Multi-technique investigation: short and medium range order

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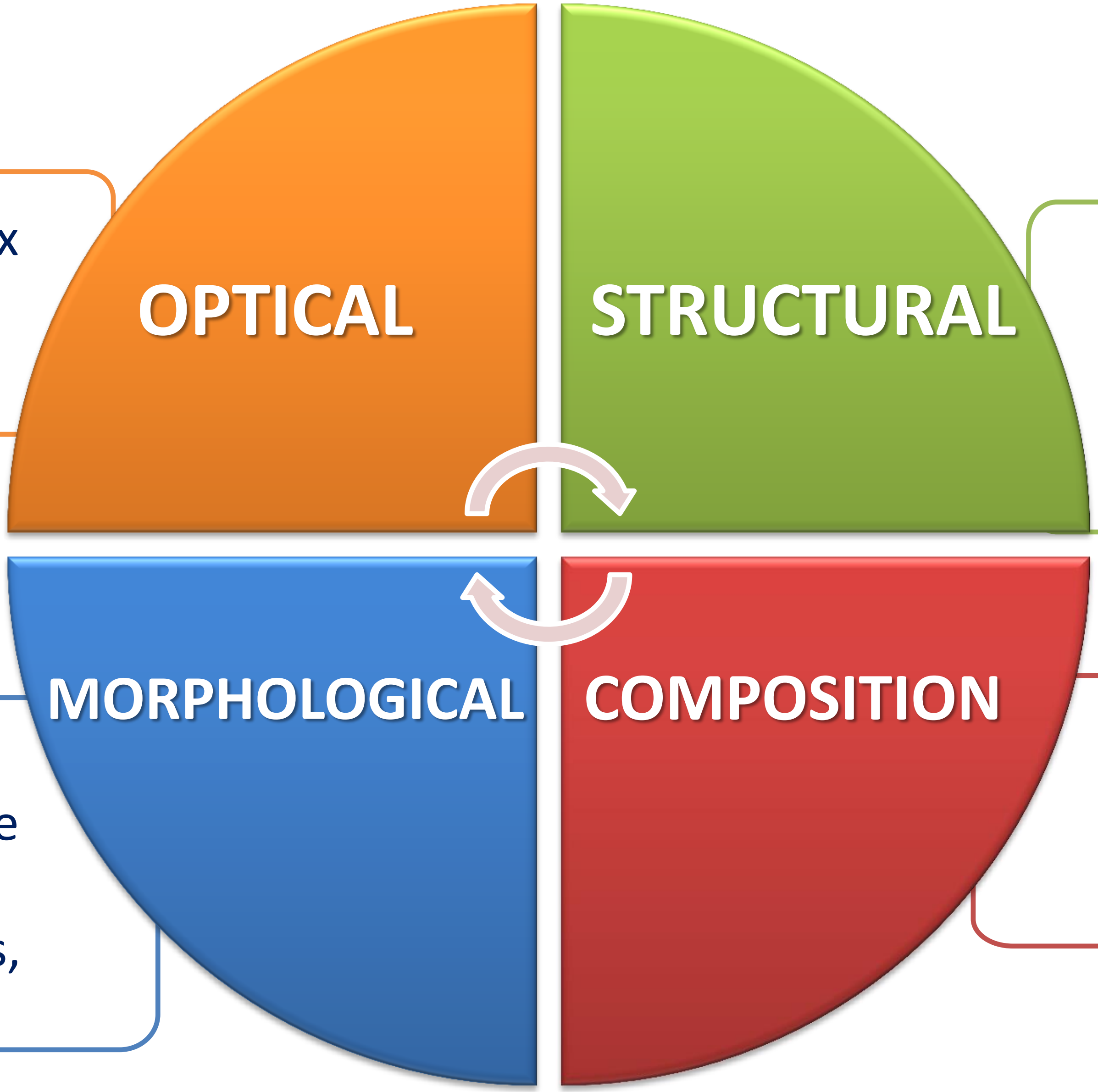
Physico-chemical characterizations

- Refractive index
- Absorption
- Scattering



- Crystalline grains
- Density
- Glass structure
- Elastic properties

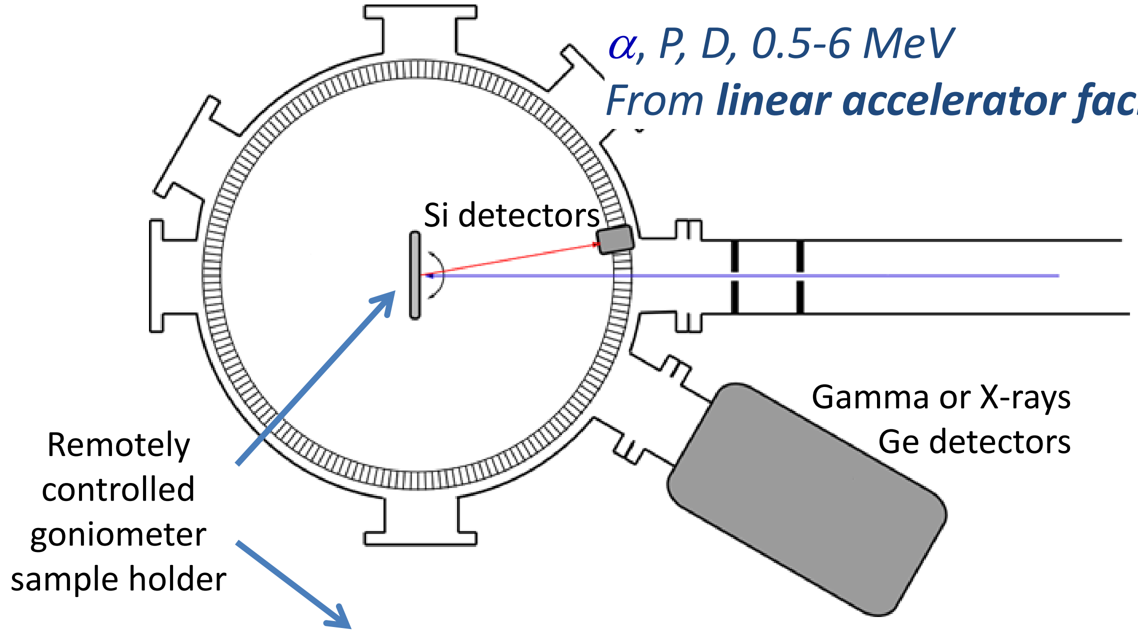
- Thickness
- Surface/interface roughness
- Defects (bubbles, cracks)

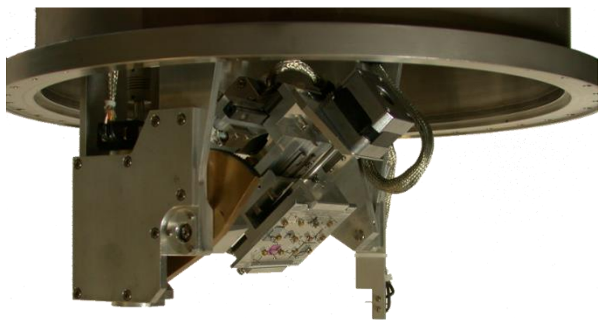
- Stoichiometry
- Contaminants
- Dopants

COMPOSITION

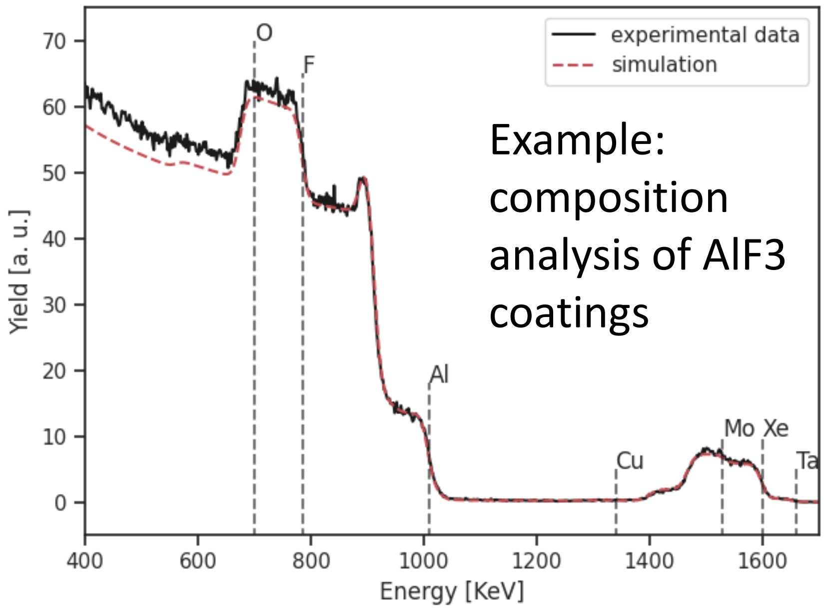
Ion Beam Backscattering Analysis (RBS-NRA- ERDA)

α, *P, D, 0.5-6 MeV*
From ***linear accelerator facilities***





- ➢ **Chemical elements absolute quantification**
- ➢ Investigated depth: from monolayer to μm's
- ➢ Sensitivity: it depends… 1 to 0.1 at %

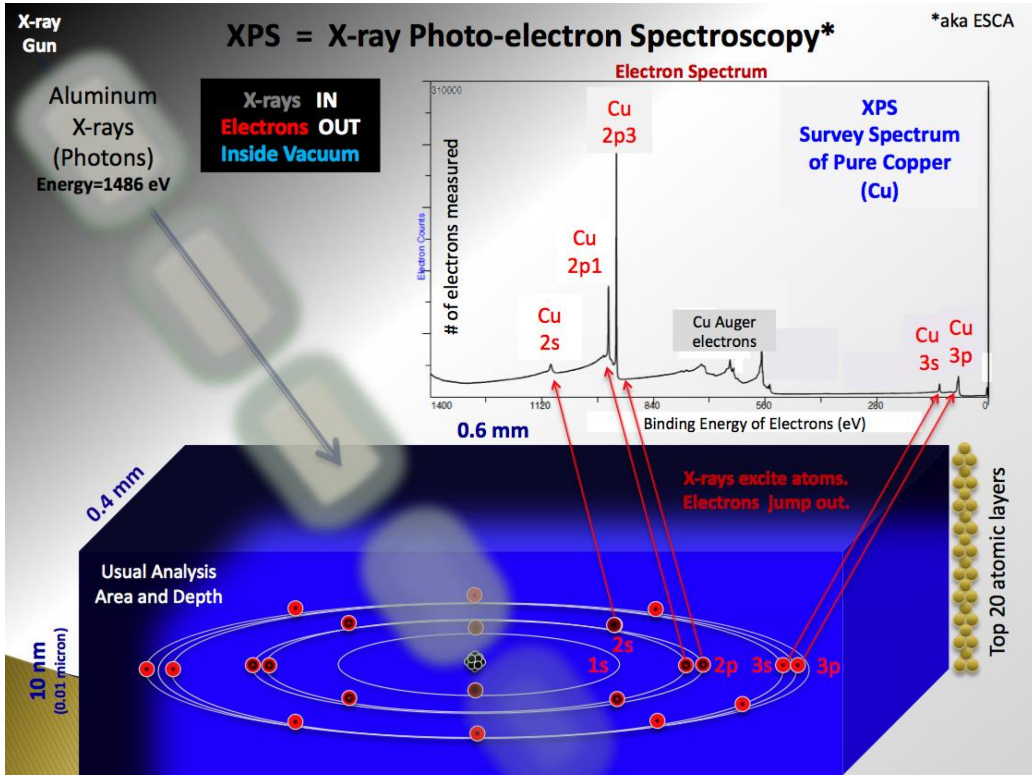


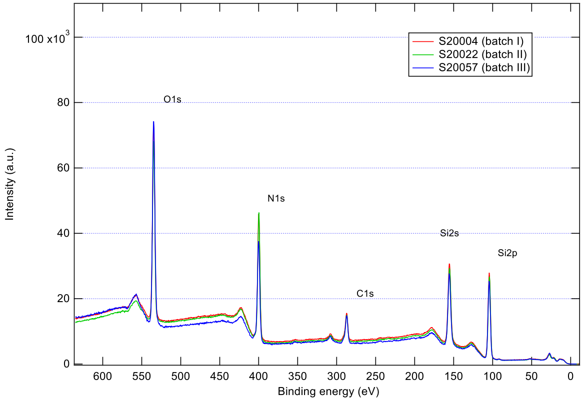
Example: composition analysis of AlF3 coatings

- Al/F = 0.4 (instead of 0.33)
- $\rho = 2.7\ g/cm^3$
- Xe, Mo contamination from process gas and grids
- Cu, Ta traces

Bischi, M., et al. "Characterization of Ion-Beam-Sputtered AlF3 Thin Films for Gravitational-Wave Interferometers." *Physical Review Applied* 18.5 (2022): 054074.

