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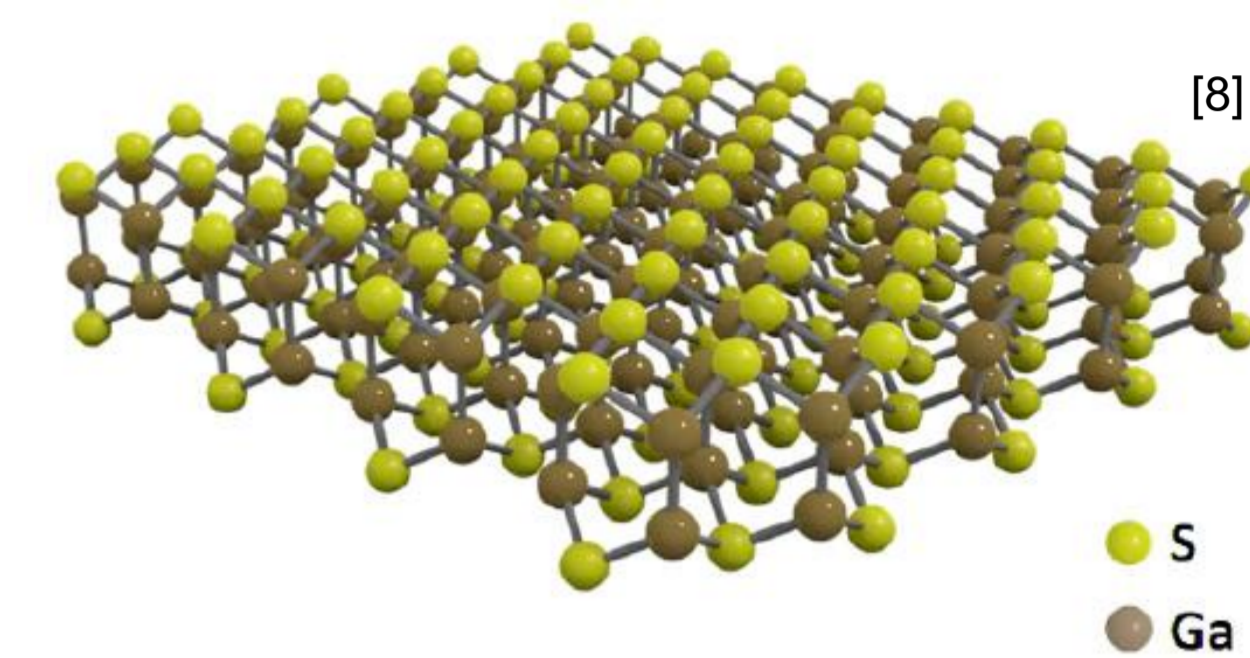
# In situ X-ray studies of lamellar metal chalcogenides GaS<sub>x</sub> prepared by Atomic Layer Deposition/Molecular Layer Deposition

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## Motivation

- 2D Lamellar Metal Dichalcogenides (LMDs) materials with tunable electrical properties hold great promises for many potential applications [1, 2, 3, 4]
- A sizeable bottleneck for the full deployment of 2D-Dichalcogenides stems from the lack of scalable fabrication methods with atomic scale precision
- Atomic/Molecular Layer Deposition (ALD/MLD) based on sequential, self limiting surface reactions are suitable techniques for the growth of scalable ultrathin layers [5]



Objectives: optimization of dichalcogenides materials GaS<sub>x</sub> by a two-step process:

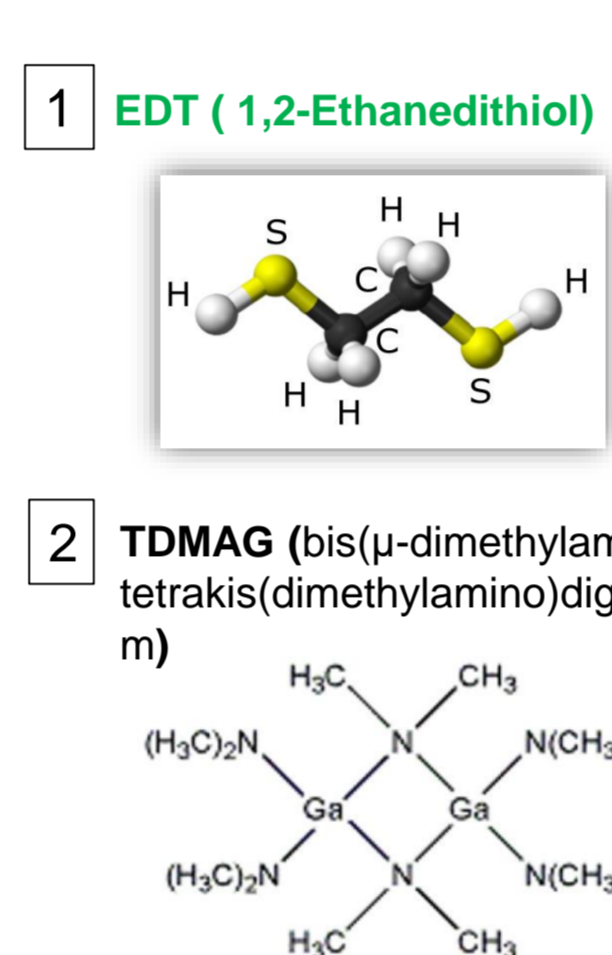
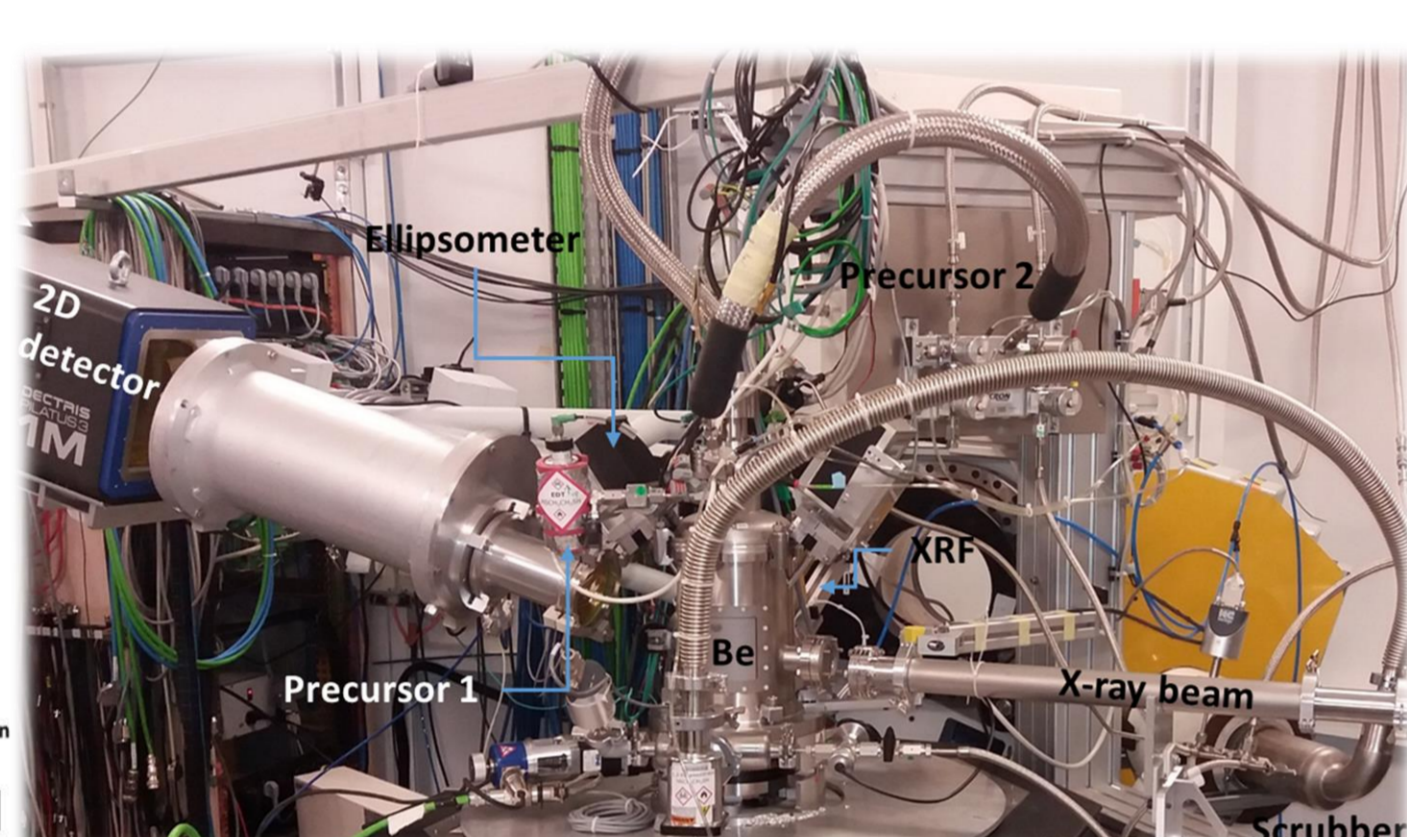
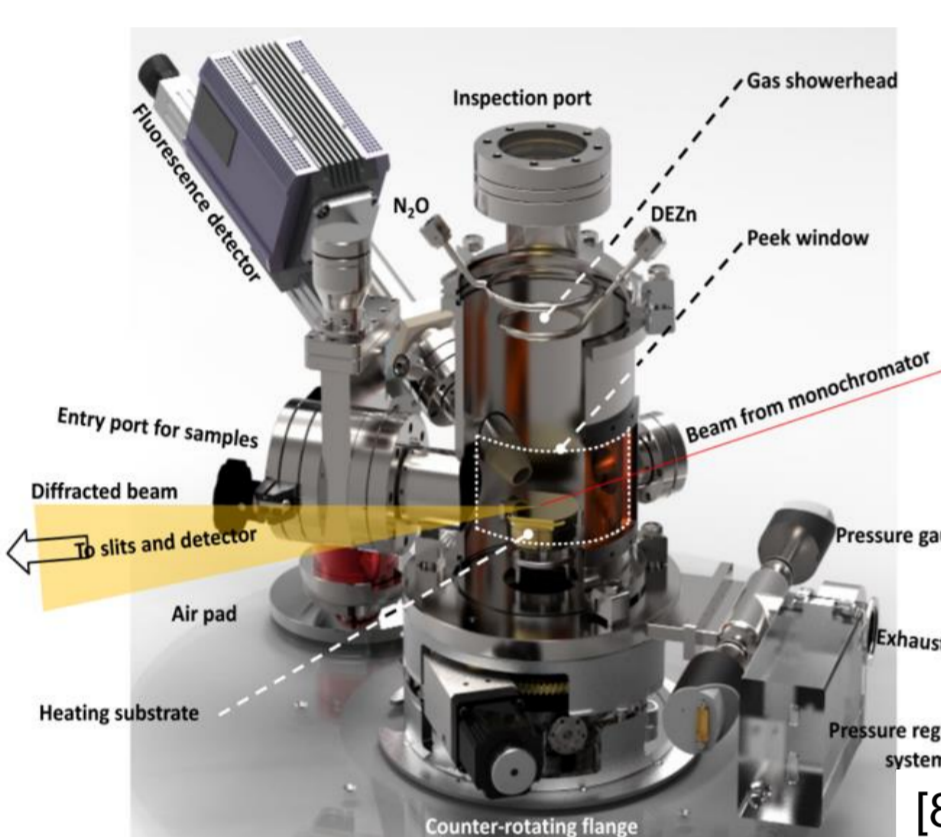
- 1) ALD/MLD of an intermediate organic layer to avoid crystallization [6]
- 2) Optimizing the annealing under a controlled atmosphere to obtain crystalline 2D ultrathin layer

