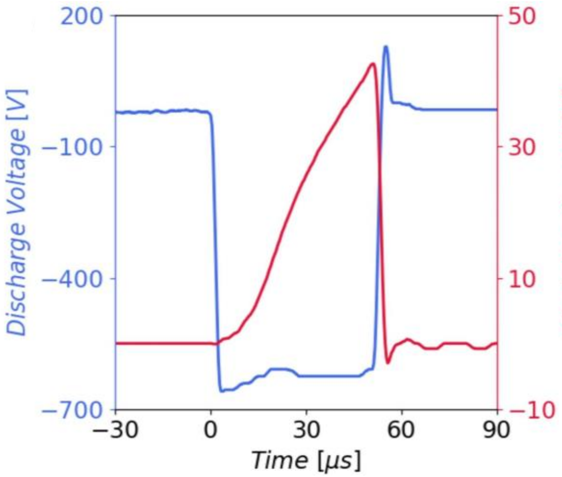
- Pressure: 0.5 Pa
- Pulse length: 50 µs
- Frequency: 300 Hz
- Duty Cycle: 1.75%

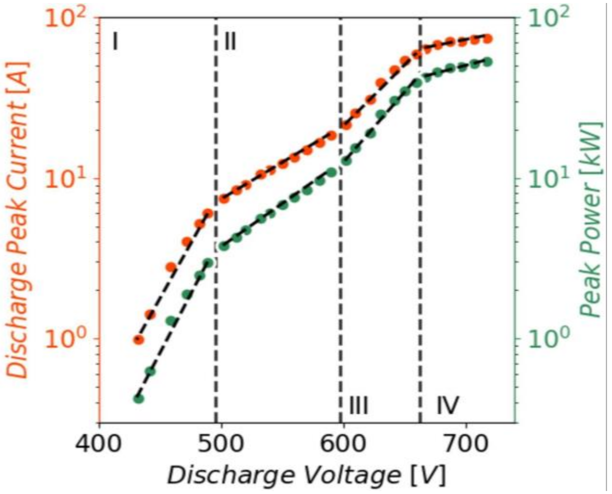
Varied parameters

- Bias voltage (U_S) : 0, -300, -500 V
- Deposition time: 15÷180 min
- Voltage (V_D): 550-660 V
- Peak current ($I_{D,\,Peak}$): 10-55 A

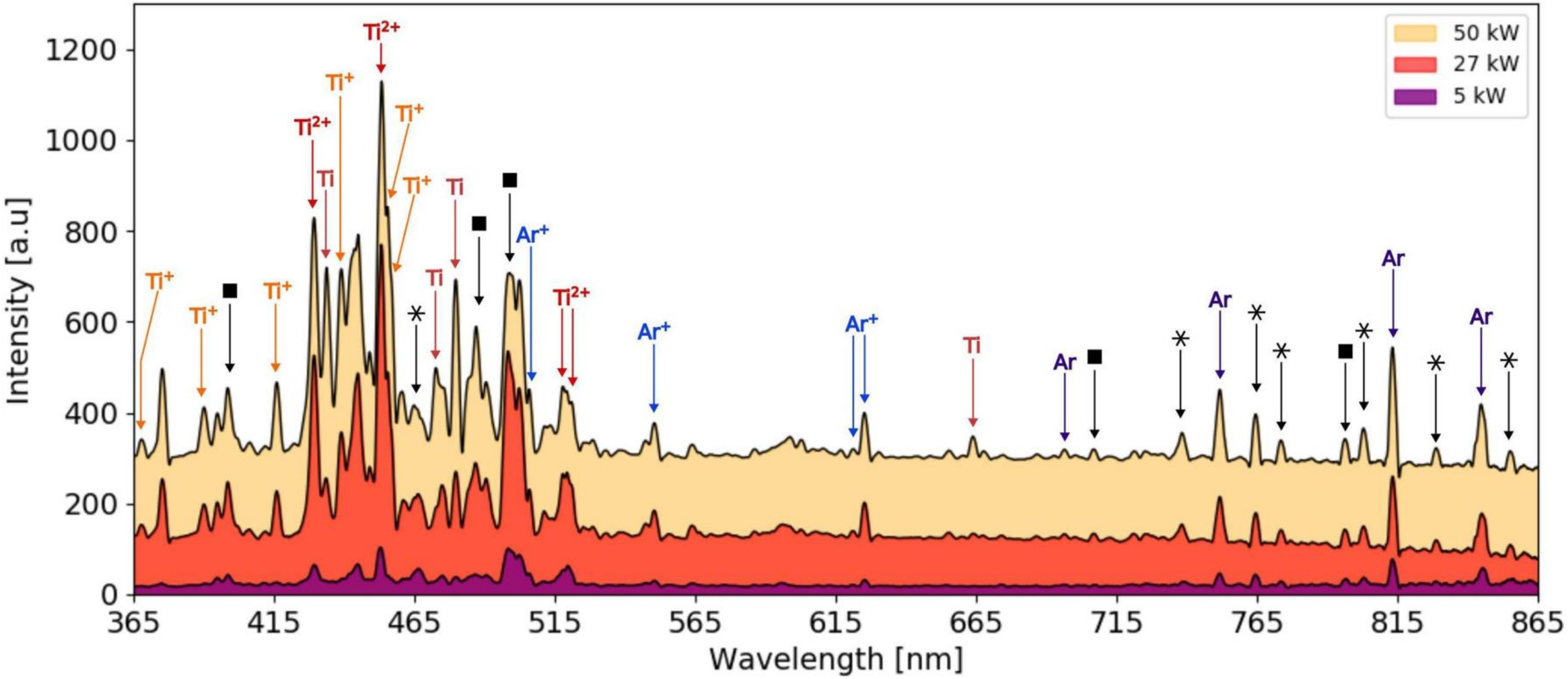
→ As working parameter, we used the peak power P_{Peak} defined as:

$$P_{Peak}=I_{D,\,Peak}\cdot V_D$$



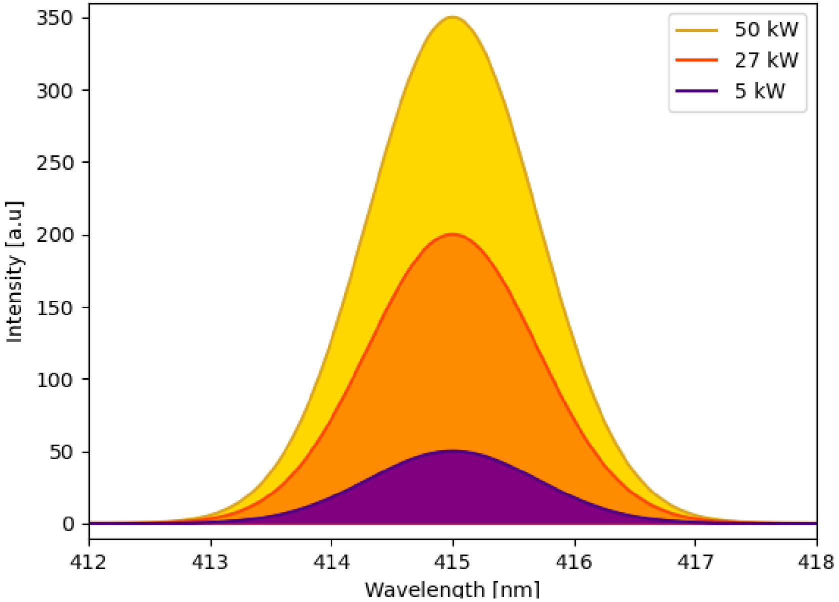


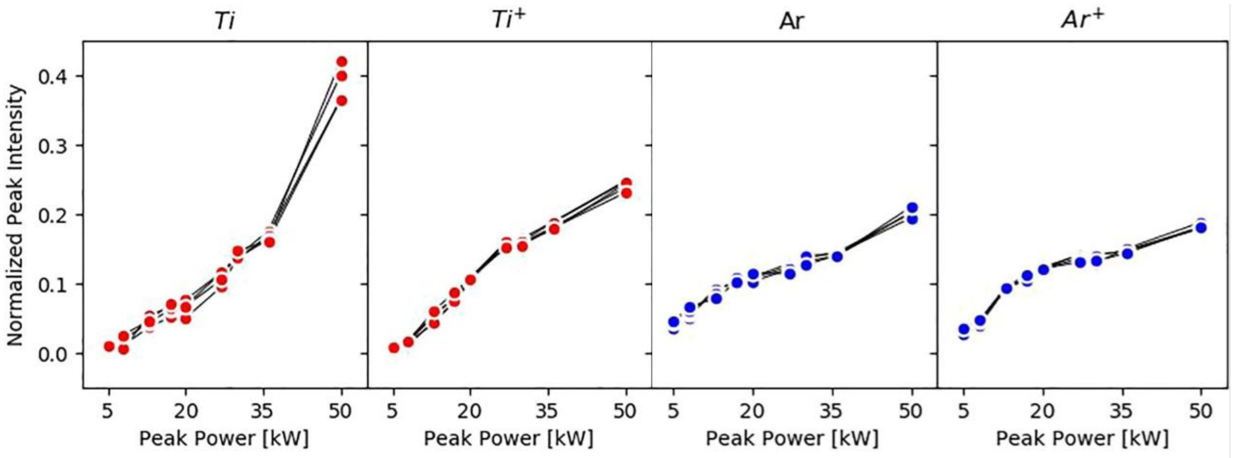
Plasma characterization: Optical Emission Spectroscopy



- P_{Peak} level → **species present** in the plasma and the **peak intensities**
- P_{Peak} varied in the range 5-50 kW.