Composition: X-ray Photoemission Spectroscopy



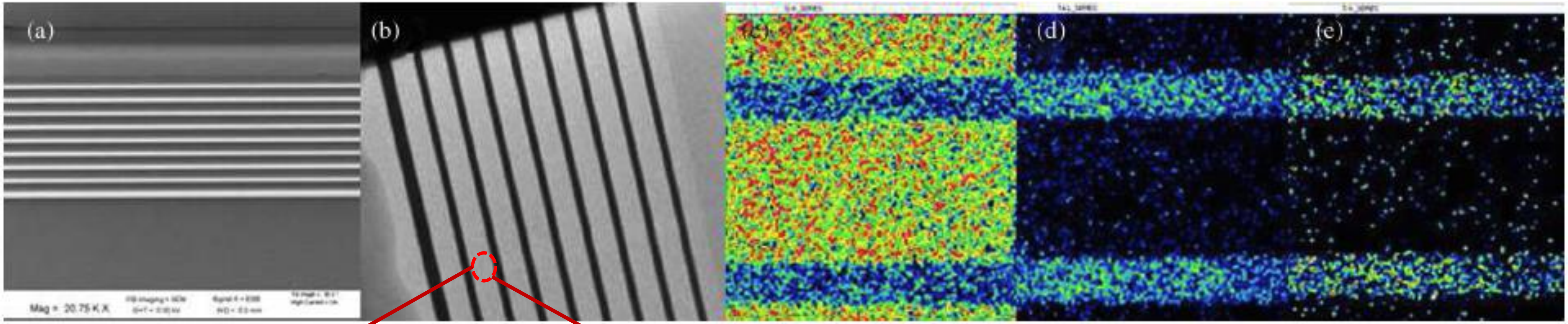


- **Relative quantification of elements and chemical state**
- Investigated depth: from monolayer to few nm
- Sensitivity: it depends… (1 to 0.1 % at)

Composition:

SEM -EDX

SiO2/Ti:Ta2O5 multilayer



Bright field

Dark field

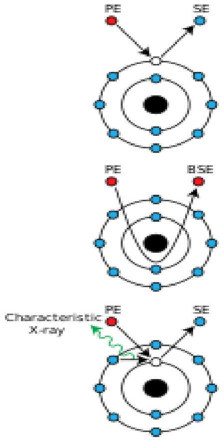
Si

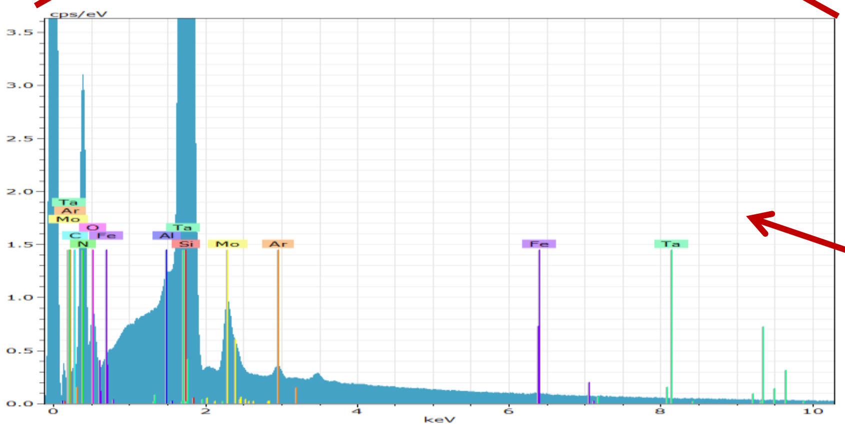
Ta

Ti

Granata, Massimo, et al. "Mechanical loss in state-of-the-art amorphous optical coatings." *Physical Review D* 93.1 (2016): 012007.

Magnozzi et al. VIR-0375A-21

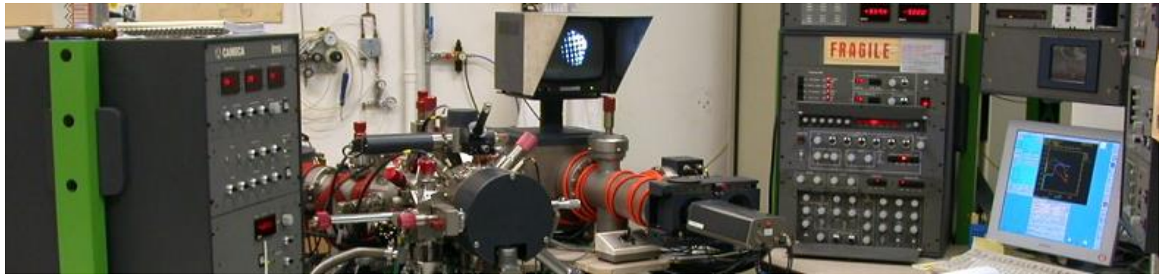




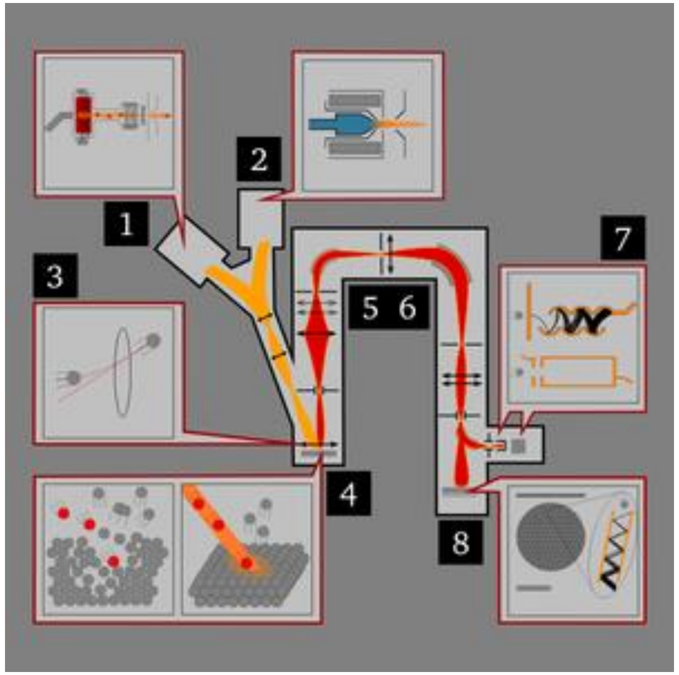
X-ray spectrum

- **Spatial mapping of elements**
- Investigated depth: from few nm to microns
- Imaging magnification: up to x 10^6
- Sensitivity: a few at %

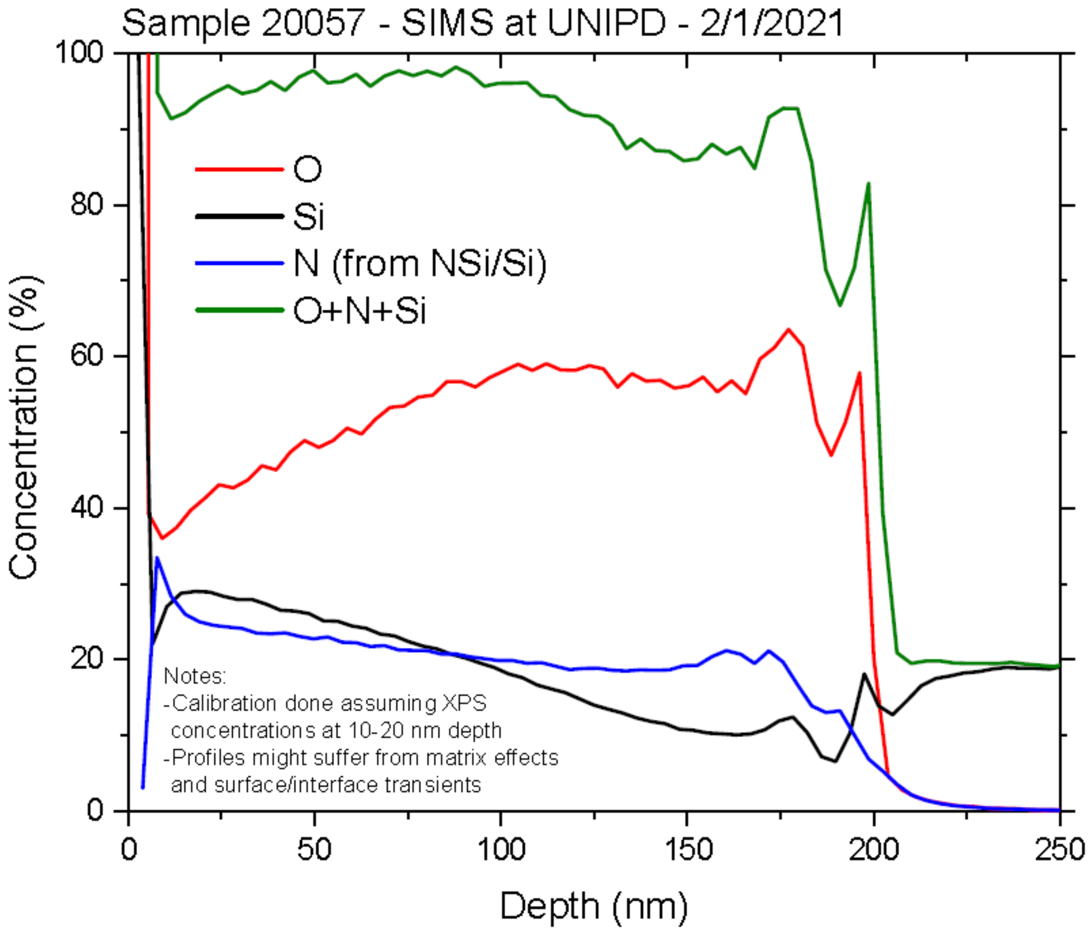
Composition: Secondary Ion Mass Spectrometry



SiN3 with heavy oxygen contamination and nonuniform stoichiometry



- **Elemental depth profiling**
- Investigated depth: from few nm to about 1 -2 microns
- Sensitivity: it depends but it can be very high (ppm…)
- Not absolute, needs an independent calibration



