

# Identification of Defects and Secondary Phases in Reactively Sputtered $\text{Cu}_2\text{ZnSnS}_4$ Thin Films

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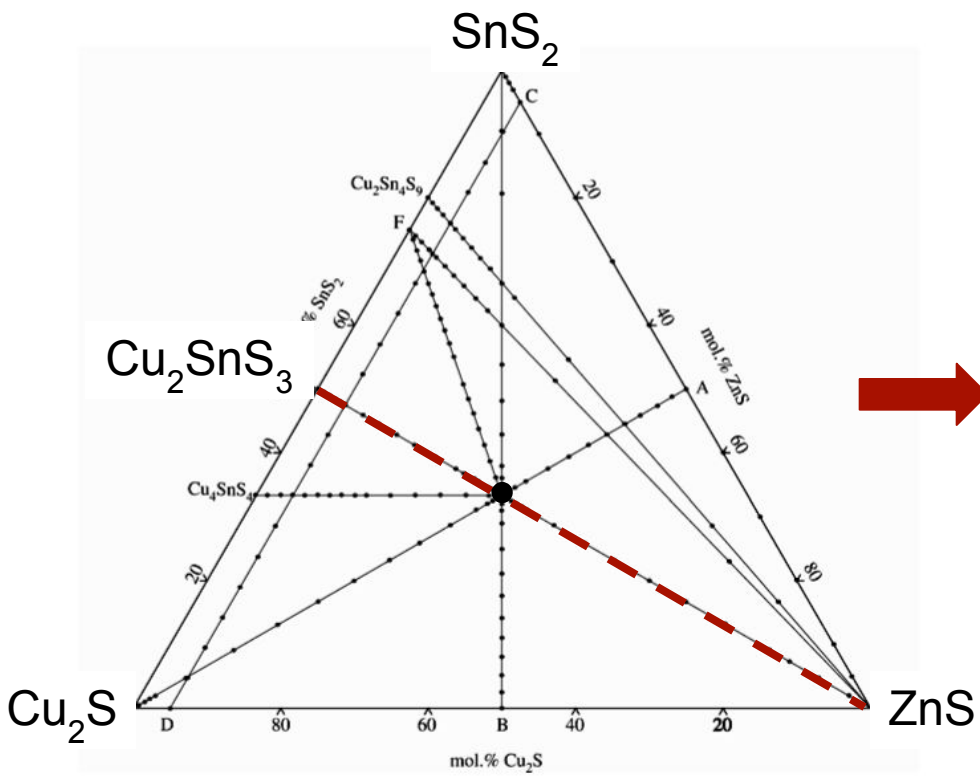
# Outline

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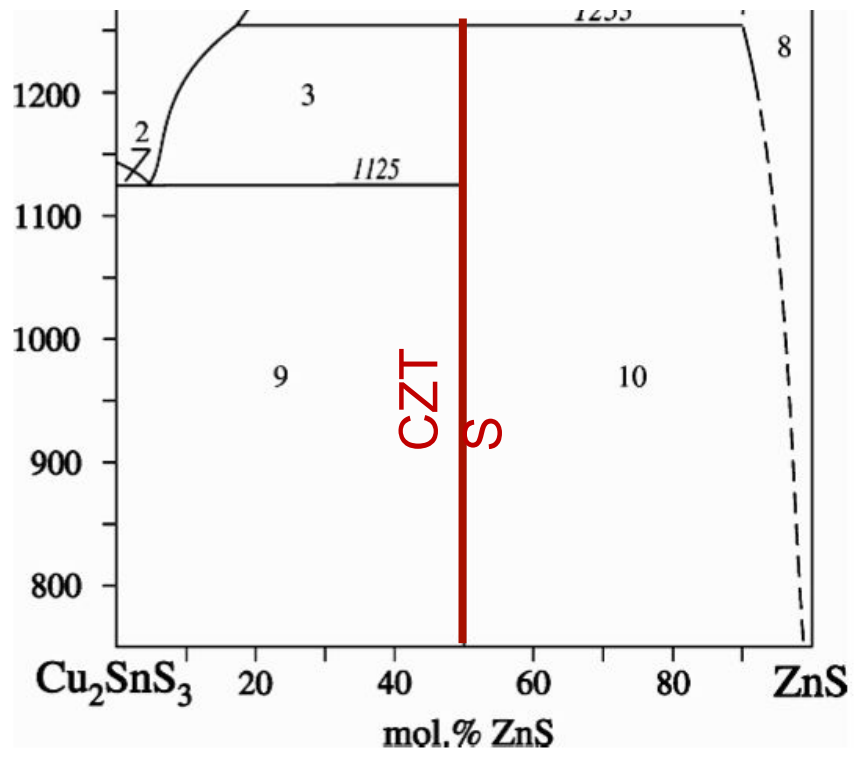


- Motivation
  - Problems with characterization of thin films
- Experimental approach
- Results
  - X-ray diffraction
  - Raman Spectroscopy
  - Transmission Electron Microscopy
  - Scanning Auger Microscopy
- Summary & Acknowledgements