OES peaks identification

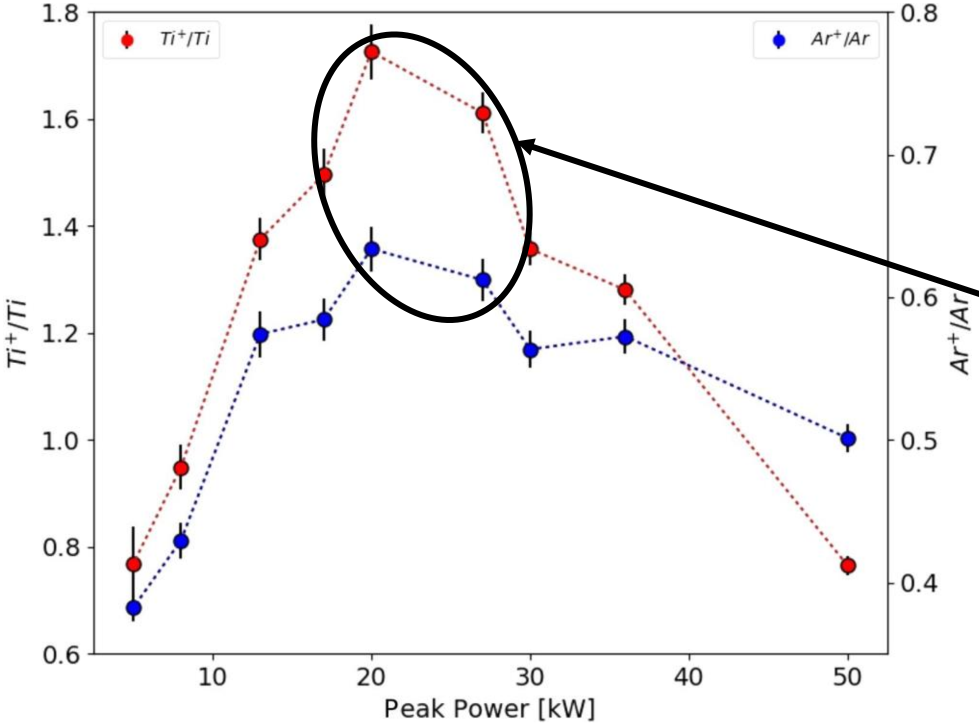




For the peak identification:

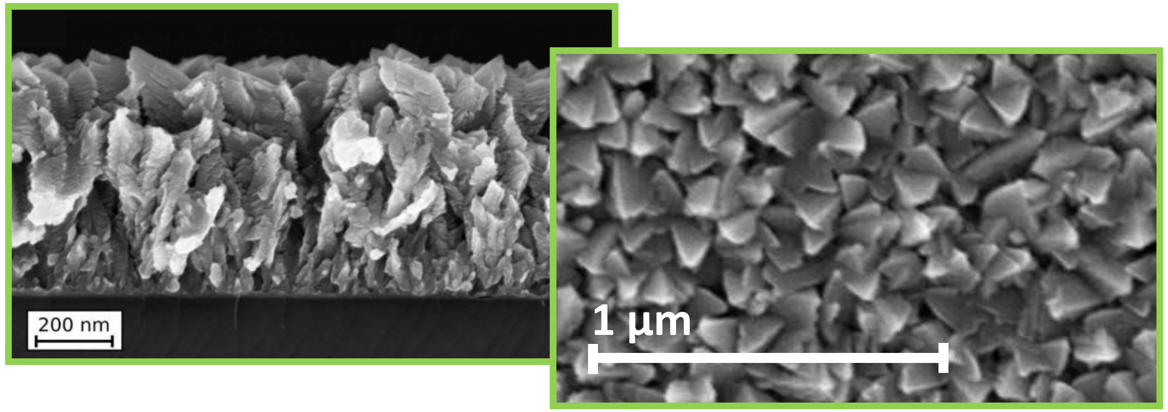
- Spectra acquired at different P_{Peak}
- **Intensity $I_{i,j}$** of the j-*th* peak acquired at the i-*th* P_{Peak} (e.g in the figure i = 5 kW, 27 kW and 50 kW and j = 415 nm)
- Peaks associated to the same species exhibit a **characteristic P_{Peak} vs $I_{i,j}$ relationship**
- If the calculated $I_{i,j}$ of the j-*th* peak is **normalized** over the sum of all the intensities at different P_{Peak} ($I_{TOT,j} = \sum_{i=1}^{n_P} I_{i,j}$,) the **trends associated to one specific species collapse** on the same curve

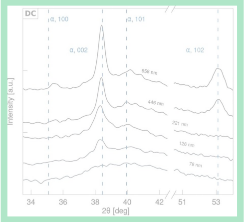
Emission intensity ratio

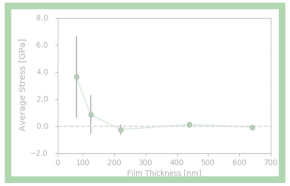


- **Ti and Ti$^+$** exhibit **similar excitation energies** (exclude dependence of excitation probability on excitation energy)
- We do **not consider Ti^{2+}**
- Similar considerations for Ar and Ar$^+$
- Emission intensity ratios show a **maximum value** in the region **between 20 and 30 kW**
- To maximize the Ti$^+$ ion flux, we **set the $P_{Peak} \approx$ 27 kW**

