Amorphous Ta_2O_5 Crystallization: a strategy to improve coating thermal noise of GW interferometers

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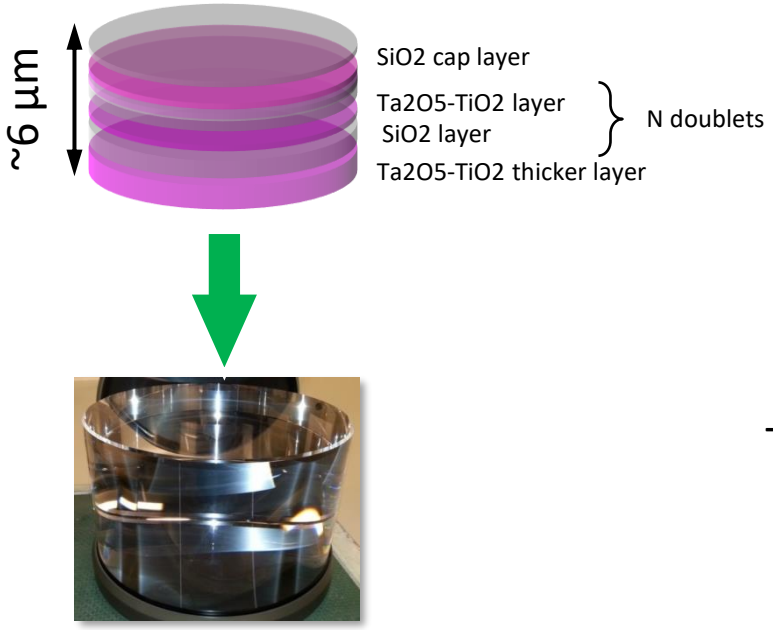
On behalf of Virgo Coating R&D Collaboration

Coating Thermal Noise power spectrum



Harry et al, Class. Quantum Grav. 19 (2002)

In a Fabry-Perot geometry:

$$S_{\mathrm{CTN}} \propto T \frac{d\phi}{w^2}$$

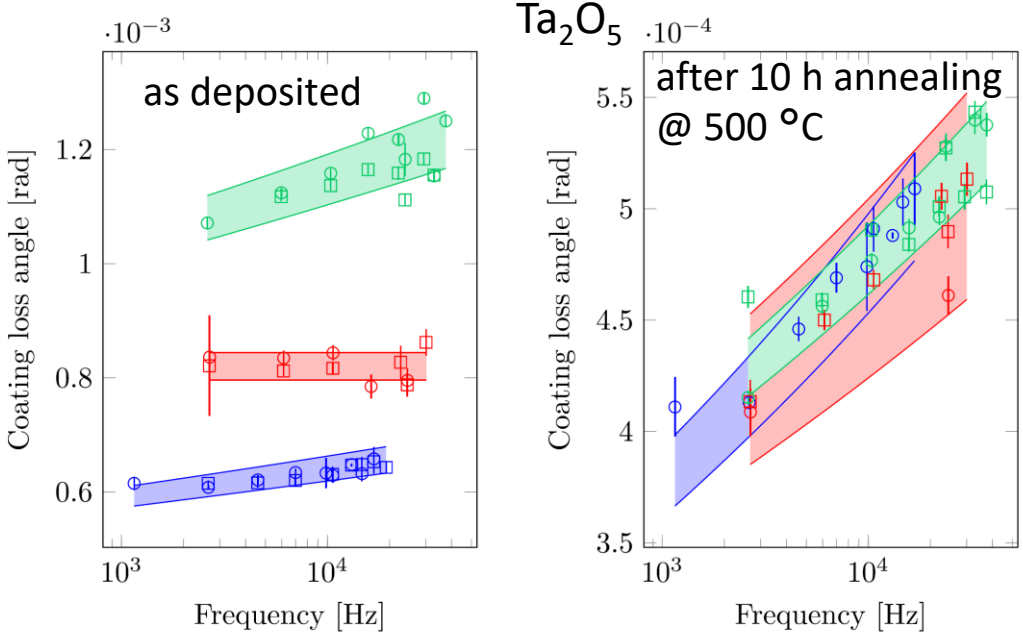
- T: Temperature
- d: Coating thickness
- ϕ: **Mechanical Loss angle**
- w: Beam Waist

Lossy materials are noisy!

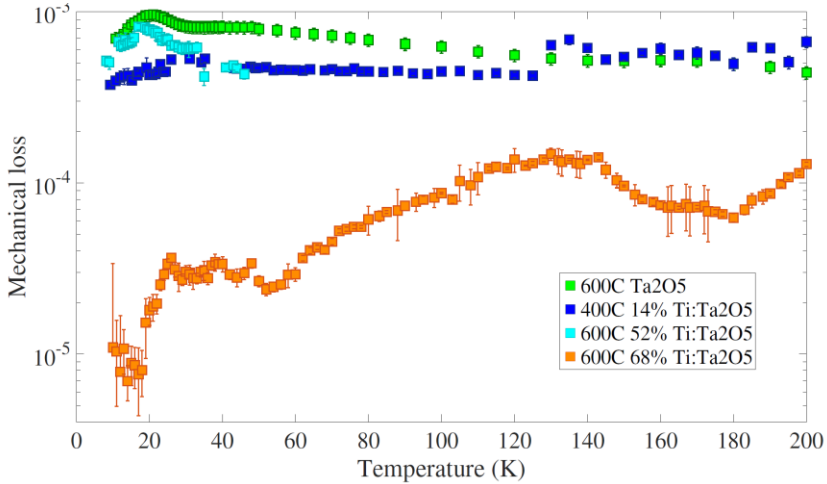
Annealing process to reduce mechanical losses