MORPHOLOGY

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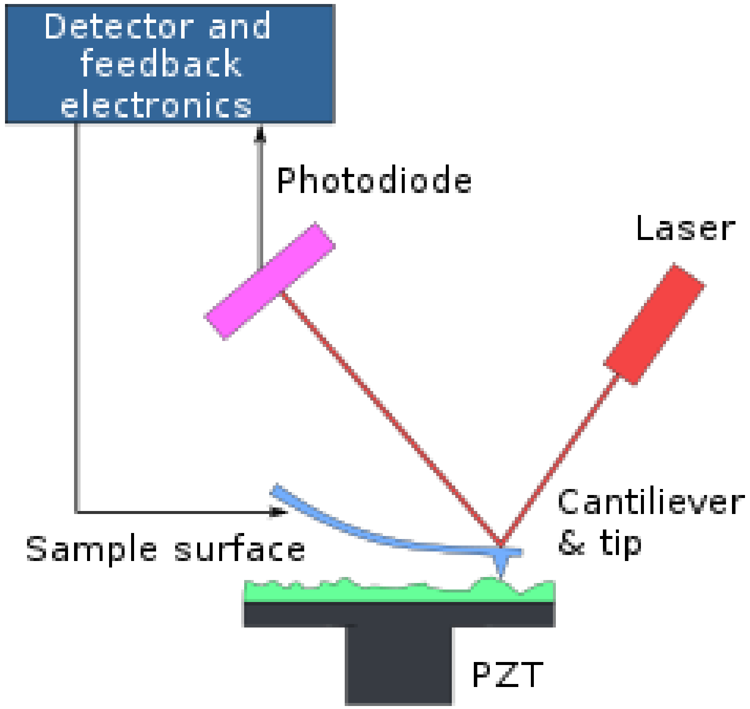
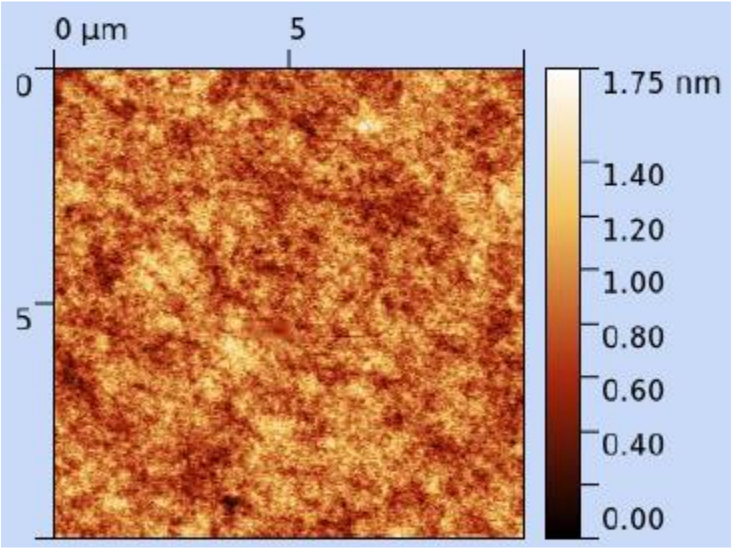
Dipartimento di Fisica e Astronomia Galileo Galilei

INFN Padova

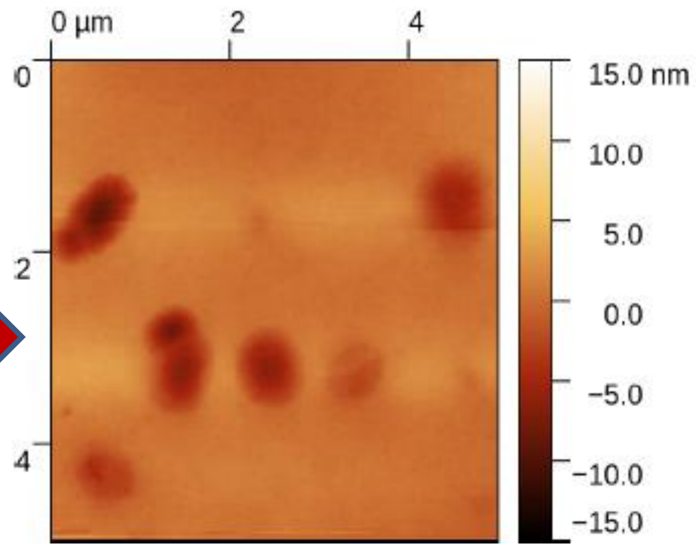
ET Italy Einstein Telescope

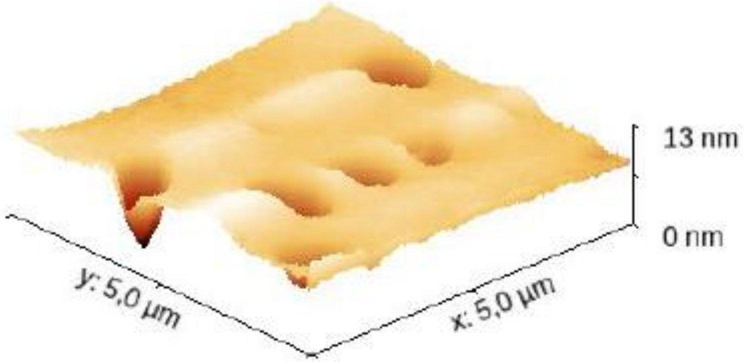
Morphology: Atomic Force Microscopy



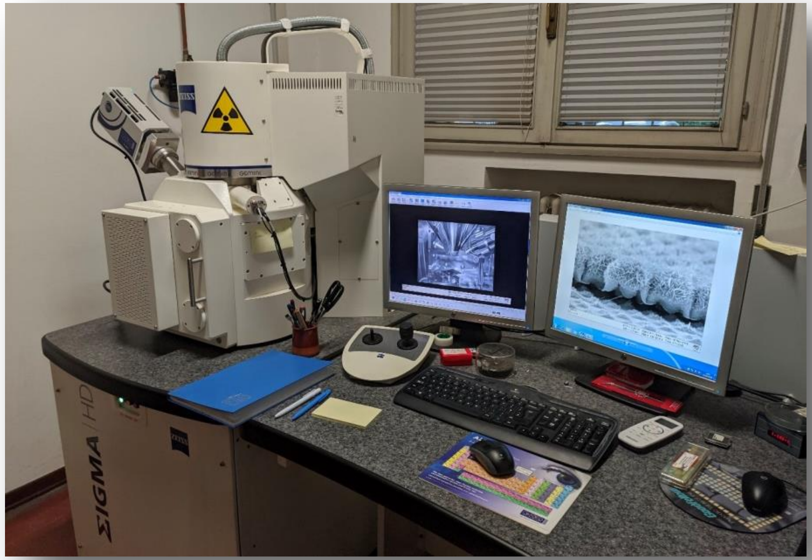


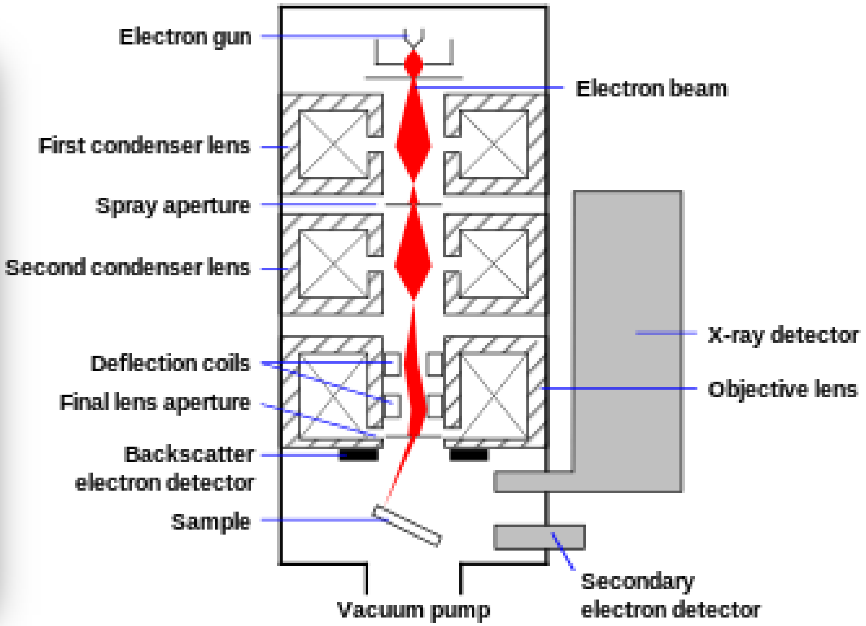
Crystalline grains formation in Ta2O5 upon annealing 630°C 9 h

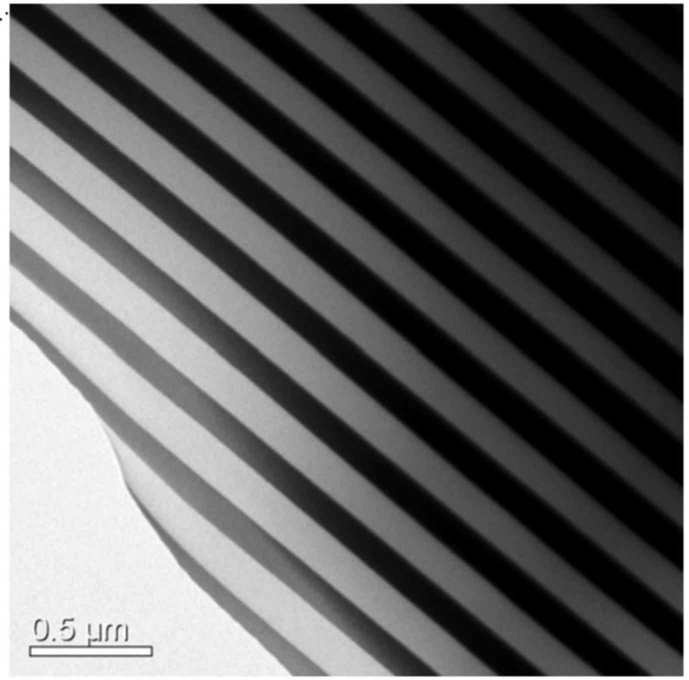




- **Surface topography**
- Very good height resolution (down to 1 Ang)
- Many different measure mode (contact, non-contact, lateral force, etc.)





