Identification of Defects and Secondary Phases in Reactively Sputtered Cu_2ZnSnS_4 Thin Films

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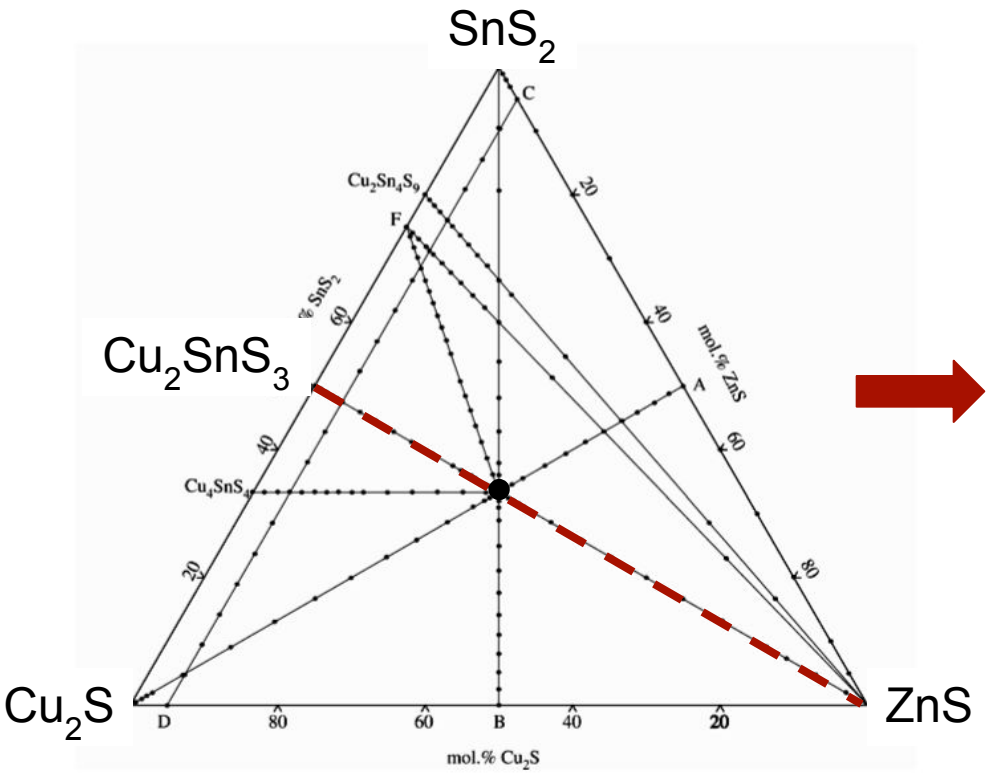
Outline

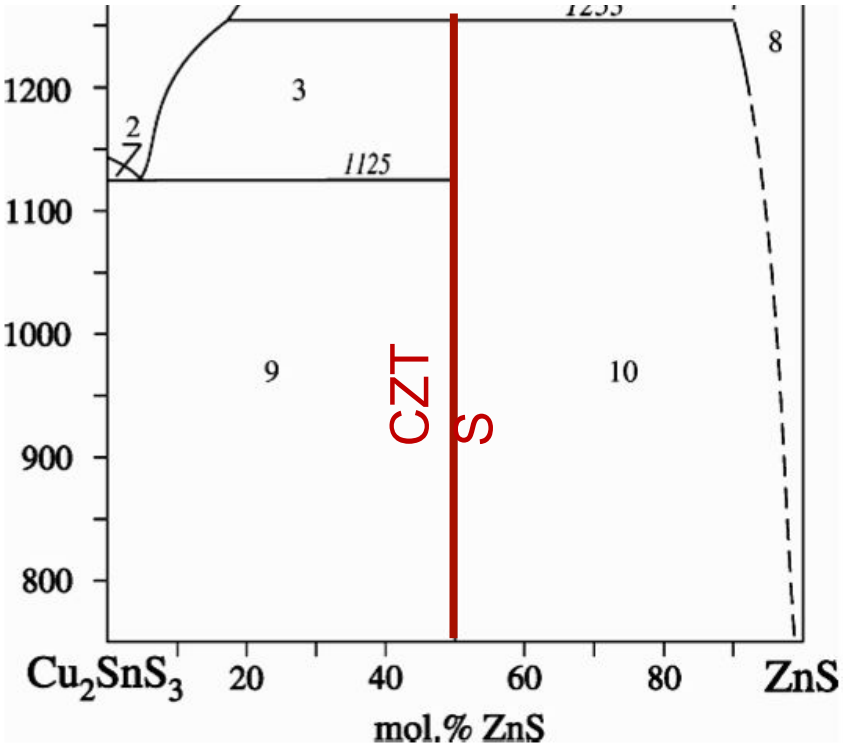
- Motivation
  - Problems with characterization of thin films
- Experimental approach
- Results
  - X-ray diffraction
  - Raman Spectroscopy
  - Transmission Electron Microscopy
  - Scanning Auger Microscopy
- Summary & Acknowledgements