## Ternary Phase Diagram



## Binary Phase Diagram



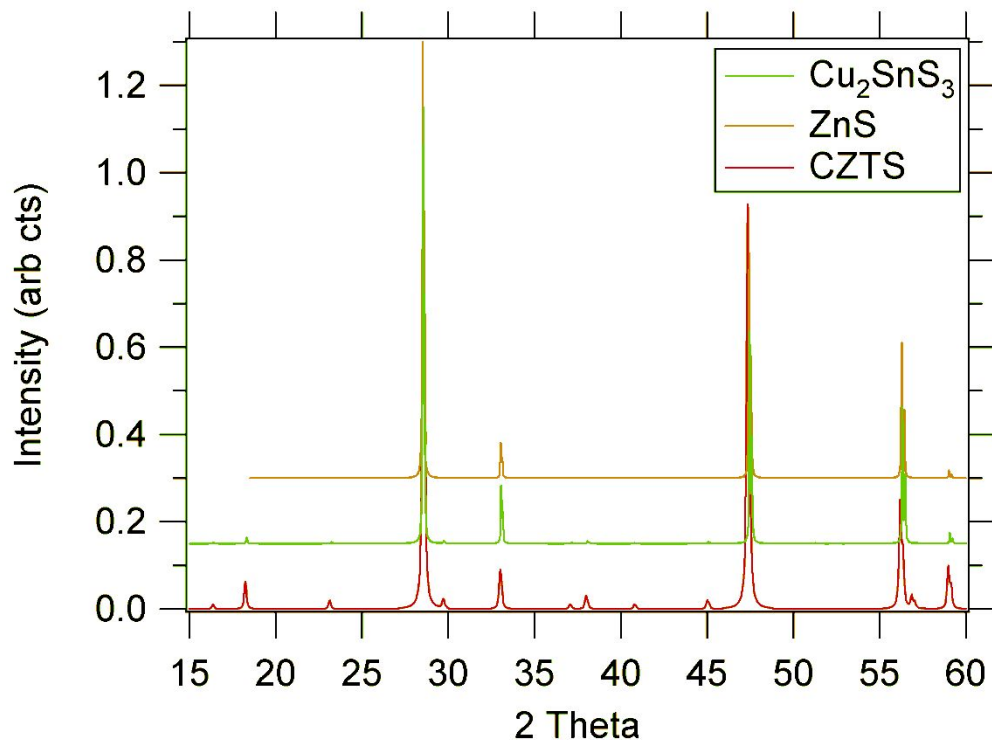
- CZTS is a line compound between  $\text{Cu}_2\text{SnS}_3$  and  $\text{ZnS}$
- Theoretically even a 2-3% compositional variation could lead to phase separation