Effect of crystallization on losses still not well understood and controlled

Ta_2O_5



- M Granata et al 2020 Class. Quantum Grav. 37 095004

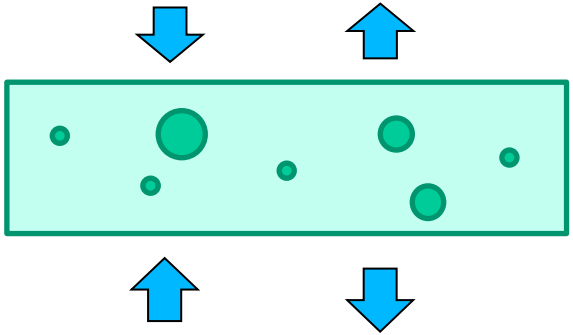


- R. Robie, Ph D Thesis, University of Glasgow, 2018

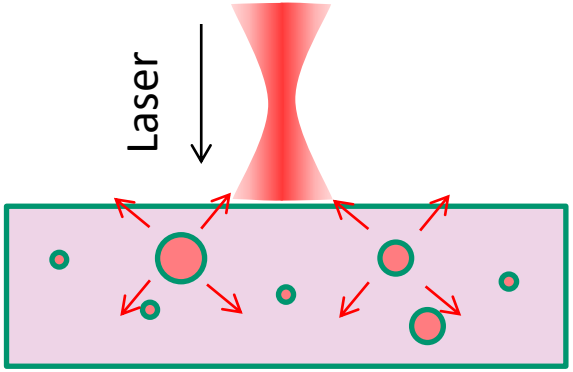
"….while displaying low mechanical loss, this coating has visual evidence of crystallization"

Post-deposition annealing process brings the structure of material coatings down to a stable optimal configuration for lowest loss. Often, but not always, crystallization can be detrimental.

The Crystallization strategy



Improve the mechanical properties by favoring the controlled formation of nanocrystals inside the amorphous matrix!



However: avoid scattering form the nanocrystals

Required:

- Precise control of the crystallization process
- Optical and mechanical characterization
- Theoretical modelling

Crystallization from the Amorphous state

Crystallization kinetics depends on:

- Nucleation rate
- Growth rate

$$N(T) = f_0(T)\exp(-g^*/RT)$$

$$g^*_{3D} = 16\pi\gamma^3/3\Delta G^2$$

$$\Delta T = T_m - T$$

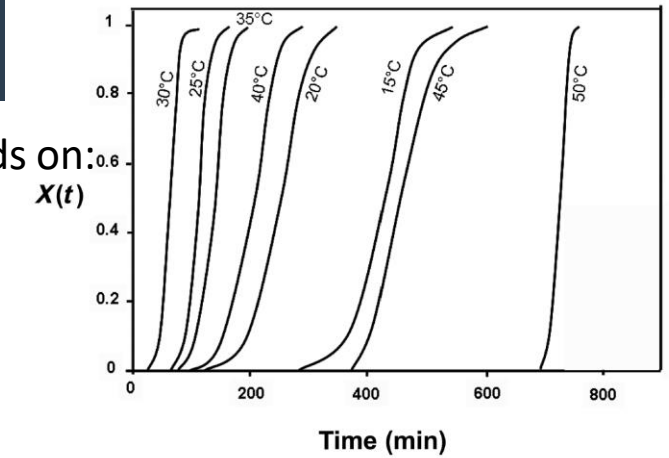
$$\Delta G \approx \Delta S_m \cdot \Delta T = \Delta H_m \cdot \Delta T/T_m$$

