PhD DAYS 2025

TOR VERGATA
UNIVERSITÀ DEGLI STUDI DI ROMA

Growth and characterization of Chalcogenides-based compounds:

Heterostructures and novel materials

Christian Petrucci
Ph.D. Student
XXXIX° Cycle

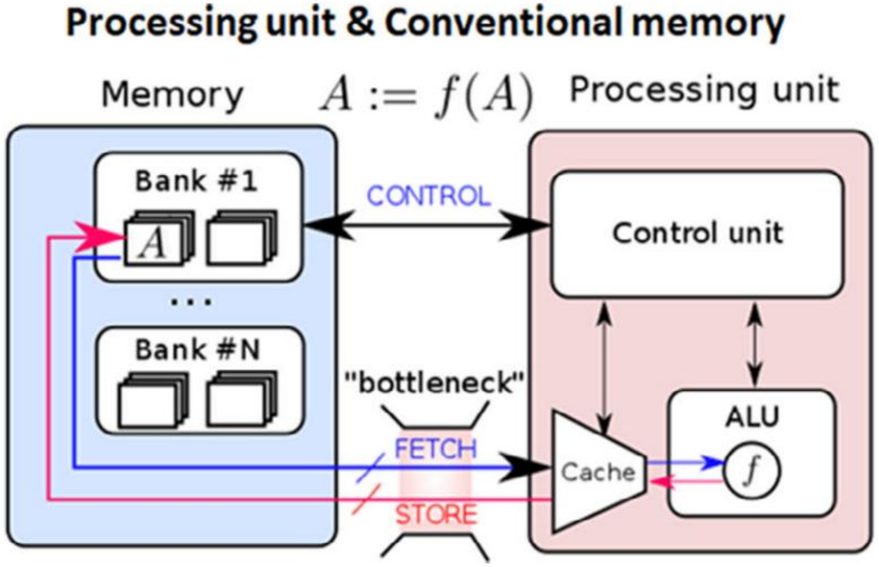
Supervisor
Prof. Fabrizio Arciprete

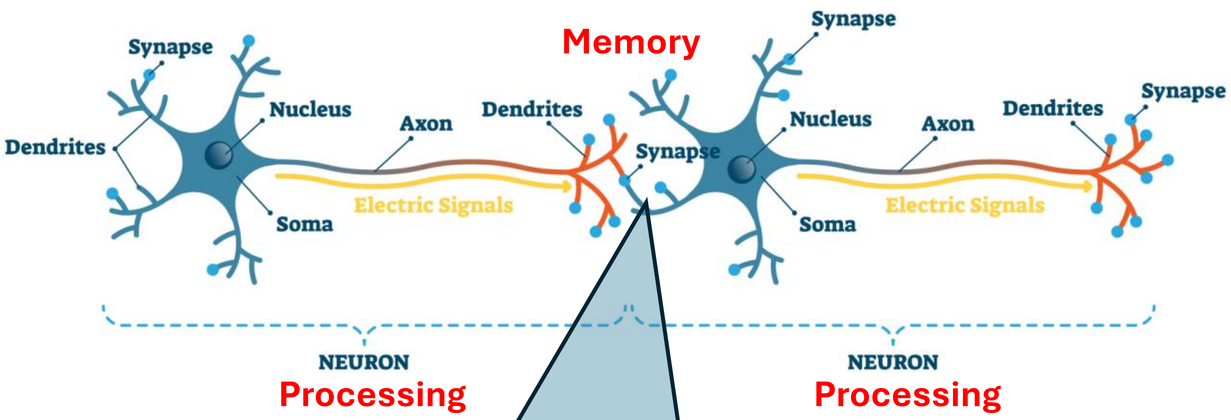
Outlook

- **Introduction**
- Experimental setup
- Results
  - Ti doped Ge-Sb-Te alloy
  - In-Ge-Te alloy
- Conclusion

Neuromorphic Computing

https://www.simplypsychology.org/synapse.html



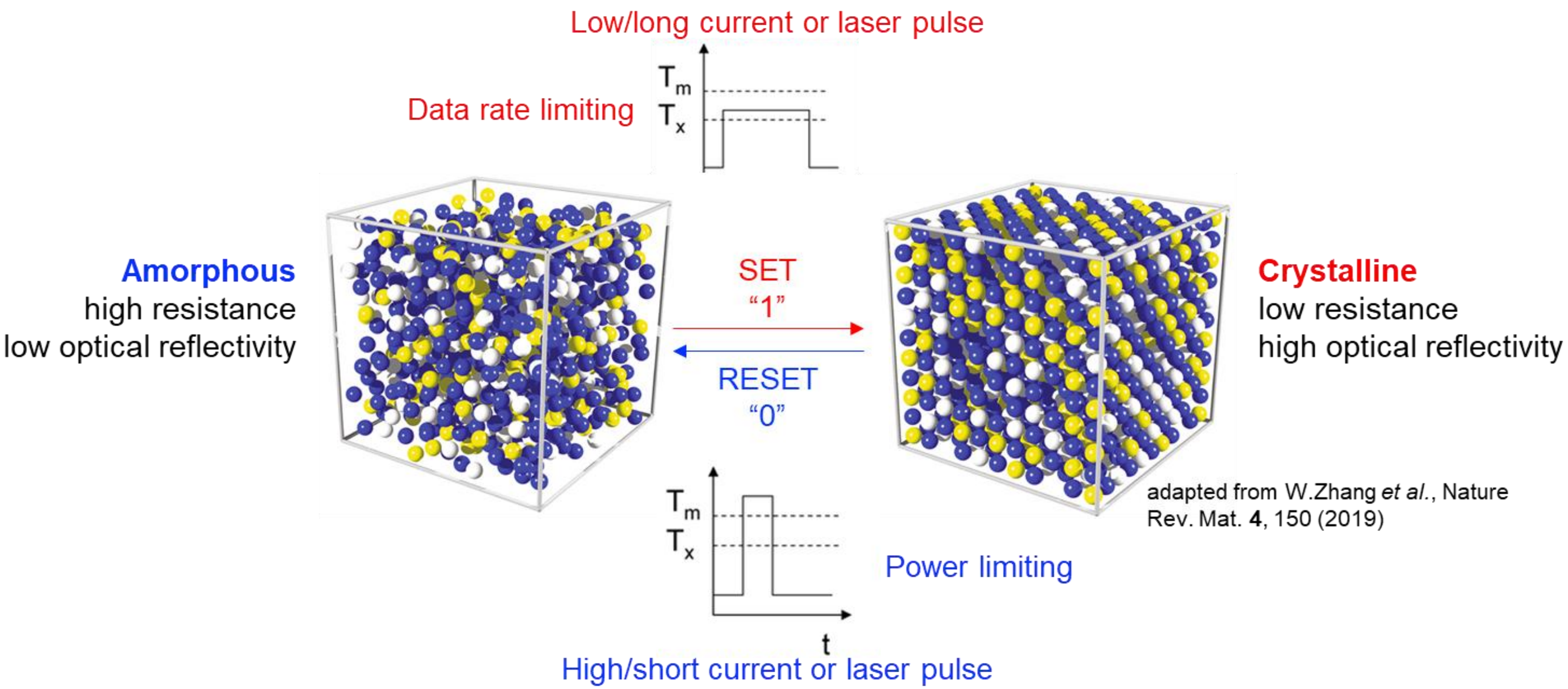


- High power consumption
- Heavy processing of big data

10 pJ

10 fJ

Phase Change Materials

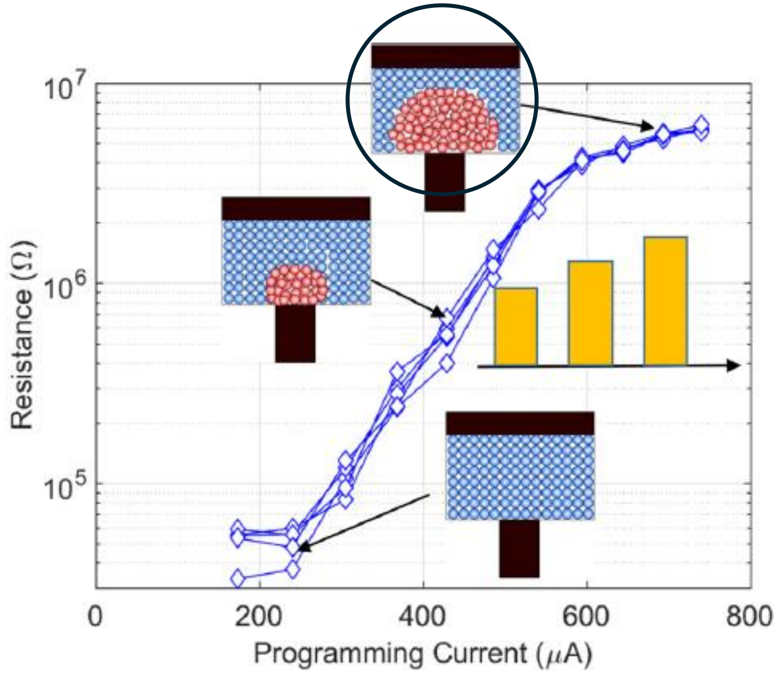


adapted from W.Zhang *et al.*, Nature Rev. Mat. **4**, 150 (2019)

- Used in non-volatile Random Access Memory

PCMs issues:
- Resistance drift over time
- High energy consumption

Programmable region: resistance range depending on the amount of material in amorphous/crystalline state



Adapted from: A. Sebastian *et al* «Tutorial: Brain-inspired computing using phase-change memory devices», *J. Appl. Phys.*, vol. 124, fasc. 11, p. 111101, set. 2018

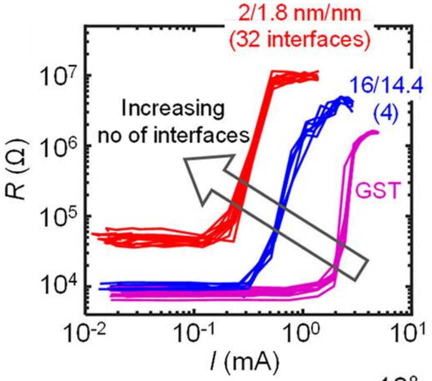
Phase Change Heterostructures

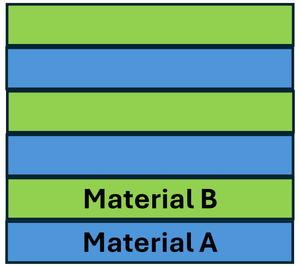
Interfacial PCM

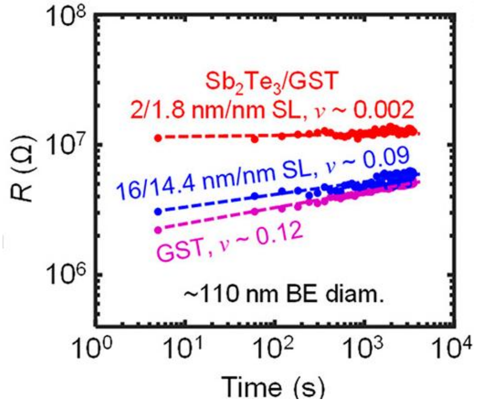
- Lowering of $\mathbf{R_{drift}}$ and $\mathbf{I_{reset}}$ incresing interfaces number
- Role of **vdW** gap

- PCM/TMDs heterostructures: $TiTe_2$ as **Confinement Material** (CM)
- Sharp interfaces to prevent atoms **migration** and to **confine heat**

- Strong Ti **migration** and **segregation**

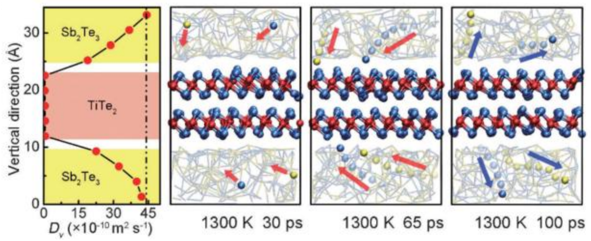




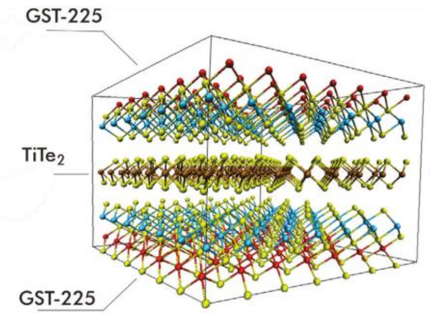


Khan, A. I. *et al.*, Nano Lett. **22**, 6285 (2022)

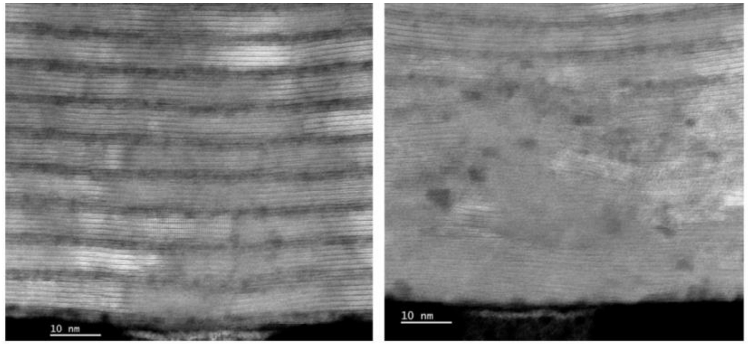
Sb_2Te_3/$TiTe_2$ Ding, K. et al., Science **366**, 210 (2019)



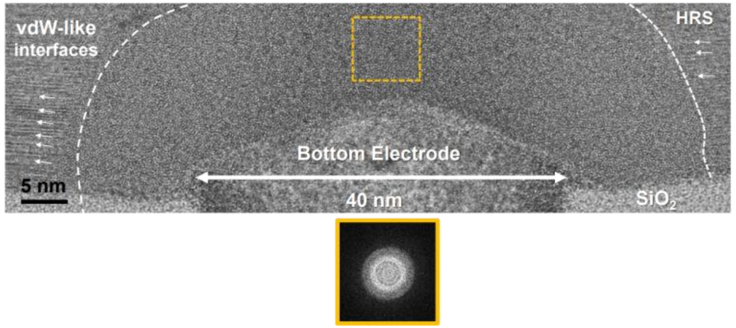
GST/$TiTe_2$ Piombo, R. et al., Adv. Sci. 2402375 (2024)



Wu, X *et al.* Nature Comm. **15**, 13 (2024)



Cohen, G.M. *et al.*, PSS RRL 2300426 (2024)



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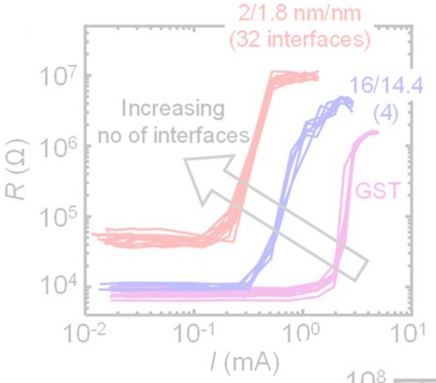

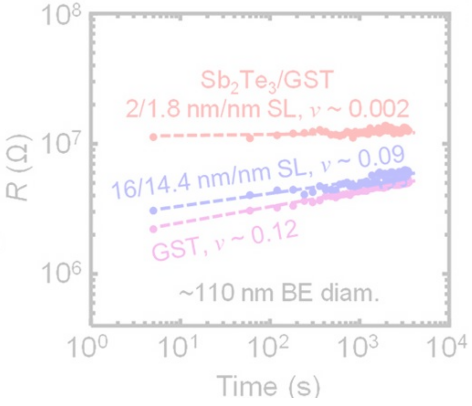

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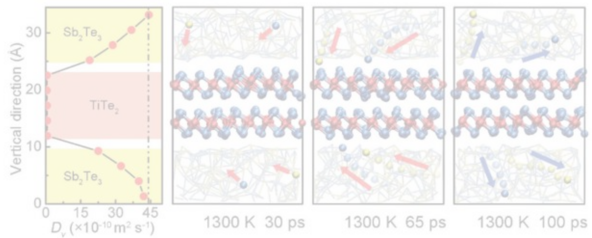
- PCM/TMDs heterostructures: $TiTe_2$ as **Confinement Material** (CM)
- Sharp interfaces to prevent atoms **migration** and to **confine heat**

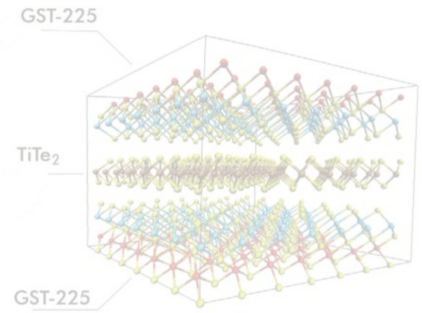
$Sb_2Te_3/TiTe_2$

Ding, K. et al., Science **366**, 210 (2019)



GST/$TiTe_2$

Piombo, R. et al., Adv. Sci. 2402375 (2024)



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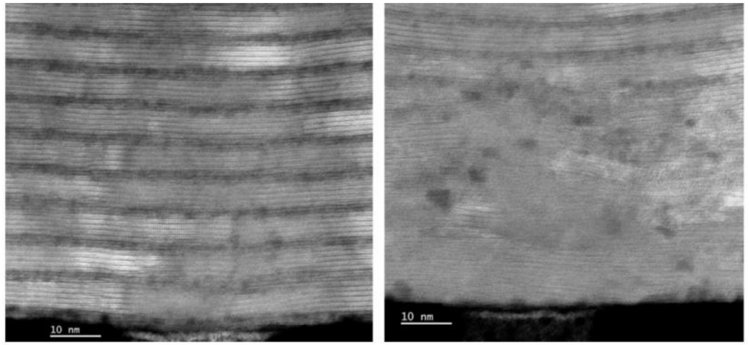
- Strong Ti **migration** and **segregation**



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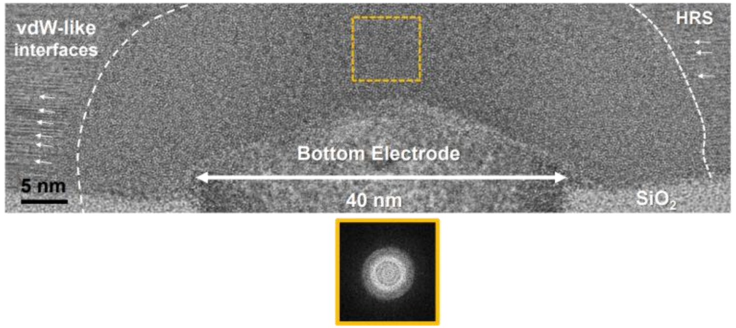


Not perfect interface!

