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## Lab-scale Hard X-ray Photoelectron Spectroscopy (HAXPES) characterization of Transition Metal Dichalcogenide TiS<sub>2</sub> grown by Molecular Layer Deposition and thermal annealing

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### Motivation

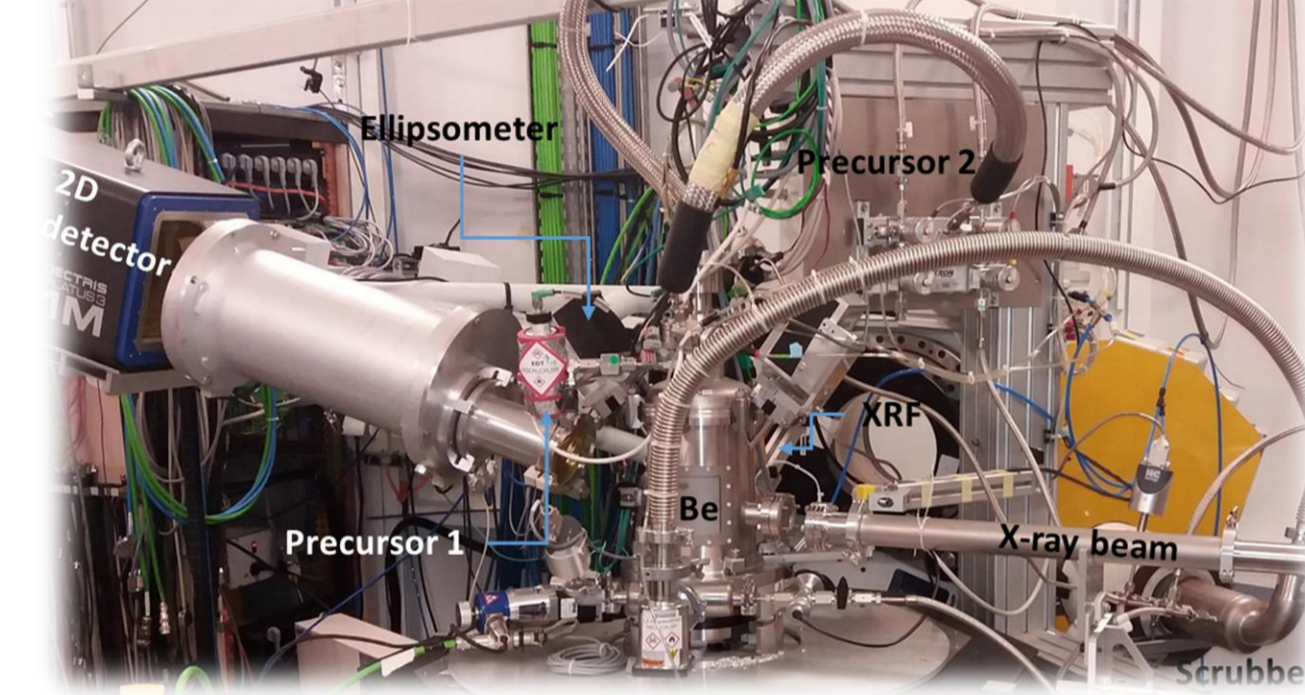
- 2D Transition Metal Dichalcogenides (TMDs) materials with tunable electrical properties hold great promises for many potential applications
- A sizeable bottleneck for the full deployment of 2D-Dichalcogenides stems from the lack of scalable fabrication methods with atomic scale precision
- Hybrid ALD/MLD followed by a thermal annealing at low temperature avoid the co-occurrence of growth and crystallization during the process (which is considered as a complicating factor to obtain textured TMD material)
- **Evidencing that lab-based hard x-ray sources (HAXPES) is a powerful tool for 2D materials characterization,**
  - 1- To study buried interfaces and especially in this study, since the obtained TiS<sub>2</sub> layers are oxidized in ambient conditions.
  - 2- To investigate the chemical composition at the dichalcogenide surface after analyzing TiS<sub>2</sub> and TiO<sub>2</sub> powder references
  - 3- To evaluate the in-depth distribution of TiO<sub>2</sub> within the TiS<sub>2</sub> layer.