Motivation – Phase Equilibrium

Ternary Phase Diagram



Binary Phase Diagram

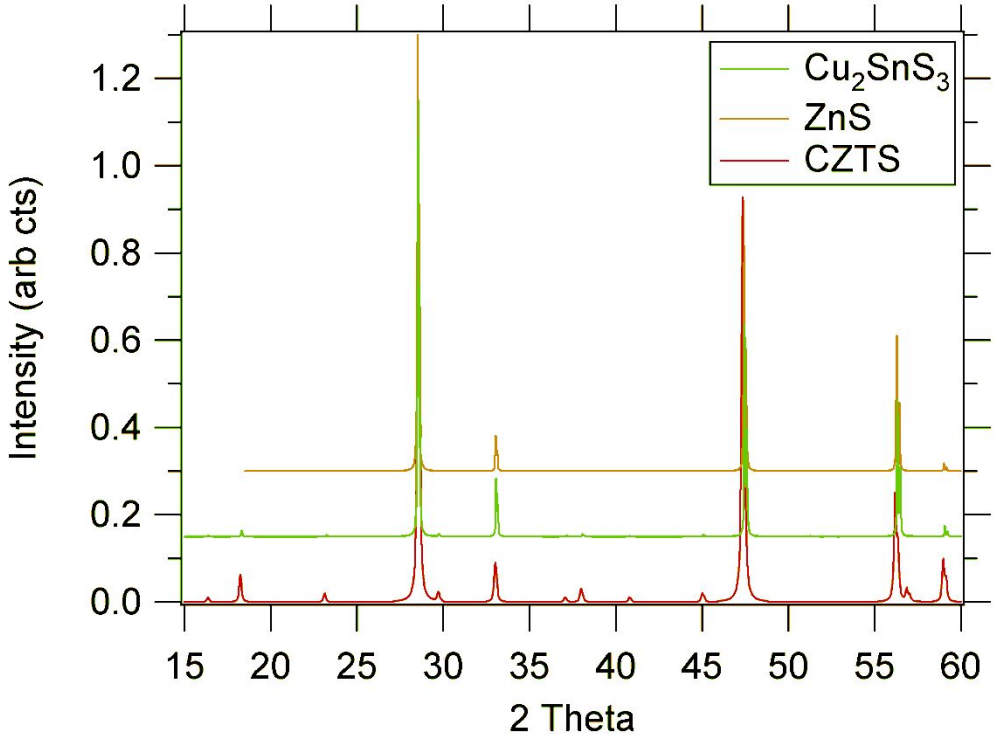


- CZTS is a line compound between Cu_2SnS_3 and ZnS
- Theoretically even a 2-3% compositional variation could lead to phase separation

Olekseyuk, I.D. "Phase Equilibria in the Cu2S-ZnS-SnS2 System." *Journal of Alloys and Compounds*. 368. (2004): 135-143. Print.