DCMS films: SEM, XRD and stress analysis

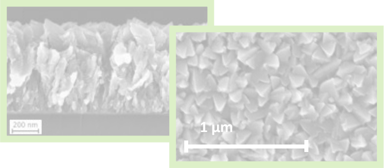


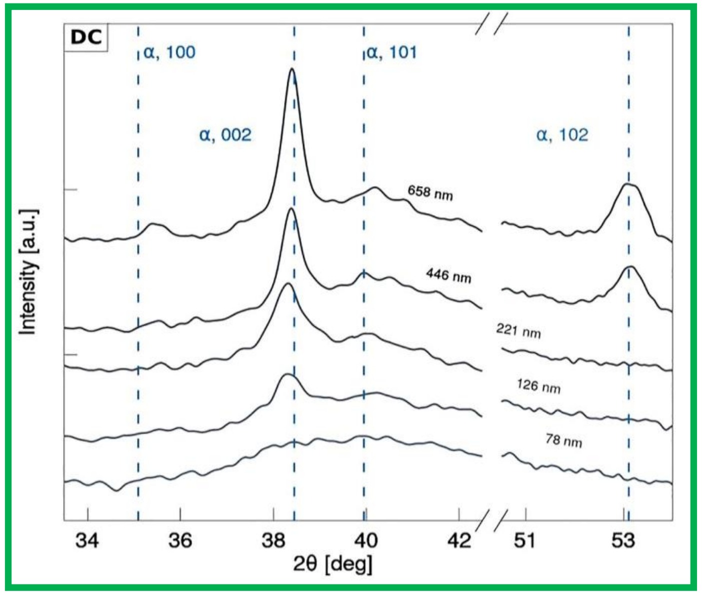


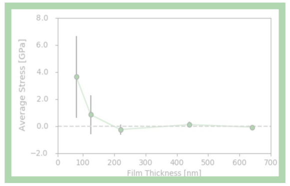


- **Columnar structure** with a **pyramidal** shaped **superficial pattern**

DCMS films: SEM, XRD and stress analysis



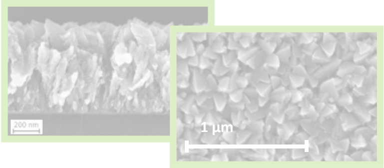


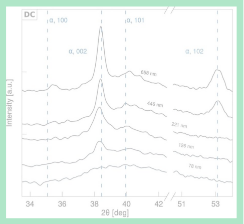


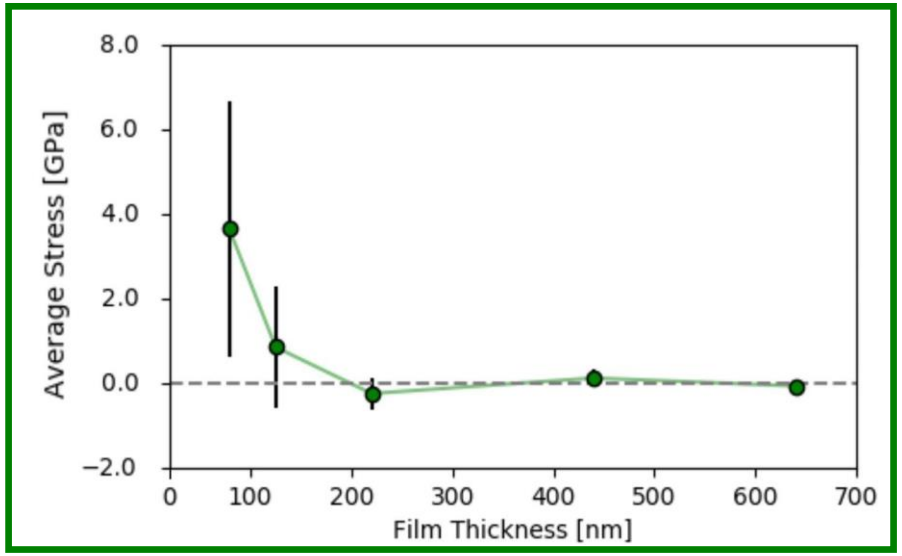
- **Columnar structure** with a **pyramidal** shaped **superficial pattern**

- Peaks related to the **α-phase only**
- At lowest thicknesses only the **(002) reflection** appears→ **minimization of the surface energy**
- For higher thicknesses also the (100), (101) and (102) reflections appear

DCMS films: SEM, XRD and stress analysis







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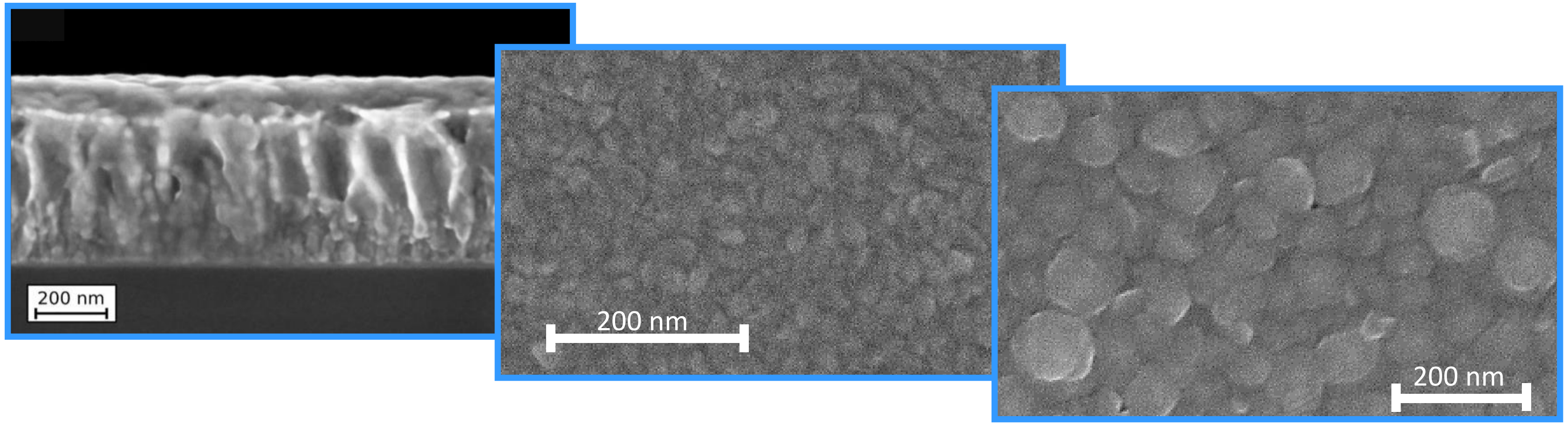
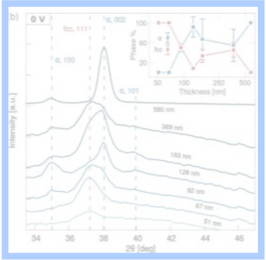
- Initial high tensile state
- A stress relaxation occurs for increasing thickness
- For films **thicker than 200 nm** the average **stress** state is almost **negligible**