## GaS<sub>x</sub> Growth on 100 nm SiO<sub>2</sub> substrate (SOLEIL)

### ALD/MLD Reactor

### SIRIUS Beamline

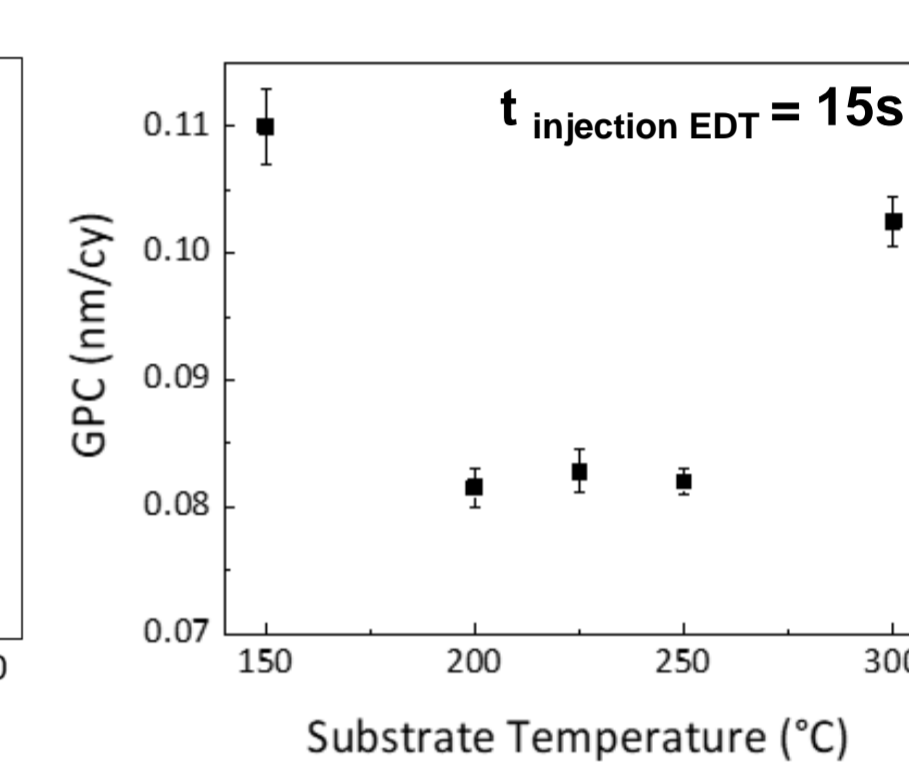
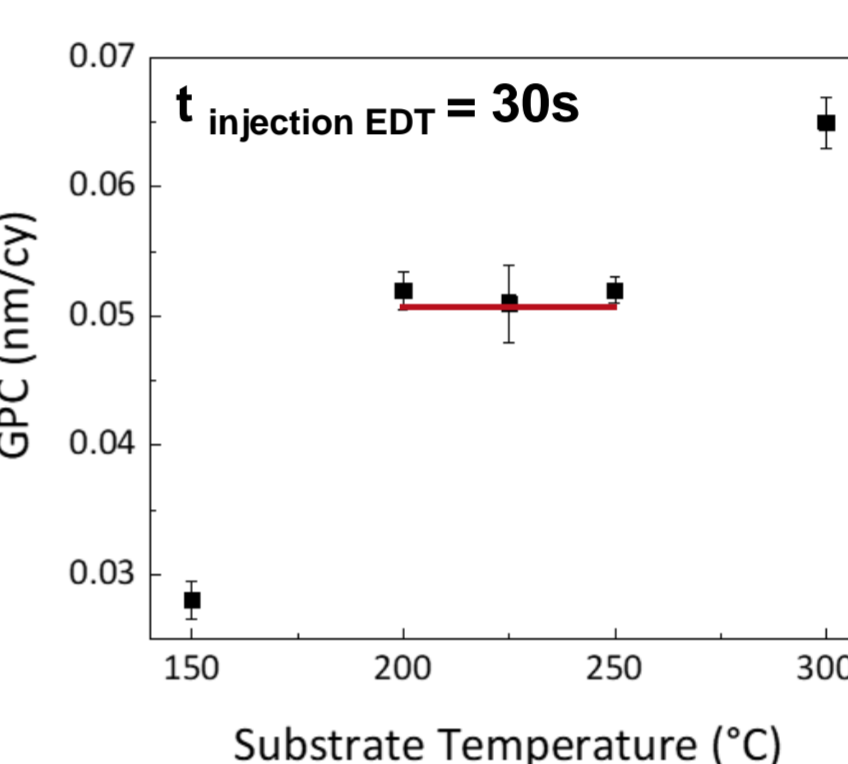
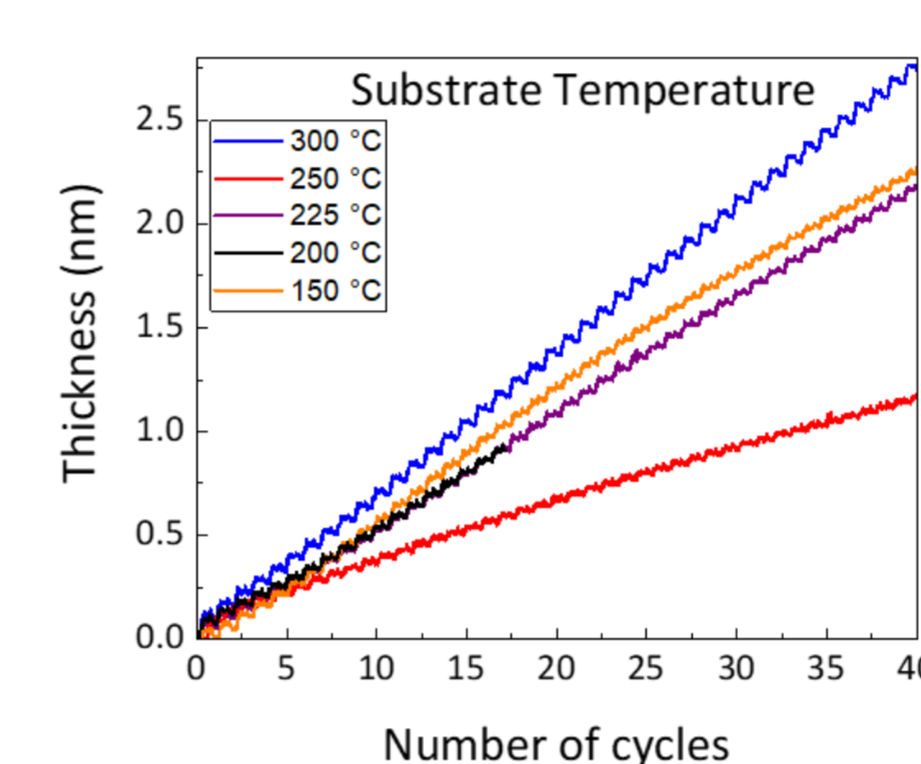
### Precursors