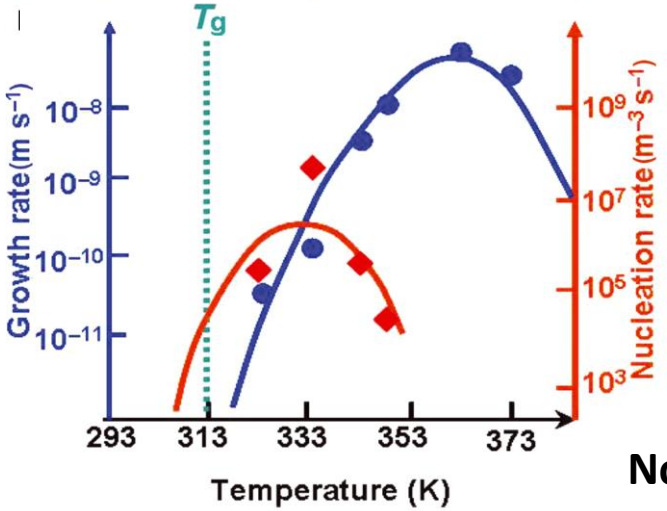
$$g^*_{3D}(T) \sim 1/\Delta T^2.$$

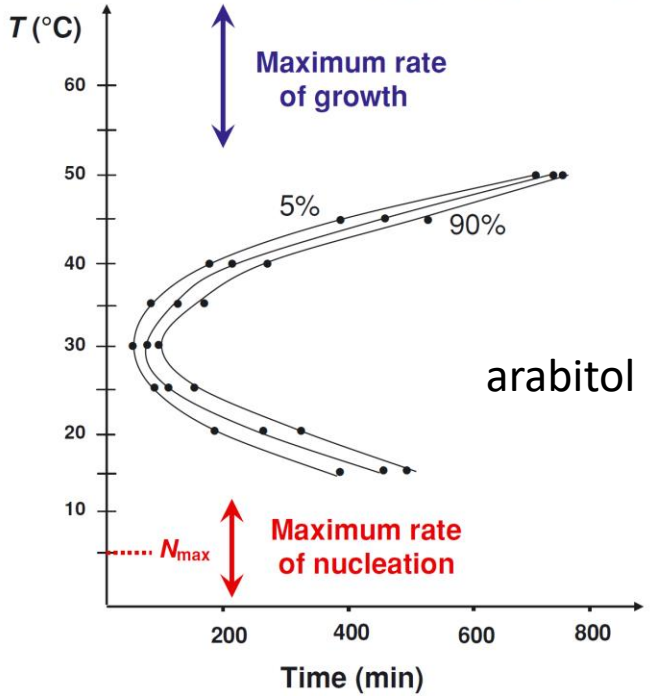
Non monotonic Nucl rate

Critical 3D nucleus

$$r^*_{3D}(T) \sim 1/\Delta T$$







arabitol

- M Descamps et al 2014 J. Pharm. Sci. 103 2615

$$V(T) \propto V_0(T) \cdot \Omega \cdot [1 - \exp(-\Delta G/RT)]$$

$$V_0(T) \propto \exp(-\Delta G_a/RT)]$$

Non monotonic growth rate

Crystallization Theory

JMAK equation

$$x = 1 - \exp[-(kt)^n]$$

Fraction of crystallized material

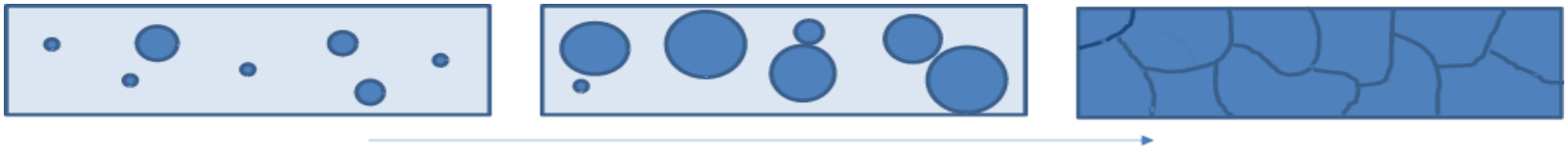
Time

Rate constant

Avrami parameter

Assumptions:

- Random and homogeneous nucleation;
- Constant and isotropic growth rate;
- Growth rate does not depend upon the fraction of crystallized volume.



Avrami parameter values:

- Constant nucleation and interface controlled growth → n=4
- Constant nucleation and diffusion controlled growth → n=5/2
- Saturated nucleation and interface controlled growth → n=3

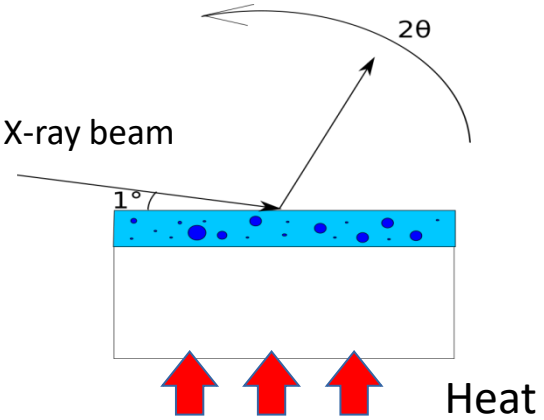
Rate constant follows an Arrhenius-like law:

$$k(T) = A\exp[\frac{-E_a}{k_B T}]$$

Samples and Experiment

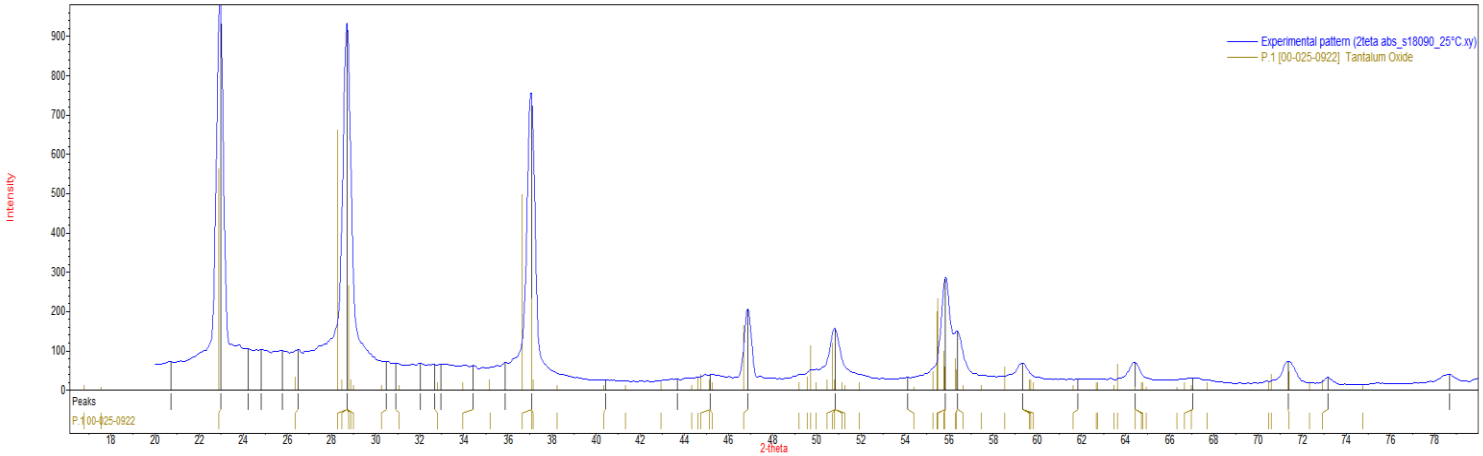
Samples:
500nm-thick films of a-Ta_2O_5 deposited on Si substrates by Ion Beam Sputtering @ LMA (France)