Unbiased HiPIMS films (U_S= 0 V) : SEM and XRD analysis





- **Compact morphology** composed of **nanometric grains**
- The **superficial** pattern reveals **globular grain**

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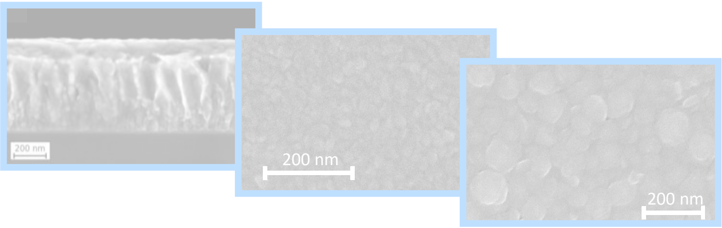

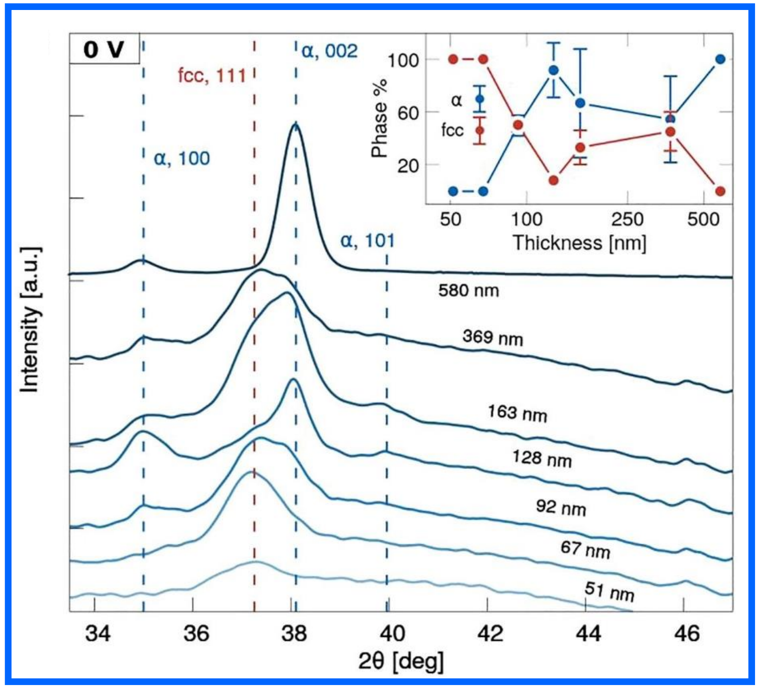

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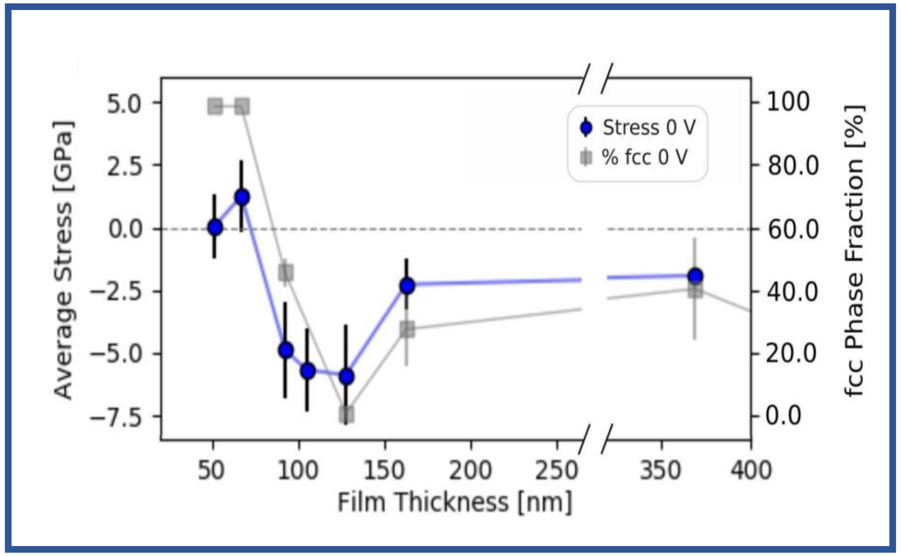
- The **superficial** pattern reveals **globular grain**

- At low thicknesses a **peak positioned at 2θ = 37.05°** → the **fcc phase** (111) reflection.
- **Coexistence** between the **fcc and α phases.**↑ **α phase (002)** reflection ↑ thickness increases (**minimization of the surface energy**)
- Complete **fcc→α-phase transition** at a critical film thickness **between 370 nm and 580 nm**