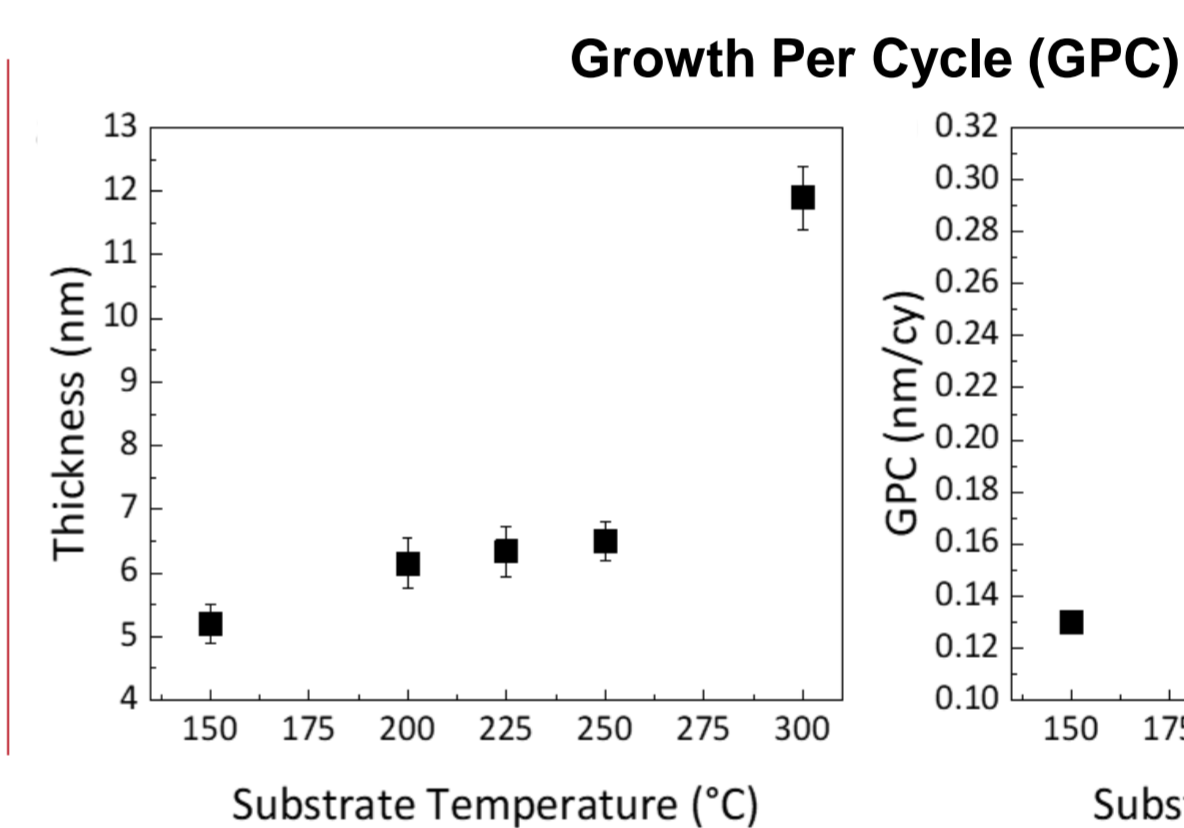
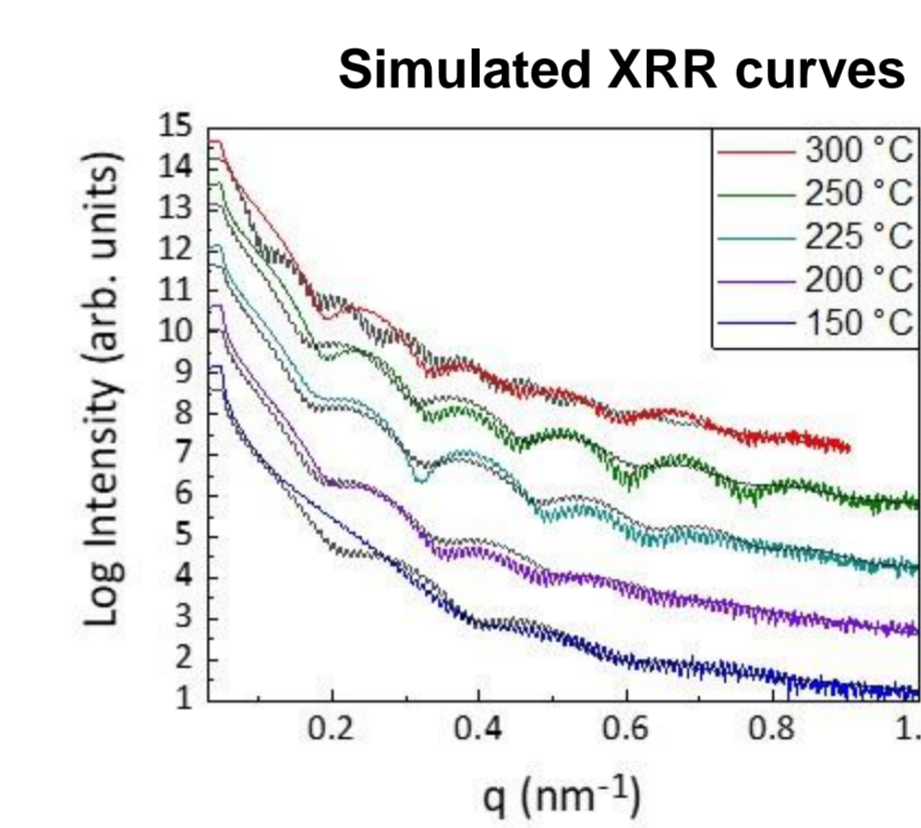
- ALD/MLD is carried out inside MOON reactor and monitored by ellipsometry *in situ*
- Organosulfur reactant EDT (1,2 ethanedithiol) is used as an alternative to the hazardous H<sub>2</sub>S molecule [9]
- Thiolate-derivative film deposited at low temperature on flat 100nm thick thermal SiO<sub>2</sub> on silicon substrate