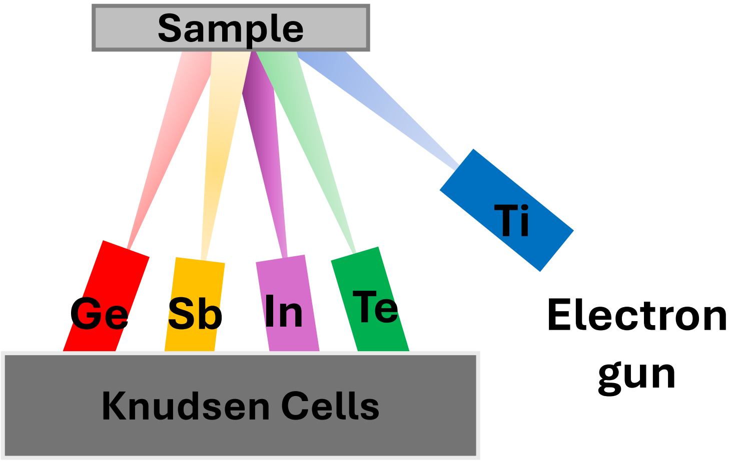
Outlook

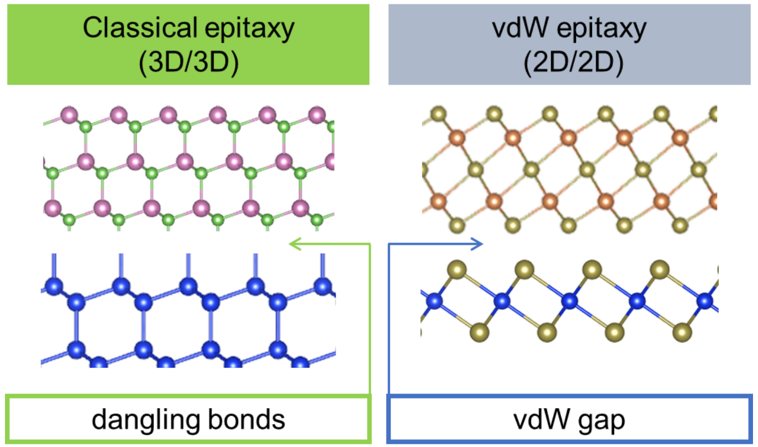
- Introduction
- **Experimental setup**
- Results
  - Ti-Ge-Sb-Te alloy
  - In-Ge-Te alloy
- Conclusion

Experimental setup

- Growth via **Molecular Beam Epitaxy**
  - Molecular regime: no interaction before absorption on substrate
  - Co-evaporation of different elements : Ge, Sb, Te, In, Ti
  - Realization of high quality crystalline samples
- **Van der Waals** epitaxy: exploitation of vdW gaps inside materials to allow a less costrictive growth (mismatch allowed up to 45%)

Materials growth rates:
- **$TiTe_2$** : 0.1 nm/min
- **Sb_2Te_3** : 0.6 nm/min
- **GST** : 0.7 nm/min
- **IGT** : 0.7 nm/min





Koma, *et al.* (1992)

Outlook

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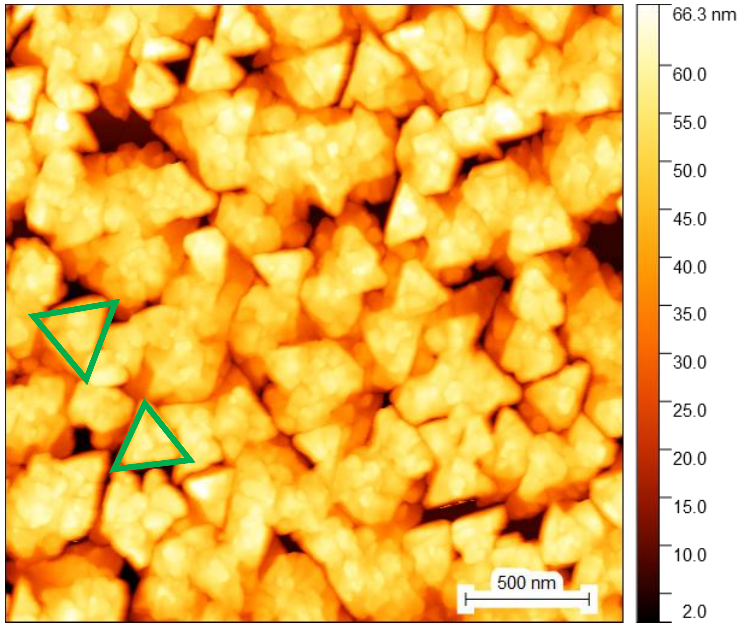
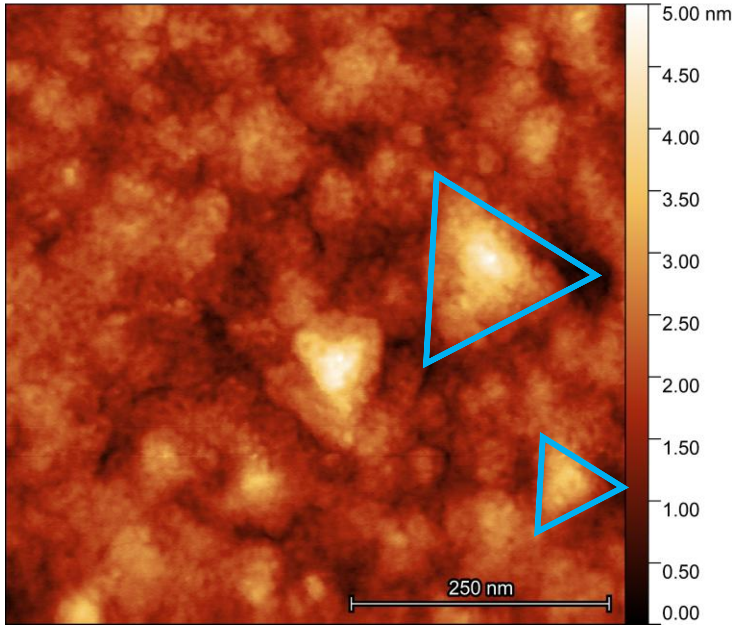
Epitaxial films growth