Motivation – Crystal Structure

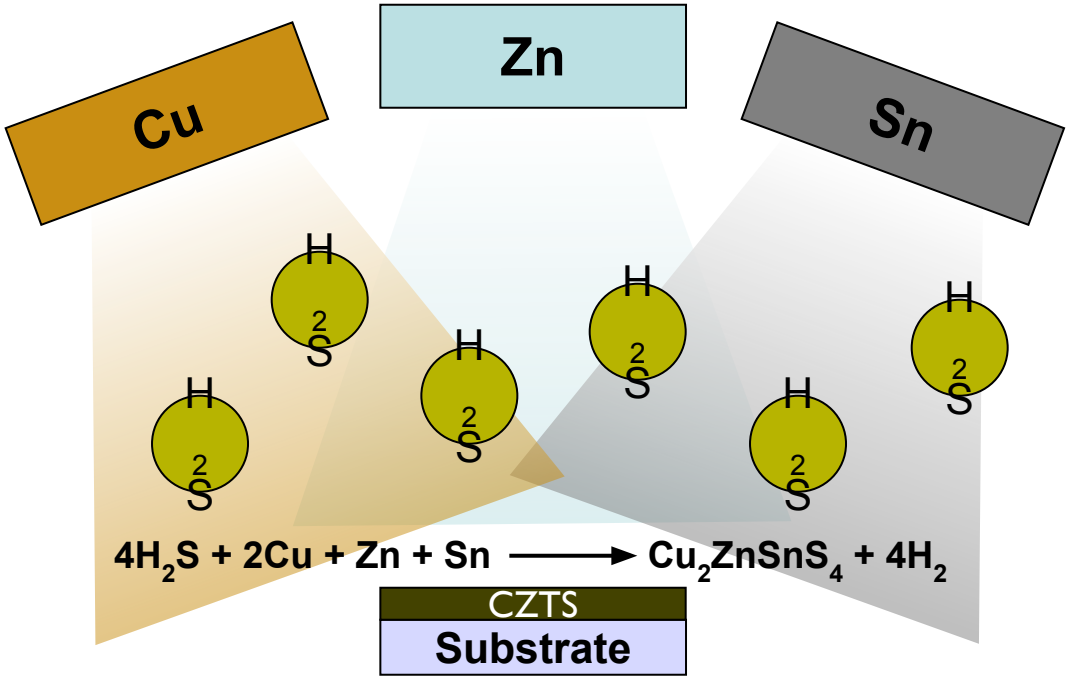
Theoretical XRD Patterns of CZTS, Cu_2SnS_3, and ZnS