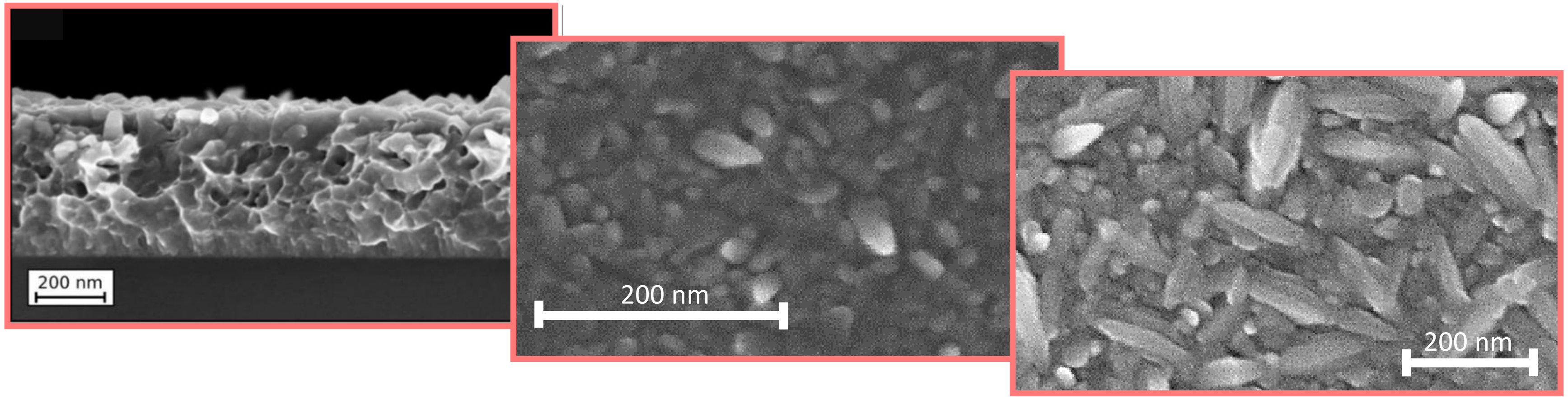
Unbiased HiPIMS films (U_S= 0 V) : stress analysis

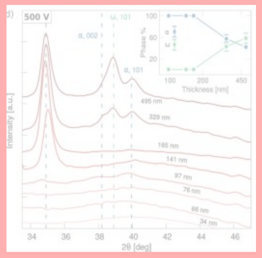
- **Mobility** of the species on the substrate → **homologous temperature** $T_h = T_s / T_m$
- In our case $T_h \approx 0.15$ (assumed T_s at room temperature) → **low mobility behavior**
- Increasing the thickness → **tensile stress state** expected
- **Steady-state stress** at high thicknesses



- **Compressive-tensile-compressive** (CTC) **behavior** associated to a 3D Volmer-Weber growth
- **High** surface **mobility** metals
- The **presence** of the **ion flux** could be related to this behavior and to the fcc phase nucleation
- Strong **correlation** between **stress** trend and **fcc fraction** trend

Biased HiPIMS films (U_S= -500 V) : SEM and XRD analysis





- The cross section appears as result of **plastic deformation** and **nanovoids** are visible
- **Elongated grains** appear. Quantity and dimension increase with the films thickness

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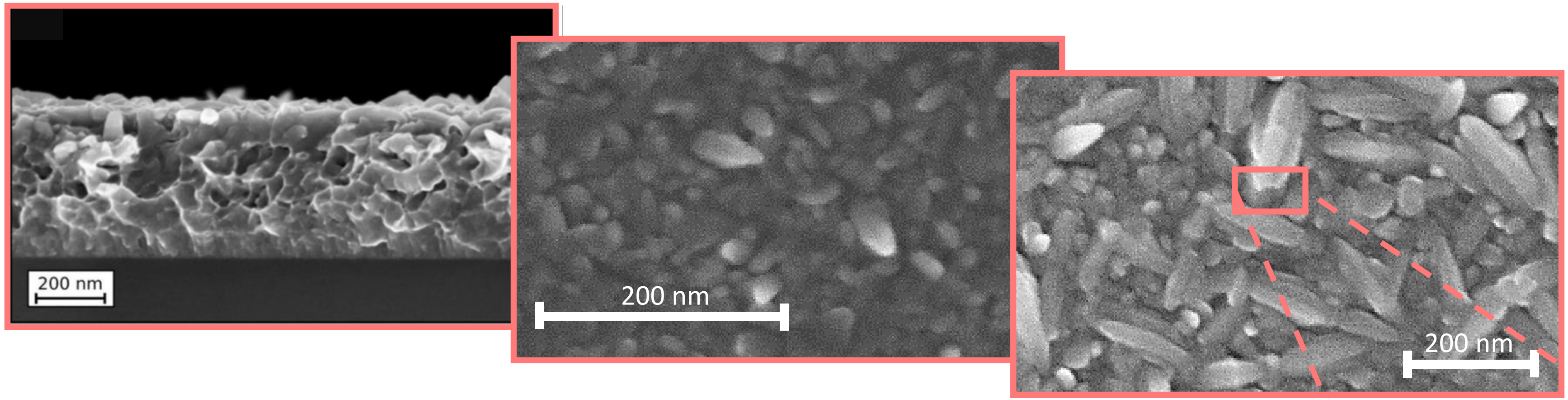