### Cr K $\alpha$ HAXPES

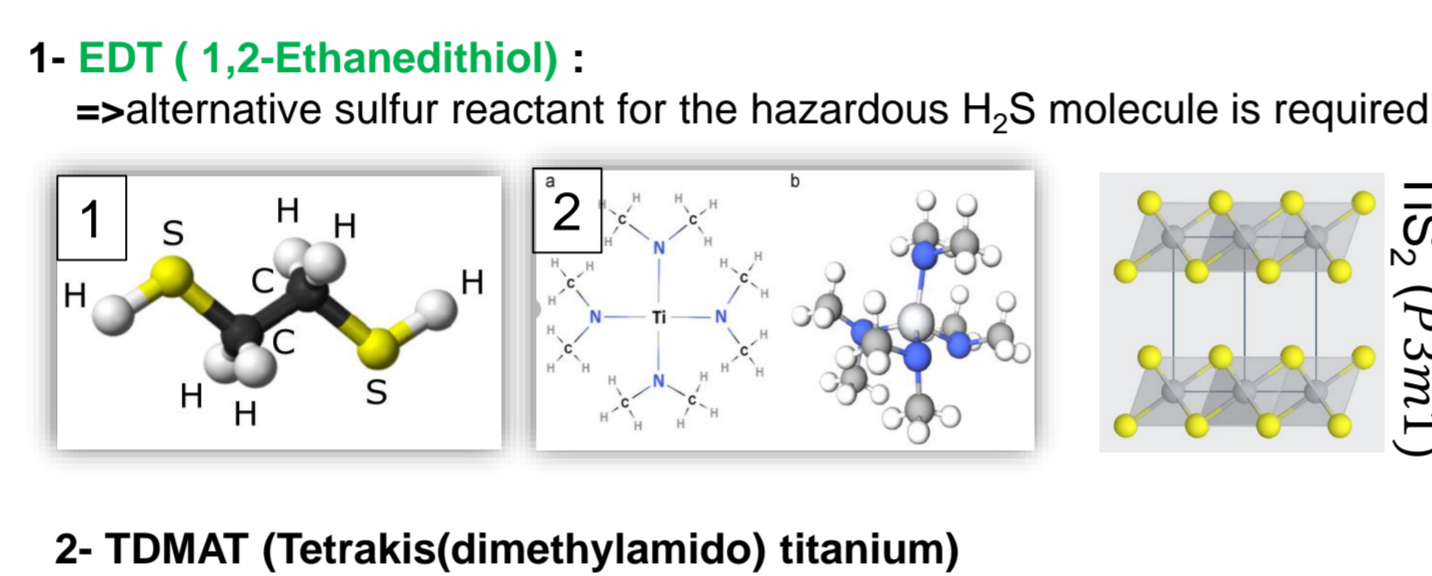


### Ti-thiolate Growth on SiO<sub>2</sub> substrate (SOLEIL)

#### SIRIUS Beamline



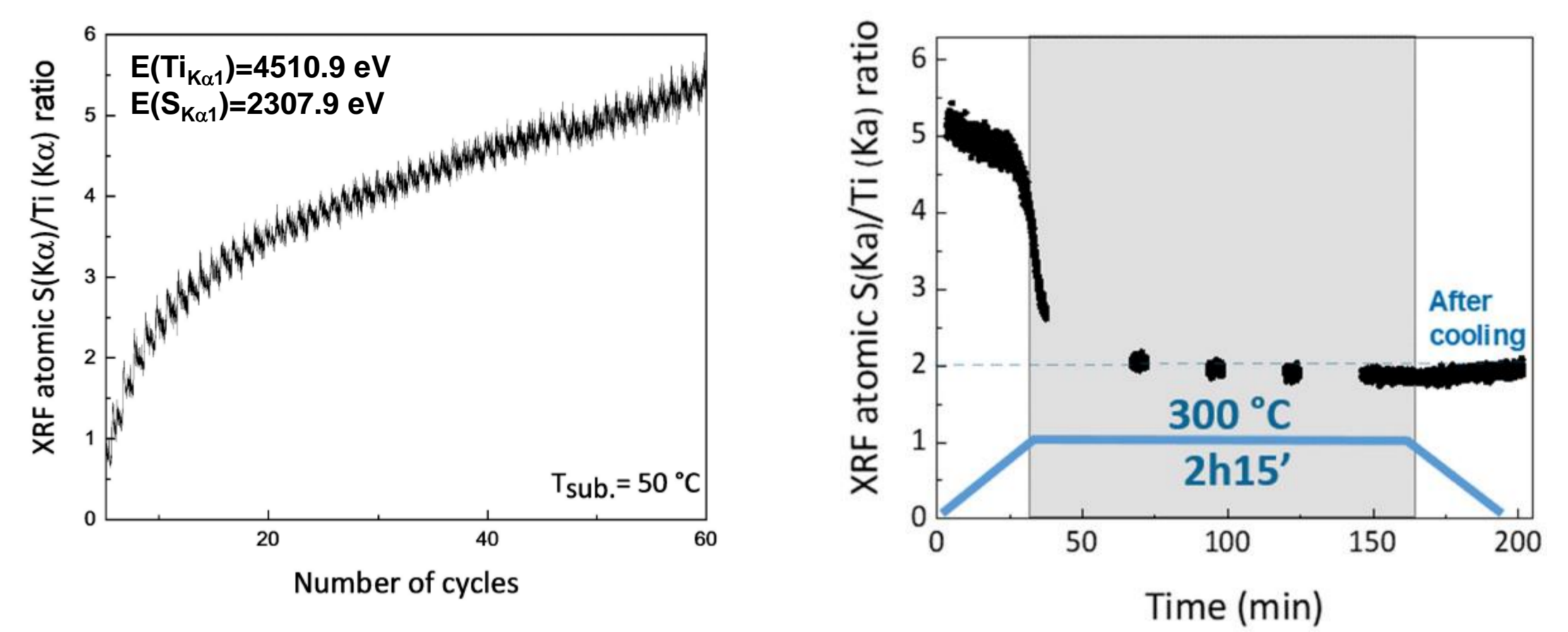
#### Precursors



- 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 [1]
- Polymer film deposited at low temperature on flat 100nm thick thermal SiO<sub>2</sub> on silicon substrate

➤ **Objective: optimization of dichalcogenides materials (TiS<sub>2</sub> and GaS) by a two-step process: ALD/MLD of an intermediate organic layer (Thiolate) at low Temperature and an annealing under a controlled atmosphere to obtain crystalline 2D ultrathin layer**