- 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

Experimental Approach

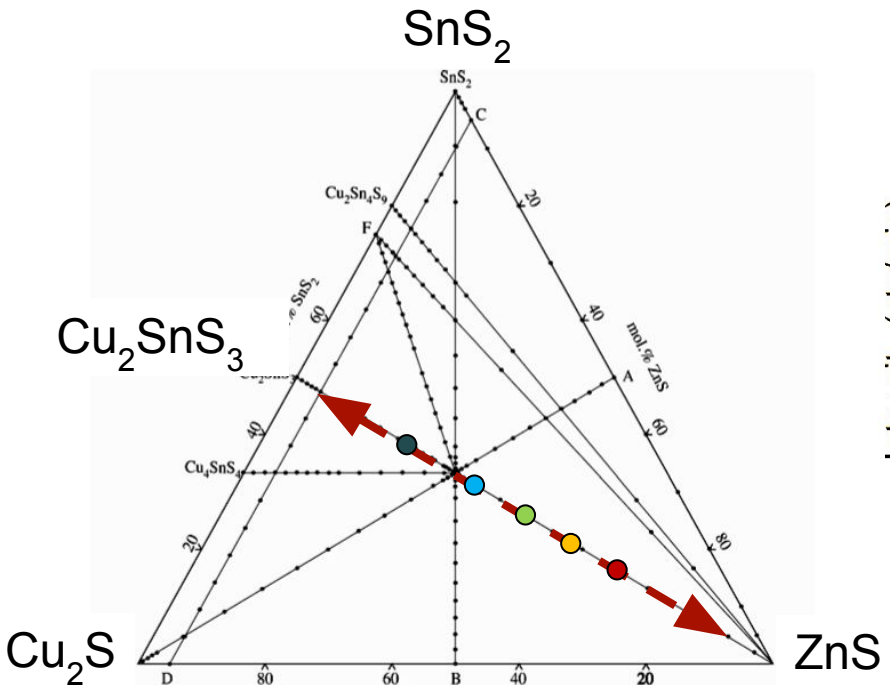
Reactive Sputtering

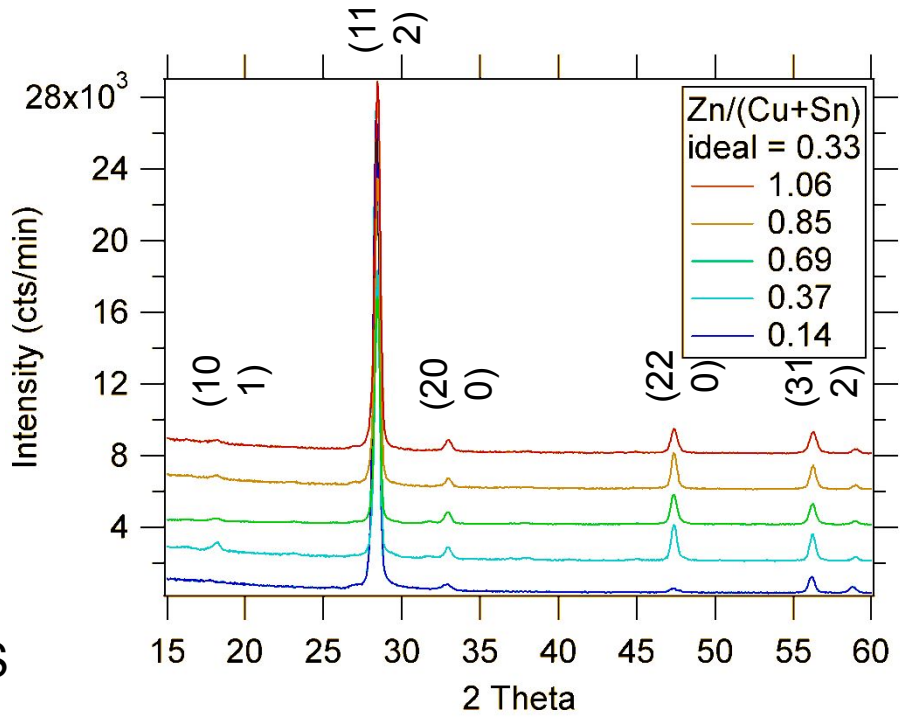


- Introduce H_2S into chamber during sputter deposition
- Sulfur is incorporated into the film in one step (no anneal)
- Expect to see higher densities and improved film quality