Experiment:
Samples heated at fixed temperatures and monitored with Grazing Incidence X-Ray Diffraction @ INFN and University of Padova (Italy)

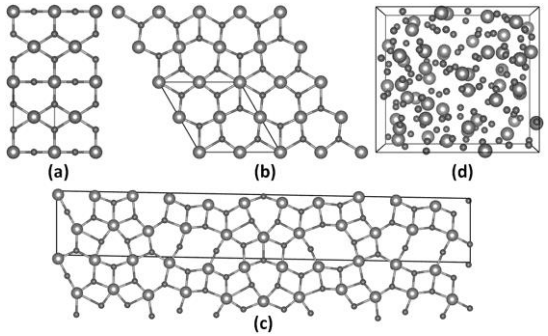


Goal:
Studying the crystallization kinetics of amorphous Ta_2O_5 thin films.

Structure assignment



Diffraction spectrum of a crystallized sample



The Ta – O system crystallizes in many different polymorphs. The assignment of the diffraction spectrum is still under discussion (probably orthorombic β-Ta_2O_5)

J. Lee; et al.; *Appl. Phys. Lett.* **105,** 202108 (2014)

Ta_2O_5 Thin Films Crystallization

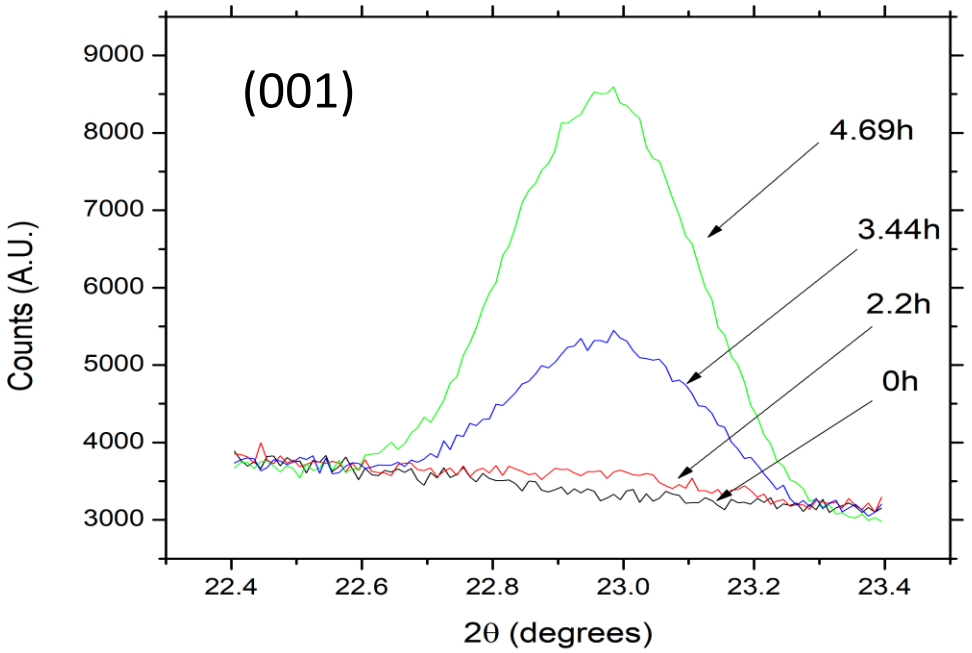
Measurements focused on the (001) peak of orthorombic Ta_2O_5

Peak height proportional to crystallized volume.