# Motivation – Crystal Structure

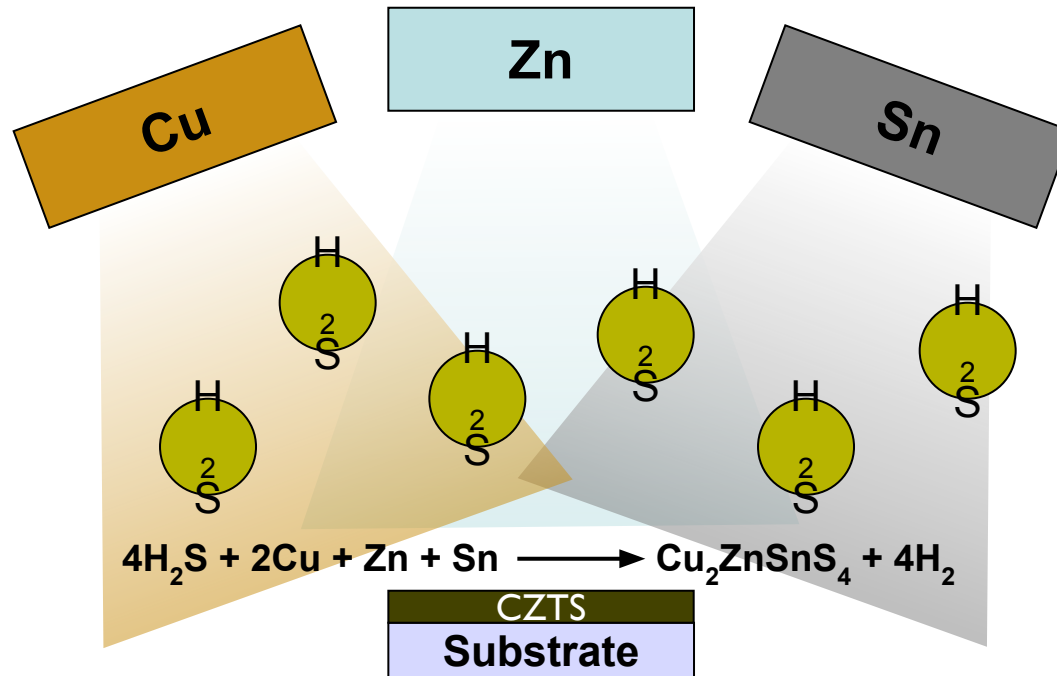


## Theoretical XRD Patterns of CZTS, $\text{Cu}_2\text{SnS}_3$ , and ZnS



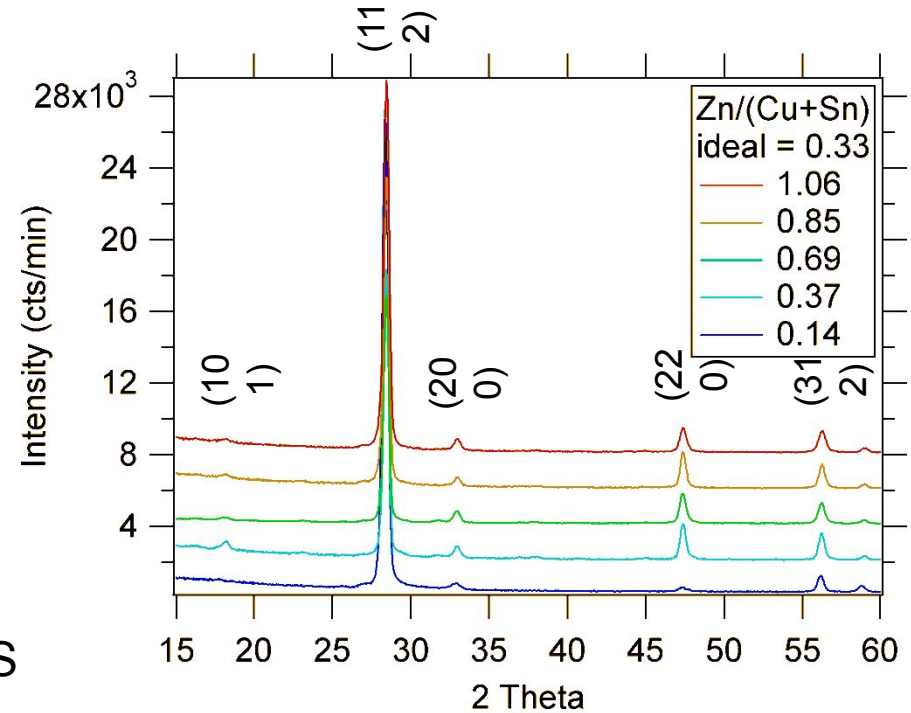
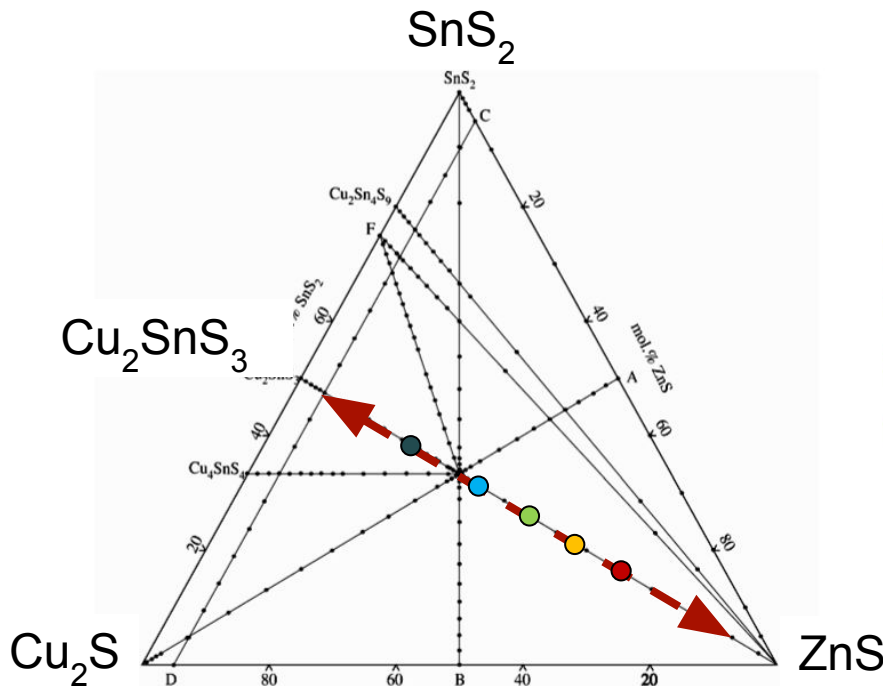
- Crystal structures of secondary phases similar to CZTS
- All primary peaks overlap and hard to separate
- Low intensity peaks cannot be seen easily in thin films

## Reactive Sputtering



- Introduce  $\text{H}_2\text{S}$  into chamber during sputter deposition
- Sulfur is incorporated into the film in one step (**no anneal**)
- Expect to see higher densities and improved film quality

## Varying Zn/(Cu+Sn) Ratio



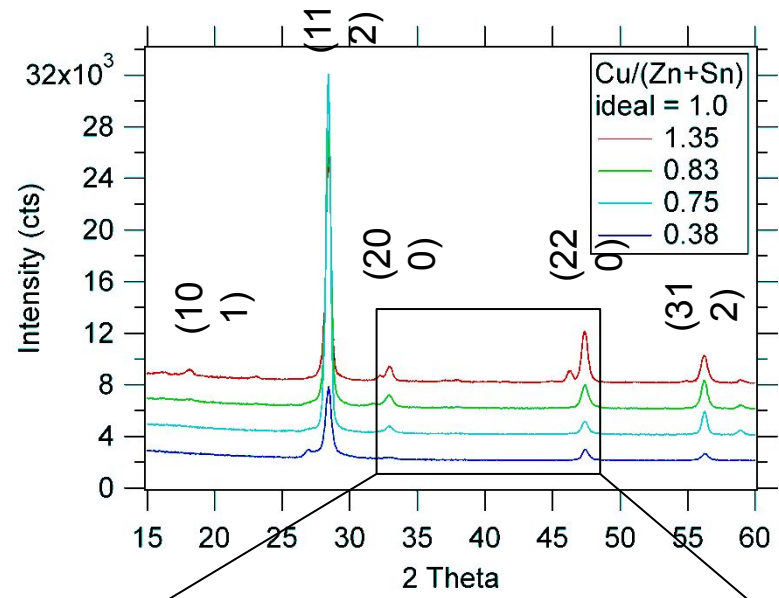
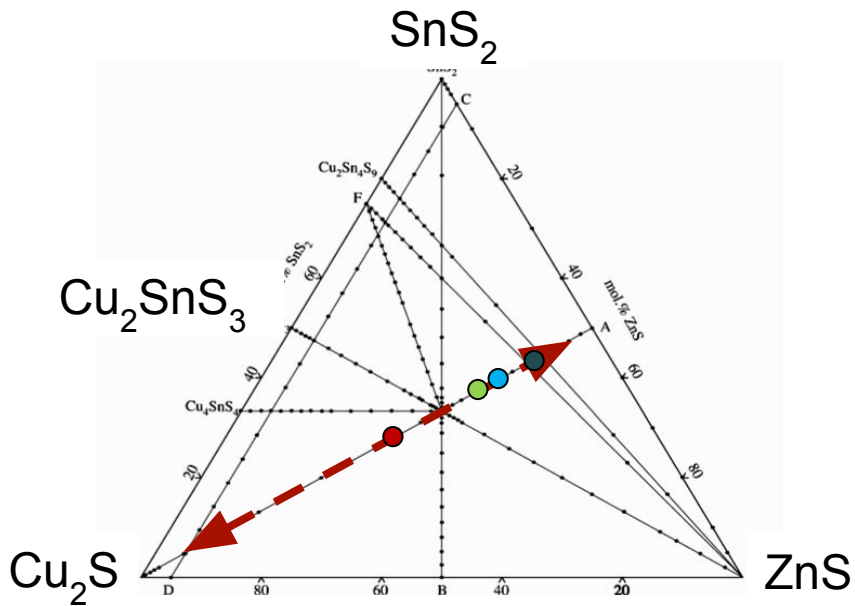
- Zn/(Cu+Sn) ratio is varied while holding Cu/Sn ratio constant
- Impossible to determine difference between CZTS, CTS, and ZnS from XRD pattern