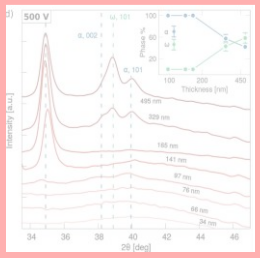

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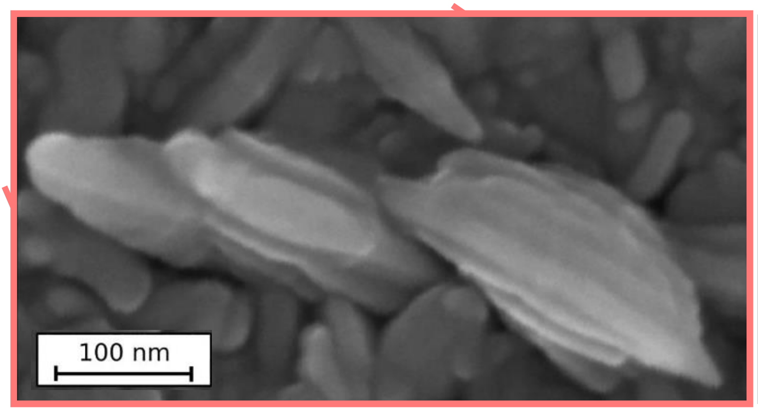
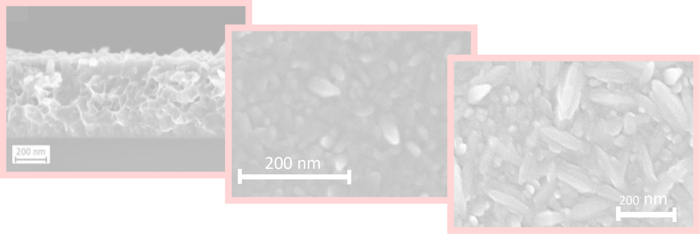
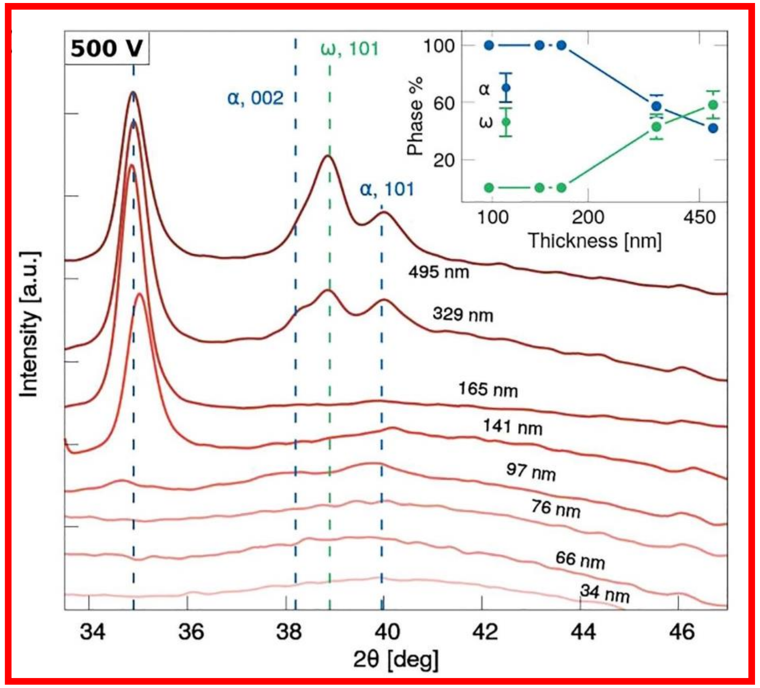


Biased HiPIMS films (U_S= -500 V) : SEM and XRD analysis





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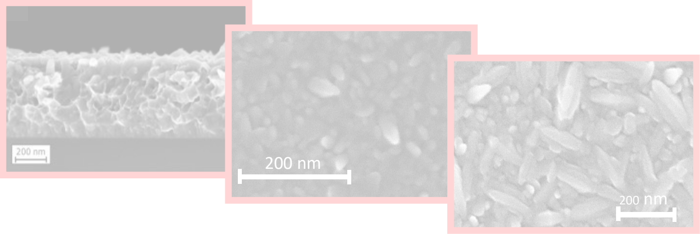
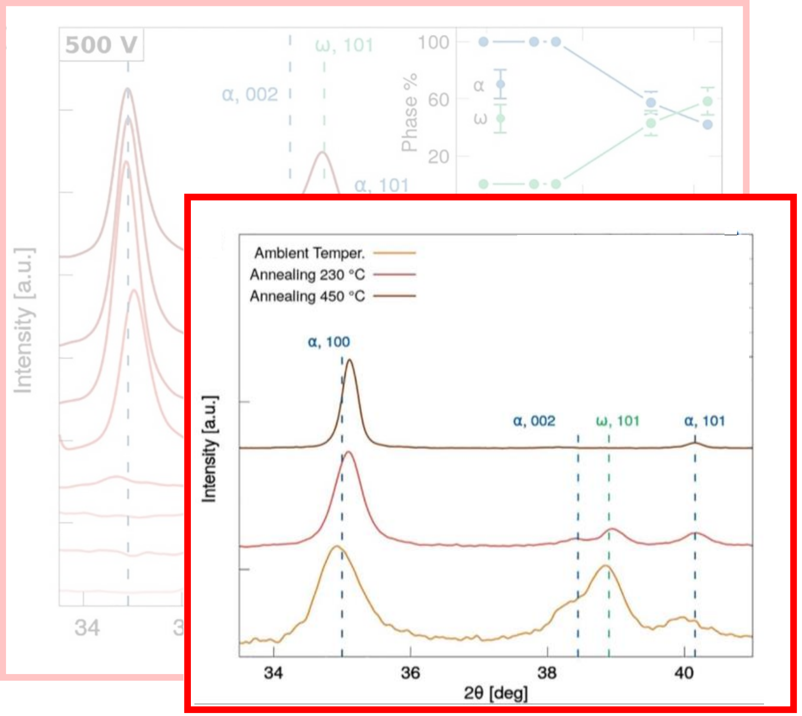
- At **lowest thicknesses** → **no peaks** presence
- **α-phase peaks** appear → strong orientation along the **(100)** direction (**minimization of strain energy**)
- A **new peak** appears at **2θ = 39°** → **(101) reflection** of the **ω-phase** (correlation with **elongated grains**)