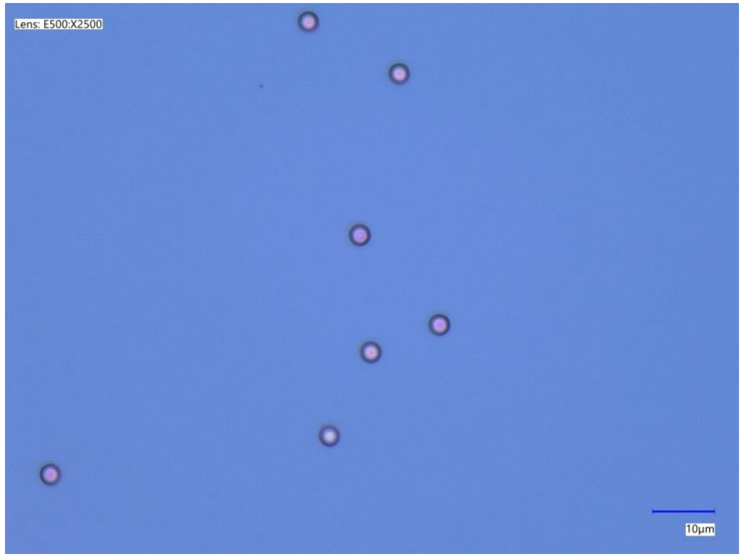


SEM image of an ion beam-sputtered λ/4 multilayer stack of SiO_2 (light) and TiO_2 doped Ta_2O_5 (dark) designed for high-reflectivity at 1064 nm

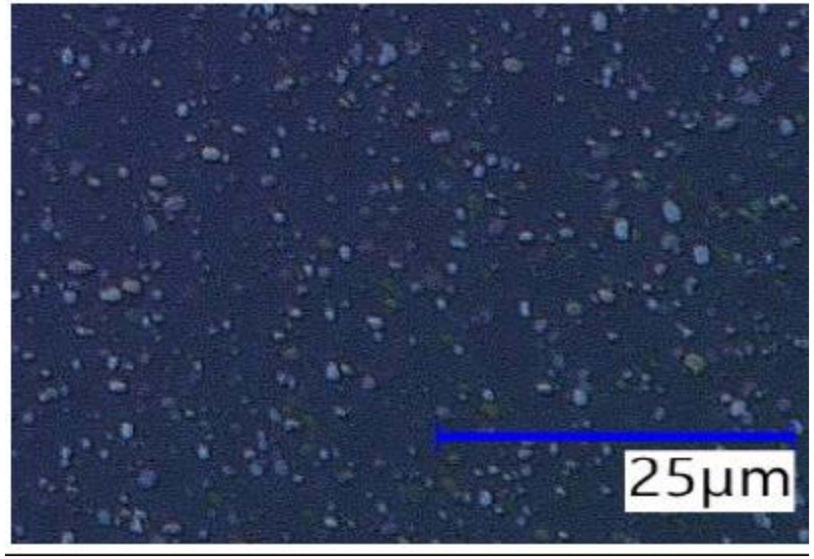
- **Surface topography**
- **Cross sectioning**
- Very good height resolution (down to 1 Ang)
- Possibilty to use different probes

Reid, S.; Martin, I.W. Development of Mirror Coatings for Gravitational Wave Detectors. *Coatings* **2016**, *6*, 61. https://doi.org/10.3390/coatings6040061

Morphology: Digital Optical Microscopy



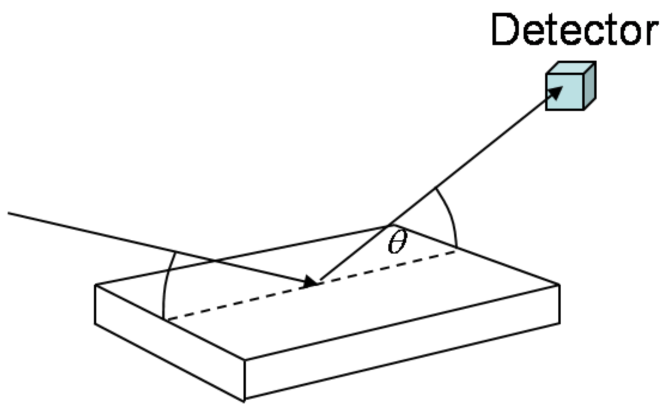
Bubbles in Hf:Ta2O5 annealed



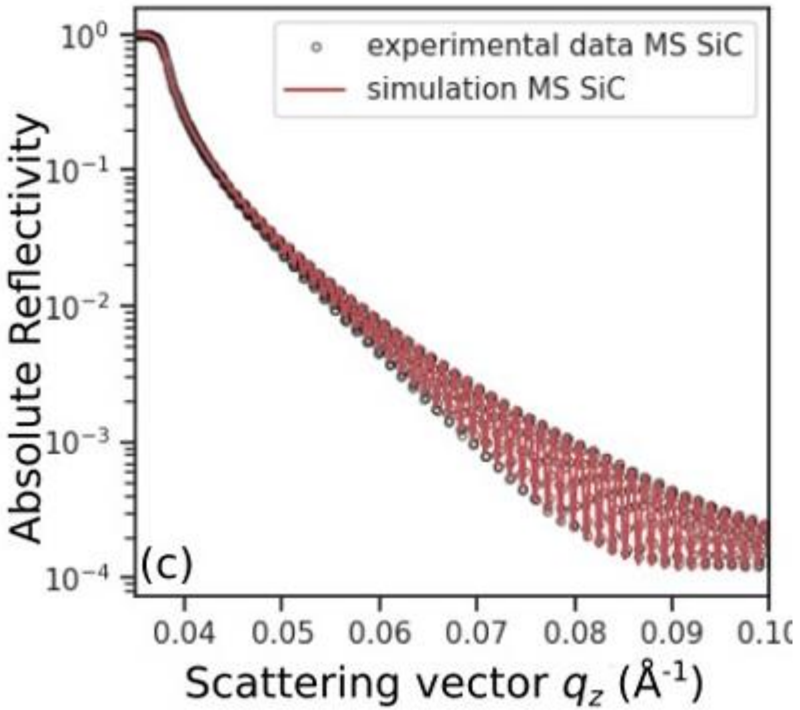
Crystalline grains in Ta2O5 after annealing

- **Surface observation**
- Sub-micron resolution
- Possiblity to perform large area mapping
- Software for analysis of images
- Defects (bubble, cracks, crystallites)

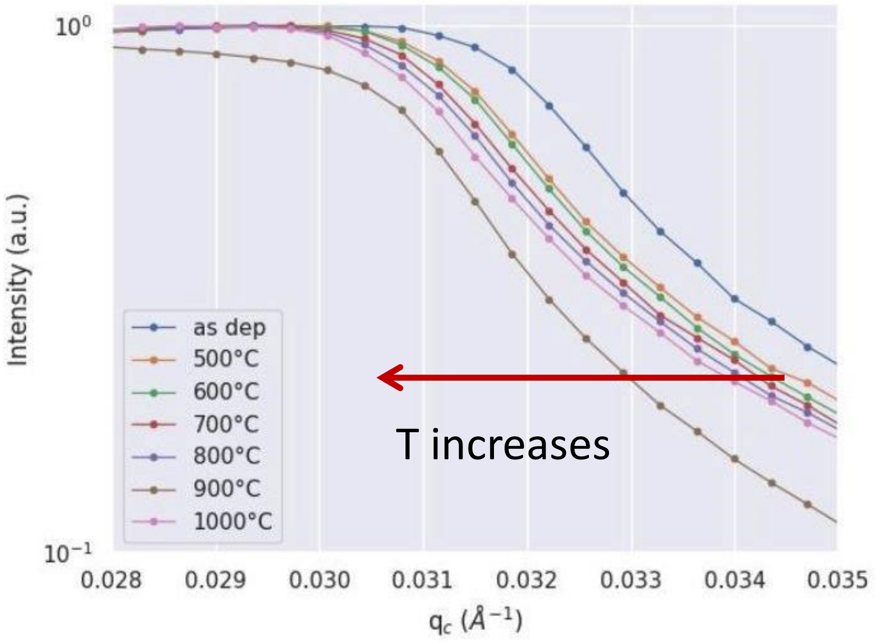
Morphology: X-Ray Reflectivity



- **Non- destructive**
- **Film Density**
- **Coating thickness (up to 500 nm)**
- **Interfaces study (roughness, conformatio etc.), also for ML.**



Characterization of a SiC layer on Si deposited by magnetron sputtering,
Thickness: t = (423.1 ± 0.1) nm ;
Density ρ = (2.82 ± 0.05) g/cm3
RMS Roughness: σ = (2.3 ±0.1) nm



De-densification of a SiO2 layer upon thermal annealing

Favaro, G., et al. *Physical Review Applied* 18.4 (2022): 044030.

L.Silenzi et al. GWADW 2023

OPTICAL PROPERTIES

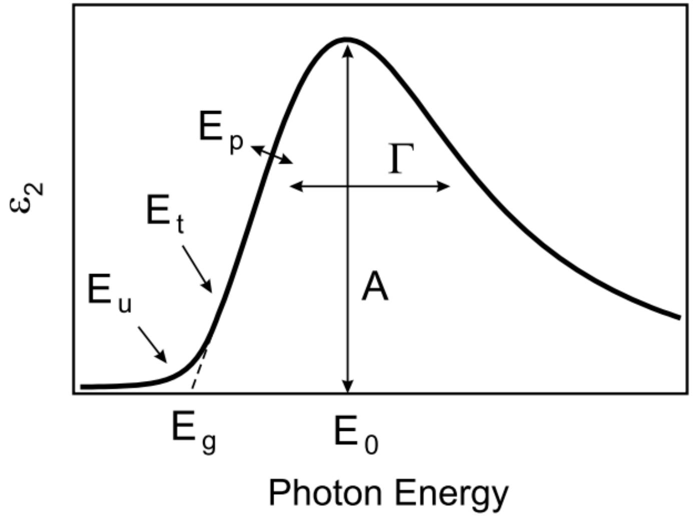
Optical properties: Ellipsometry

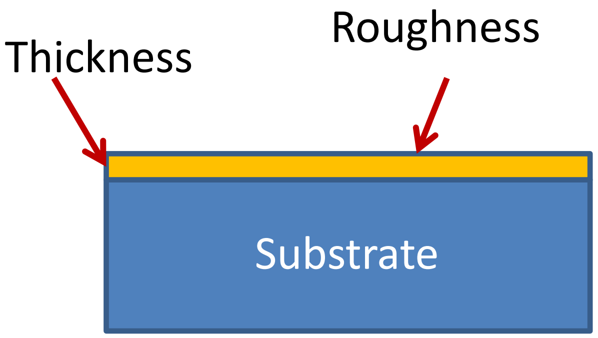
Cody-Lorentz dispersion model

Spectroscopic ellipsometer
Measures the reflected beam polarization as a function of:

- Input polarization
- Wavelength
- Angle of incidence

In general, the obtained data must be analyzed **assuming** an optical model: no direct inversion is possible



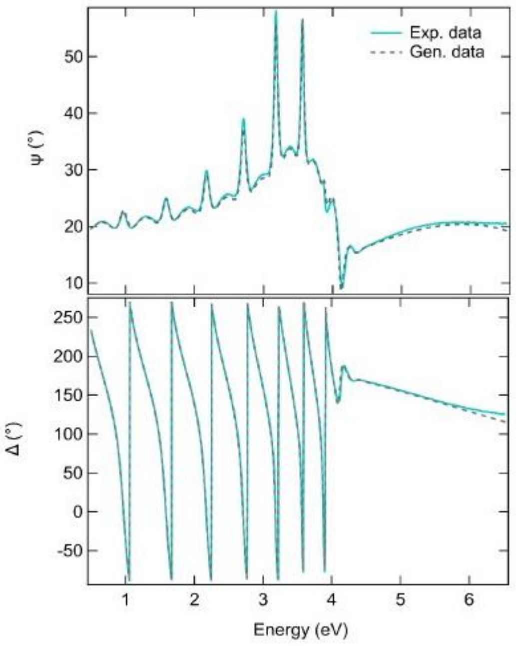


$$\epsilon_2(E) = \begin{cases} \frac{E_t G(E_t) L(E_t)}{E} \exp\left(\frac{E-E_t}{E_u}\right), & 0 < E \leq E_t \\ G(E)L(E) = \frac{(E-E_g)^2}{(E-E_g)^2+E_p^2} \frac{A E_0 \Gamma E}{(E^2-E_0^2)^2+\Gamma^2 E^2}, & E > E_t \end{cases}$$