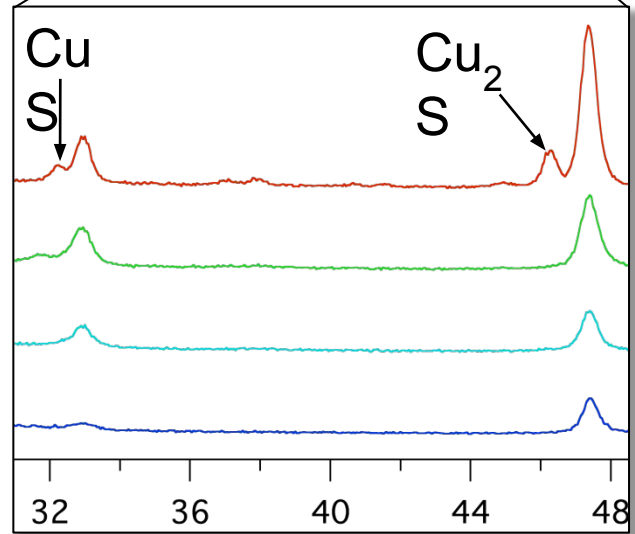
# Characterization - XRD



## Varying Cu/(Zn+Sn) Ratio



- Cu/(Zn+Sn) ratio is varied while holding Zn/Sn ratio constant
- Need to get very far off 2:1:1 stoichiometry before any  $Cu_xS$  phases can be seen
- $Cu_xS$  can be removed with KCN etch