## Investigation of ALD/MLD window

### In Situ Ellipsometry



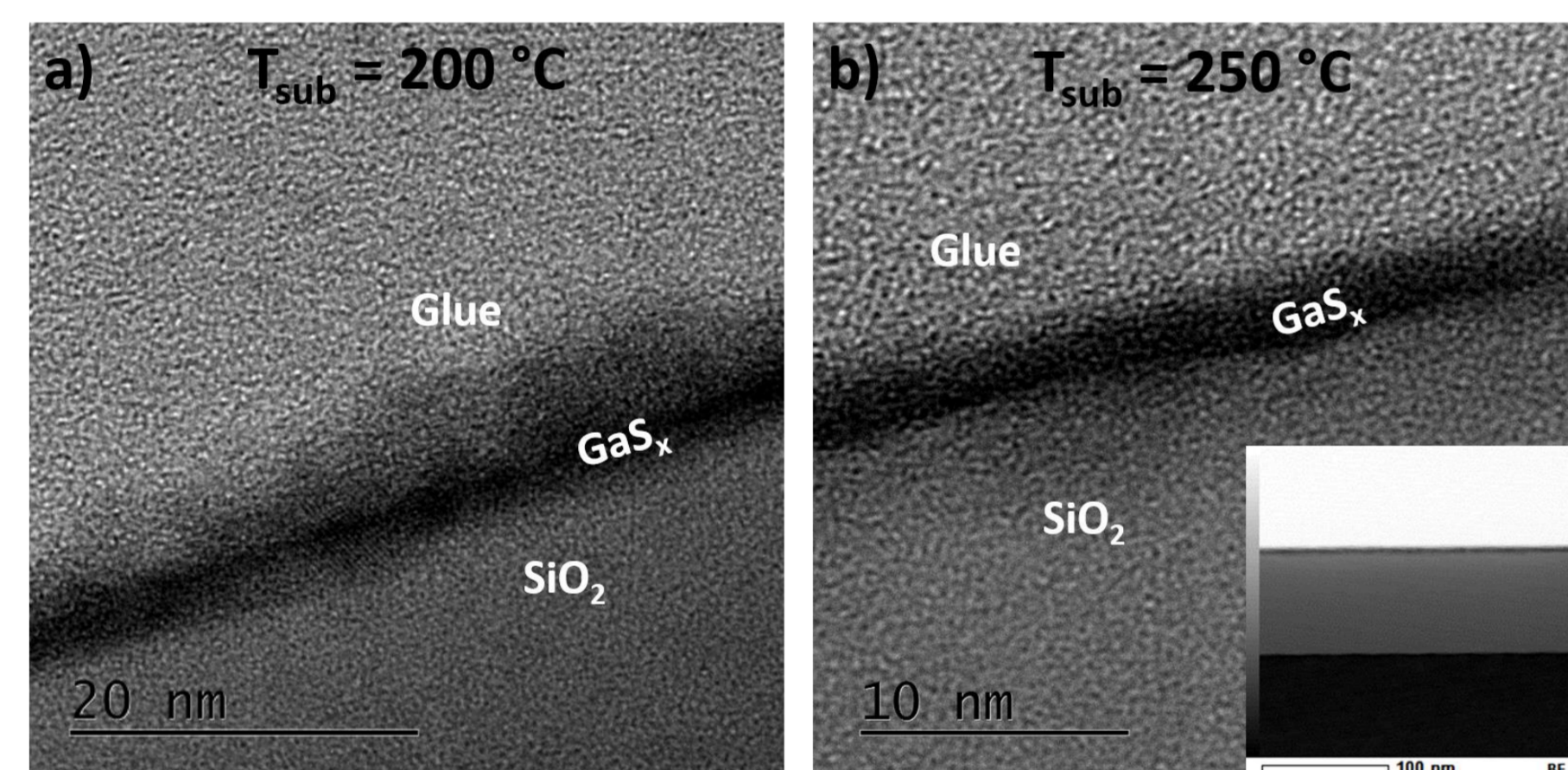
### Ex Situ XRR



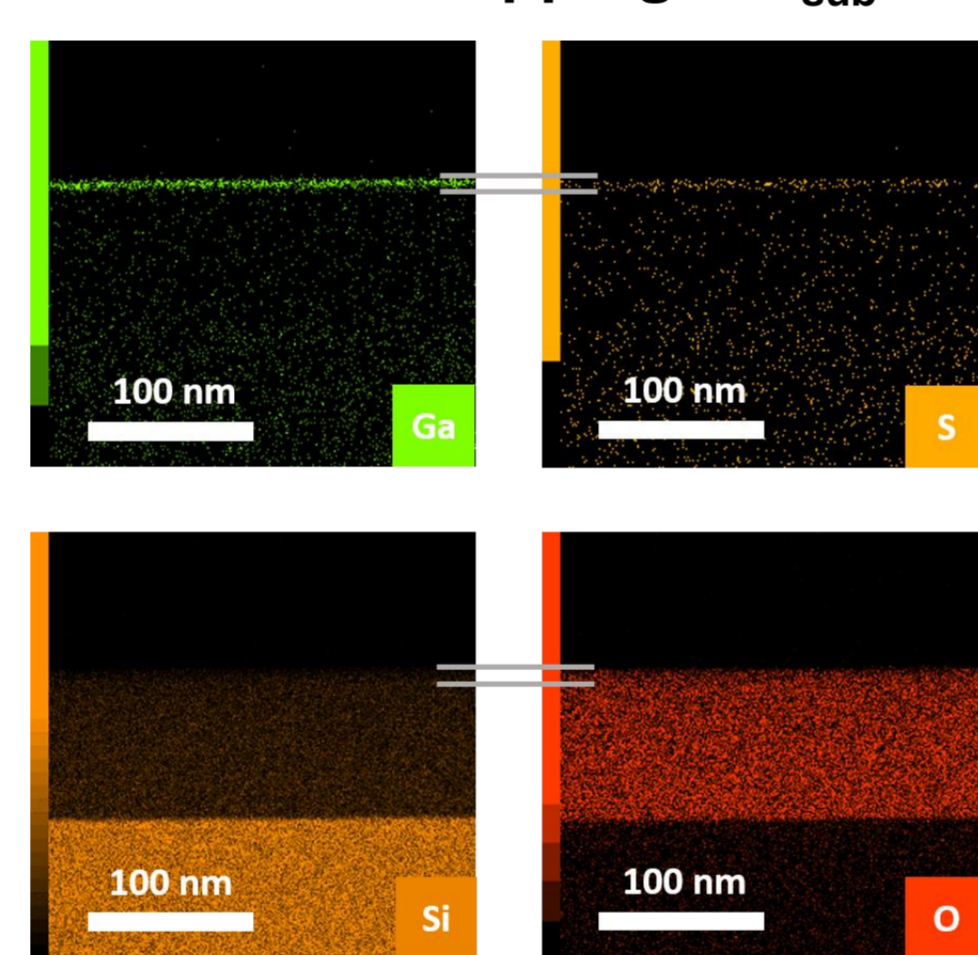
- Both *in situ* Ellipsometry and *ex situ* XRR curves allow to evaluate the ALD/MLD window in the region of [200 °C -250 °C]