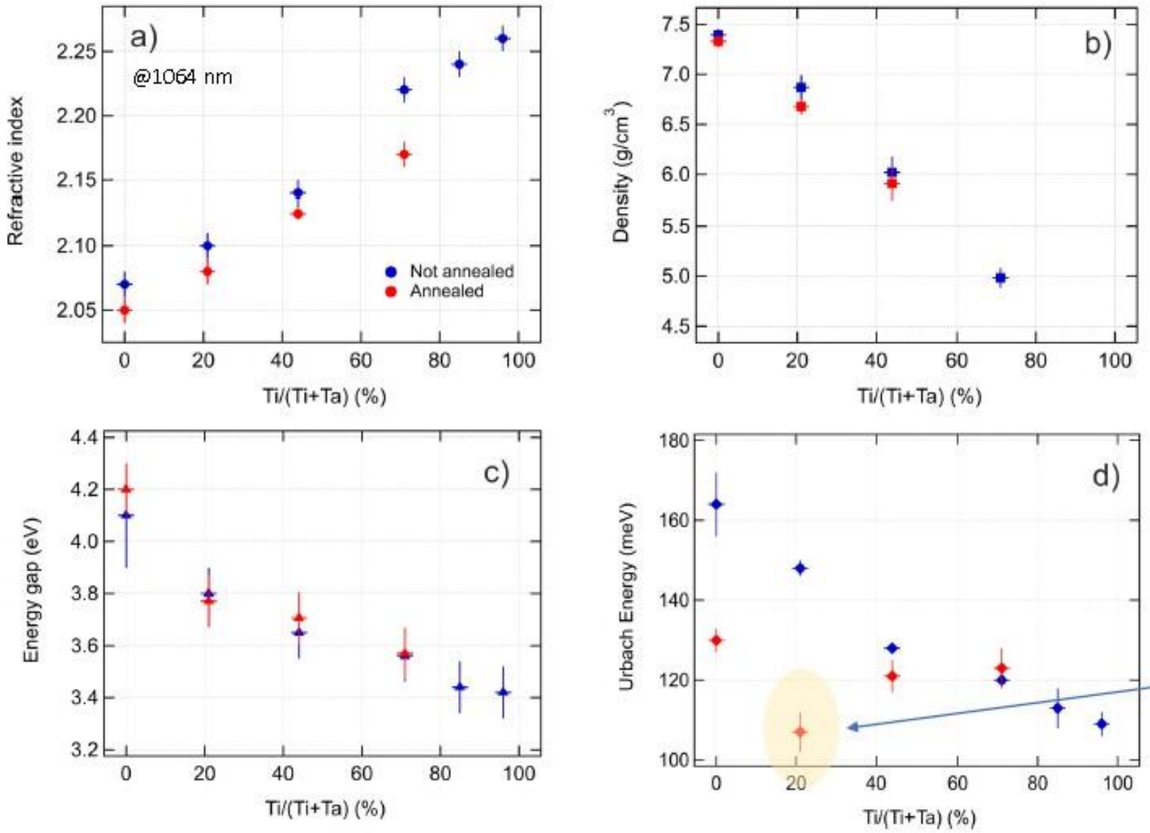
- **Refractve index and absorption at different wavelenghts**
- **Thickness and roughness**
- Investigated depth: from monolayer to μm's
- Sensitivity: it depends…

M. Magnozzi et al. VIR-0615A-22

Example: Ti:Ta2O5



Measurement example :
Ti: Ta2O5 sample with
Ti/(Ti+Ta) = 0.21



Composition dependence of optical properties in titania-doped tantala

Monotonous trends:

- Refractive index
- Density
- Energy gap
- Urbach energy, not annealed

Non-monotonous trend:

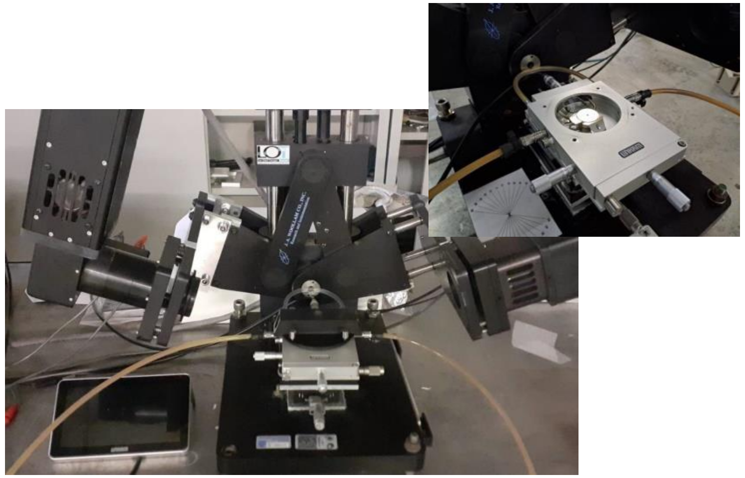
- Urbach energy, annealed

This sample is the one with the best performances (lowest optical absorption, lowest thermal noise)

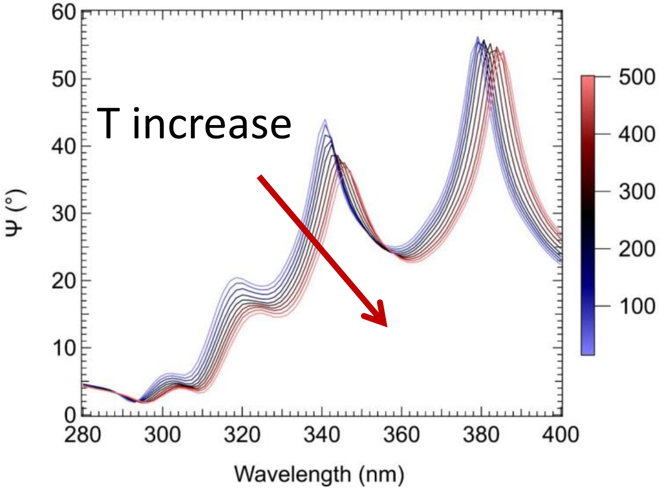
Amato, Alex, et al. "Observation of a correlation between internal friction and Urbach energy in amorphous oxides thin films." *Scientific Reports* 10.1 (2020): 1670.