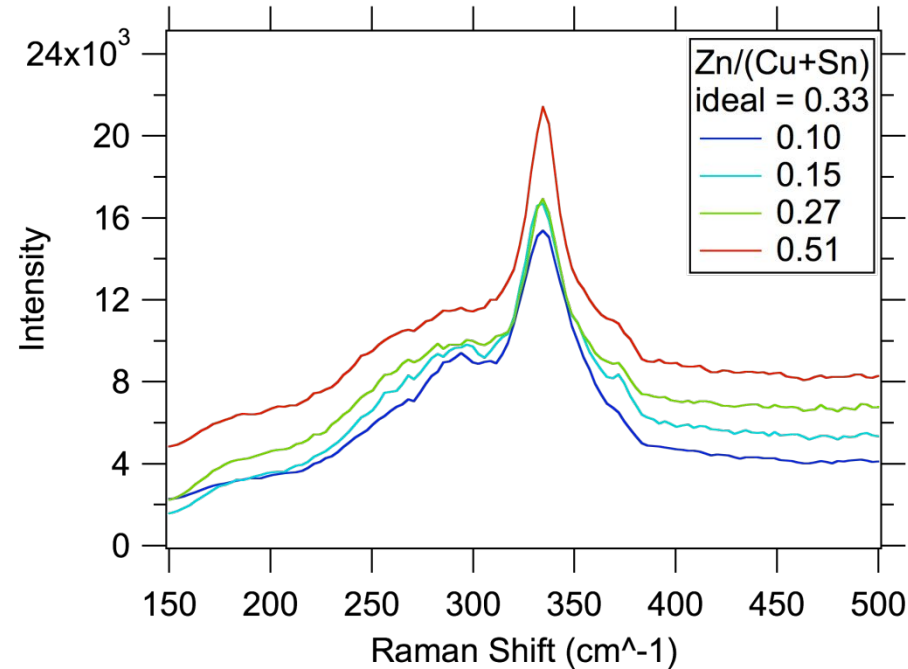




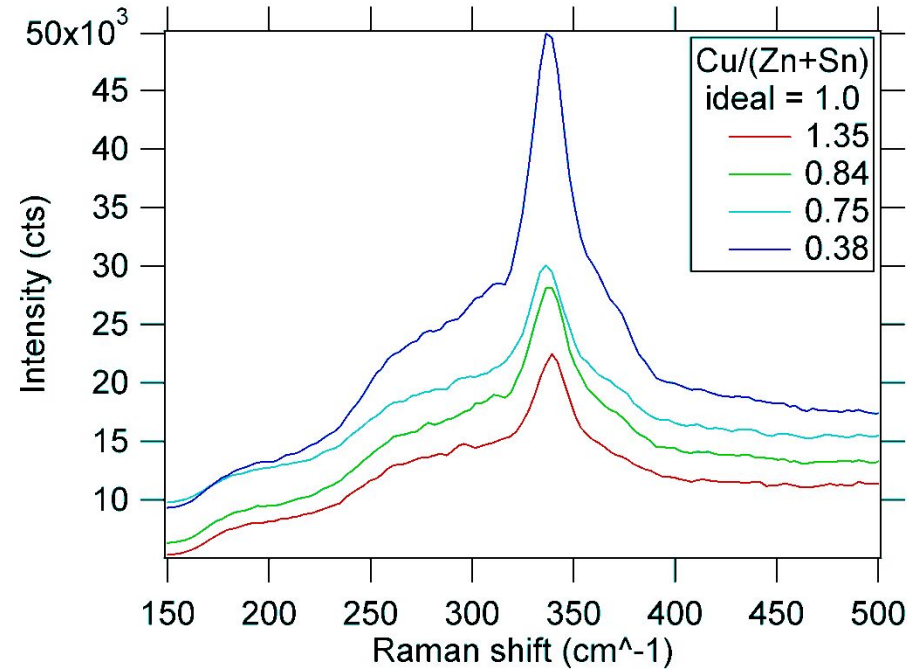
# Characterization – Raman



## Varying Zn/(Cu+Sn) Ratio



## Varying Cu/(Zn+Sn) Ratio

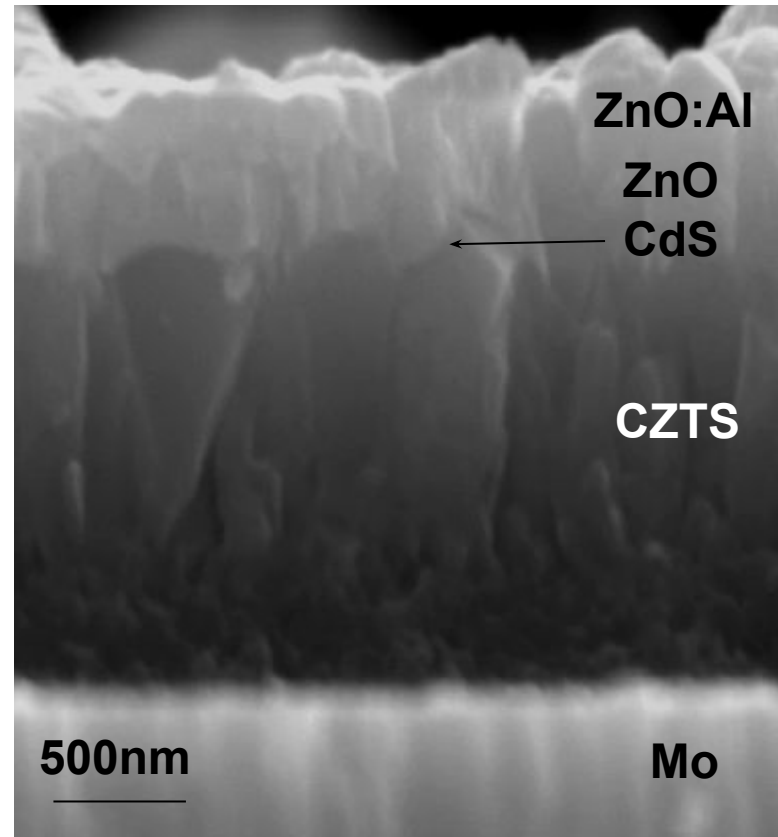
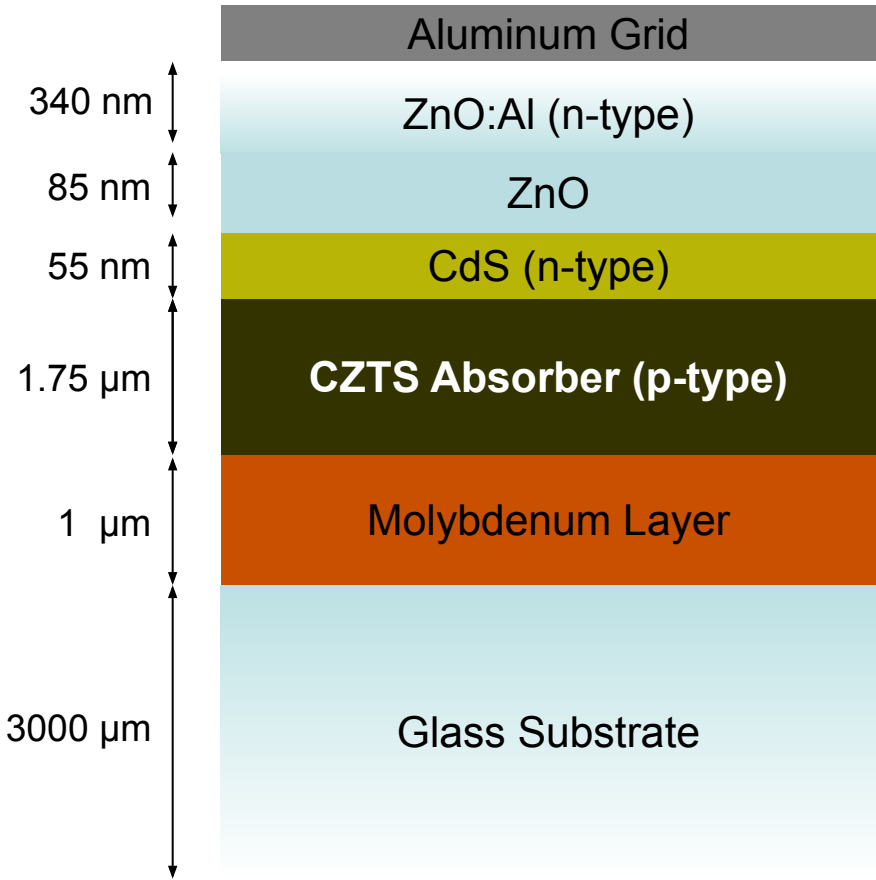


- Raman spectra show only minor changes even though composition is varied dramatically
- No evidence of the  $\text{Cu}_x\text{S}$  phase shown by other groups at growth temperatures higher than 500C



## CZTS Device Stack

## SEM Image



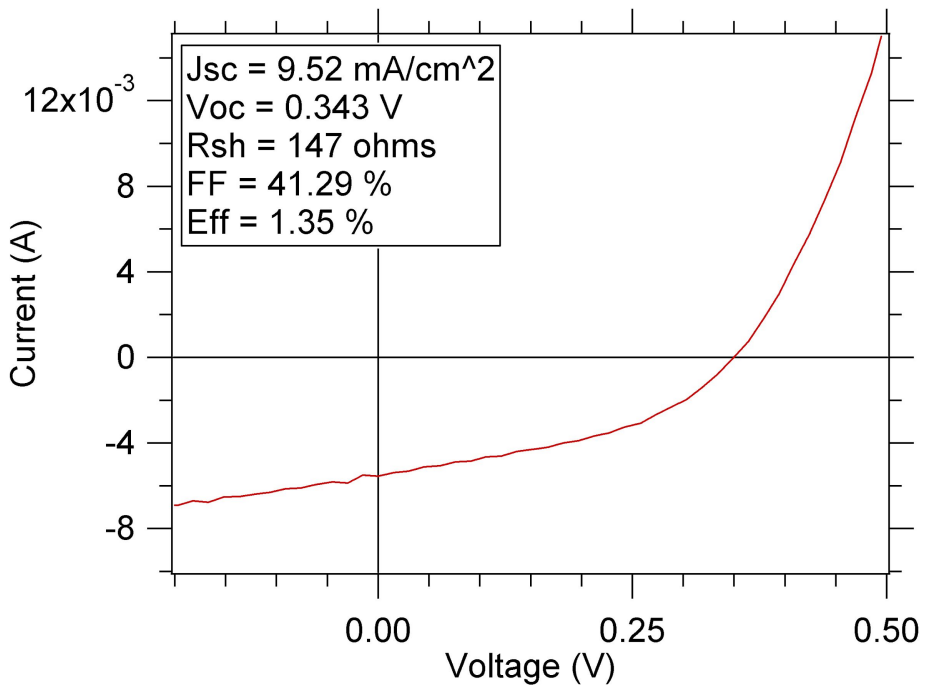
- Zn-rich films incorporated into standard CIGS device stack for testing