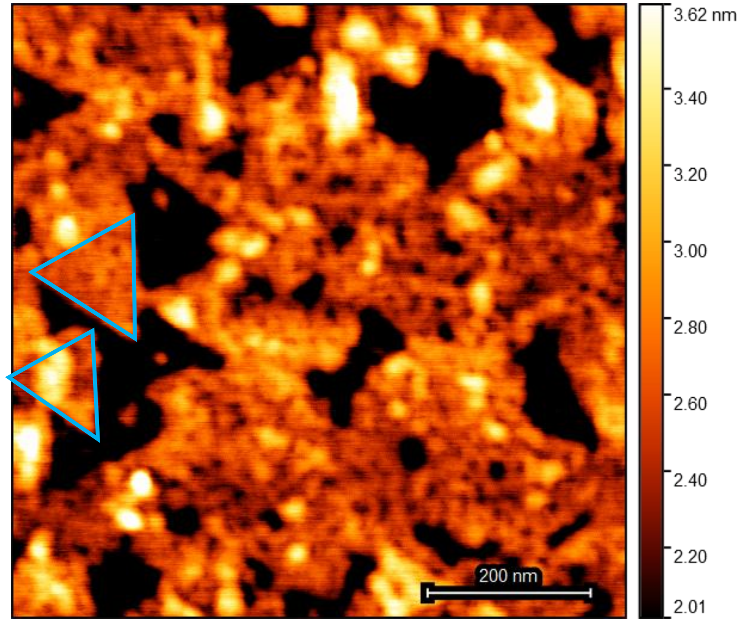
- **Sb_2Te_3**



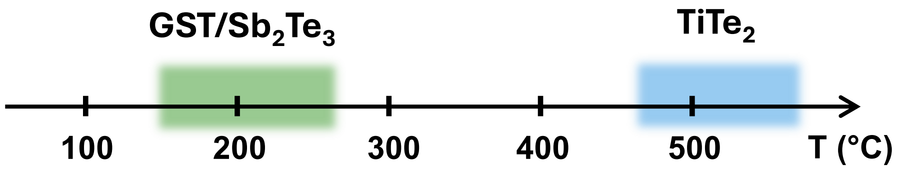
- **GST**

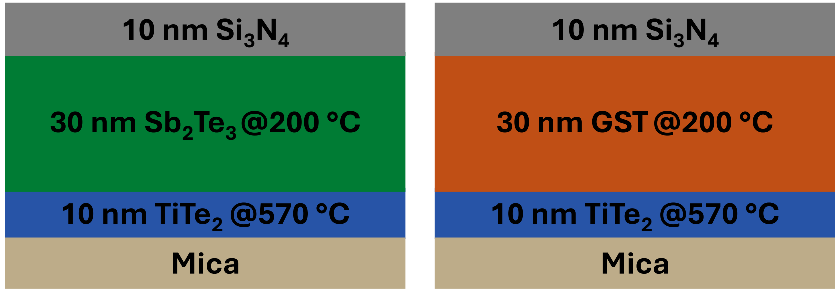


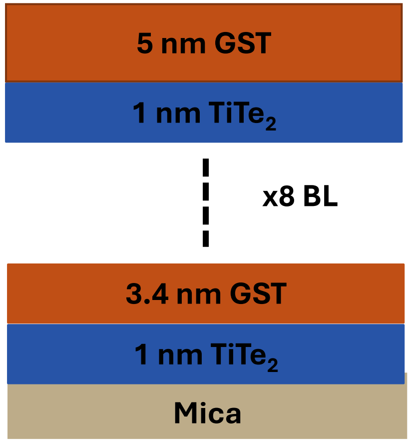
- **$TiTe_2$**



Atomic Force Microscopy (**AFM**) images



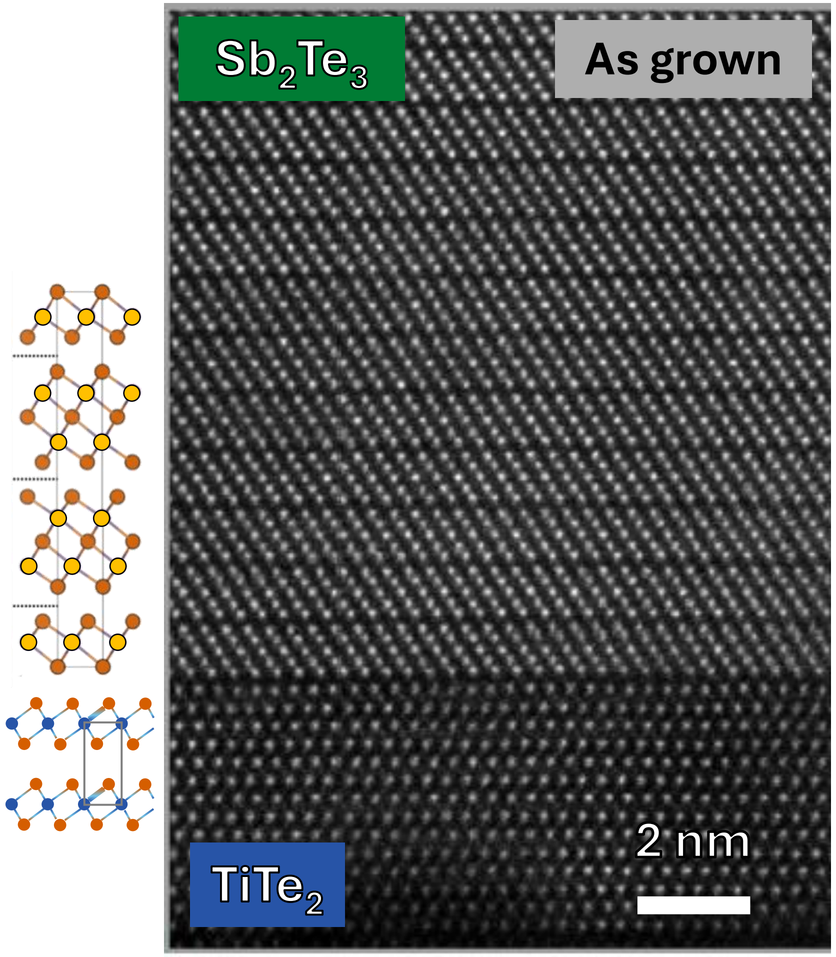


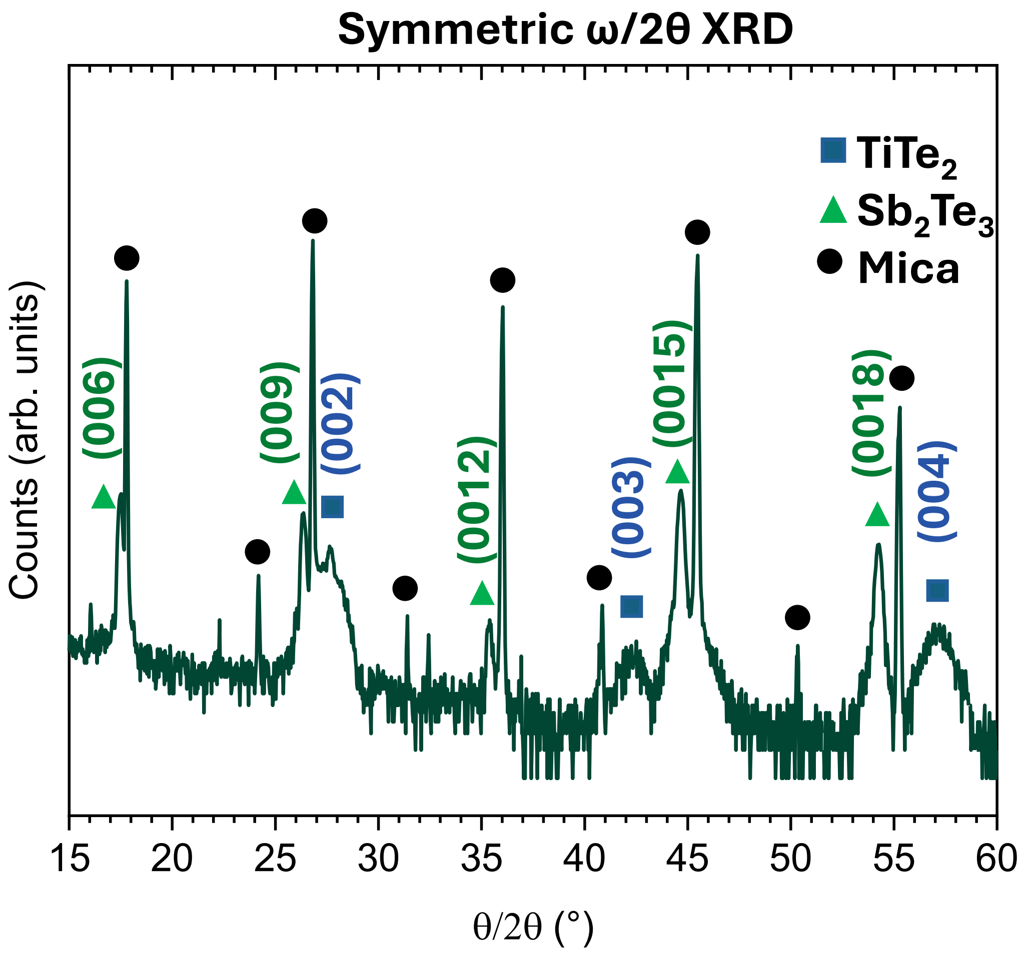


! **Different** growth windows

Bilayers growth

High Resolution-Transmission Electron Microscopy **(HR-TEM)**

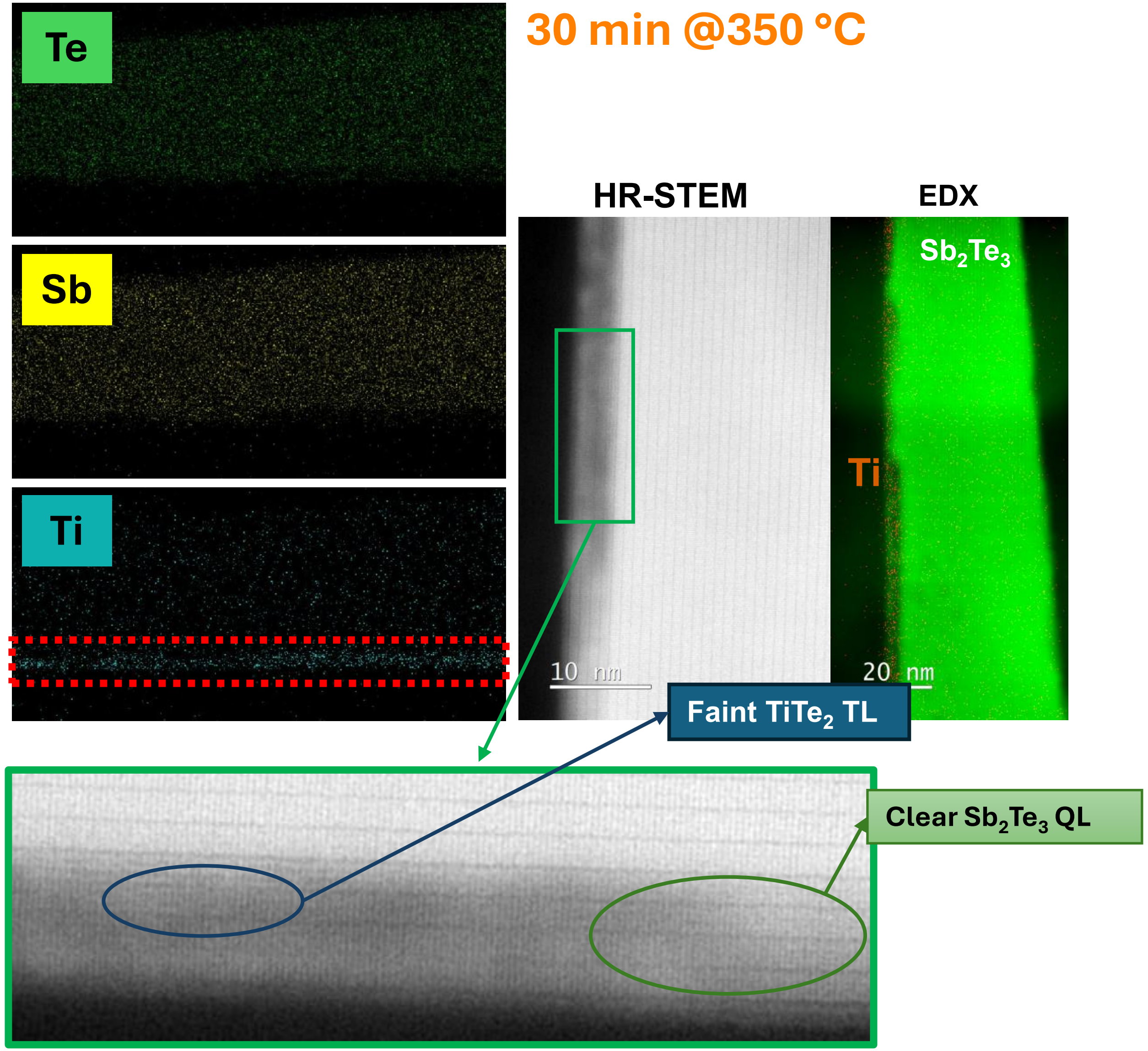




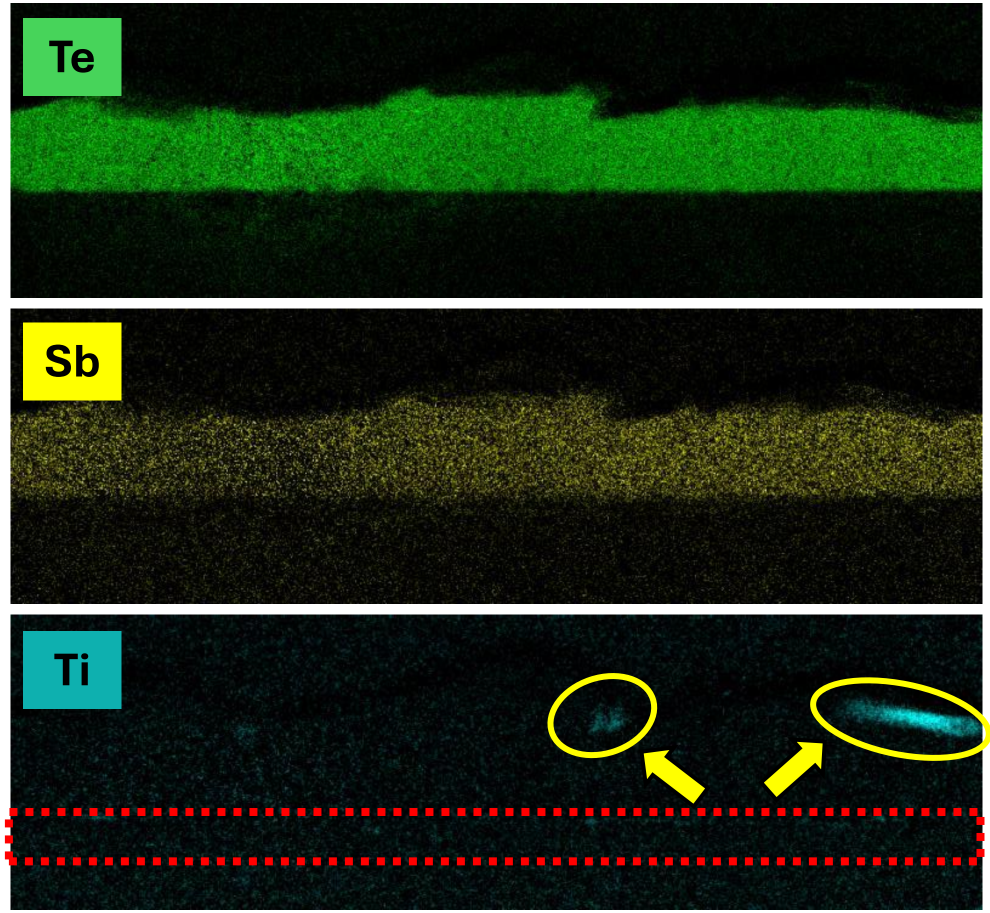
- Highly oriented sample

$TiTe_2$-Sb_2Te_3 Bilayer

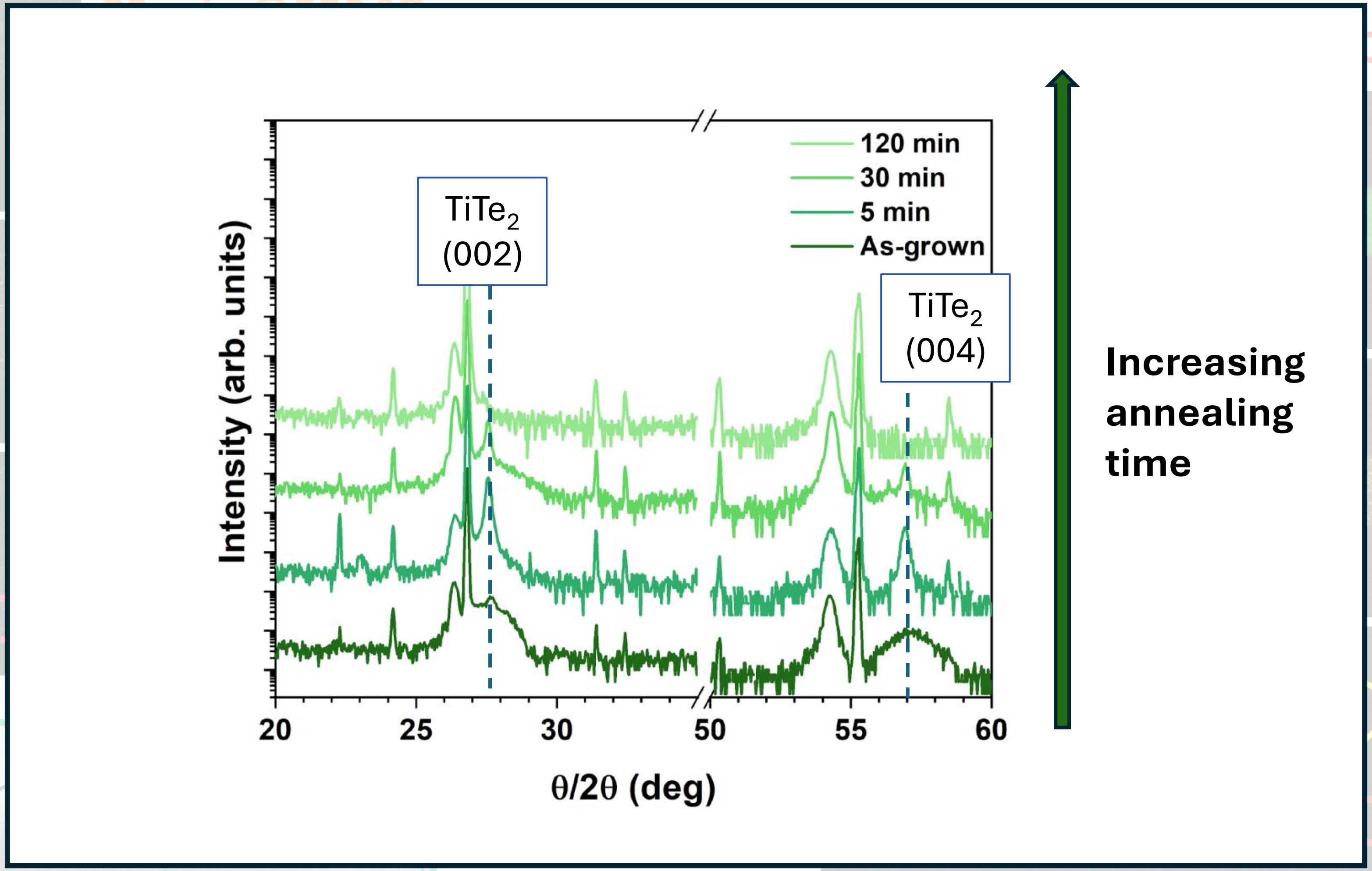
30 min @350 °C



30 min @400 °C



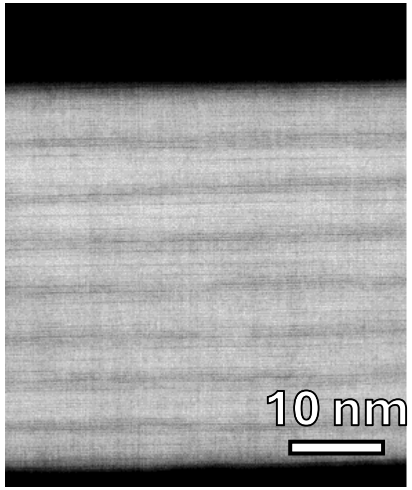
$TiTe_2$-Sb_2Te_3 Bilayer

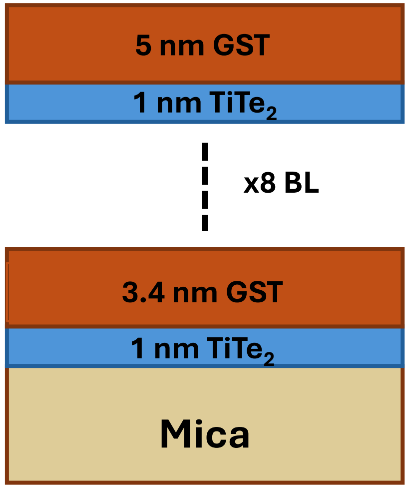


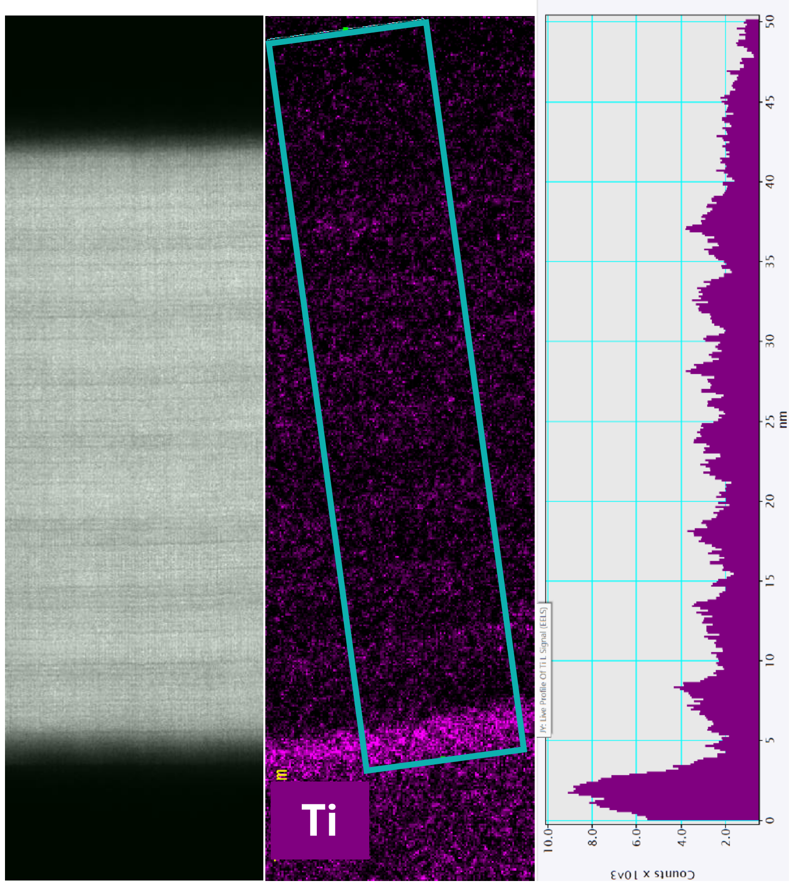
The kinetics of **Ti migration** determines the **stability** of the bilayer