Characterization - XRD

Varying Zn/(Cu+Sn) Ratio



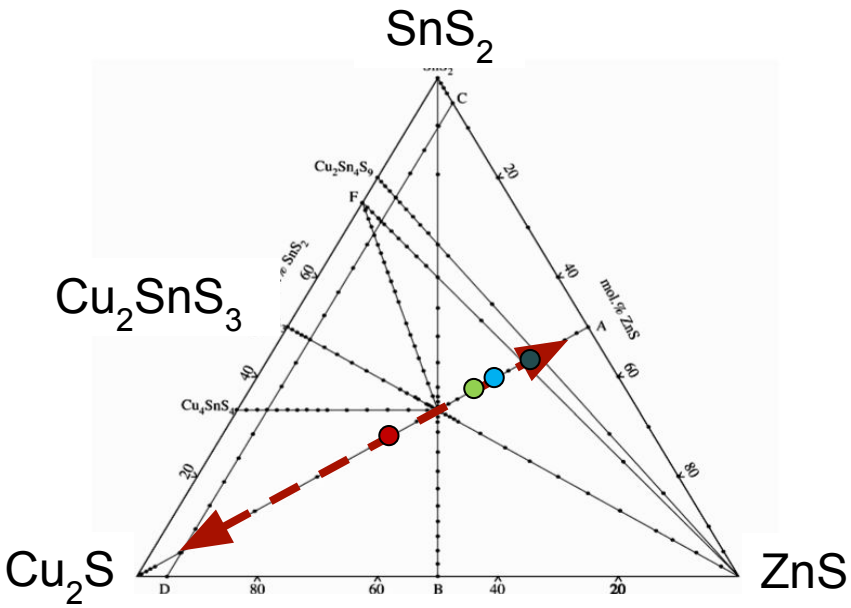


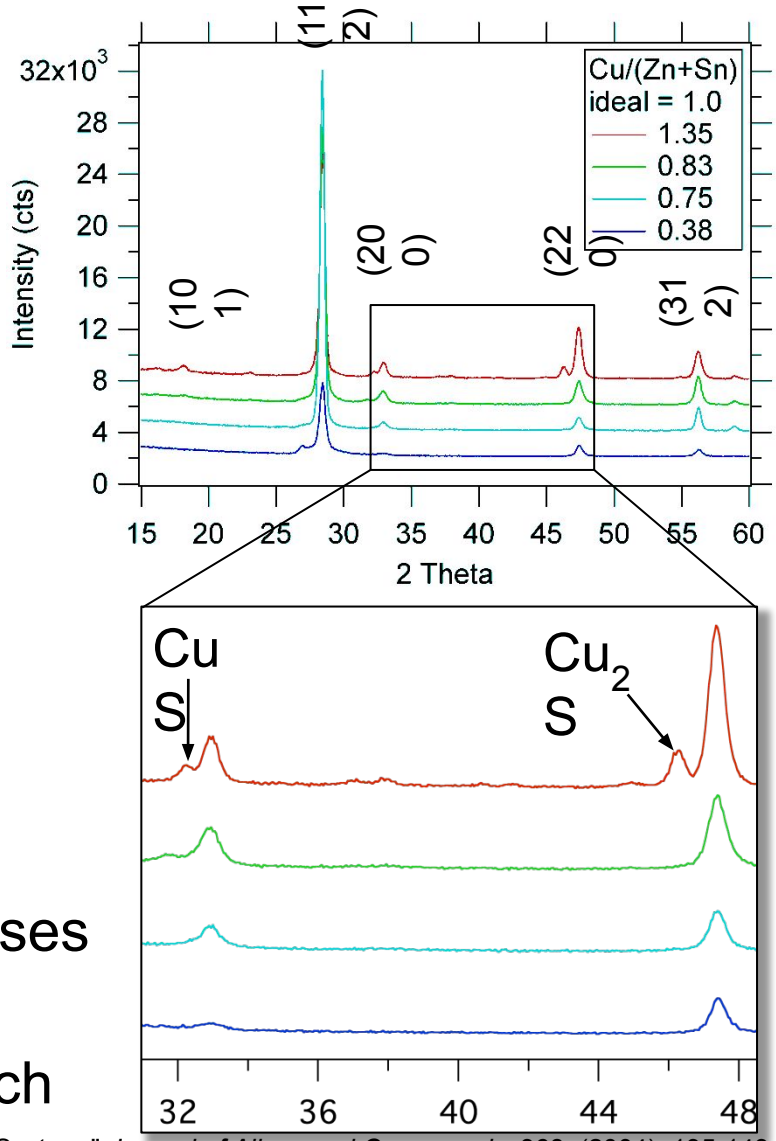
- Zn/(Cu+Sn) ratio is varied while holding Cu/Sn ratio constant
- Impossible to determine difference between CZTS, CTS, and ZnS from XRD pattern

Olekseyuk, I.D. "Phase Equilibria in the Cu2S-ZnS-SnS2 System." *Journal of Alloys and Compounds*. 368. (2004): 135-143. Print.