Biased HiPIMS films (U_S= -500 V) : SEM and XRD analysis





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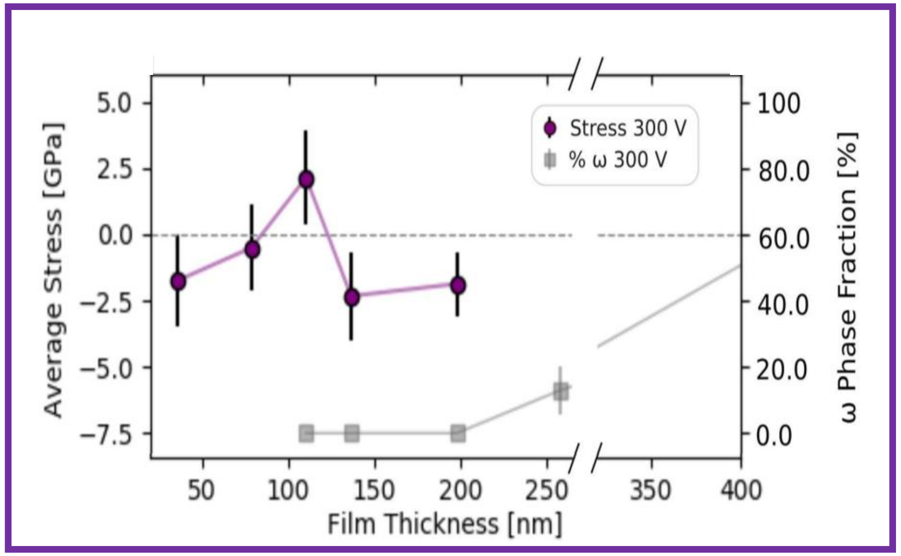
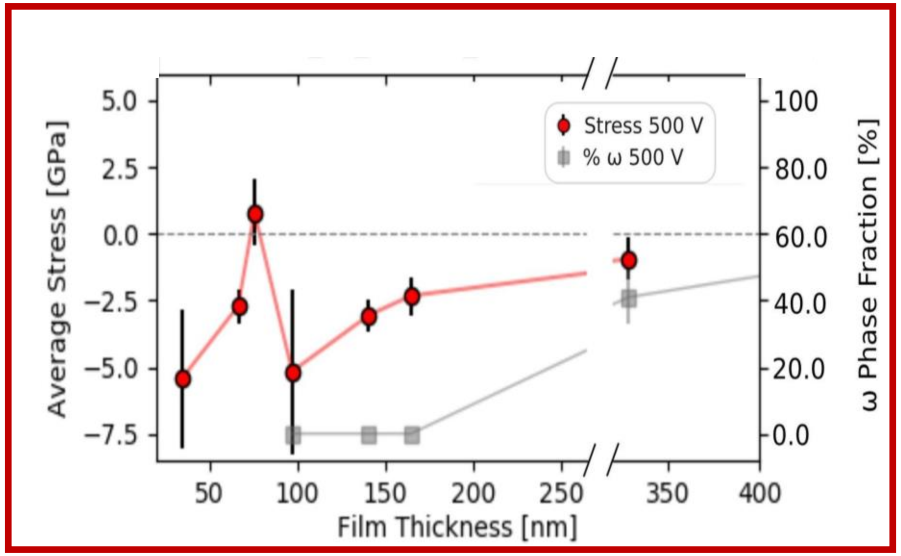
- **Annealing** → **decrease** up to a complete **absence** of the **ω-phase peak**

Biased HiPIMS films (U_S= -300 and -500 V): stress analysis

- In both cases a **CTC behaviour** is observed
- Strong initial compressive stress in the system
- Development of the **ω-phase for relatively low stress**
- Out of equilibrium condition → **α-phase rearranging** to the structure of **ω-phase**





Conclusions

By optimizing deposition parameters, HiPIMS allows to to obtain Ti films exhibiting not only the Ti α-phase, but also other uncommon crystalline phases.

- The **ion fraction** has been **maximized** by analyzing the plasma composition **in a range of** P_{Peak} (5 - 50 kW).
- **Comparison** of Ti films grown both in a **low Ti ions** (DCMS) and **high Ti ions** (HiPIMS) **environments**
- **Comparison** of Ti films grown both in **a low energy Ti ions** (U_S = 0 *V*) and **high energy Ti ions** (U_S = -300 V and -500 V) **environments**
- The presence of a **low energy and high fraction ion environment** leads to **fcc phase formation** to the lowest thicknesses
- The presence of a **high energy and high ion fraction environment** leads to the formation of **α-phase** strongly **oriented** along the **(100) direction**
- At “high” film thicknesses the **high energy regime** drives to **ω-phase nucleation** (with relatively low amount of stress)

- Activities performed within the framework of an **ERC consolidator grant** (from 2015 to 2020)

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Exploring the **N**ew **S**cience and engineering unveiled by
Ultraintense ultrashort **R**adiation interaction with matt**E**r

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D. Dellasega, F. Mirani, D. Vavassori, C. Conti and M. Passoni, Role of energetic ions in the growth of fcc and ω crystalline phases in Ti films deposited by HiPIMS, App. Surf. Sci. 556, 2021

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Principal investigator

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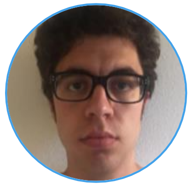
V. Russo

A. Pola

A. Maffini

A. Formenti

F. Mirani



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Thank you for your kind attention!

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