$TiTe_2$-GST systems

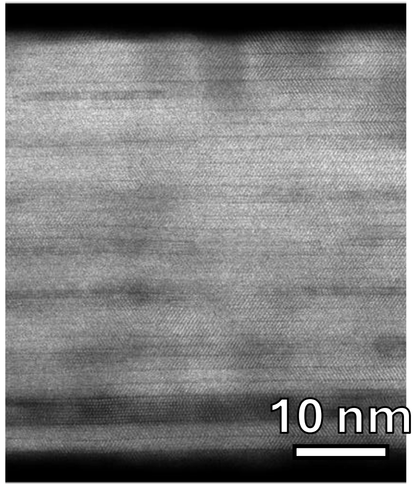
As grown

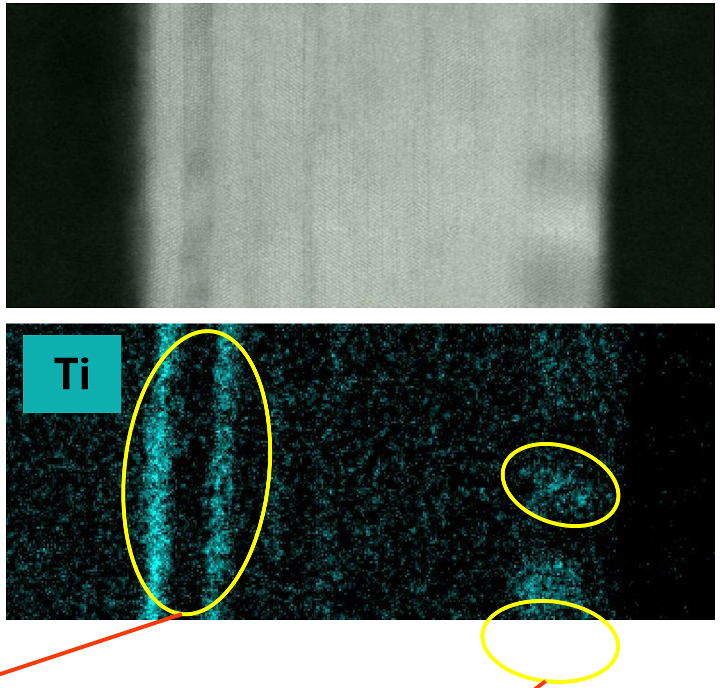






30 min @350 °C



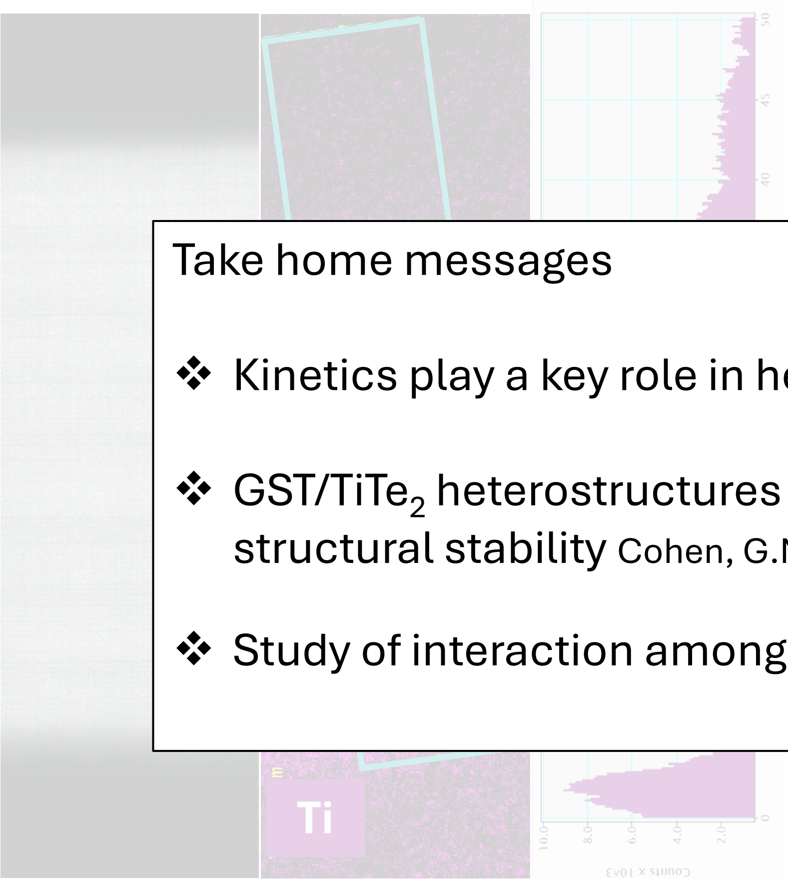


Ti migration towards first $TiTe_2$ layer increasing Ti signal

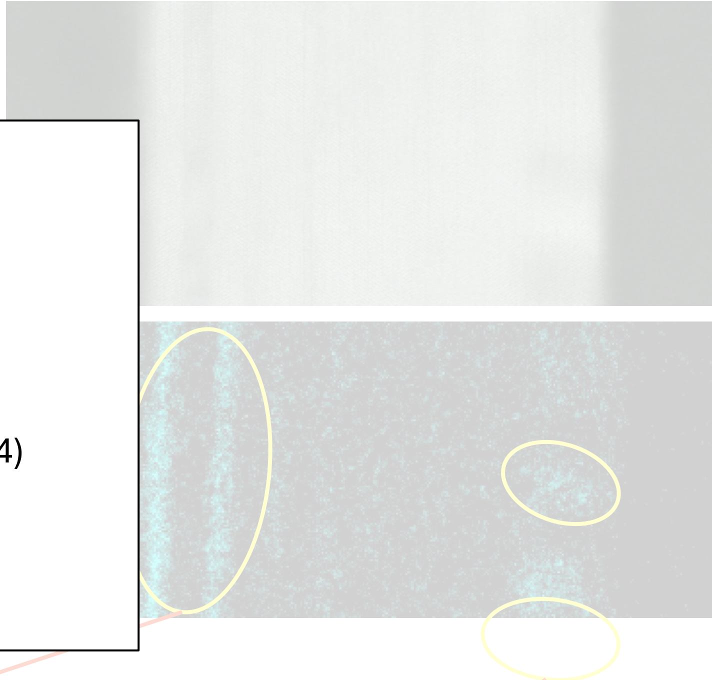
Ti migration in GST layers

$TiTe_2$-GST systems

As grown



30 min @350 °C



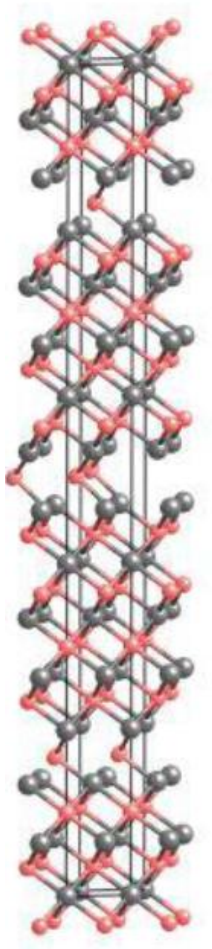
Take home messages

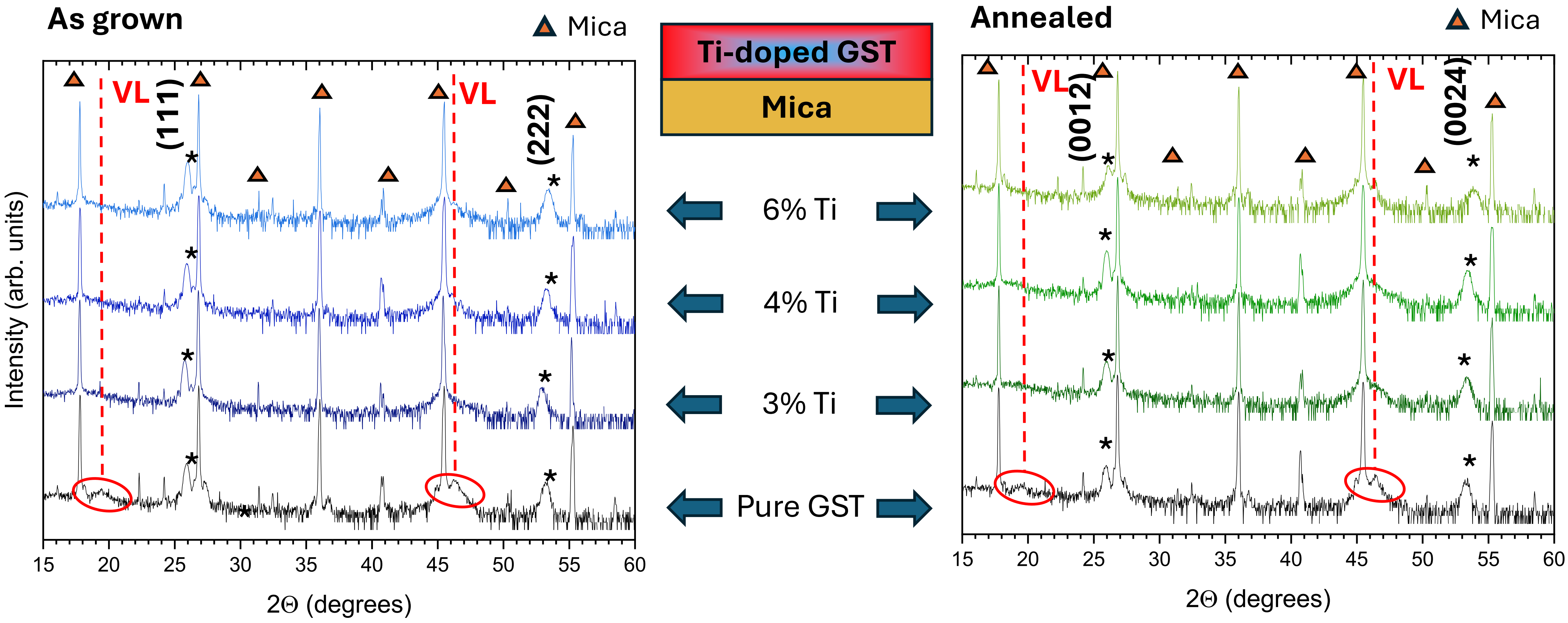
- Kinetics play a key role in heterostructures stability
- GST/$TiTe_2$ heterostructures operate also with poor structural stability Cohen, G.M. *et al.*, PSS RRL 2300426 (2024)
- Study of interaction among Ti and GST

Ti migration towards first $TiTe_2$ layer increasing Ti signal

Ti migration in GST layers

Ti-doped GST

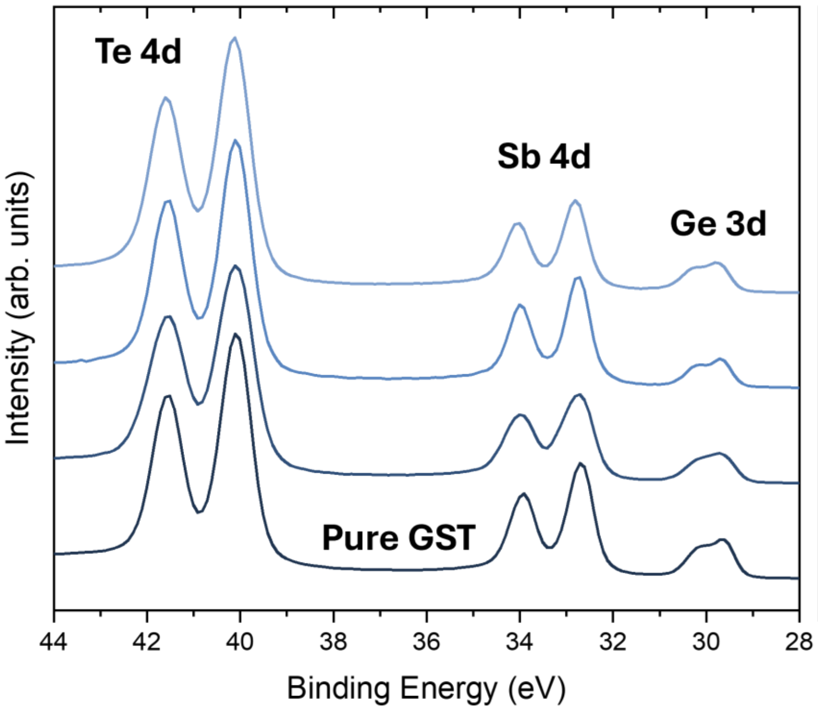


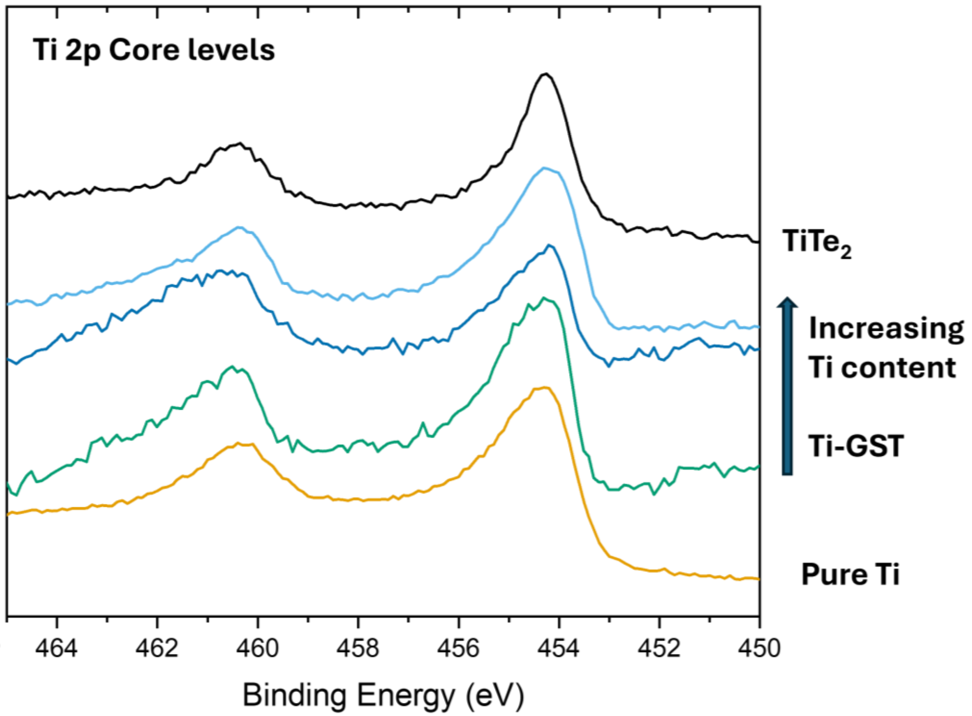


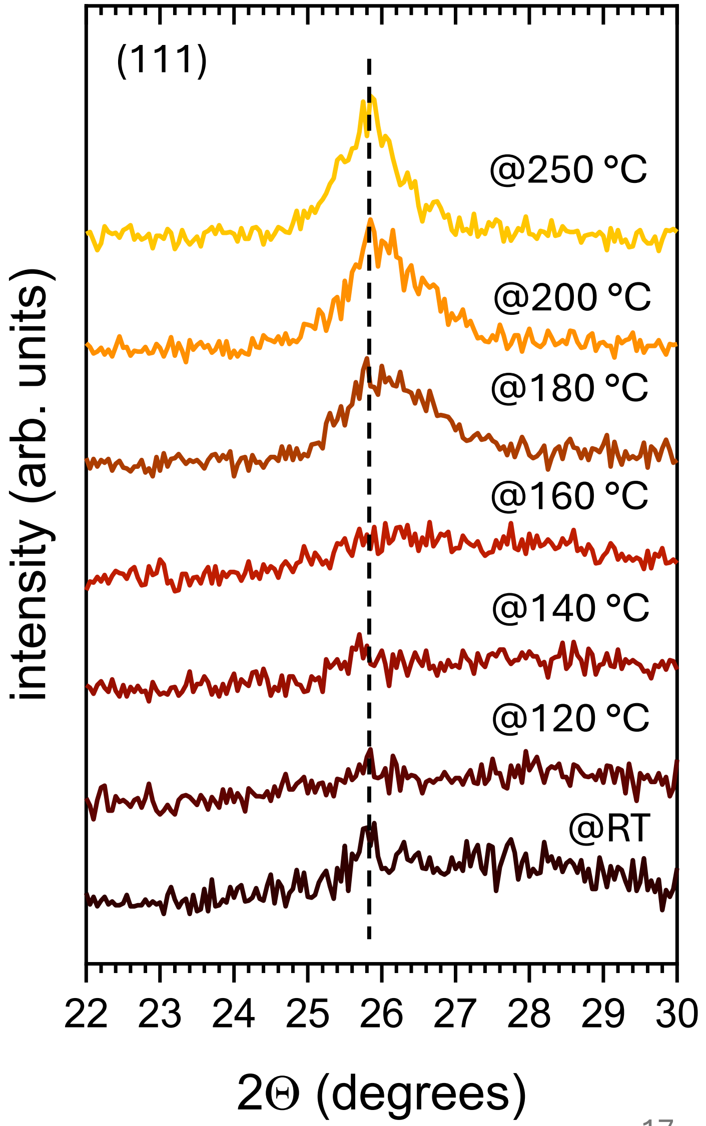
- **No evidences of Vacancy Layers** features (red dashed lines) in Ti-GST samples
- **No evidences of secondary compounds** (e.g. $TiTe_2$) in the samples

Ti-doped GST

X-Ray photoemission Spectroscopy (**XPS**)







- Evolution of intensity of **111 peak** upon annealing suggest a crystallization temperature between **160 °C** and **180 °C** (Ref. GST: 100-160 °C)