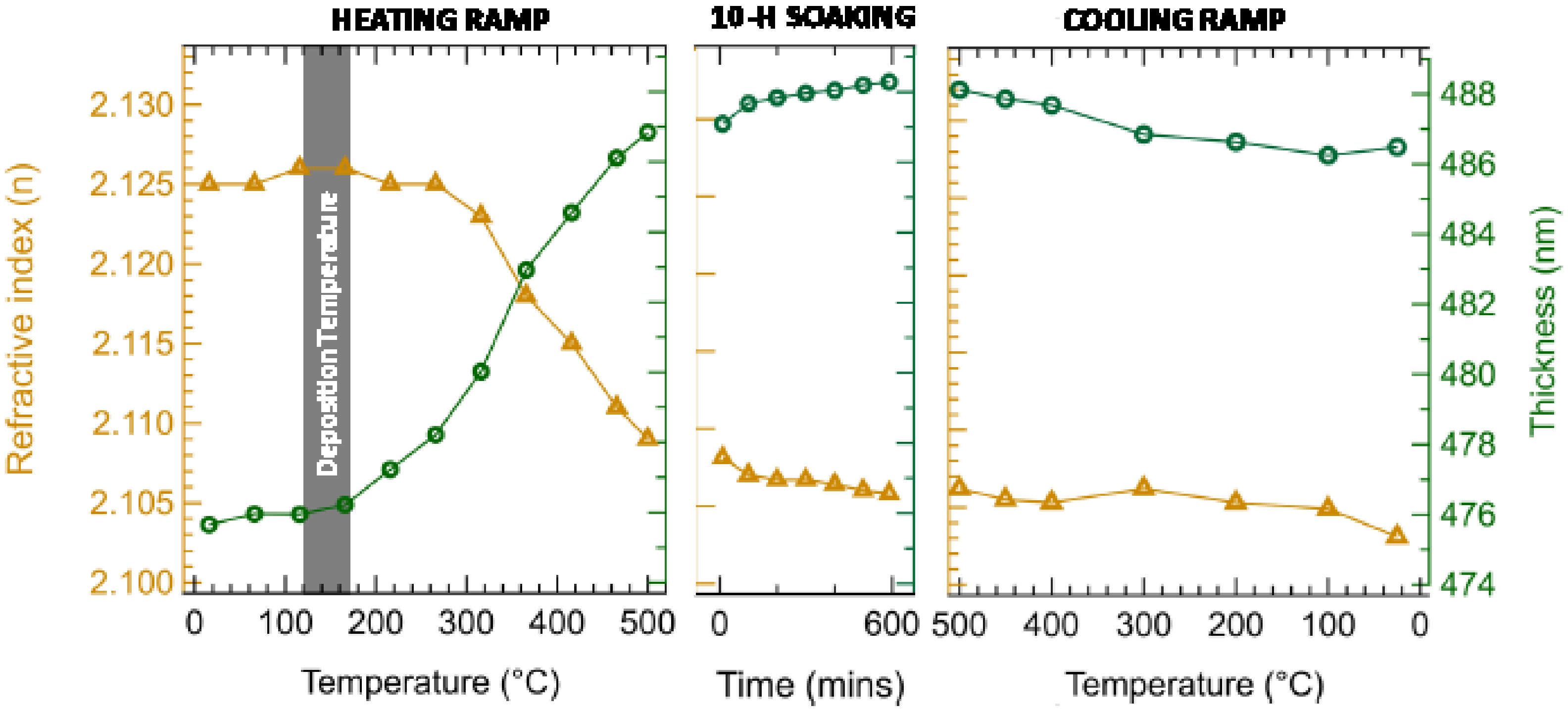
M. Magnozzi et al. VIR-0615A-22

Optical properties: In situ ellipsometry



Heating/Cooling sample cell
For in-situ measurement





Evolution of single layer Ti:Ta2O5 during standard 10h 500°C annealing

M. Magnozzi et al. VIR-0367A-24

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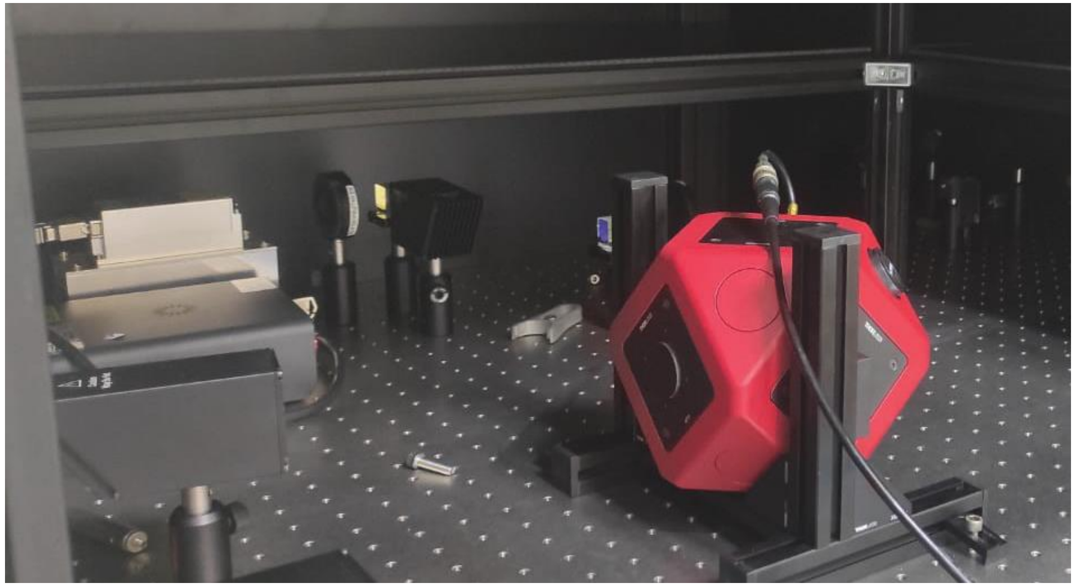
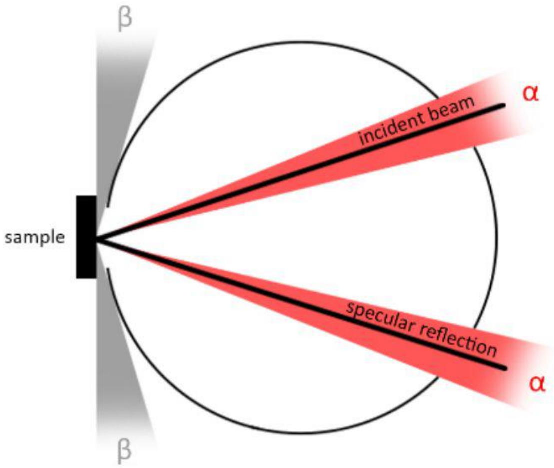
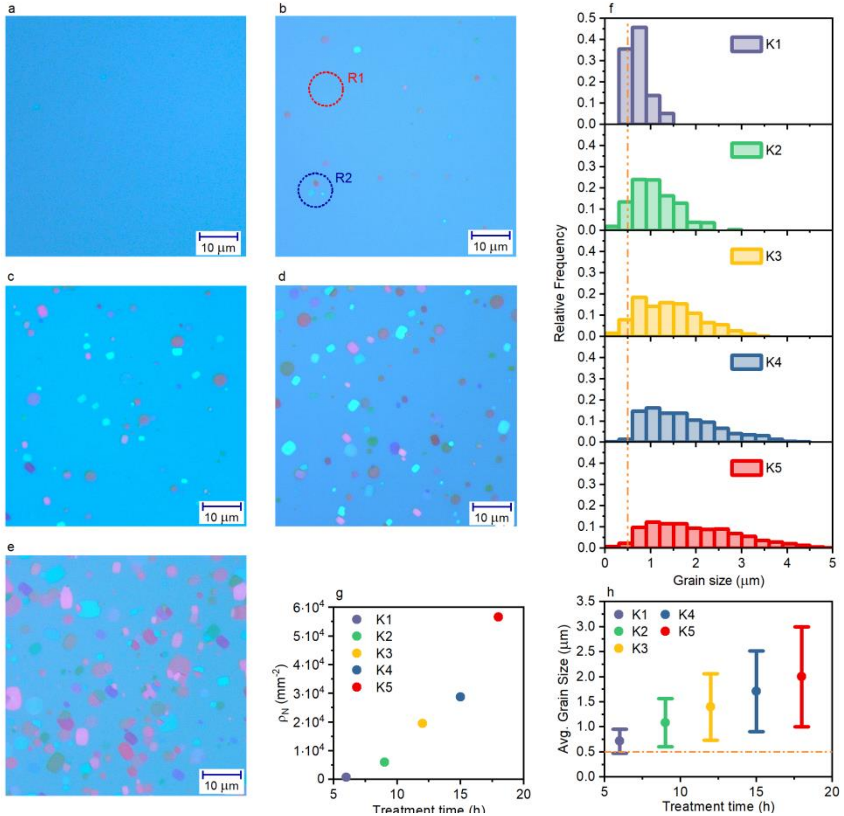
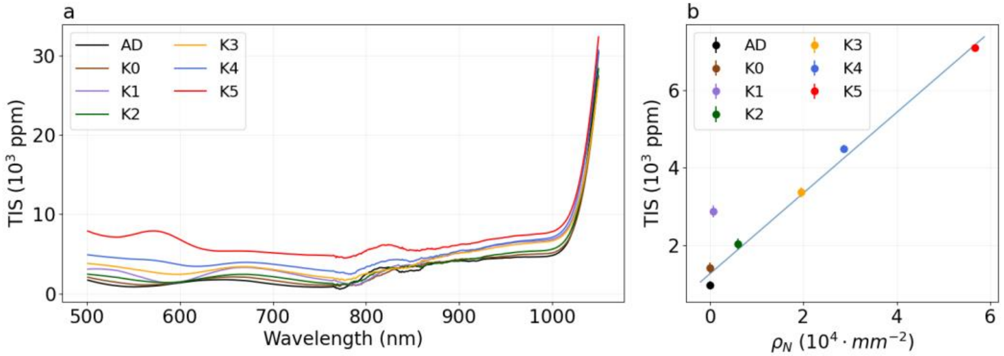
Optical properties: Total Integrated Scattering





TIS = PD/P0

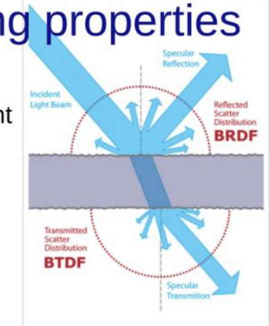




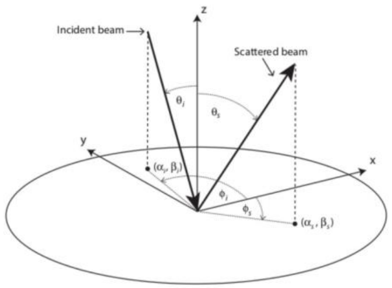
Favaro, Giulio, et al. "Reduction of mechanical losses in ion-beam sputtered tantalum oxide thin films via partial crystallization." *Classical and Quantum Gravity* 41.10 (2024): 105009.

Optical properties: BSDF

BSDF: characterization of scattering properties



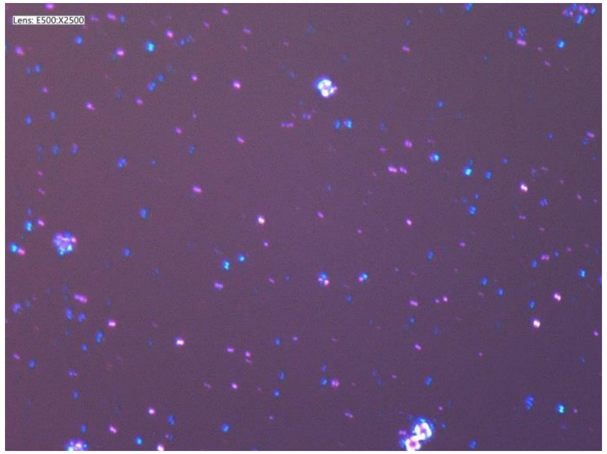
Bi-directional Scattering Distribution Function (BSDF), the ratio of the scattered radiance (ph/s-unit area -sr) to the incident irradiance (ph/s-unit area).
A sort of 'reflectance per solid angle'.

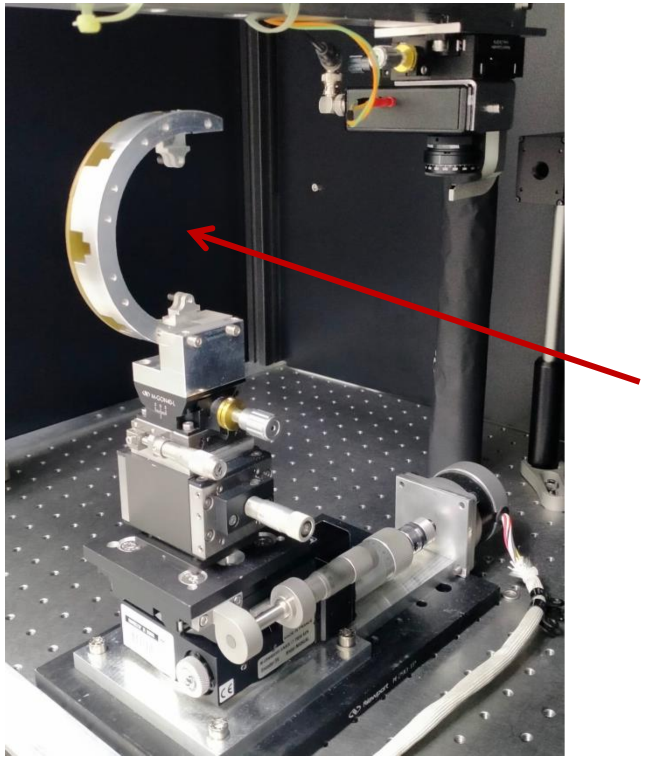


$$BSDF = \frac{d\Phi_s / d\Omega_s}{(d\Phi_i)\cos\theta_s}$$

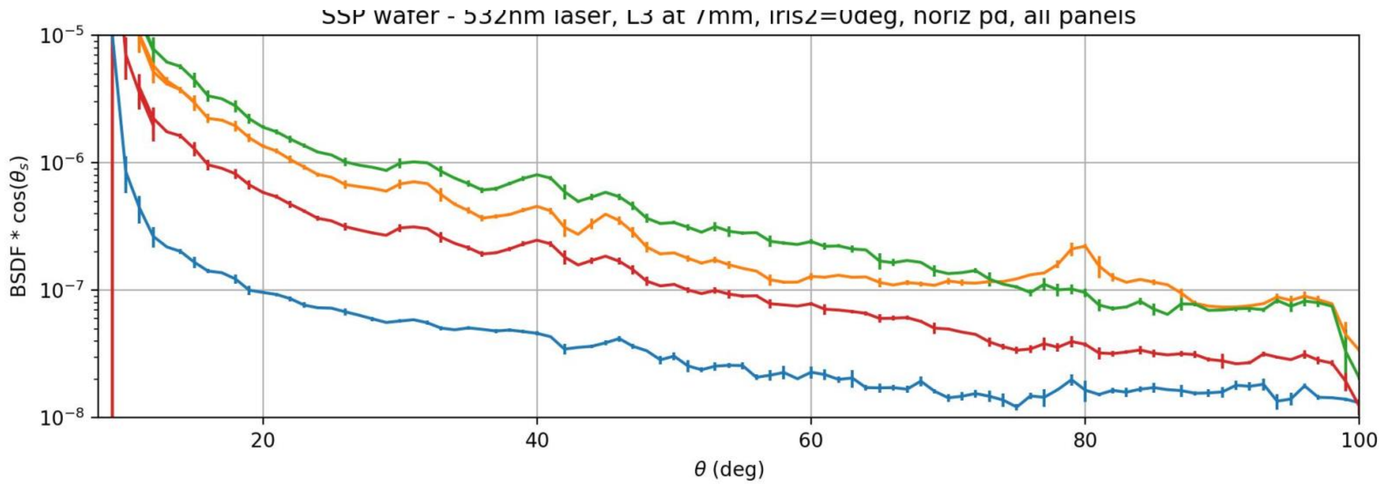
Energy conservation: BSDF must be the same if the incident and scattered rays are reversed ('*Bidirectional*')

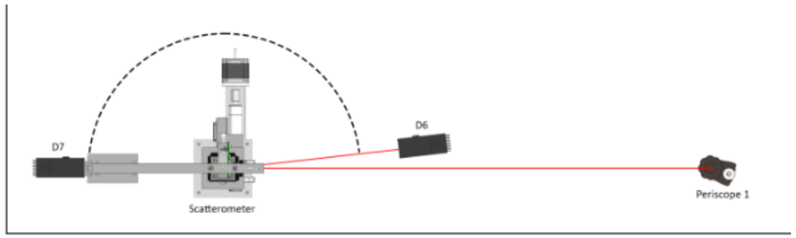
$$BSDF(\theta_i, \phi_i, \theta_s, \phi_s) = BSDF(\theta_s, \phi_s, \theta_i, \phi_i)$$