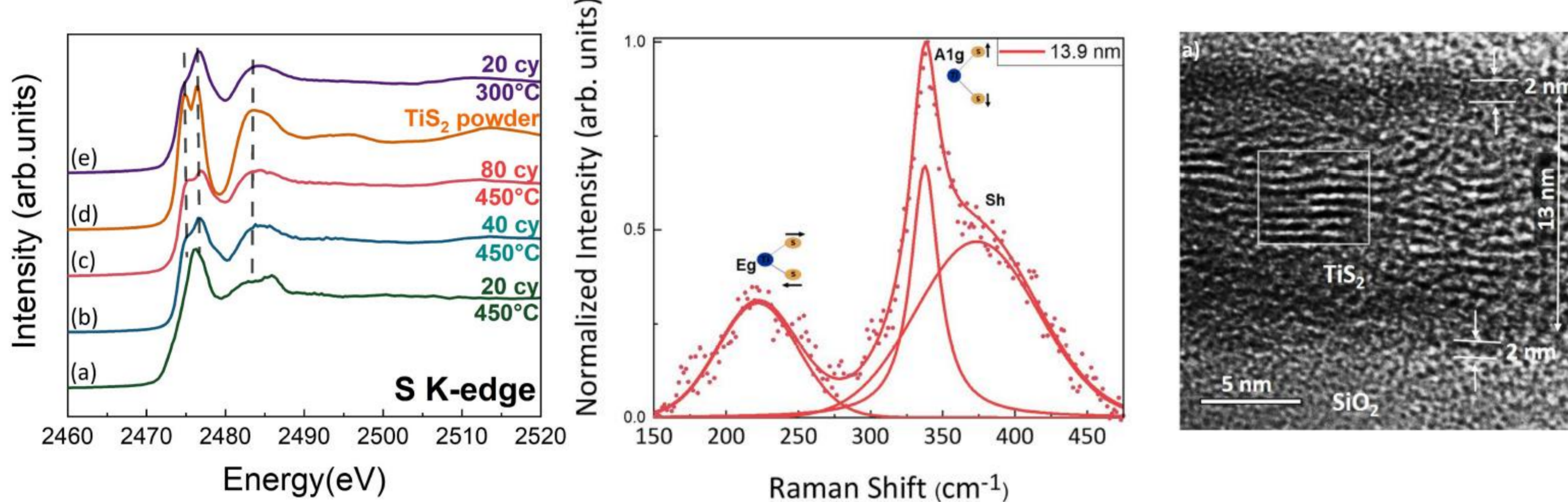
### In Situ X-ray Fluorescence (XRF)



- Ti- and S- K $\alpha$  yields are proportional to the mass concentration of the Ti and S atoms
- XRF S/Ti ratio curve shows a linear growth behavior with a slight non linearity in the early stages of growth
- XRF data confirms the grafting of the precursors leading to a Ti-thiolate deposit on SiO<sub>2</sub>

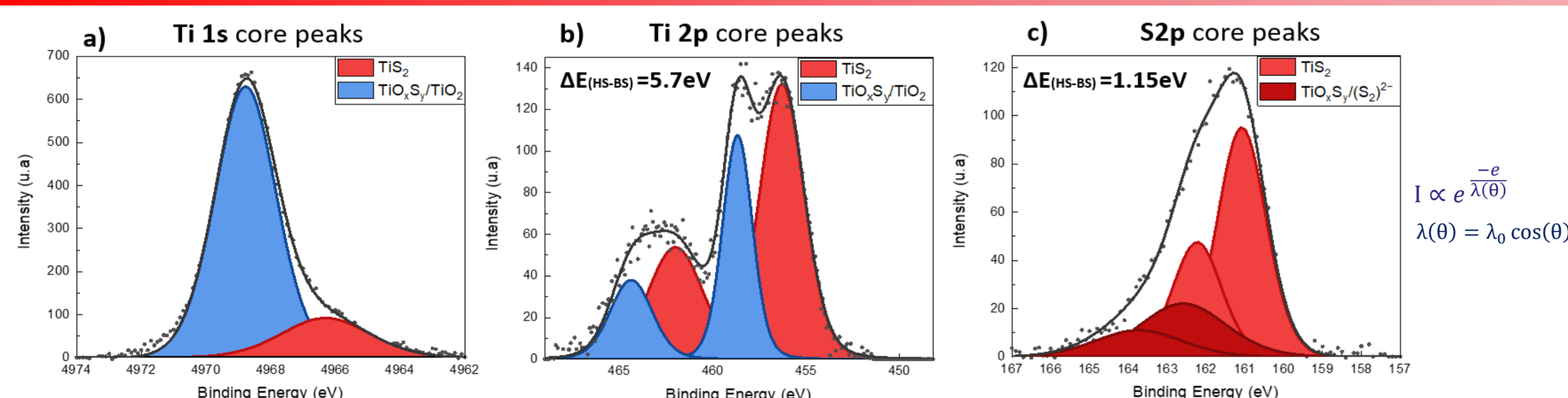
### Ex situ measurement after Thermal Annealing (2h15' at 300°C, Ar+4%H<sub>2</sub>)