Peak FWHM inversely proportional to crystallite size. (Scherrer's formula)

$$D = k\frac{\lambda}{\Delta \cos\theta}$$

- D = crystallite size
- λ = wavelength of the incident beam
- Δ = peak FWHM
- 2θ = peak position in the spectrum

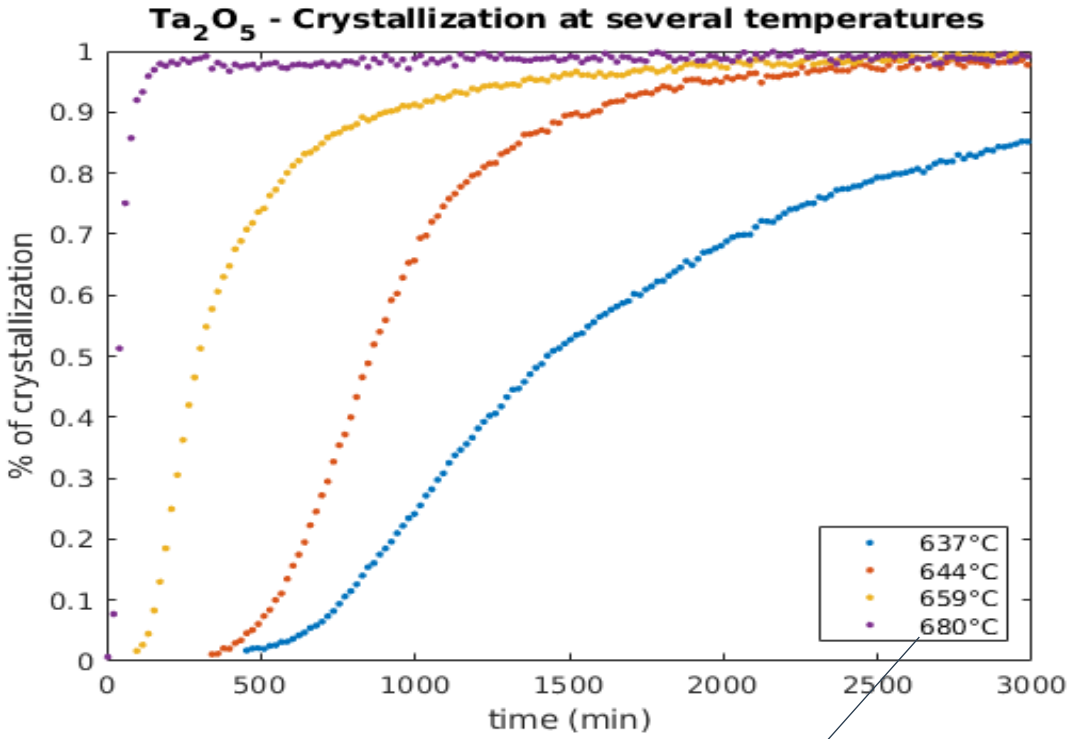


Ta_2O_5 Thin Films Crystallization

JMAK equation

$$x = 1 - \exp[-(kt)^n]$$

- x → Fraction of the crystallized volume.
- $n = D + 1$ → information about the dimensionality D of the growth.
- k →crystallization rate



Temperatures corrected for substrate thermal conductivity

Avrami Plots

Linearized JMAK equation:

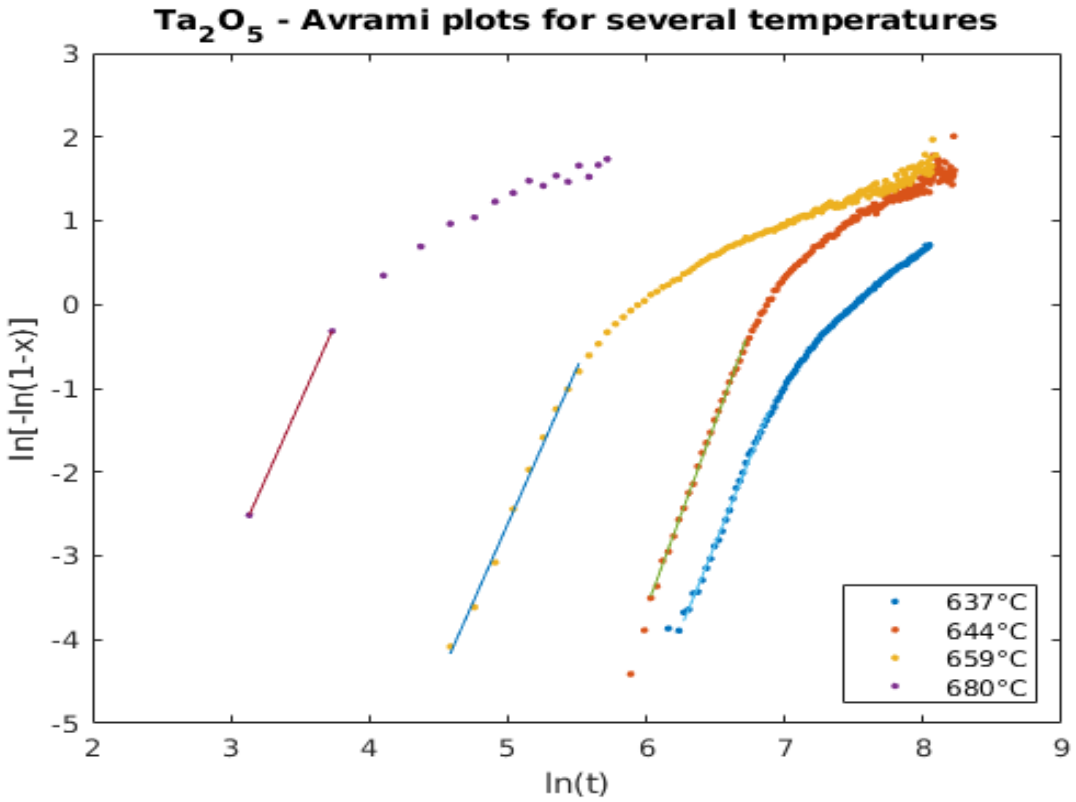
$$\ln[1 - \ln x] = n \ln t + n \ln k$$

From the fit of the first part of the curves:

$$n = 4.11 \pm 0.05$$

Strong indication of a constant nucleation rate and a 3D growth

Highly homogeneous films



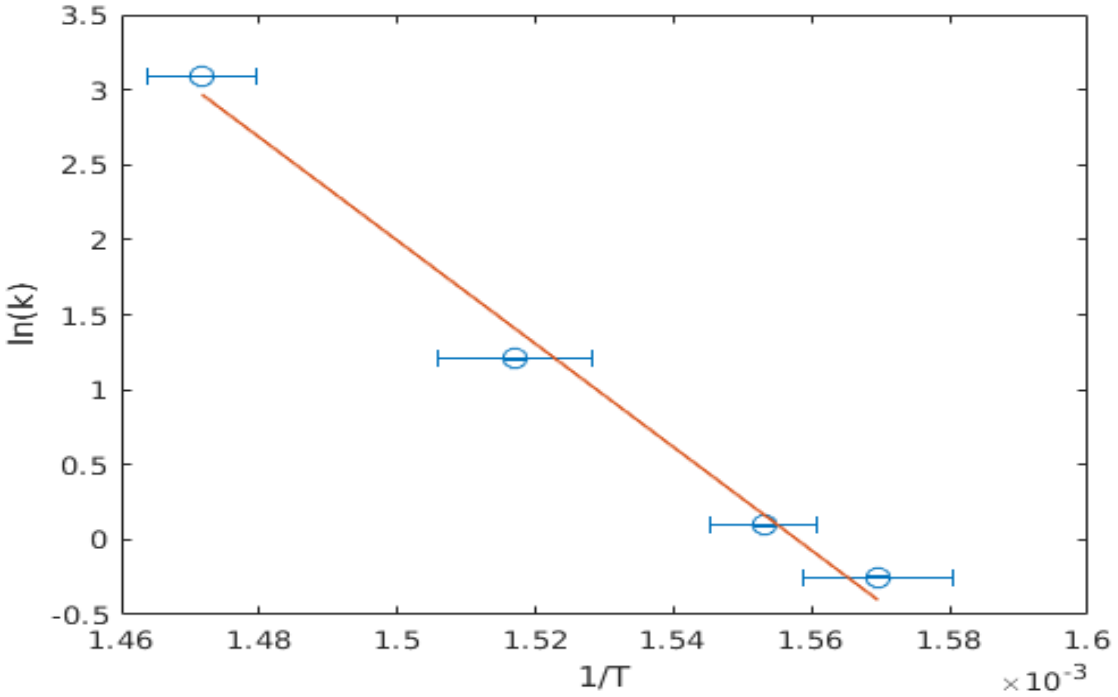
Activation Energy

Arrhenius' law:

$$k(T) = A\exp[\frac{-E_a}{k_B T}]$$

$$\ln(k) = \ln(A) - \frac{E_a}{k_B T}$$

$$E_a = 290 \pm 20\, kJ/mol$$

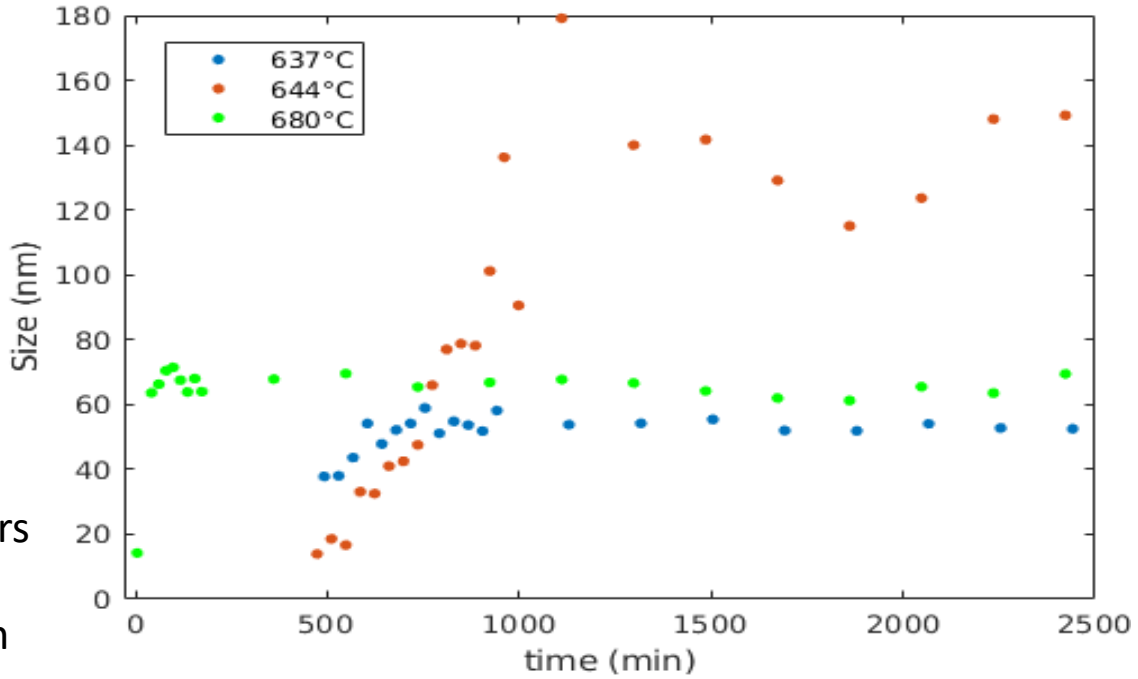


Average Cristallite Size

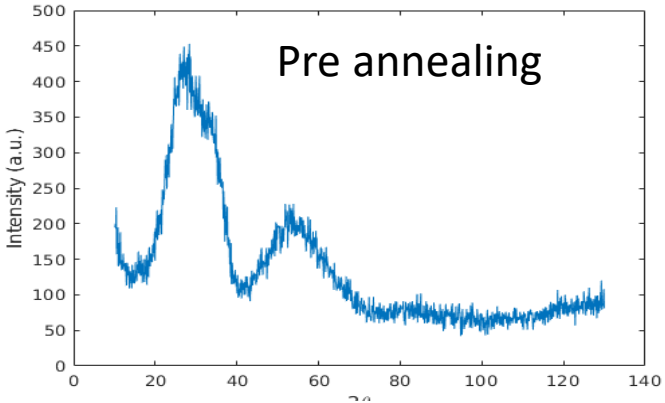
Average crystallite size estimated with Scherrer's formula after correcting for instrumental broadening:

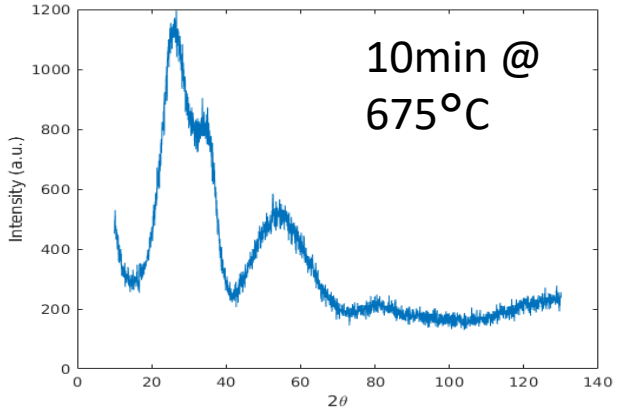
$$D = \frac{\lambda k}{\Delta \cos(\theta)}$$

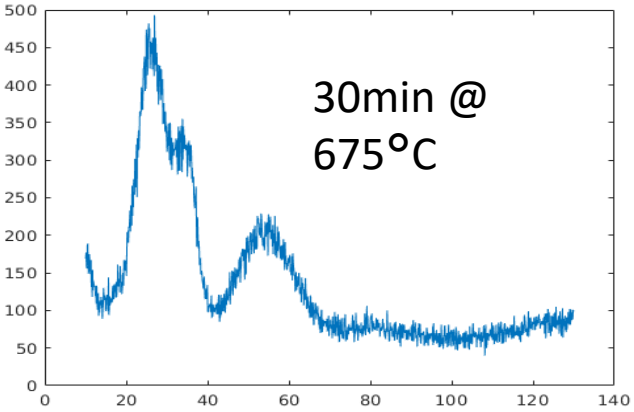
- Crystallites start to be detected when they are already around 17 - 18 nm.
- The final average crystallite size appears to depend on the annealing temperature, which is reasonable from thermodynamic arguments.