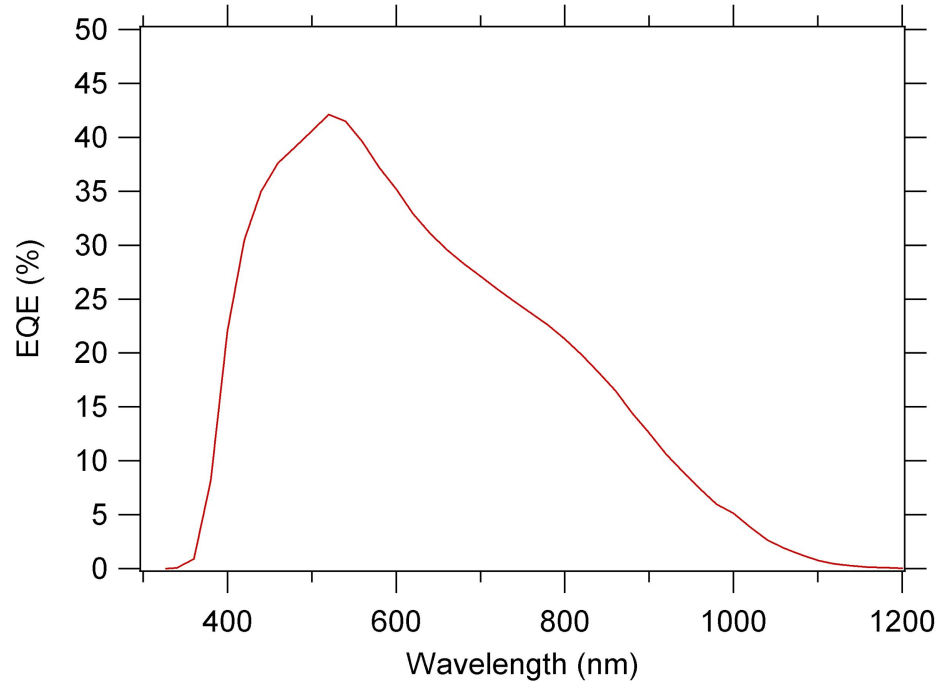
# Device Characterization



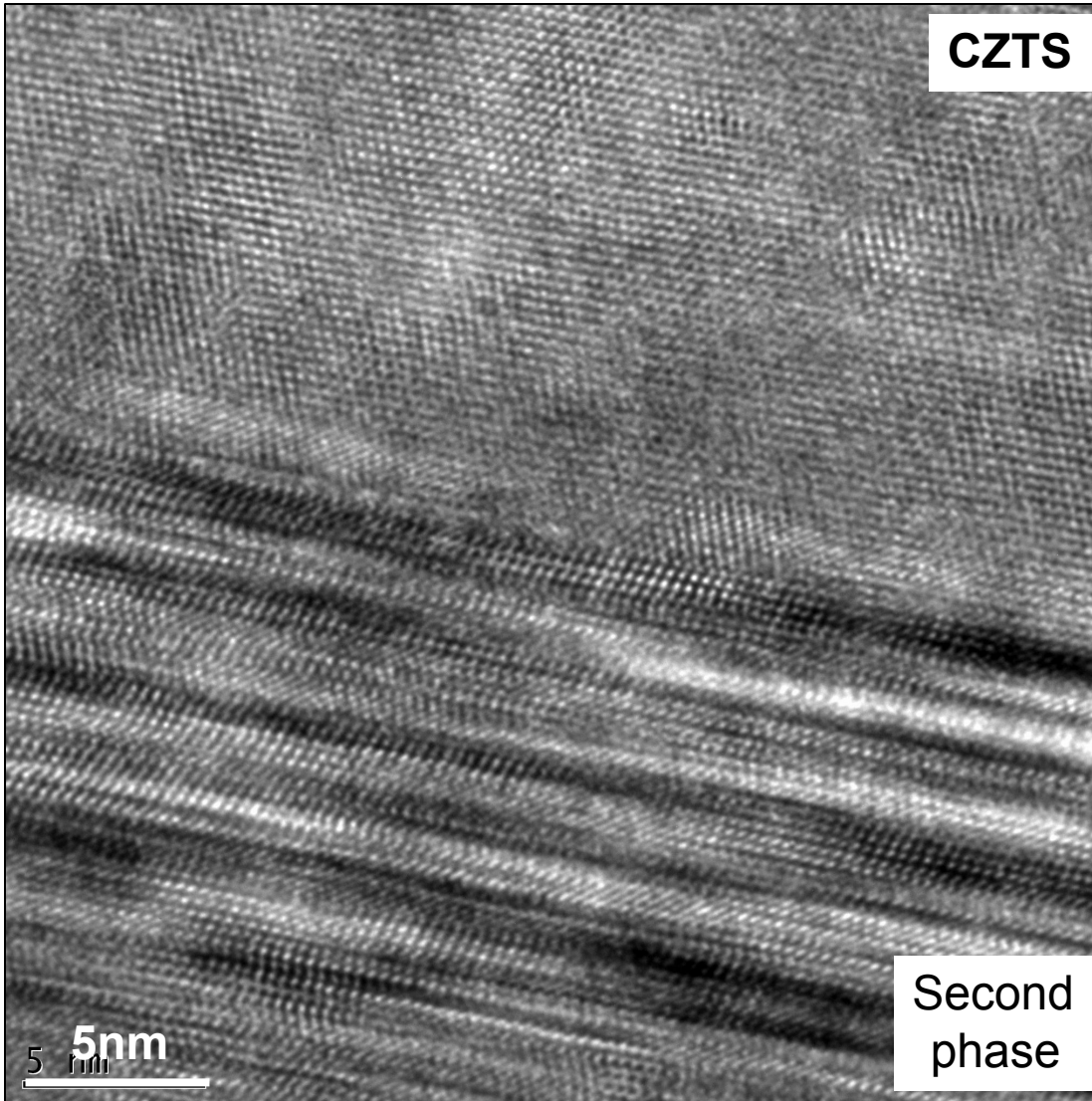
## I-V Measurement



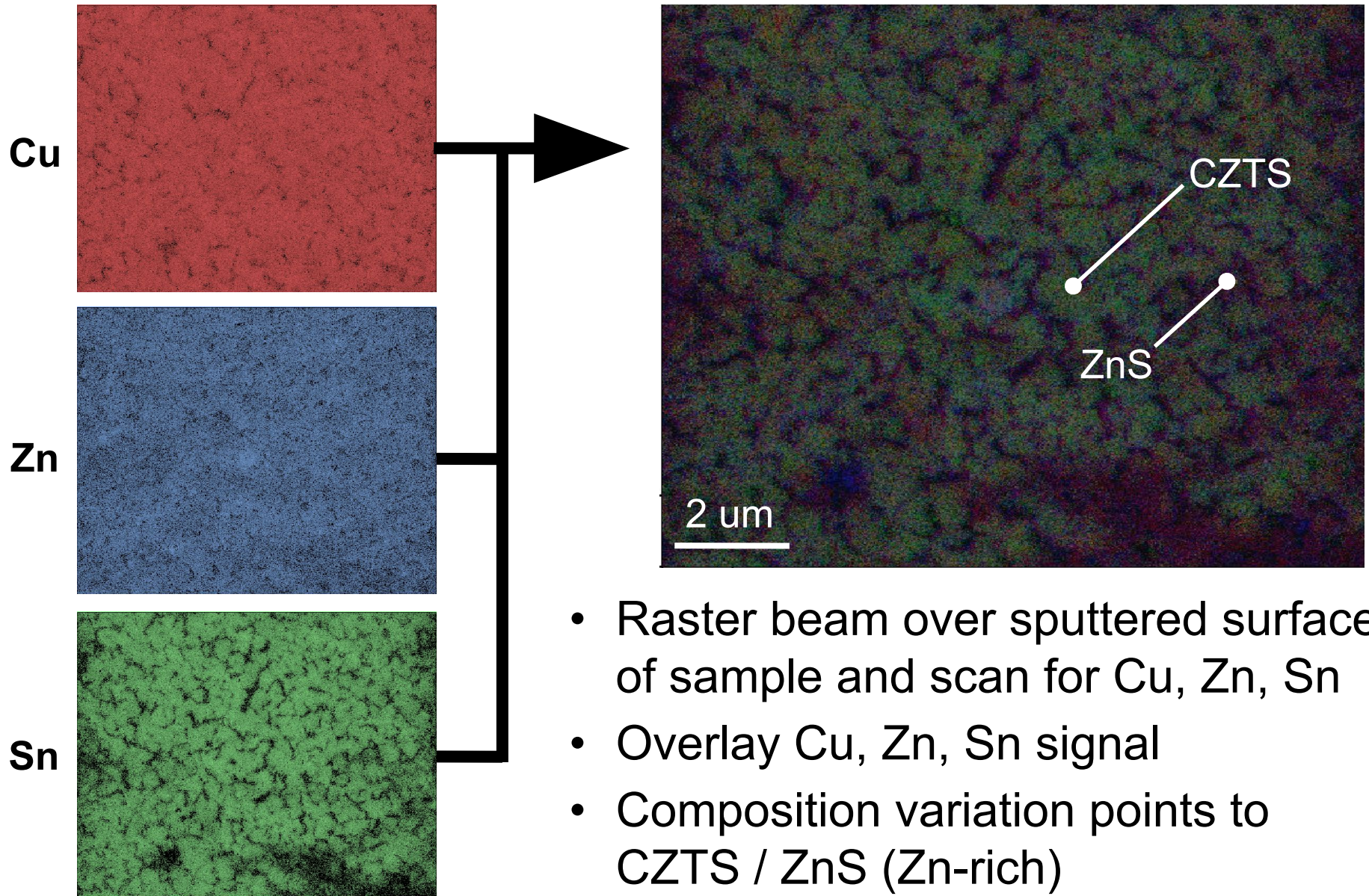