Input beam





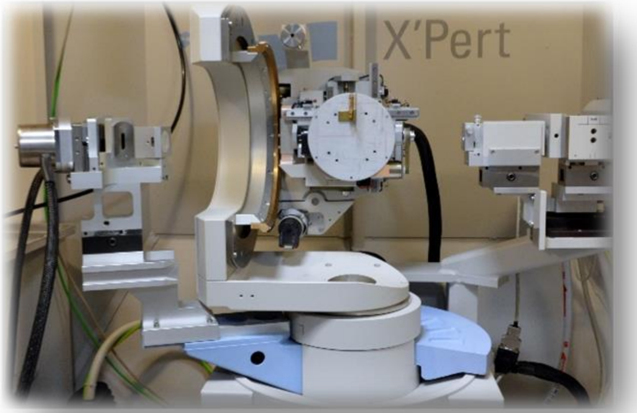
L Conti - EPS HEP 2023 ; VIR-0518B-23

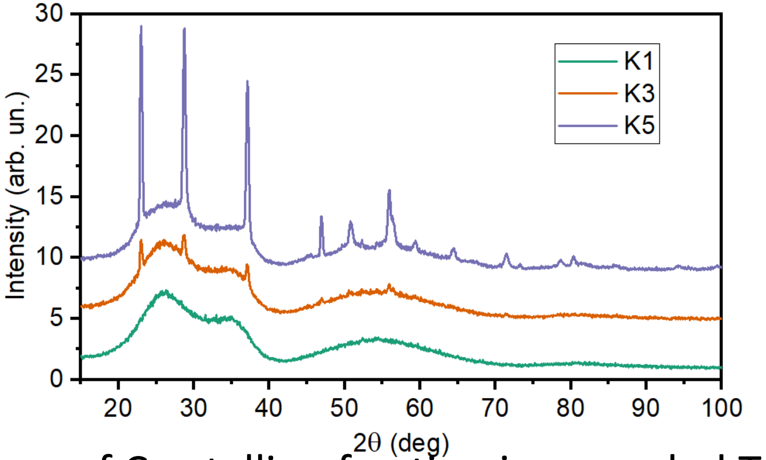
Optical properties: In situ Scattering measurement

J. Smith et al. LIGO DCC G2400567-v5

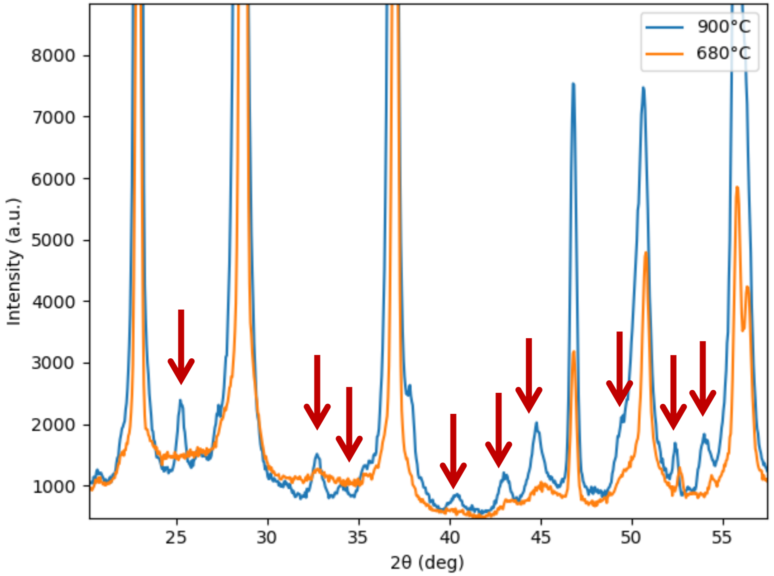
STRUCTURAL PROPERTIES

Structural properties: X-Ray diffraction

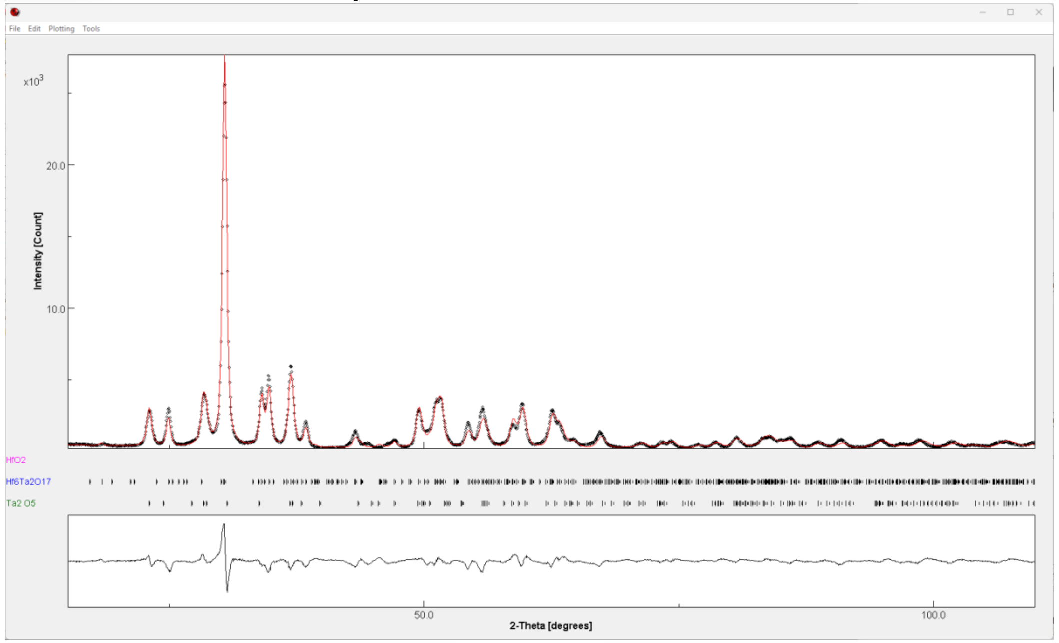




Increase of Crystalline fraction in annealed Ta_2O_5



Phase separation of TiO_2 (Anatase) in Ti:Ta_2O_5 annealed at high T.



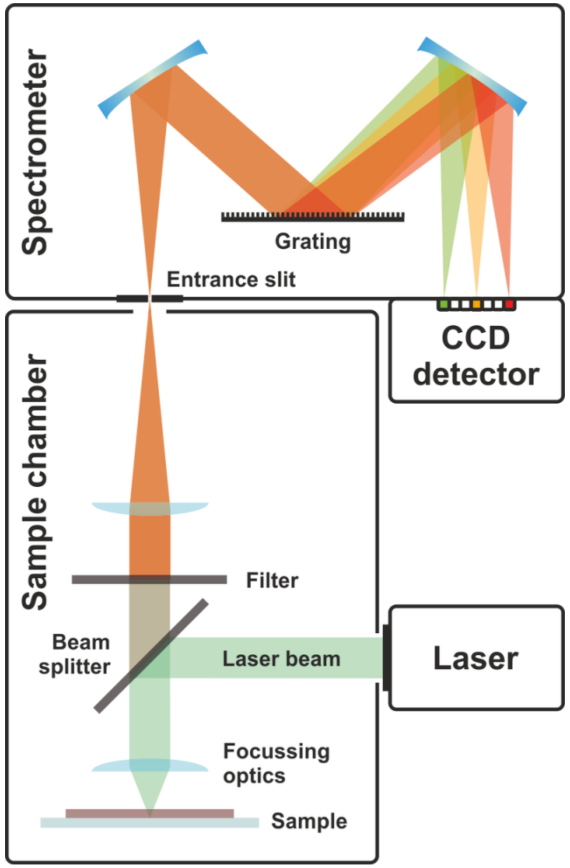
Rietveld fitting of Hf:Ta_2O_5 annealed: the volume fraction of the different phases can be estimated:

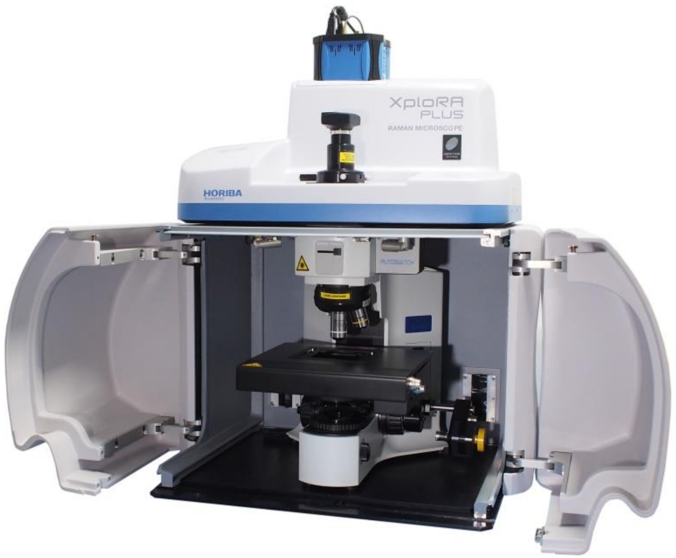
Ta_2O_5 wt% = 20.8

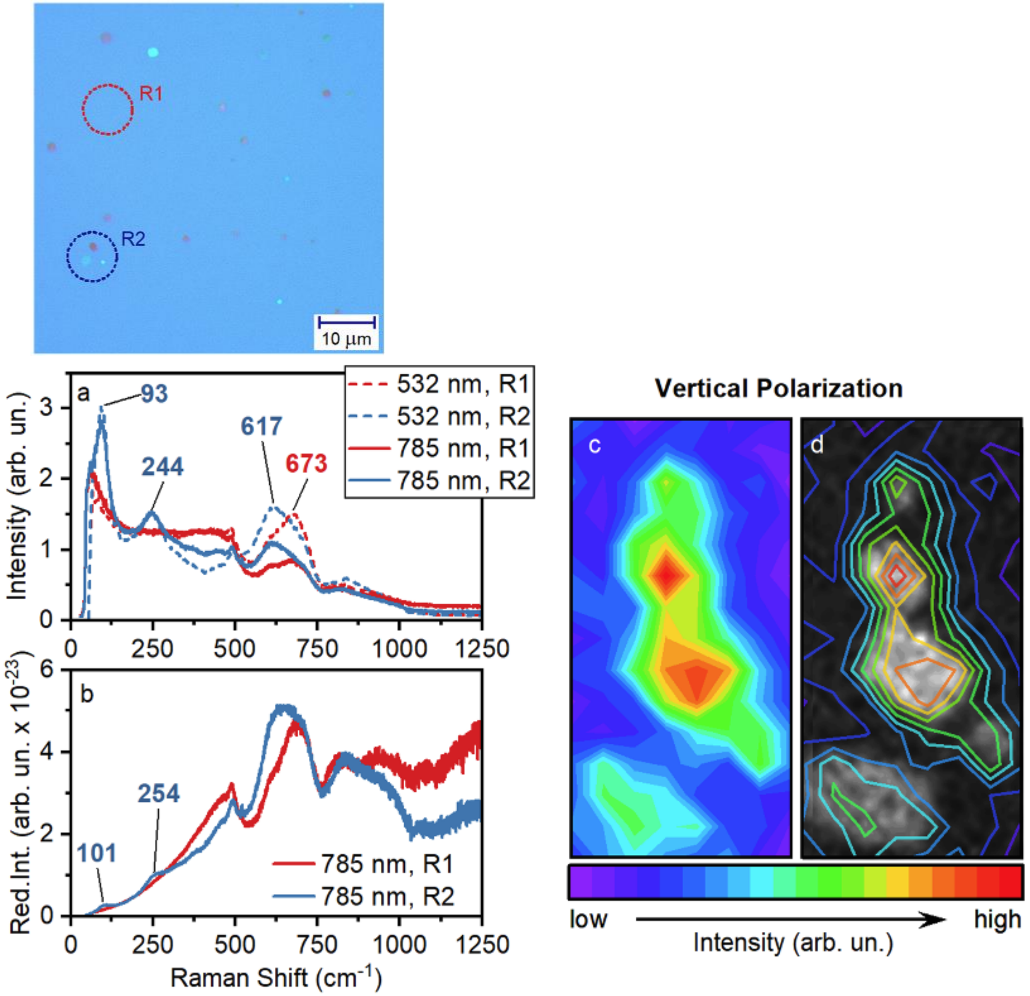
$Hf_6Ta_2O_{17}$ wt % = 79.2

- **Detection of crystalline formation**
- **Crystalline Phase identification**
- **Structural information (lattice parameters etc.)**
- Sensitivity: it depends…

Optical properties: Raman Spectroscopy







- **Sensitive to vibrational states -> short-range chemical bond signature**
- **Can be coupled to a microscope to provide spatial-resolved measurement**
- Not trivial interpretation.