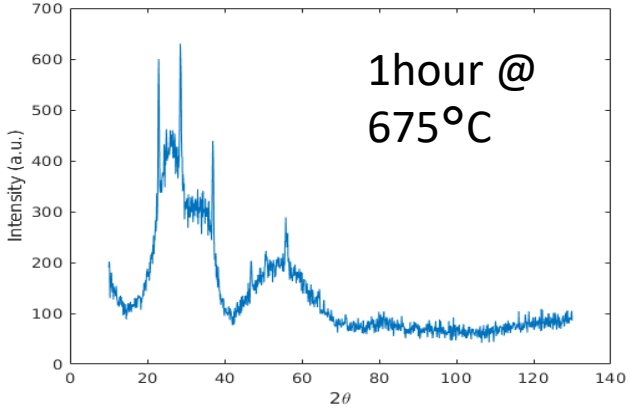


First Tests





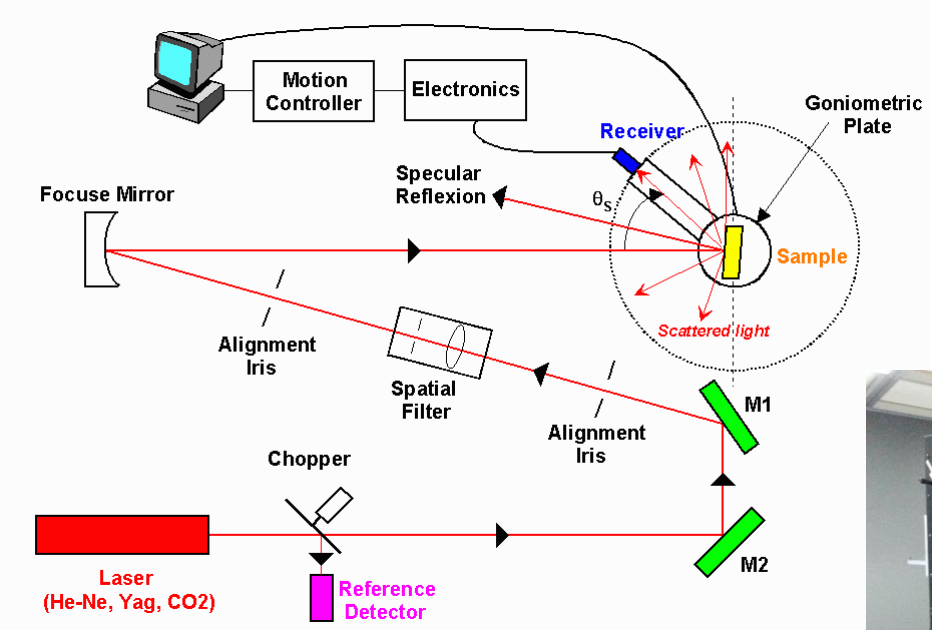




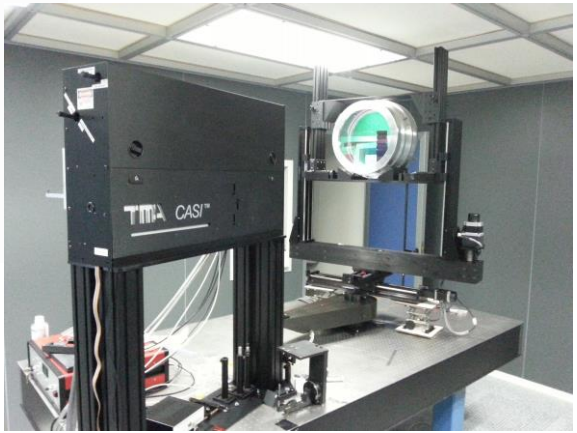
A set of samples with varying crystallization degrees have been prepared and are now undergoing structural/optical characterizations

Stay tuned!

First Test: light scattering @ LMA in progress



A set of samples with varying crystallization degrees are under test for light scattering



In progress

Scattering by nanodiffusers in the ITF: an estimate

- We have to set the maximum length scale or minimum density of nanocrystals so that the scattered light is negligible compared to the requirements.
- L_{RT} measured for the the cold cavity, are around 60 ppm. 20 ppm are due to the roughness high spatial frequency (measured with a scatterometer), **10 ppm** per mirror (see https://wiki.virgo-gw.eu/Commissioning/OptChar/WebHome and VIR-0270A-15)
- In general, losses due to scattering of photons are: $l_{scatt} = \frac{N_{scatt}}{N_{TOT}}$

scattered over total number of photons

- If we study the problem from the energetic point of view we can translate the number of photon in term of power. Wher *I* is the intensity of our electro-magnetic field:

$$l_{scatt} = \frac{I \cdot S_{scatt}}{I \cdot S_{TOT}} = \frac{S_{scatt}}{S_{TOT}} = \frac{\sigma \cdot n}{\pi w^2} = \frac{\sigma \cdot \rho \pi w^2}{\pi w^2} = \sigma \cdot \rho$$

σ is the scattering cross section, ***n*** and ρ are the number and density of nano-diffusers, and ***w*** is the radius of the area out of which we considered the light scattered

σ can be calculated in first approximation using **Mie Scattering**

Mie Scattering simulation forseen

- Scattering of an electromagnetic plane wave by a homogeneous sphere, it depends on radius of the nanodiffuser (r size of the crystallite), wavelength and complex refractive index of the sphere and the refractive index of the medium around this.
- CALCMIE (MATLAB code)* calculates the amplitude scattering matrix and cross sections for the scattering of electromagnetic radiation by a single (stratified) sphere.
- The cross sections (extinction, **scattering** and absorption) and wavenumber k are returned in the structure matrix C
- Total attenuation coefficient: l_{scatt} = C(sca)*ρ
- The density of nano diffuser can be extracted from experimental data, but to use it in calculations we have to make some approximations on distribution:

  Surface density of nano-diffuser, all the crystallite are side by side $\rho_S = \frac{dn}{dS}$

  Volume density of nano-diffuser, crystallite can be also covered by others $\rho_V = \frac{dn}{dV}$

* [1] Schäfer, J.-P., PhD thesis, Univerität Ulm, 2011,http://vts.uni-ulm.de/doc.asp?id=7663
[2] Schäfer, J. and Lee, S.-C. and Kienle, A, J. Quant. Spectrosc. Radiat. Trans. 113(16), 2012.
[3] https://www.mathworks.com/matlabcentral/fileexchange/36831-matscat

M. Simoni Uni Roma ToV
Bachelor Thesis

Conclusions

- Crystallization kinetic of 500nm-thick films of a-Ta_2O_5 produced by IBS has been investigated;
- The crystallization is characterized by a homogeneous nucleation and a 3D growth in the first stage;
- The activation energy of the process has been estimated: **E_a = 290 ± 20 kJ/mol;**
- the as-formed crystallites have a size of the order of 20 nm and grow further to fnal size which seems to depend on the annealing temperature;
- Degree of crystallization and size of nanocrystals can be tuned at suitable annealing temperatures and times
- Samples with a low degree of crystallization have been prepared and are going to be optically and mechanically tested