## Layer Homogeneity in the ALD/MLD window: T<sub>sub</sub> = 250 °C

### Transmission Electron Microscopy (TEM) images

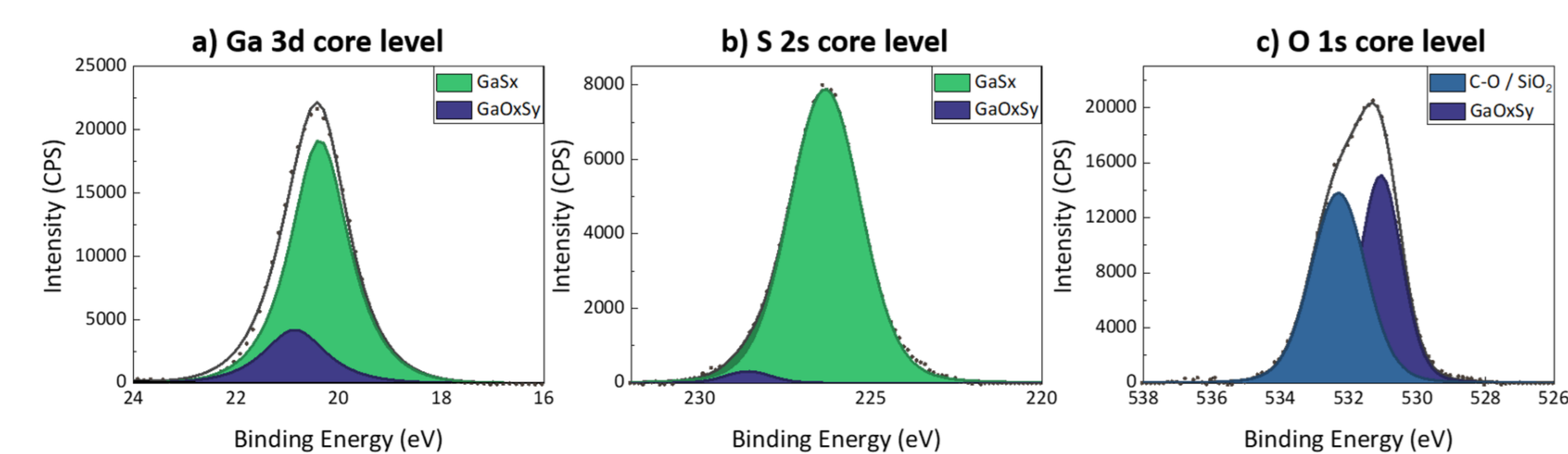


### EDX elemental mapping at T<sub>sub</sub> = 250 °C



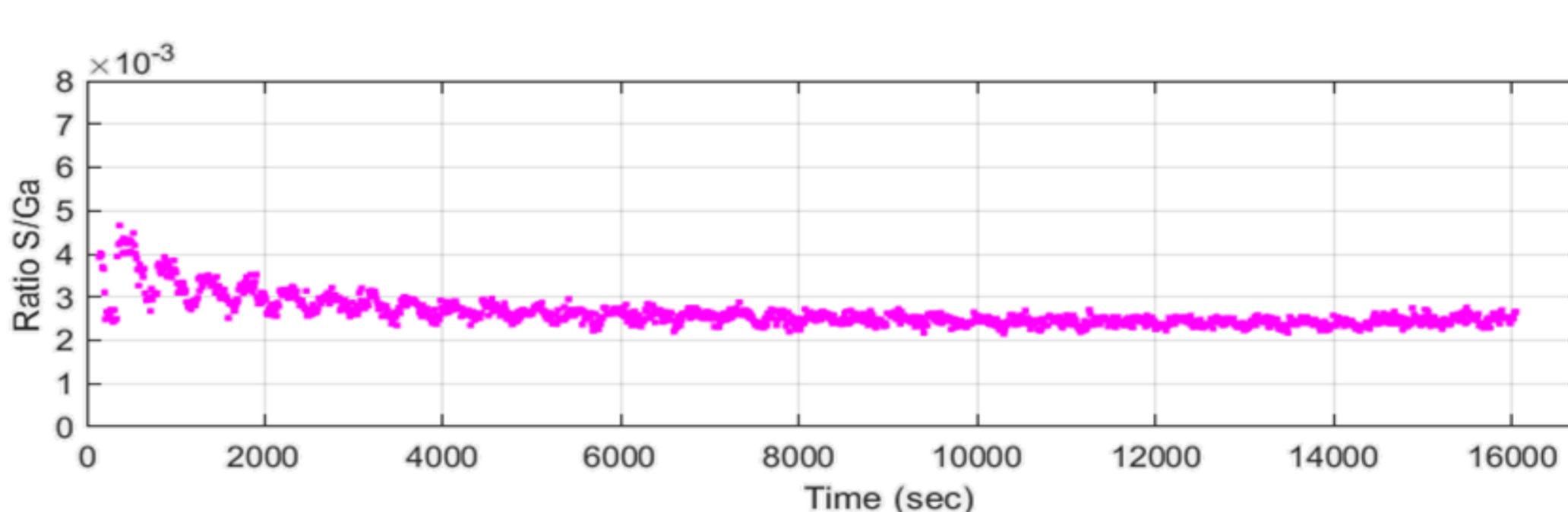
- TEM images exhibit homogeneous ultrathin layer grown at T<sub>sub</sub> = 250 °C

## XPS: Stoichiometry



- XPS (X-ray Photoelectron Spectroscopy) spectra recorded with a Al Kα source (1486.6 eV) at θ=45° (analyzed thickness depth= 4.9nm).
  - Important amount of Oxygen attributed to Gallium oxysulfide layer.
- $$\frac{[S\ 2s]_{Total} + [O\ 1s]_{GaOxSy}}{[Ga\ 3d]_{Total}} = 1.1$$