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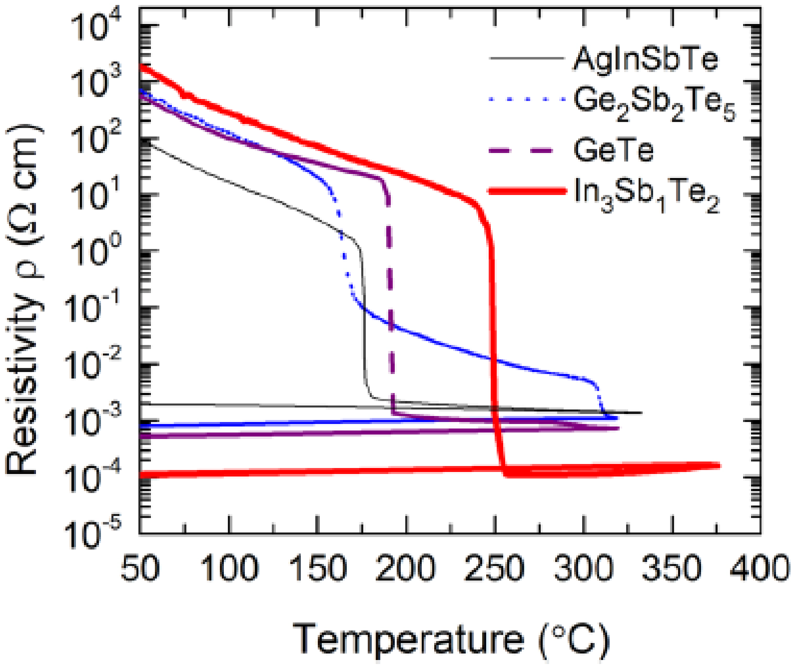
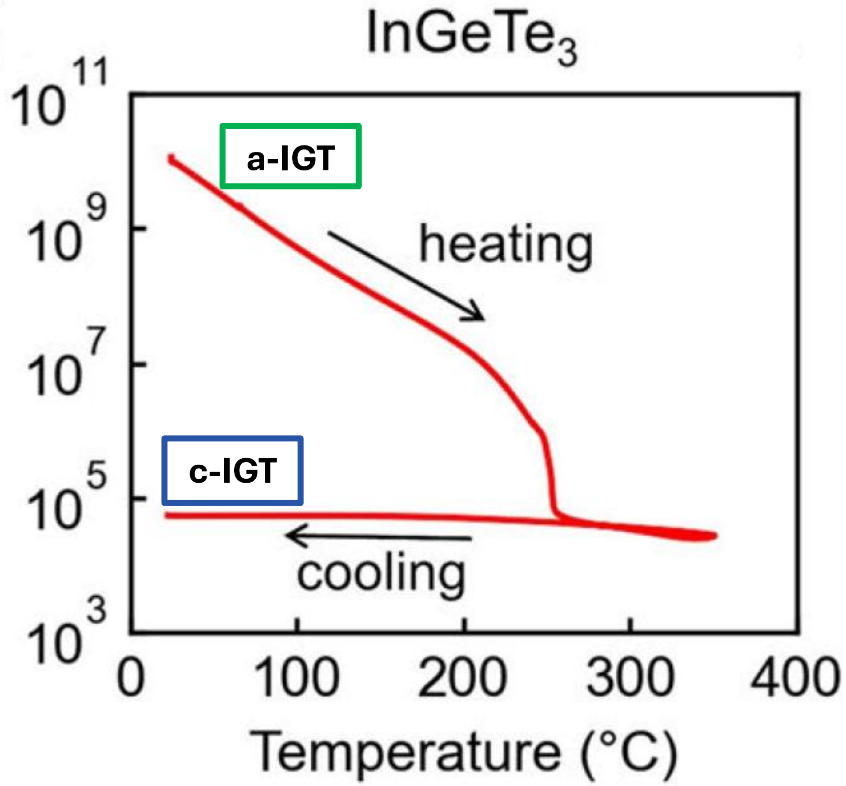
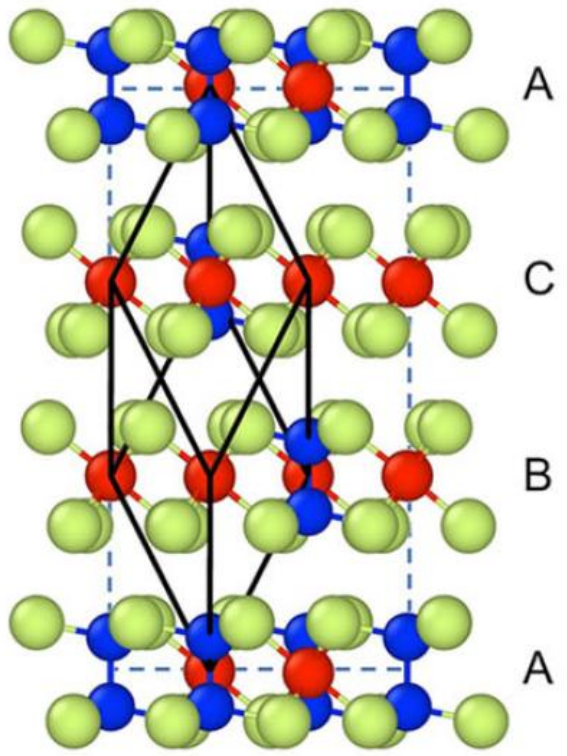
In-based PCMs







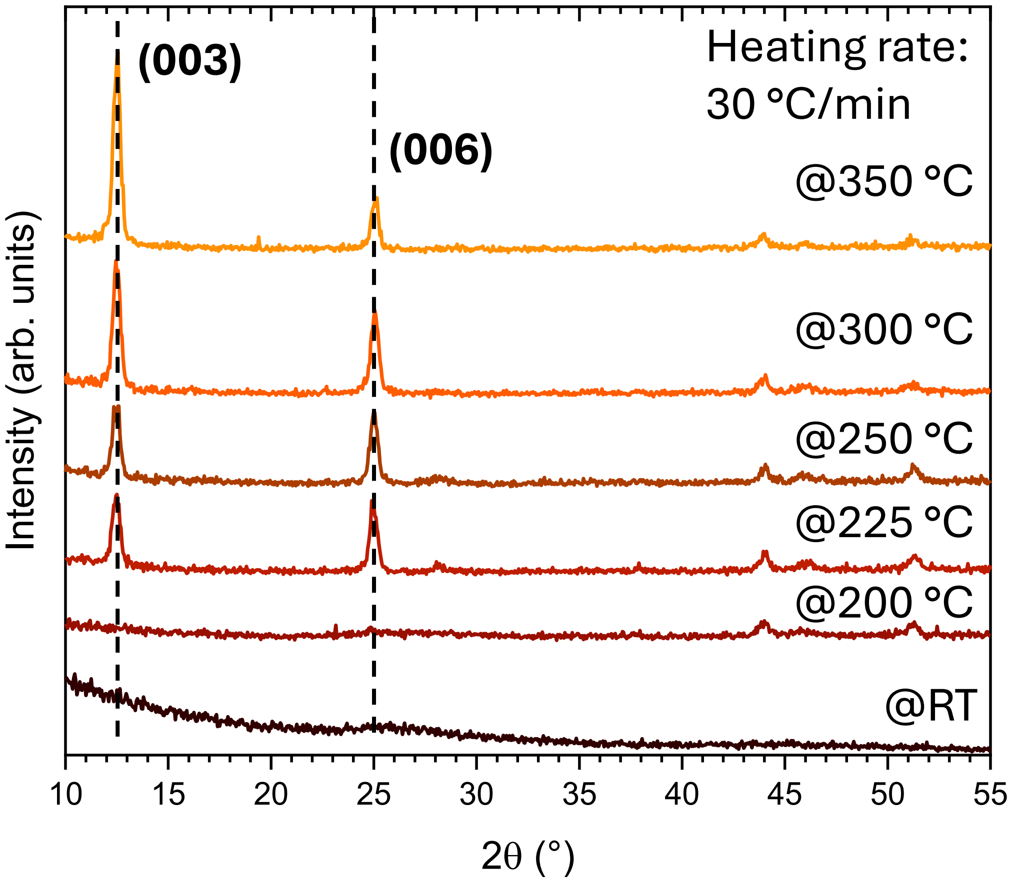
- Higher crystallization temperature, **up to 250 °C** for $In_3Sb_1Te_2$

Saxena, Nishant, *et al Scientific reports* 9.1 (2019): 19251.

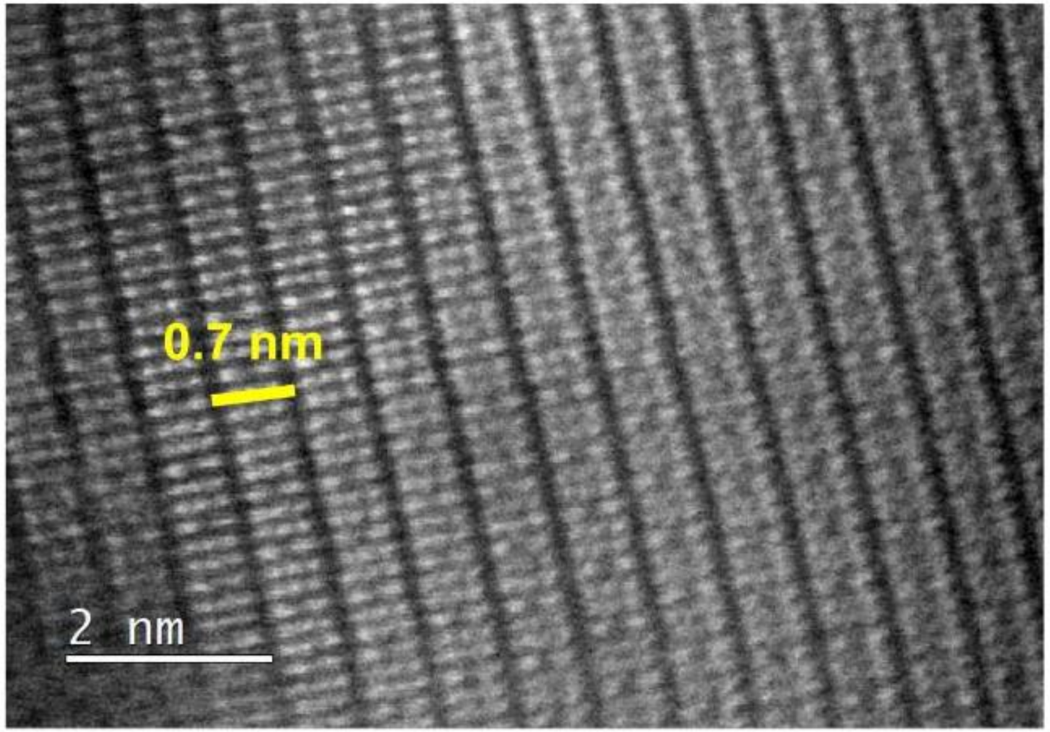
- **Huge contrast in resistivity** values among amorphous and crustalline phases (10^{10} vs 10^5)
- Layered structure for $InGeTe_3$ (IGT-113)

Sun, Suyang, et al. *npj Computational Materials* 10.1 (2024): 189.

$InGeTe_3$

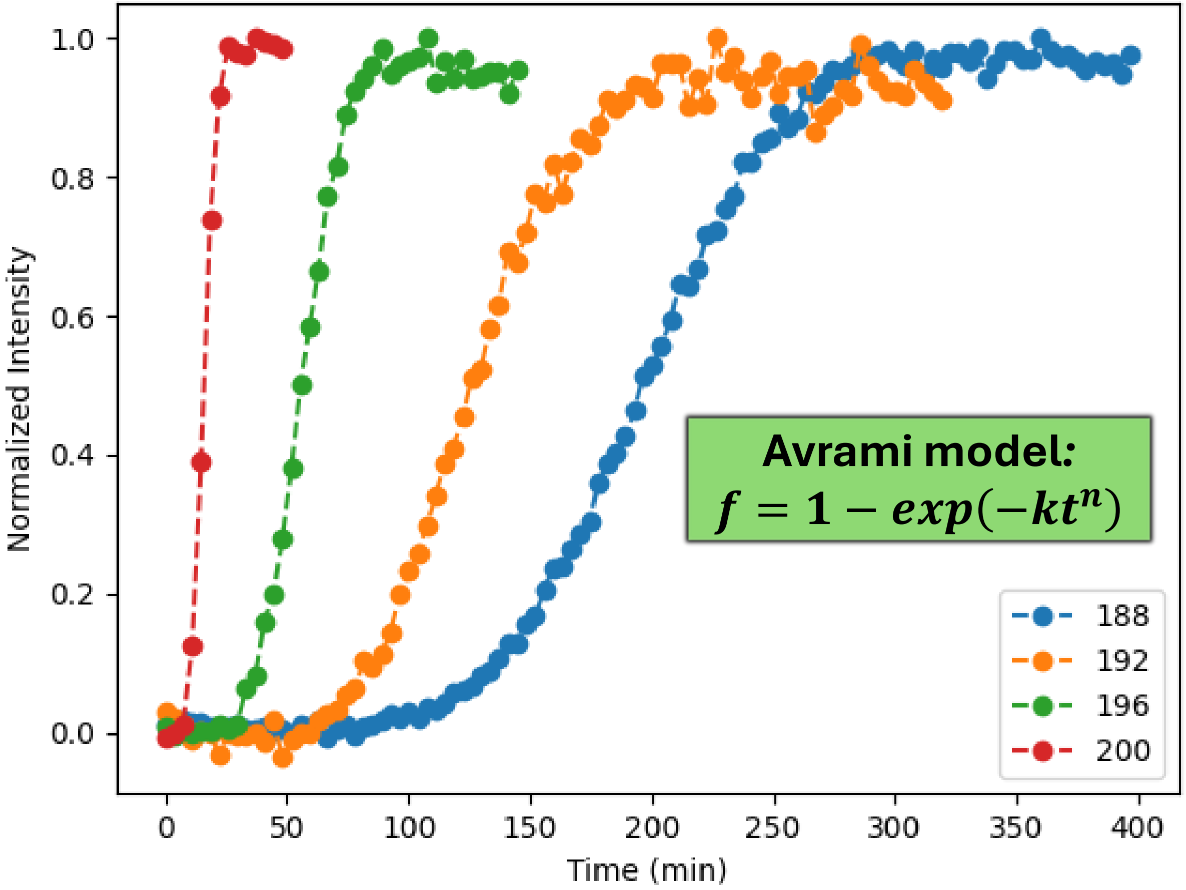


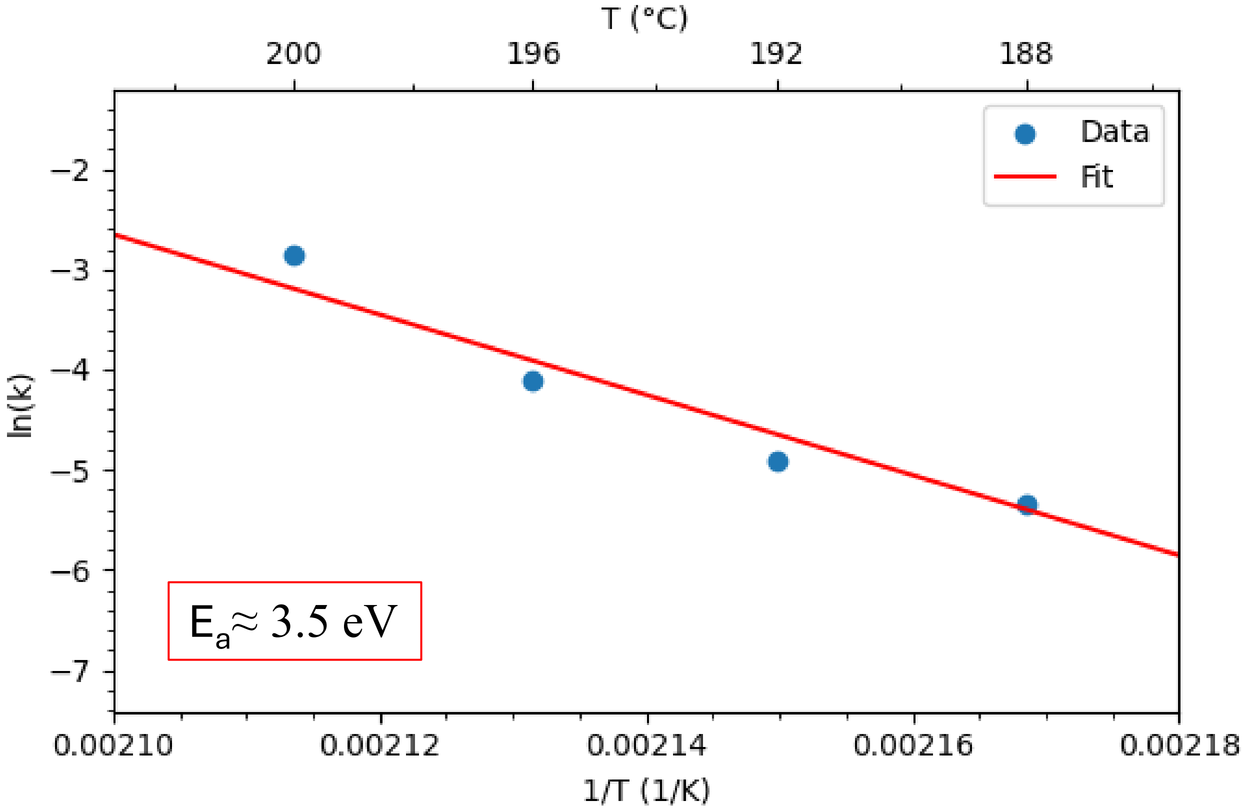
TEM image



- Evidences of **layered structure** in IGT-113
- Presence of (00l) peaks as most intense peaks confirm high orientation of the samples
- Crystallization temperature between 200 °C and 225 °C