Characterization - XRD

Varying Cu/(Zn+Sn) Ratio



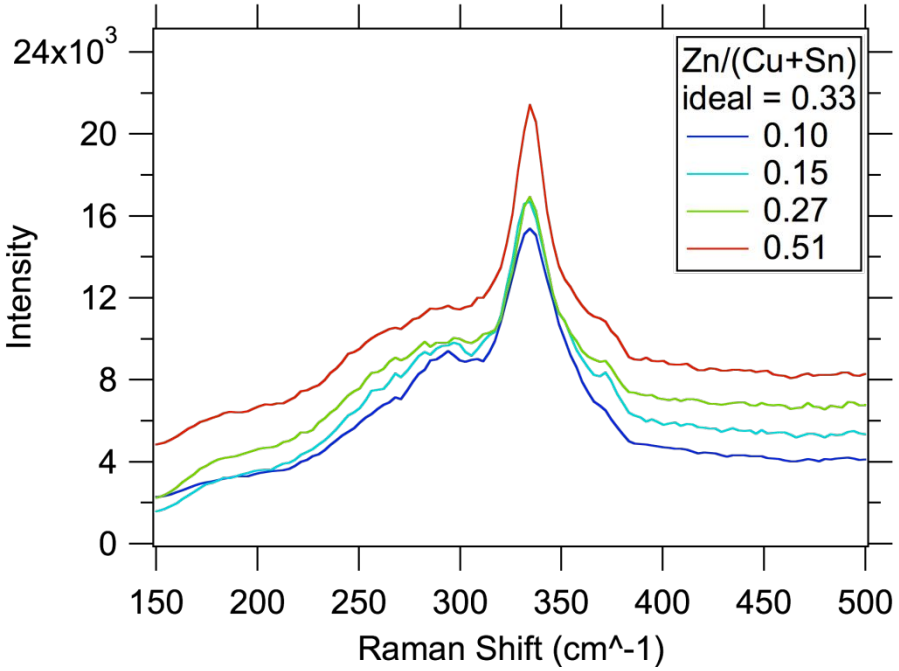


- Cu/(Zn+Sn) ratio is varied while holding Zn/Sn ratio constant
- Need to get very far off 2:1:1 stoichiometry before any Cu_xS phases can be seen
- Cu_xS can be removed with KCN etch

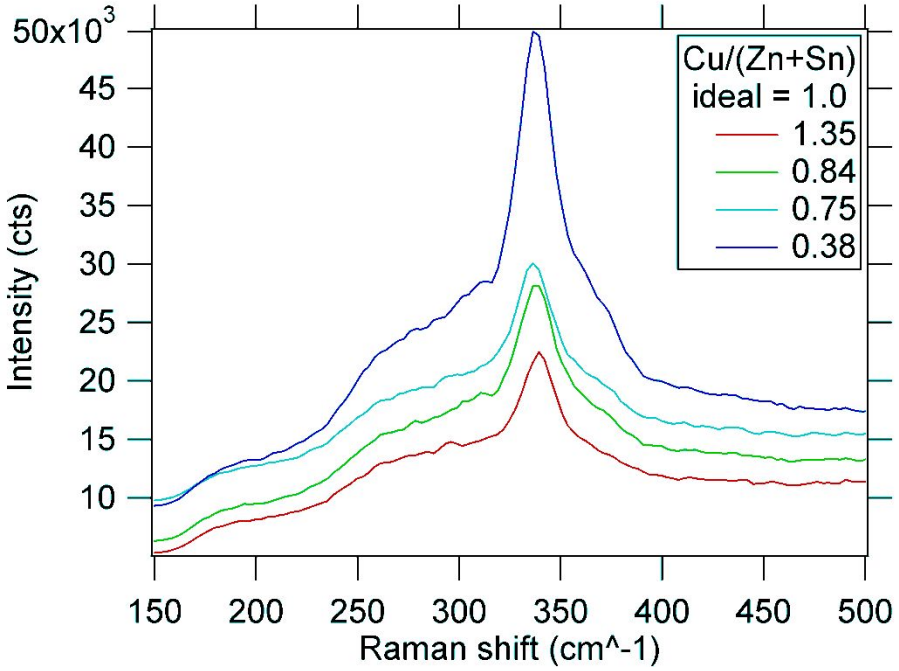
Olekseyuk, I.D. "Phase Equilibria in the Cu2S-ZnS-SnS2 System." *Journal of Alloys and Compounds*. 368. (2004): 135-143. Print.