## Growth behavior: In situ XRF

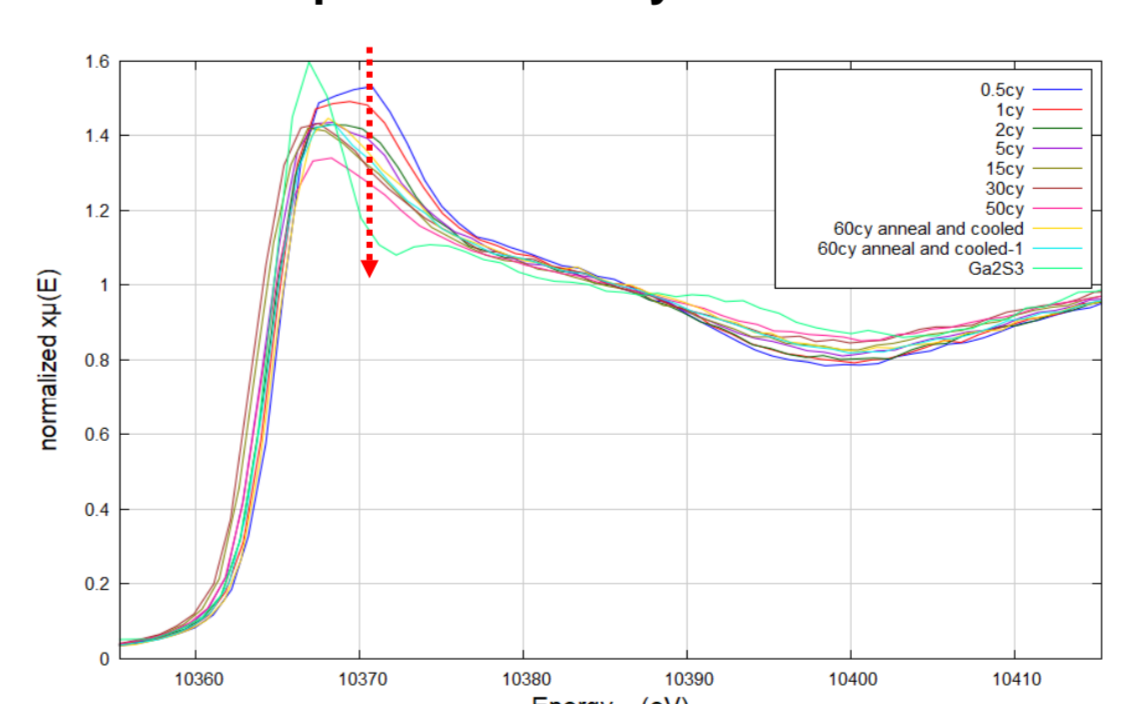


- In situ* XRF permits to evaluate growth behavior since the early stages of the growth.

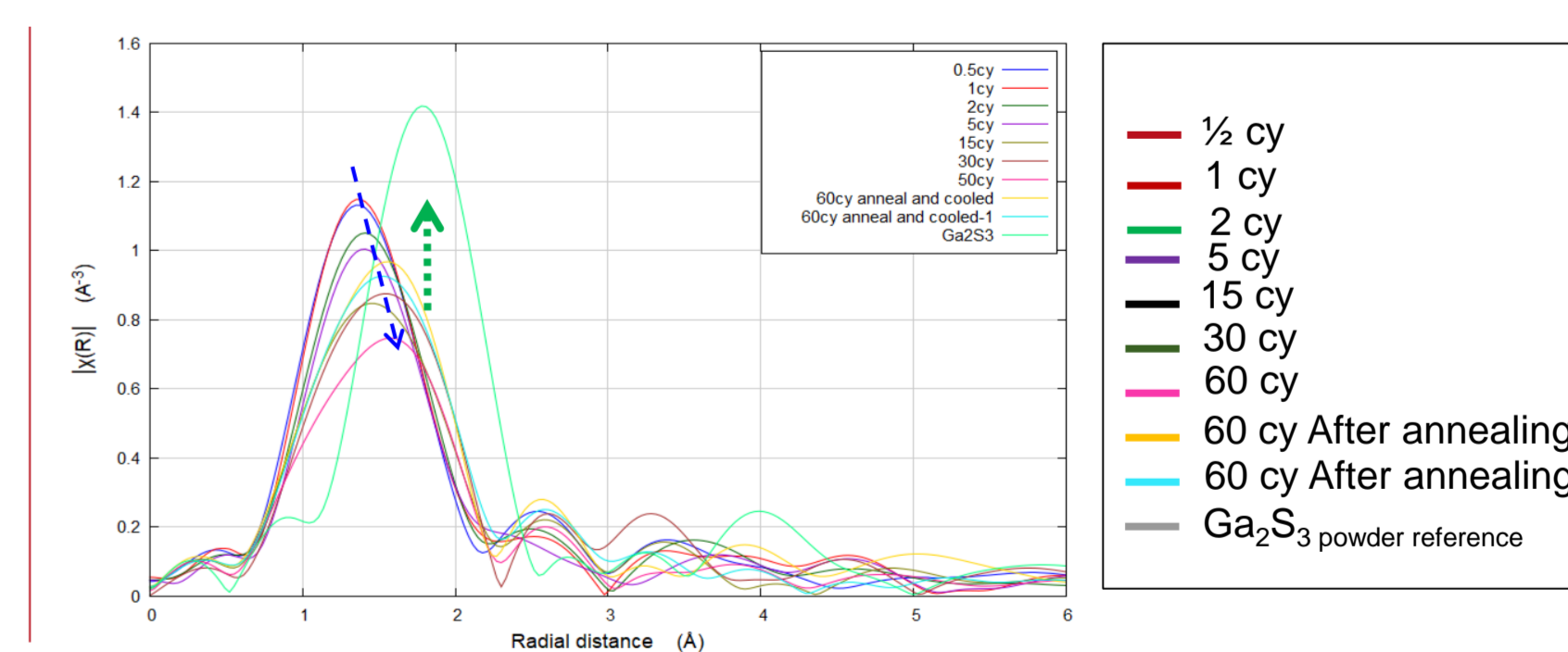
- The S/Ga ratio curve shows a constant value along the deposition (More visible after 4 cycles) => This confirms a similar growth behavior from the early stages

## XANES and EXAFS after Annealing at 415 °C

Ga K-edge XANES show systematic change of WL peak marked by the red arrow



Fourier transform spectra show reduction of Ga-N bonds and increase of Ga-S bonds with growth cycle



- Both XANES and EXAFS data confirms the importance of increasing the number of cycles (layer thickness) in order to grow Gallium Sulfide.

## Conclusions and perspectives

- GaO<sub>x</sub>S<sub>y</sub> organic film can be grown by ALD/MLD using TDMAG and EDT as precursors, at 250 °C / *In situ* XRF of Ga and S atoms confirms the self limiting growth behavior
- TEM/EDX reveals an homogeneous deposit at 250 °C
- The annealing performed under N<sub>2</sub> at 415 °C didn't succeed to confirm a local environment structure of Gallium Sulfide
- XPS data confirms the deposition of GaS<sub>x</sub>O<sub>y</sub> with x+y=1

Perspectives : Improvement of the Ga<sub>x</sub>S texture of thin layers / To deposit layered other dichalcogenides by the same process using EDT / Analysis by HAXPES after Ga<sub>x</sub>S capping

## References

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