Crystallization of $InGeTe_3$



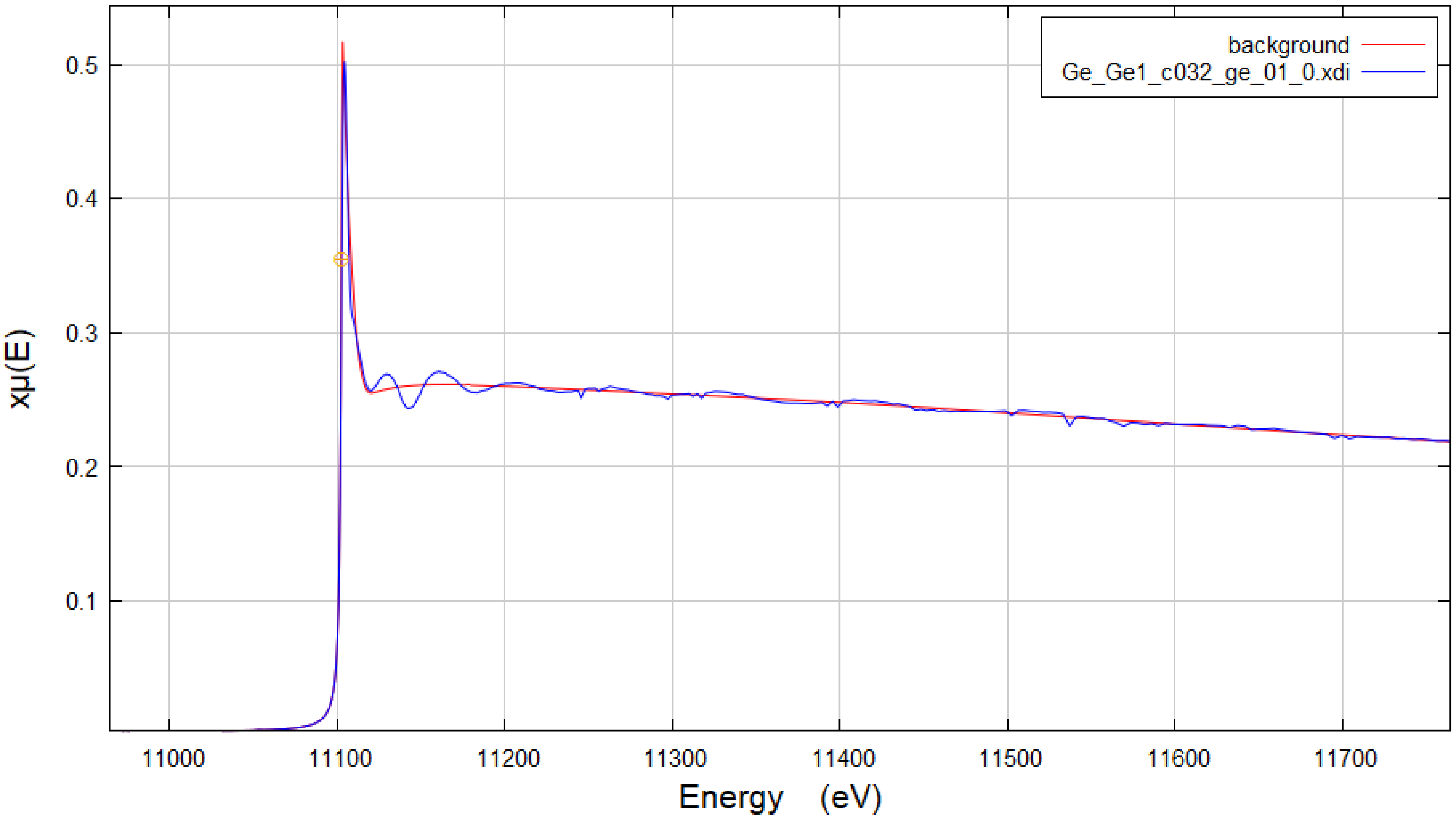


- Avrami model allows an interpretation of the crystallization process
- K follows an Arrhenius-Like law
- Parameter: intensity of **main crystalline peak** during isothermal process

What’s next?

Ge absorption edge– IGT @195 °C

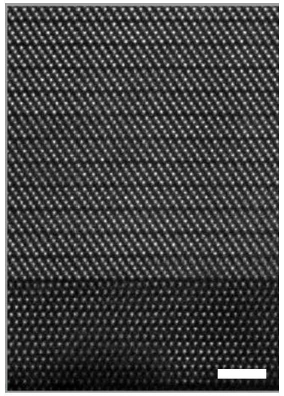
Experiment MA6822

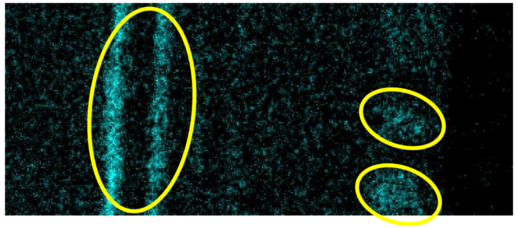


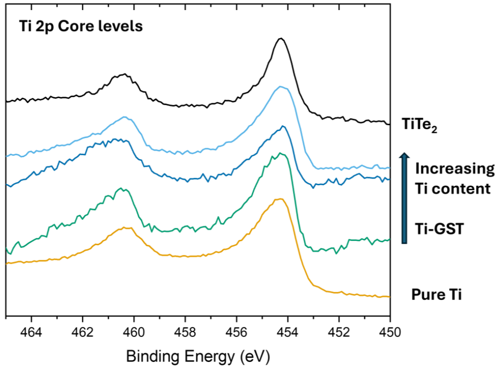
- X-ray absorption (**EXAFS**) measurements to investigate the coordination of atoms during phase transition (amorphous to crystalline)
- **Ongoing** data analysis

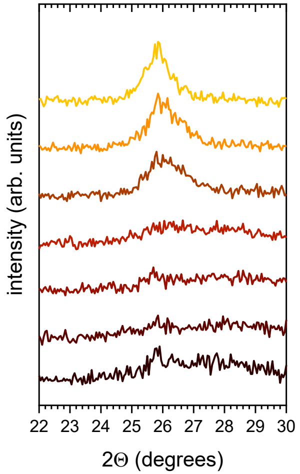
Conclusion

- Growth of high quality and oriented epitaxial $TiTe_2$, Sb_2Te_3 and GST single layers and heterostructure: thermal stability has been tested

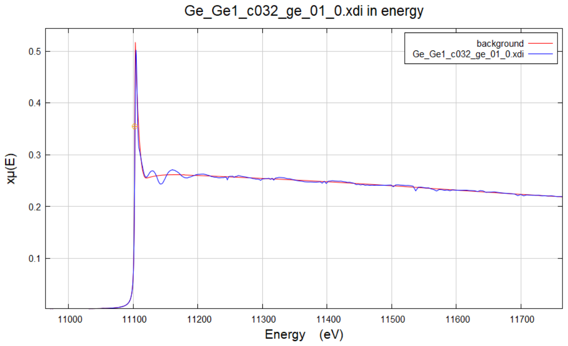


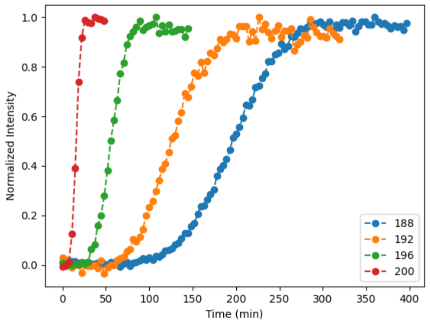






- The effect of Ti incorporation in GST matrix has been investigated





- Higly oriented layered IGT has been grown, and the study of crystallization process has started and is ongoing

Aknowledgements

TOR VERGATA
UNIVERSITÀ DEGLI STUDI DI ROMA

Dept. of Physics
- Prof. Fabrizio Arciprete
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- M. Sc. Adriano Diaz Fattorini
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- M. Sc. Agnese Foglietti
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Catania
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The European Synchrotron

LISA beamline
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- Dr. Stefano Colonna

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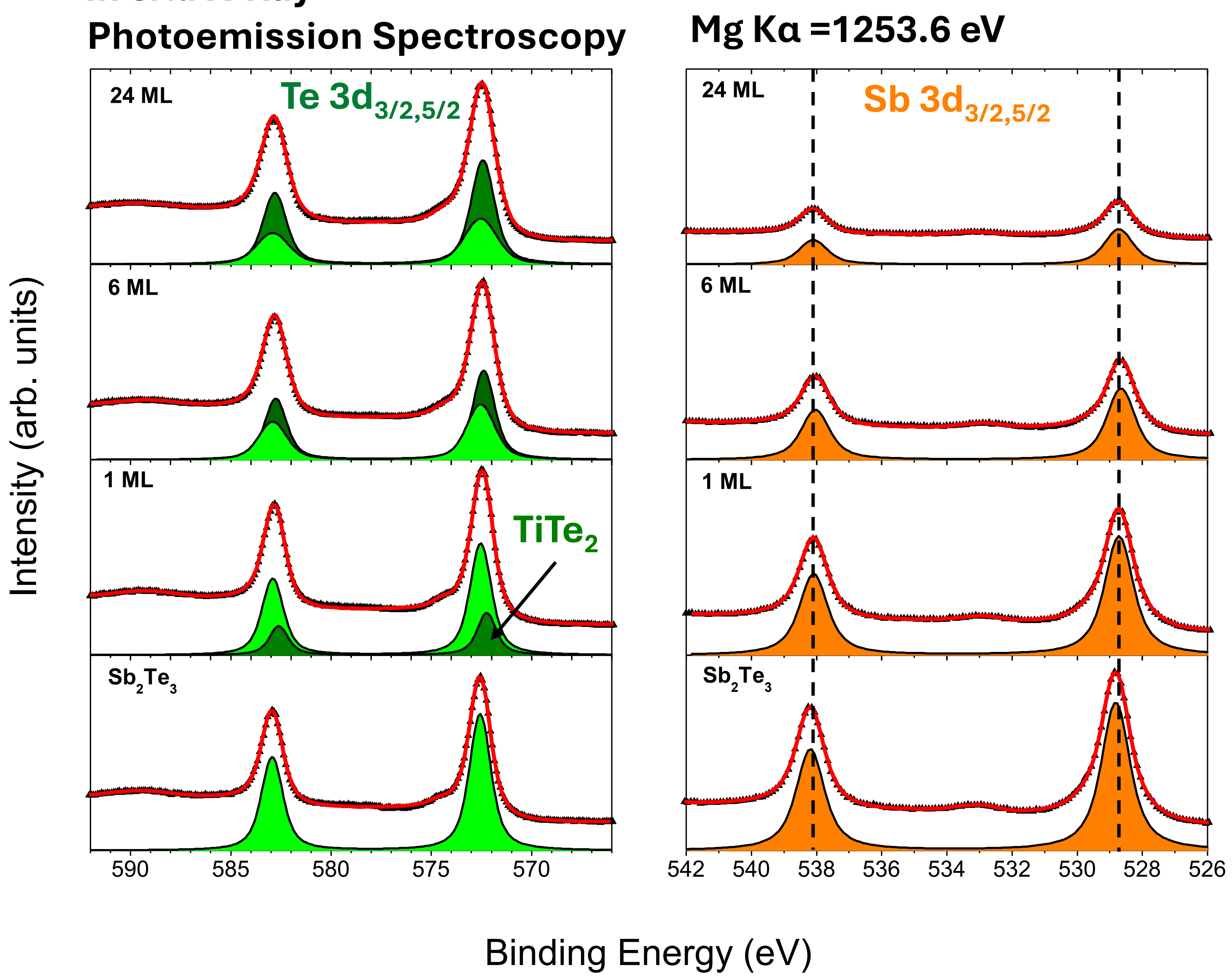
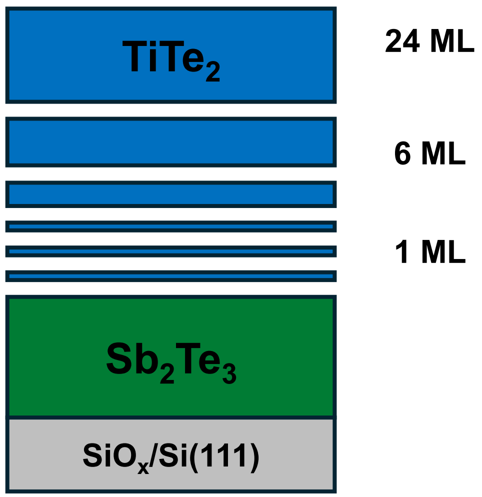
Thank you for your kind attention

Backup Slide

$TiTe_2$-Sb_2Te_3 Bilayer

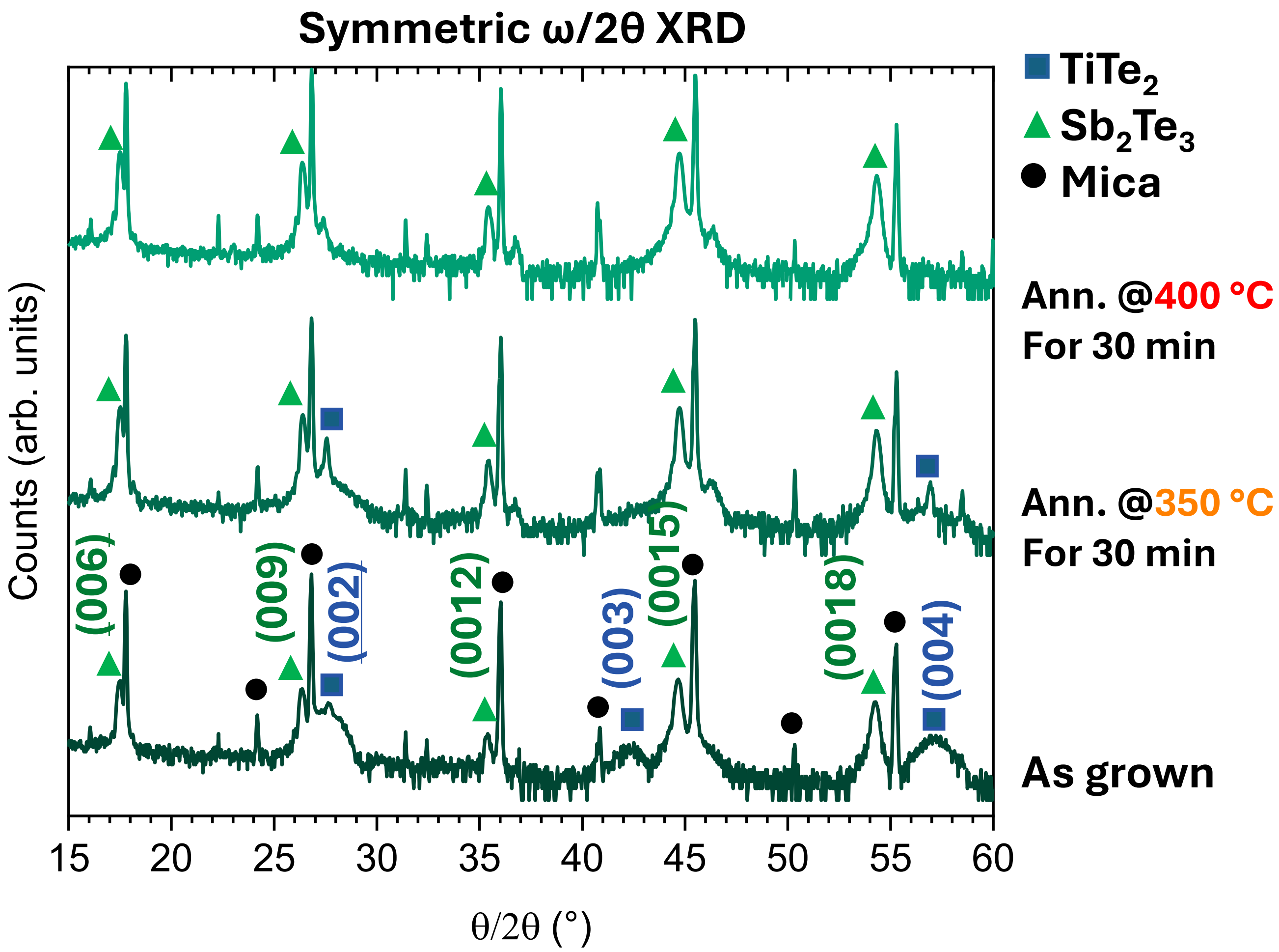
***In situ* X-Ray Photoemission Spectroscopy**

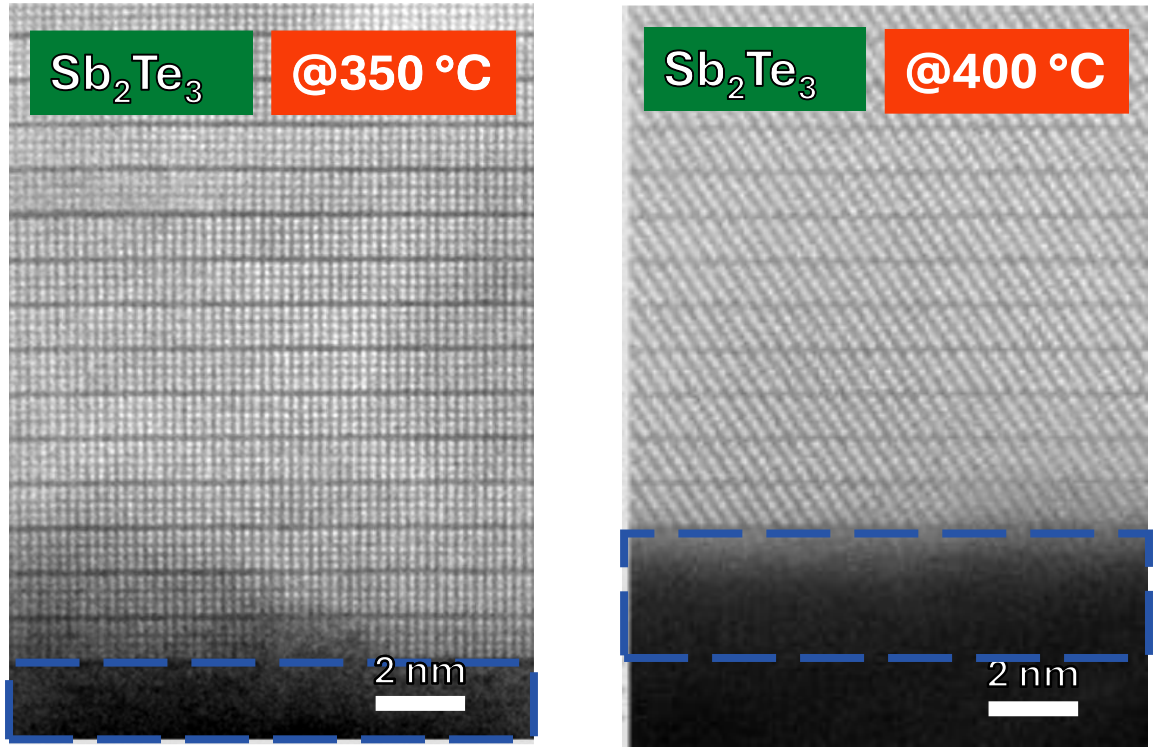




- **Step-by-step** growth and characterization on **Si** substrate
- Fitting deconvolution of the contributions of the two layers
- **No Intermixing** phenomena and Sb migration detected at the interface