## EQE Measurement



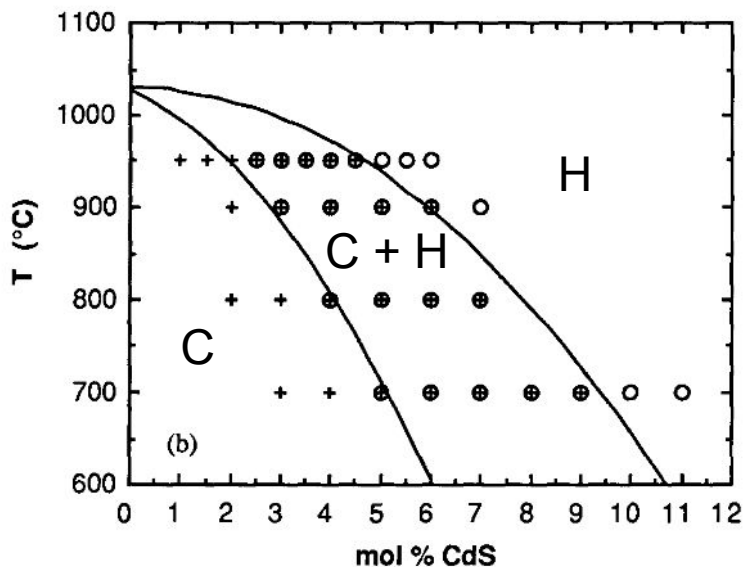
- First CZTS devices grown by a reactive sputtering process
- Efficiency = 1.35%
- **Degraded EQE clearly points to undetected defects in the absorber**