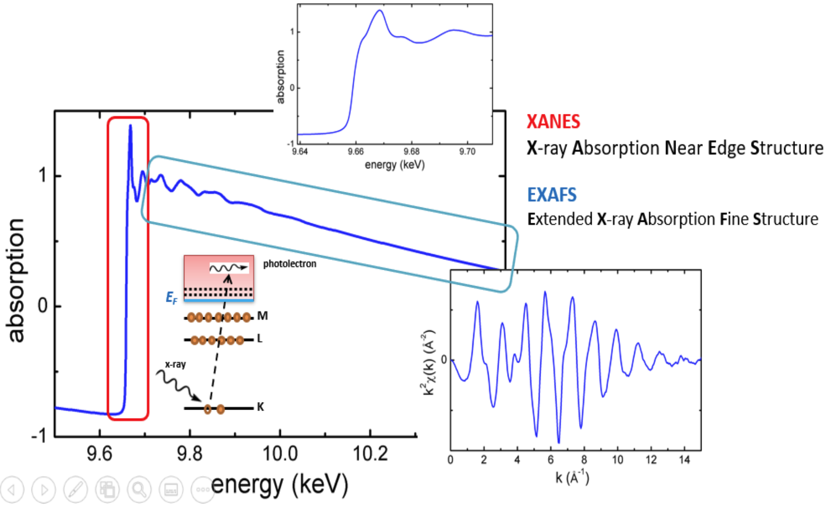
Favaro, Giulio, et al. "Reduction of mechanical losses in ion-beam sputtered tantalum oxide thin films via partial crystallization." *Classical and Quantum Gravity* 41.10 (2024): 105009.

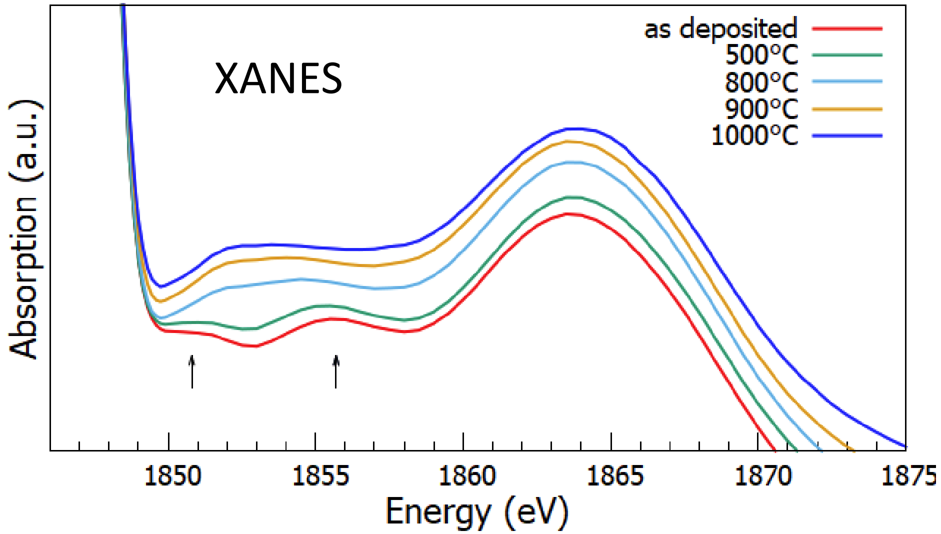
Structural properties: X-ray absorption spectroscopy

ESRF The European Synchrotron

Elettra Sincrotrone Trieste

SOLEIL SYNCHROTRON





XANES

➢ **Oxidation state and medium range order**

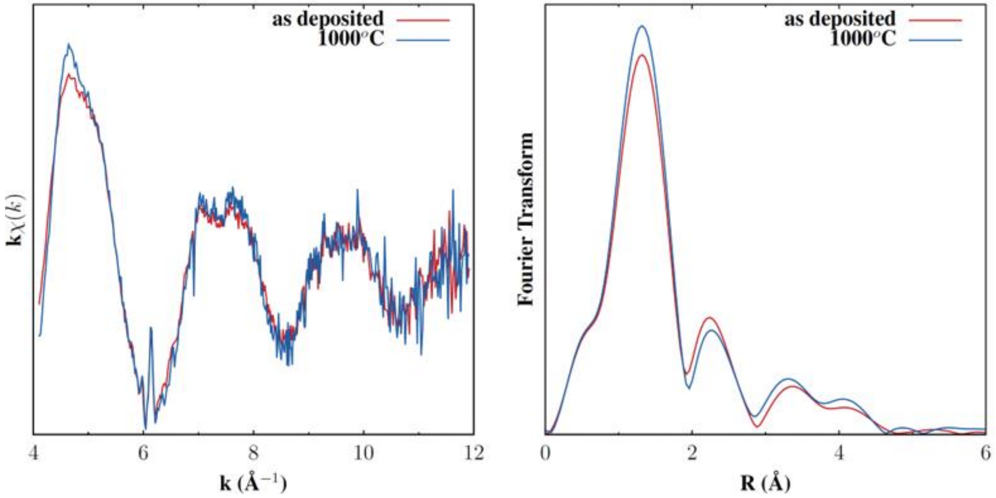
EXAFS

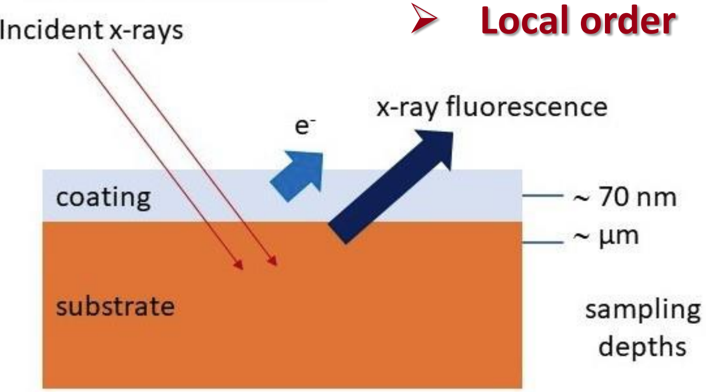
➢ **Local order**

SiO2 structure evolution upon annealing:

- The short range structure re-oganizes providing a de-densification.
- The long range order remains unaffected.

EXAFS

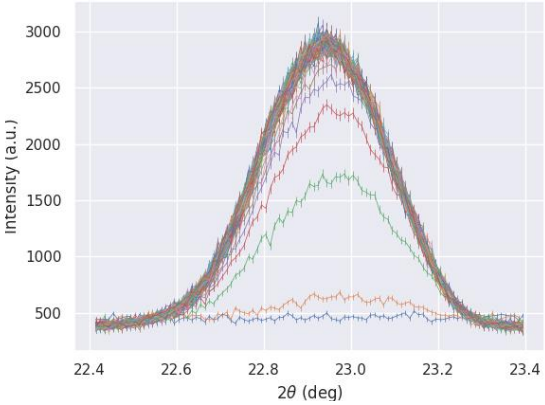


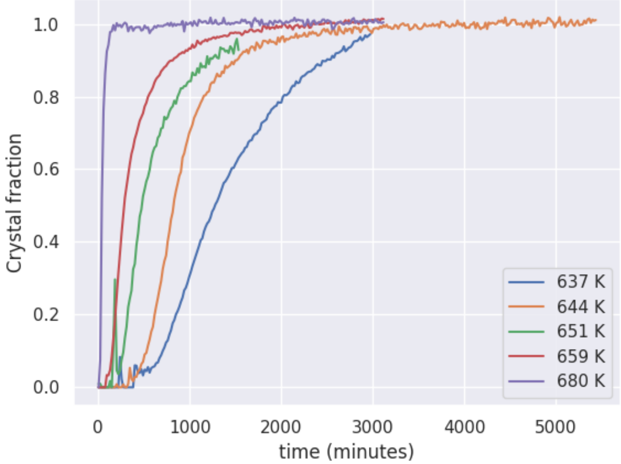


L.Silenzi et al. GWADW 2023

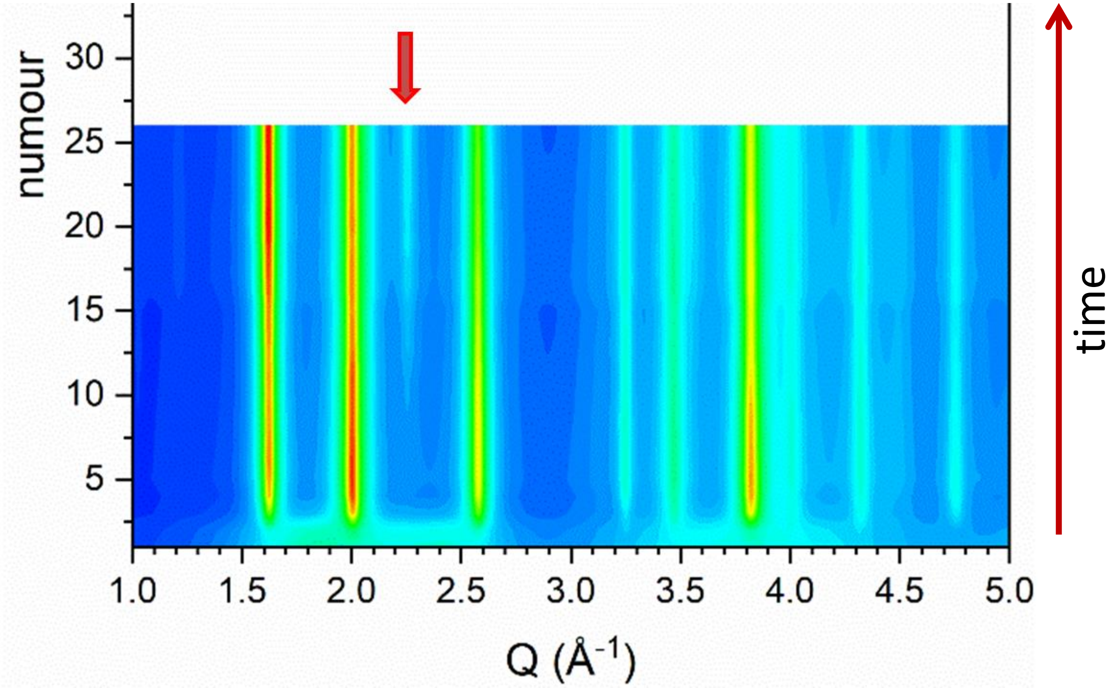
Structural properties: (In-situ) X-Ray Diffraction

Thermal stage for X-ray experiments





Crystallization Kinetics upon annealing



Evolution of different phases inside the coating

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A. Martinelli et al. to be published

Conclusions

- Modern Material science techniques are a valuable help to understand the microscopic reason of the propertes of interest for GW coatings.
- A multi-technique approach is necessary to obtain a full picture of the sample under exam.
- In-situ techniques are a valuable option e.g. to understand the effect of treatments (annealing) and of the phenomena occurring during deposition.