### XANES, $\mu$ RAMAN and TEM (40 cycles after annealing)



- ✓ Close similarity to TiS<sub>2</sub> powder spectrum
- ✓  $\mu$ Raman and TEM confirm TiS<sub>2</sub> (P3m1)

### HAXPES: Stoichiometry (40 cycles after annealing)



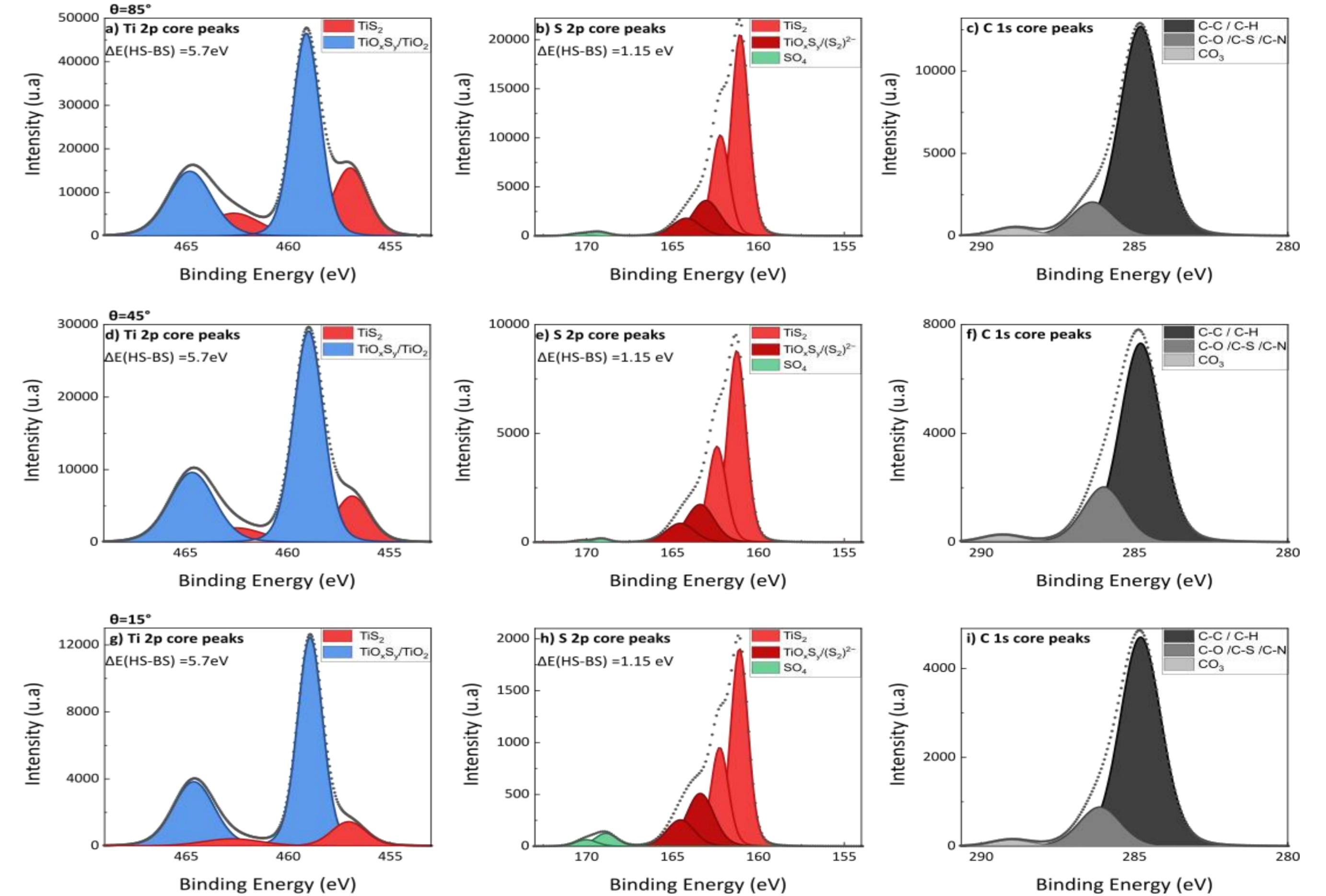
- HAXPES (Hard X-ray Photoelectron Spectroscopy) spectra recorded with a Cr K $\alpha$  source (5414.7 eV)
- Theoretical relative sensitivity factors (RSF) [3] [4] allow to calculate aspect ratios.
- HAXPES shows the in-depth presence of C atoms
- HAXPES allows to evaluate the surface oxide thickness : 2.8 nm