Characterization – Raman

Varying Zn/(Cu+Sn) Ratio



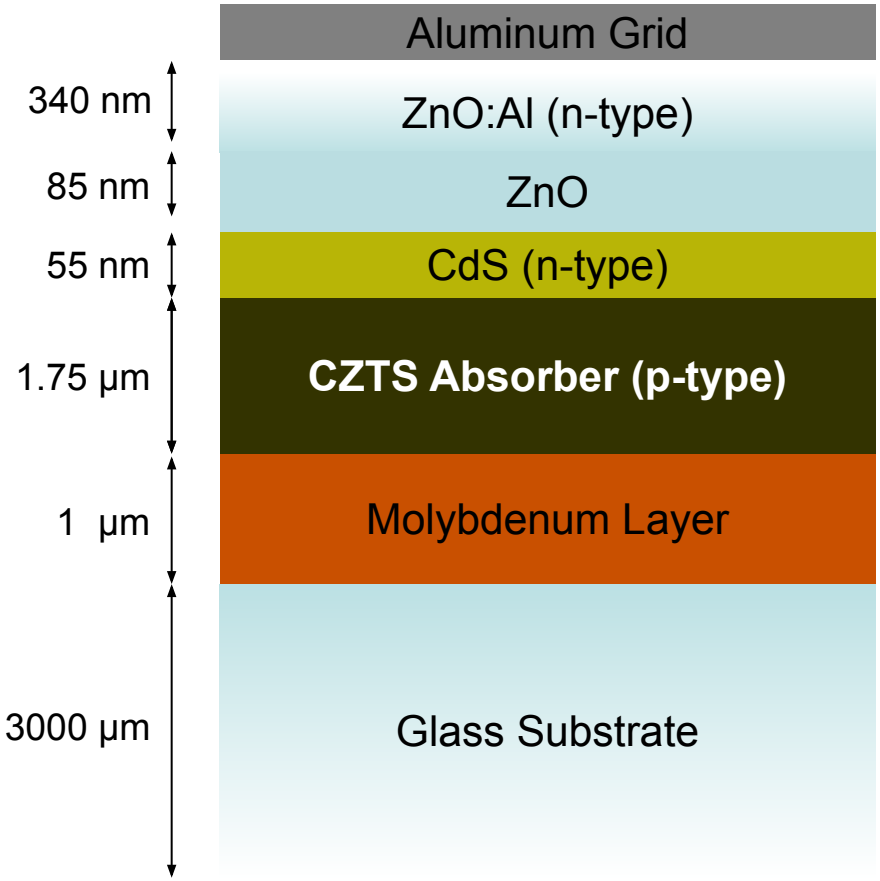
Varying Cu/(Zn+Sn) Ratio



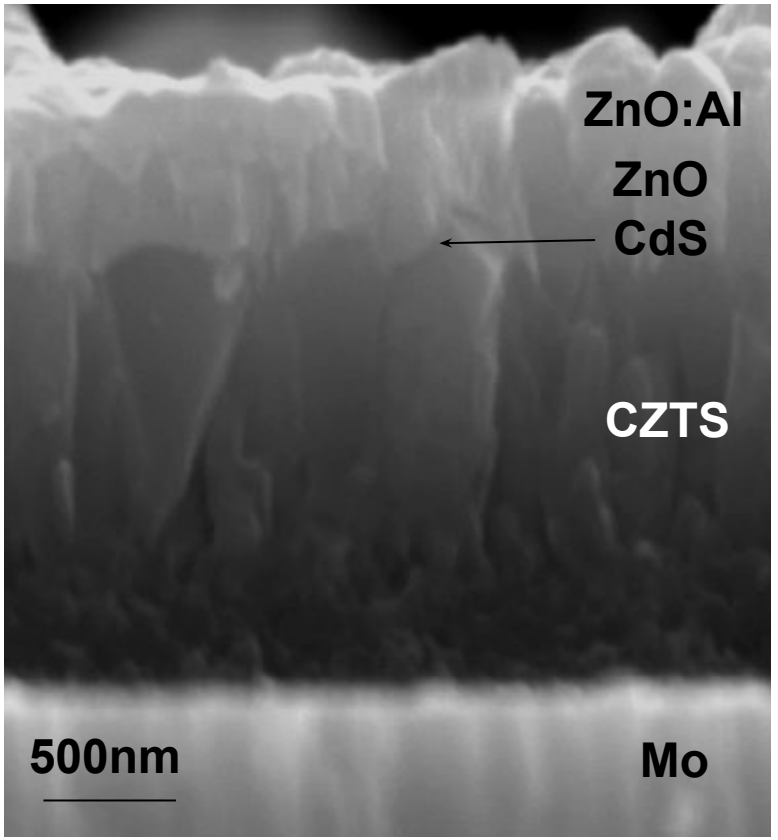
- Raman spectra show only minor changes even though composition is varied dramatically