$TiTe_2 - Sb_2Te_3$ annealing





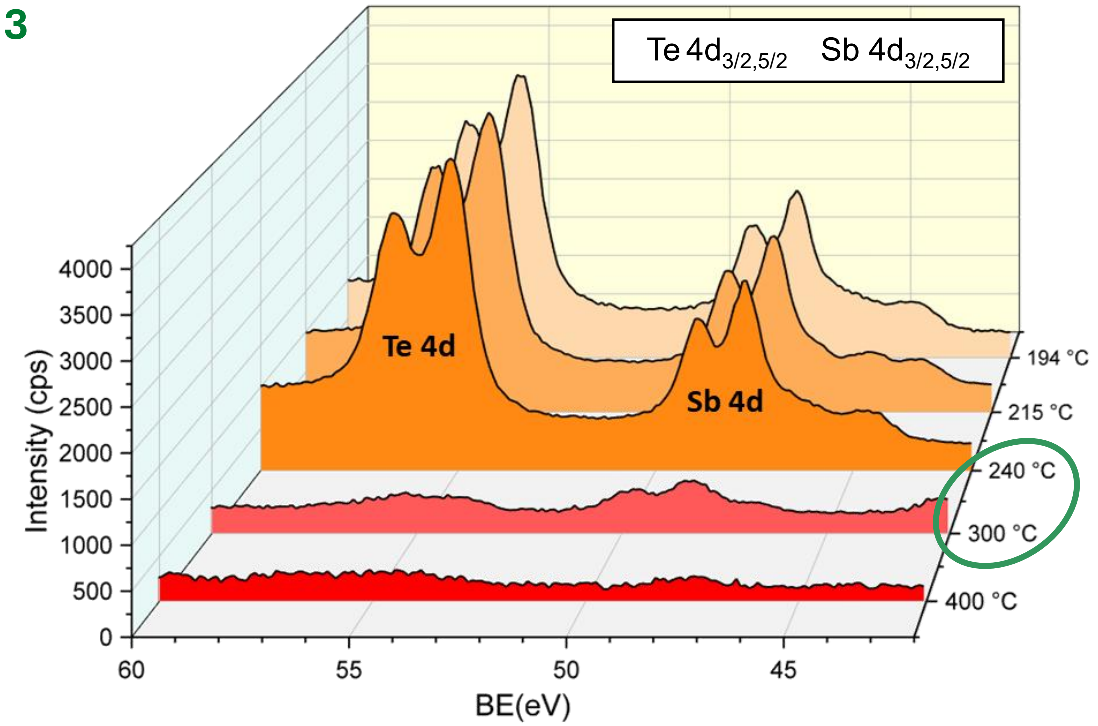
- ✓ Sb_2Te_3 displays out-of-plane orientation
- ✗ $TiTe_2$ peaks disappear increasing annealing T

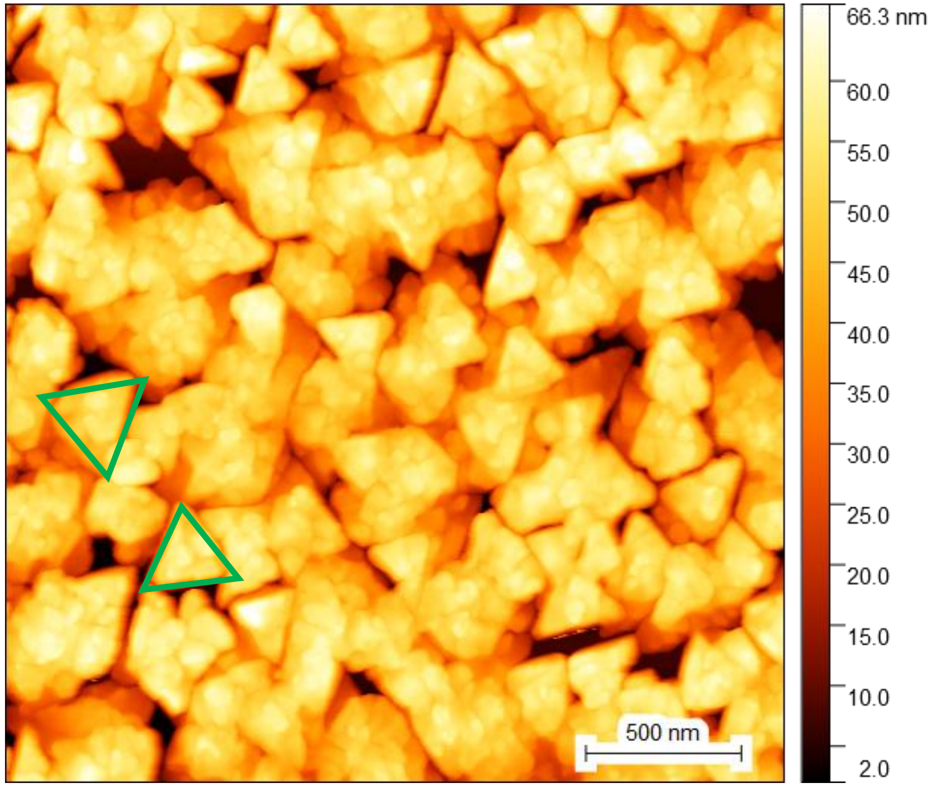
- ✓ Sb_2Te_3 displays quintuple layers
- ✗ No **$TiTe_2$** structures

Epitaxial films

- **Sb_2Te_3**

Mg Kα =1253.6 eV





- Epitaxial Sb_2Te_3 can be obtained for $T_{growth} \leq \mathbf{250}\ °C$
- Composition evaluation from Te and Sb core levels via XPS:
  - Sb:Te=**2.2:3.1**

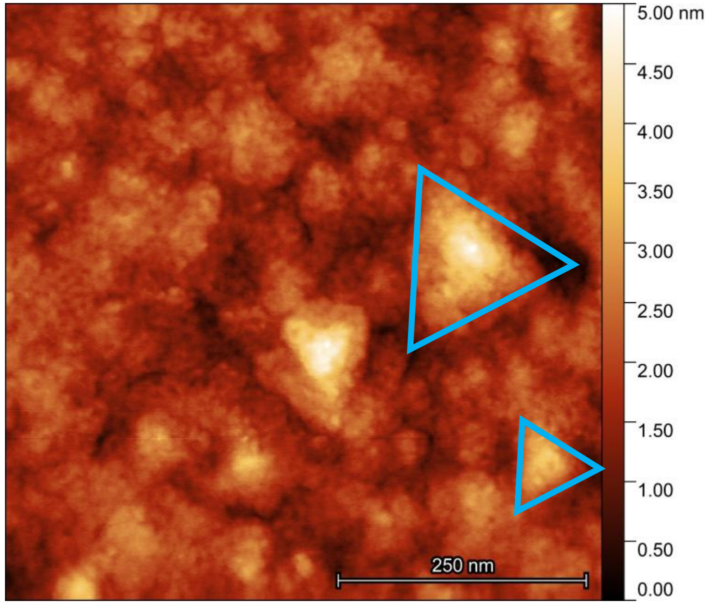
$$\boxed{x_i = \frac{I_i/S_i}{\sum_i \left(I_i/S_i\right)}}$$

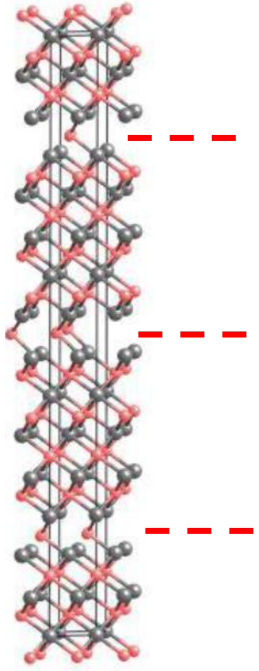
S_i from C.D.Wagner, *et al.*, Surf. Interfaces Anal.(1981)

Epitaxial films

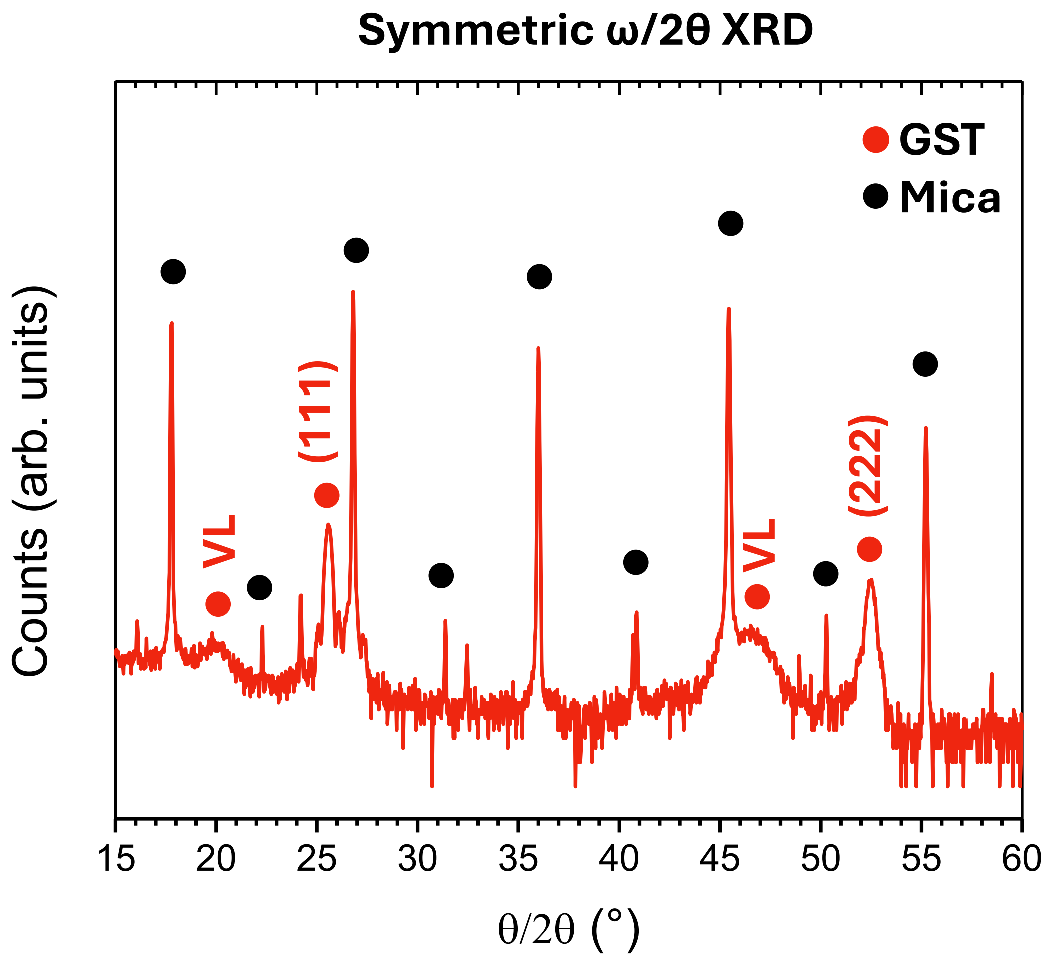
- **GST**

Bragaglia, V. *et al. AIP Advances* 7.8 (2017).





Vacancy Layers (VL)

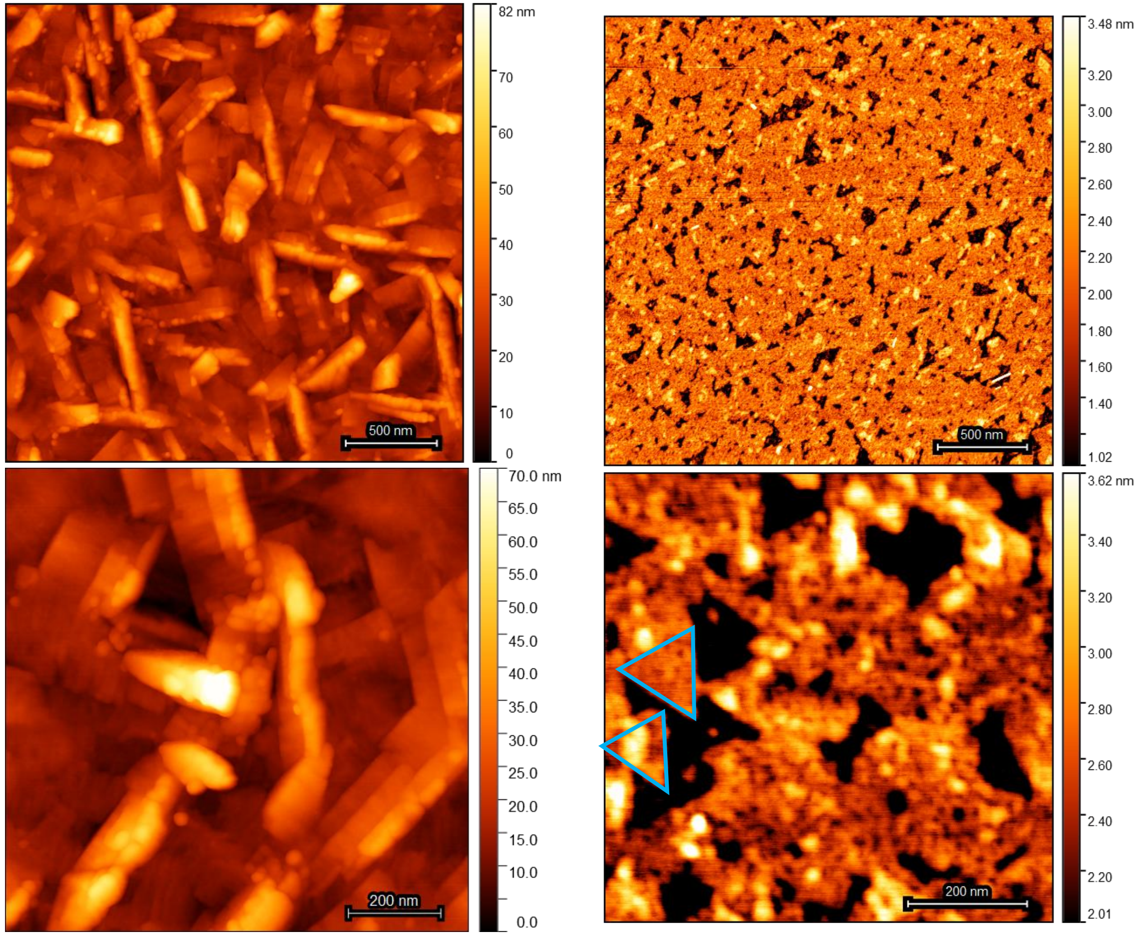


- Epitaxial **GST** can be obtained for same Sb_2Te_3
  - $T_{growth} (\leq \mathbf{250}\ °C)$
- Composition evaluation from XPS:
  - Ge:Sb:Te=**1:2:4**