$$\frac{[S\ 2p]_{TiS_2}}{[Ti\ 2p]_{TiS_2}} = 2.2$$

$$I \propto e^{-\lambda/\cos(\theta)}$$

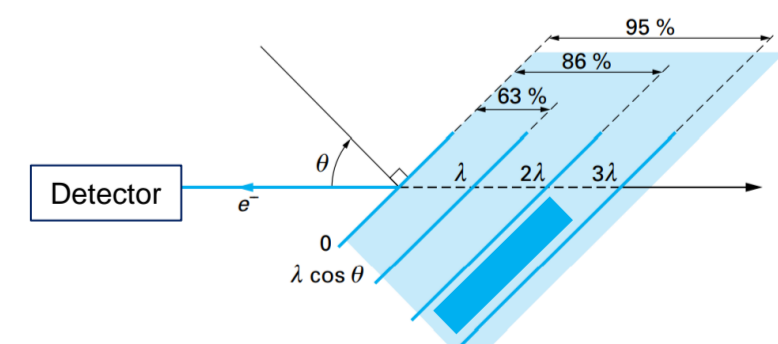
$$\lambda(\theta) = \lambda_0 \cos(\theta)$$

### ARXPS: Stoichiometry (40 cycles after annealing)



- ARXPS (X-ray Photoelectron Spectroscopy) spectra recorded with an Al K $\alpha$  source (1486.6 eV)
- Scofield relative sensitivity factors (RSF) [3] [4] allow to calculate aspect ratios.
- ARXPS allows to evaluate the surface oxide thickness : 2.7 nm
- ARXPS shows the in-depth presence of C atoms

$$\frac{r(\theta)}{r(0)} = \frac{1 - e^{-\lambda(\theta)/\cos(\theta)}}{1 - e^{-\lambda_0/\cos(\theta)}} + e^{-\lambda_0/\cos(\theta)} \frac{1 - \cos(\theta)}{\cos(\theta)}$$



### Conclusions and perspectives

- ✓ Ti-thiolate organic film can be grown by MLD using TDMAT and EDT as precursors, at 50°C / *In situ* XRF of Ti and S atoms confirms the self limiting growth and Ti-thiolate deposition
- ✓ The Raman modes E<sub>g</sub> and A<sub>1g</sub> of the layered TiS<sub>2</sub> (P3m1) are detected
- ✓ XPS data confirms the deposition of TiS<sub>2</sub> with a stoichiometric ratio S/Ti = 2.2
- ✓ Both the linear dichroism of the XANES spectra and TEM images reveal a crystalline texture i.e. the TiS<sub>2</sub> layers tend to be parallel to the substrate surface

□ **Perspectives** : Improvement of the TiS<sub>2</sub> texture of thin layers / To deposit layered GaS by the same process using TDMASn and EDT (work in progress) / Analysis of other dichalcogenides by HAXPES

#### References

- [1] S. Cadot et al. *Nanoscale* 9 (2017) 538
- [2] M. F. Smith et al. *Applied Physics Letters* 92 (2007) 142107
- [3] F. Flamarly-Mespoulie et al. *Energy Storage Materials* 26 (2020) 213
- [4] C. D. Wagner *Journal of electron spectroscopy and related phenomena* 32 (1983) 99

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