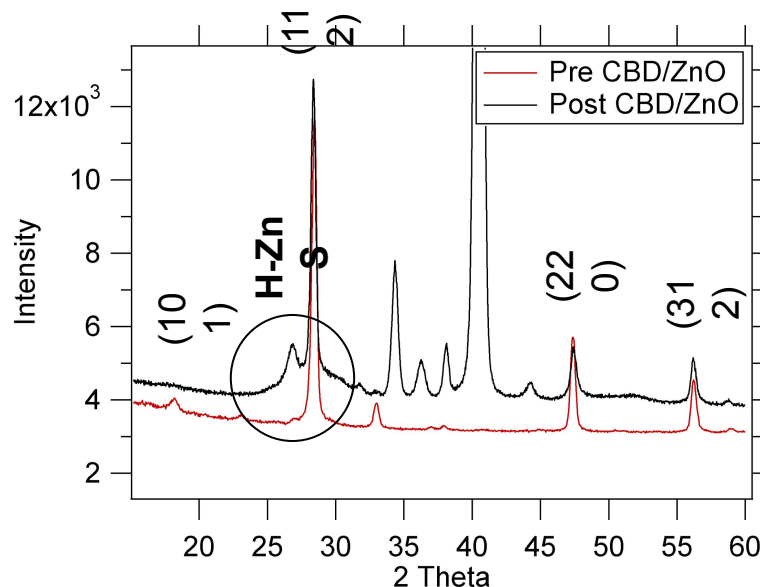
- Detrimental secondary phase interspersed in CZTS matrix
- Stacking faults in the secondary phase point to a transition between cubic and hexagonal crystal structures



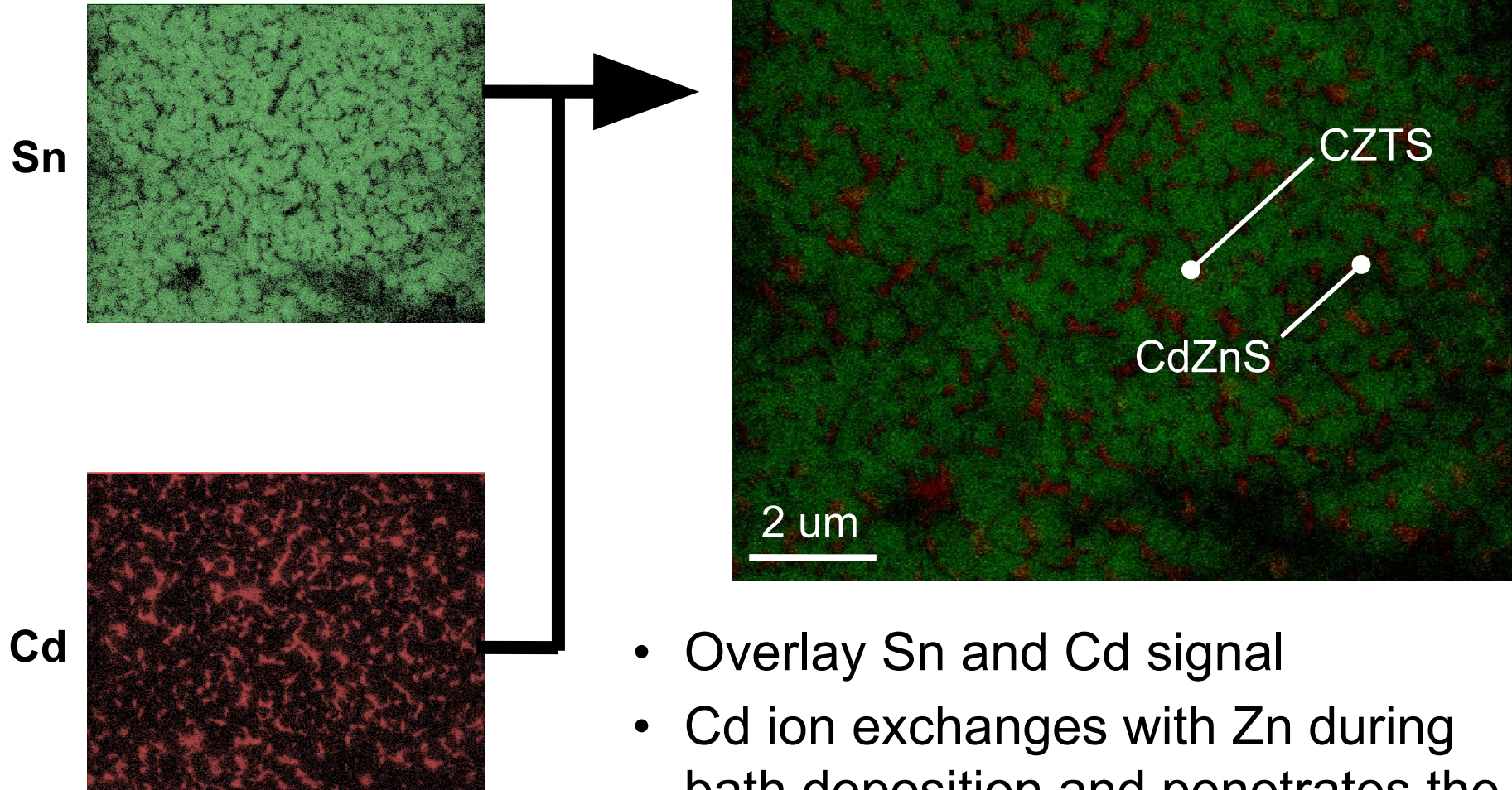
## CdS – ZnS Phase Diagram



## XRD before and after CBD



- Cd penetration into ZnS lowers the cubic-hexagonal transition temperature
- Stacking faults in TEM images are created during CBD of CdS layer



- Overlay Sn and Cd signal
- Cd ion exchanges with Zn during bath deposition and penetrates the ZnS phase



# Summary

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- CZTS thin films were grown using Reactive Sputtering
- Films were characterized using X-ray Diffraction and Raman Spectroscopy
- Full devices have been grown and tested but are limited due to secondary phases in the films
- Transmission Electron Microscopy and Scanning Auger Microscopy can be used to identify these secondary phases



# Acknowledgements

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- US Department of Energy, Office of Basic Energy Sciences as part of an Energy Frontier Research Center
  - <http://www.er.doe.gov/bes/EFRC/index.html>
- Applied Quantum Technologies
  - Local thin film solar startup
  - <http://www.aqtsolar.com>





# Questions

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# Questions?