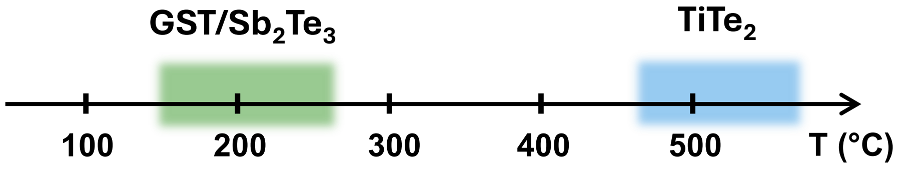
Epitaxial films

- **$TiTe_2$**

T_{growth}= 240 °C **T_{growth}= 570 °C**

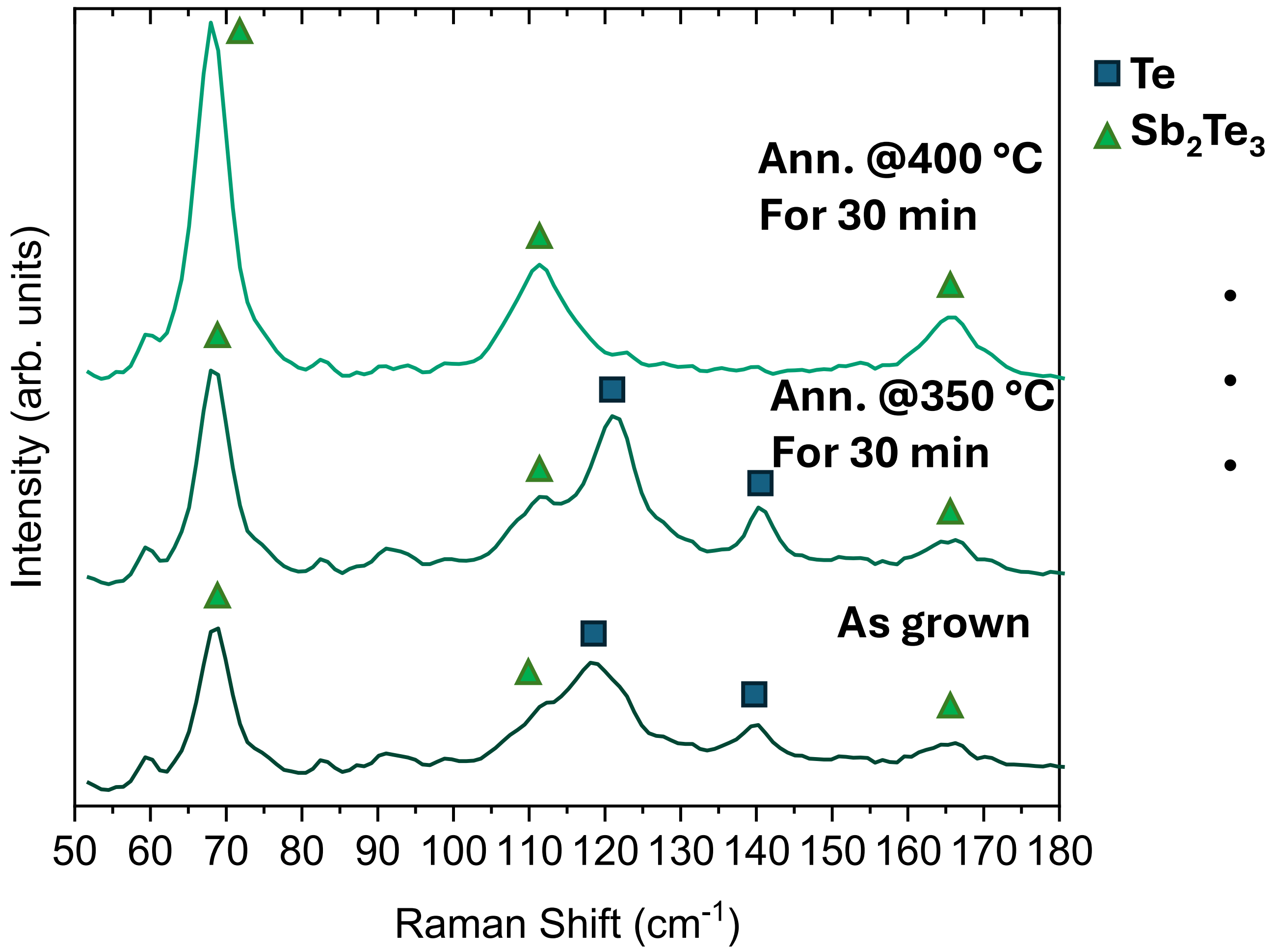


- Epitaxial $TiTe_2$ can be obtained for $T_{growth} > \mathbf{450}\ °C$



! **Different** growth windows

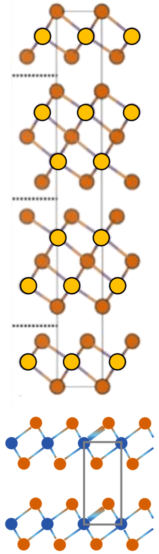
Epitaxial bilayers

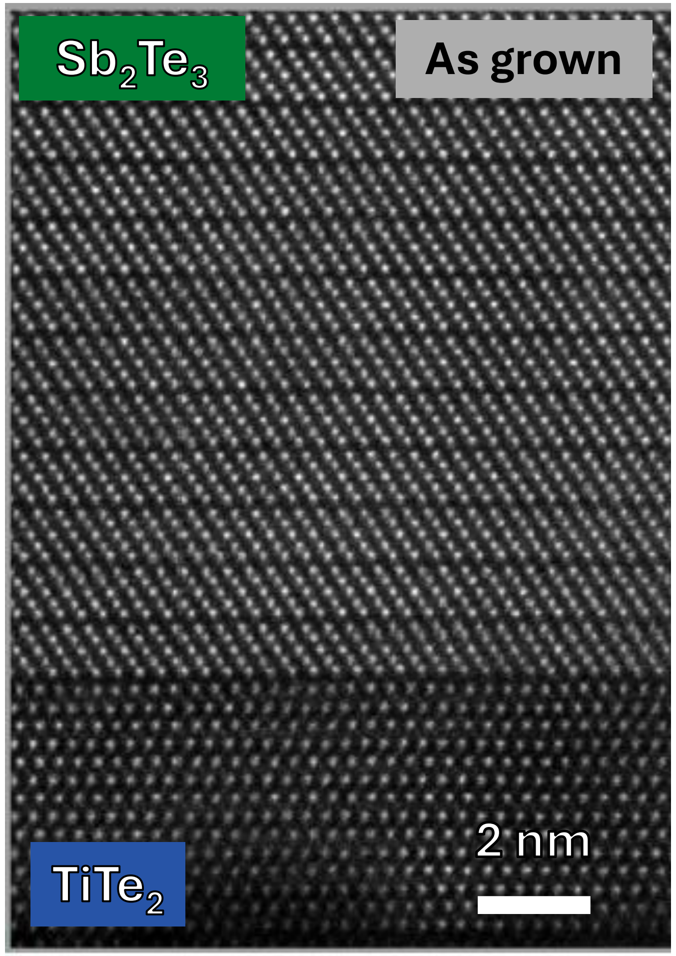


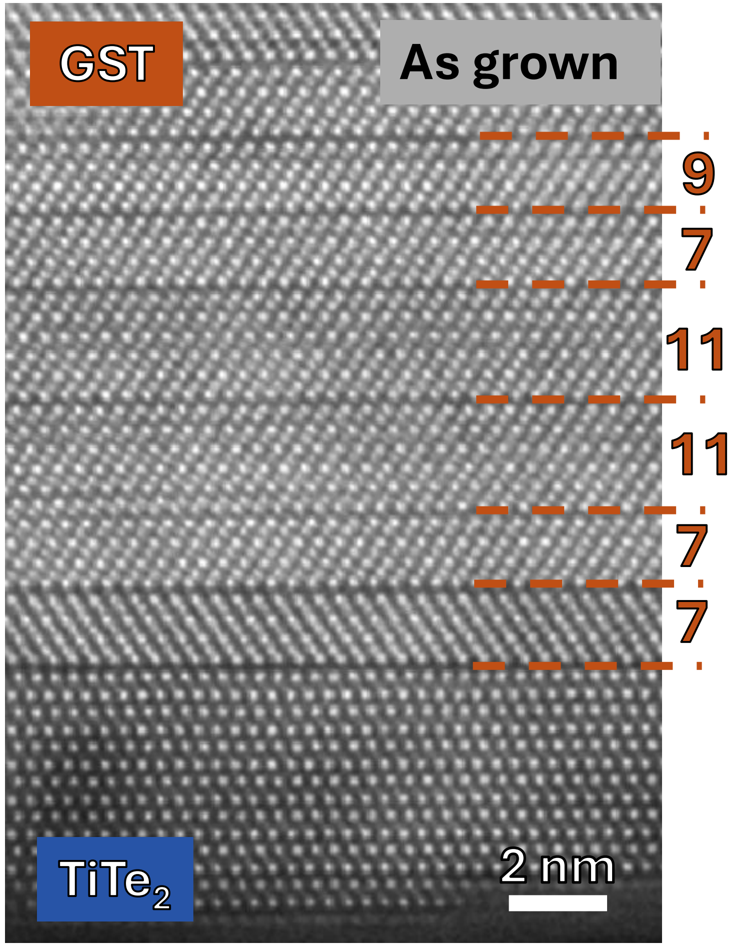
- Typical Sb_2Te_3 Raman modes
- Te instead $TiTe_2$ features
- Extinction of Te modes after 400 °C annealing

Bilayers growth

High Resolution-Transmission Electron Microscopy **(HR-TEM)**



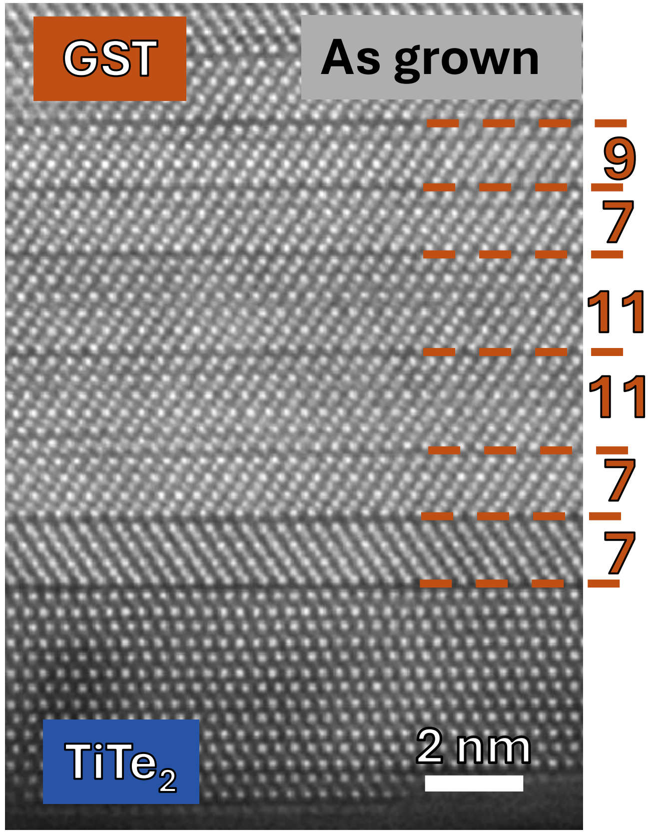


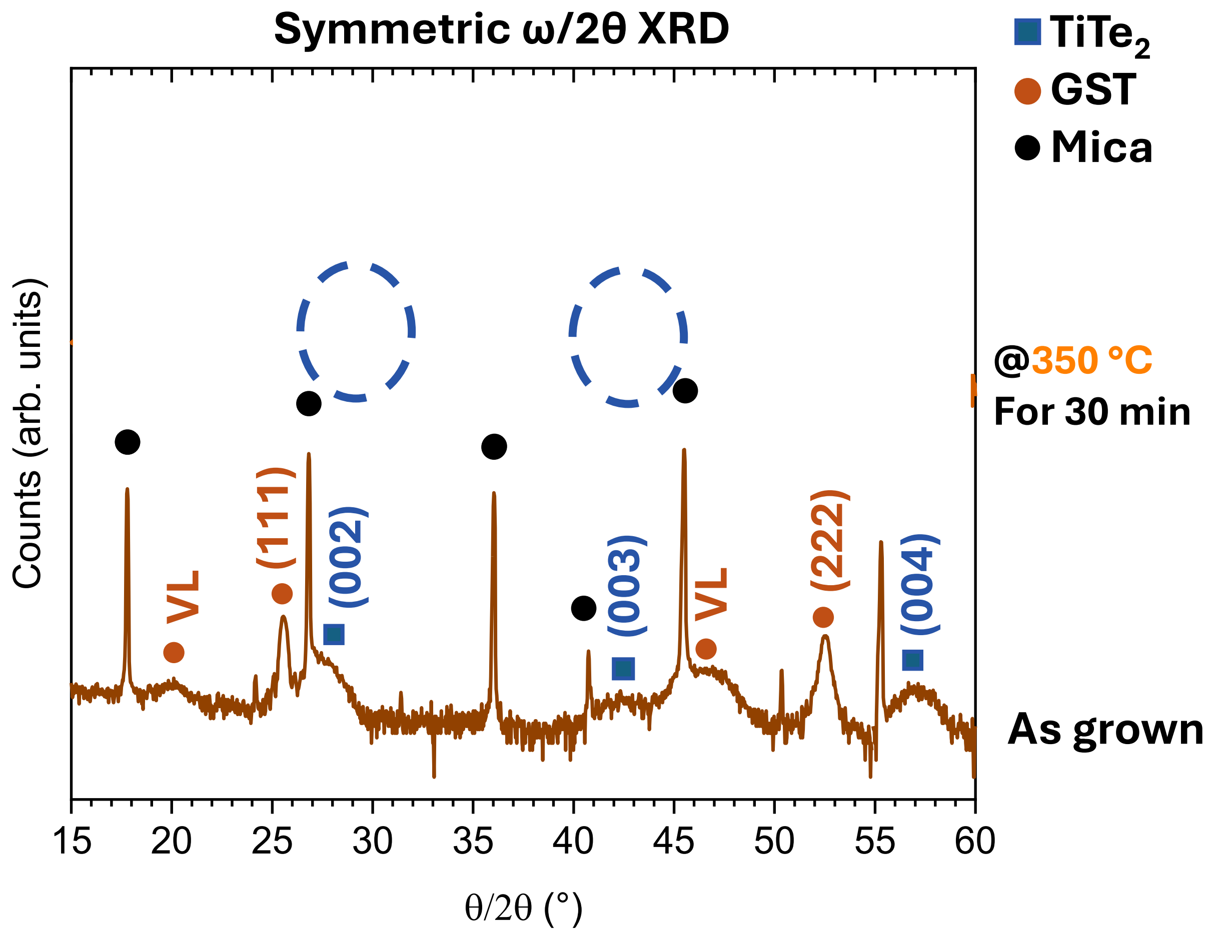


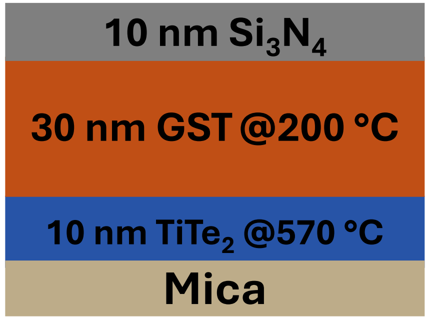
- ✓ **Sharp interface** between $TiTe_2$ and PCMs
- Evidence of **trilayers** and **quintuple layers**
- ✓ **No intermixing or segregation**

TiTe$_2$-GST systems

- Epitaxial growth of Sb_2Te_3/$TiTe_2$ and GST/$TiTe_2$ systems





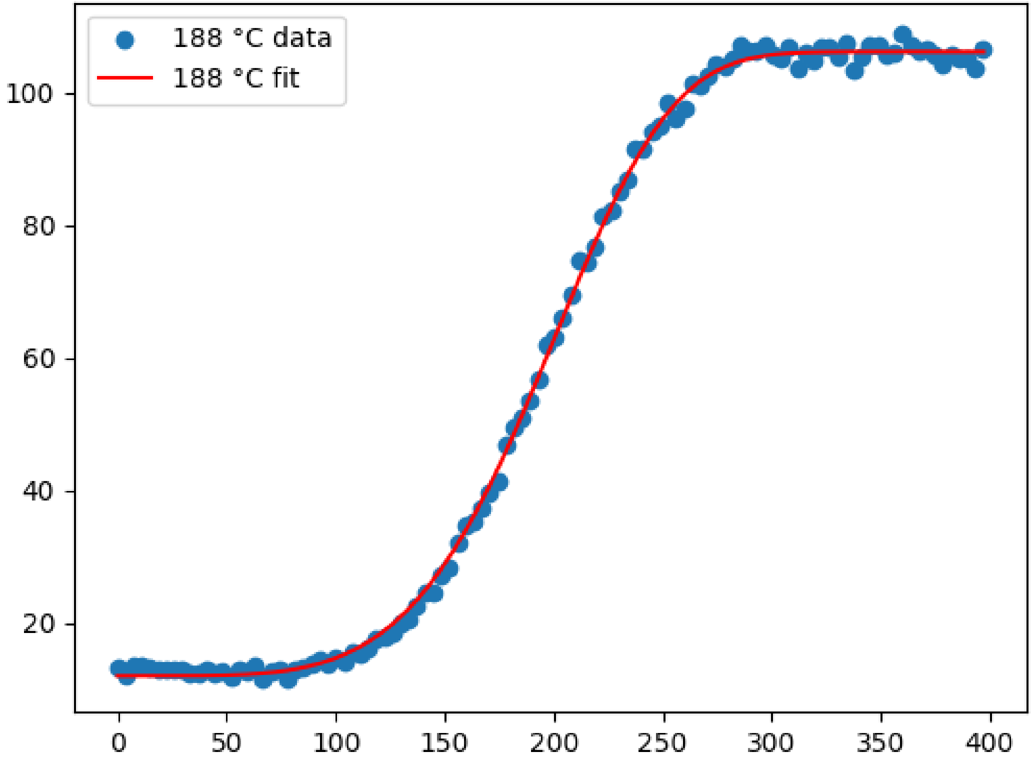


- **TEM images**

✔ GST and TiTe$_2$ diplays out-of-plane orientation with clear evidence of MLs @RT

✘ No evidence of TiTe$_2$ and TLs upon annealing !!!

$InGeTe_3$



Increasing Ti content Ti-GST