- No evidence of the Cu_xS phase shown by other groups at growth temperatures higher than 500C

Device Fabrication

CZTS Device Stack



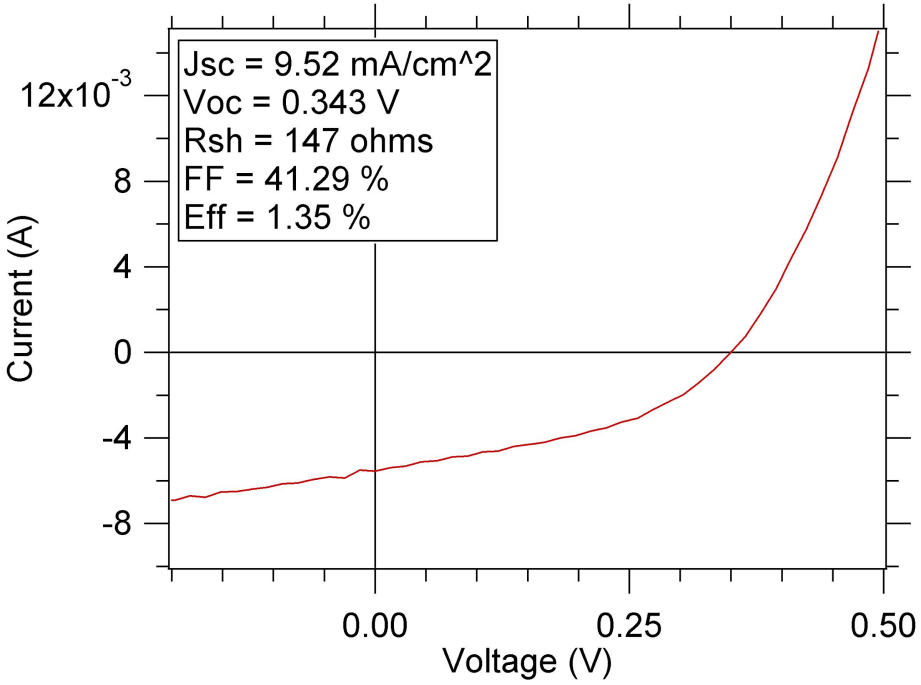
SEM Image



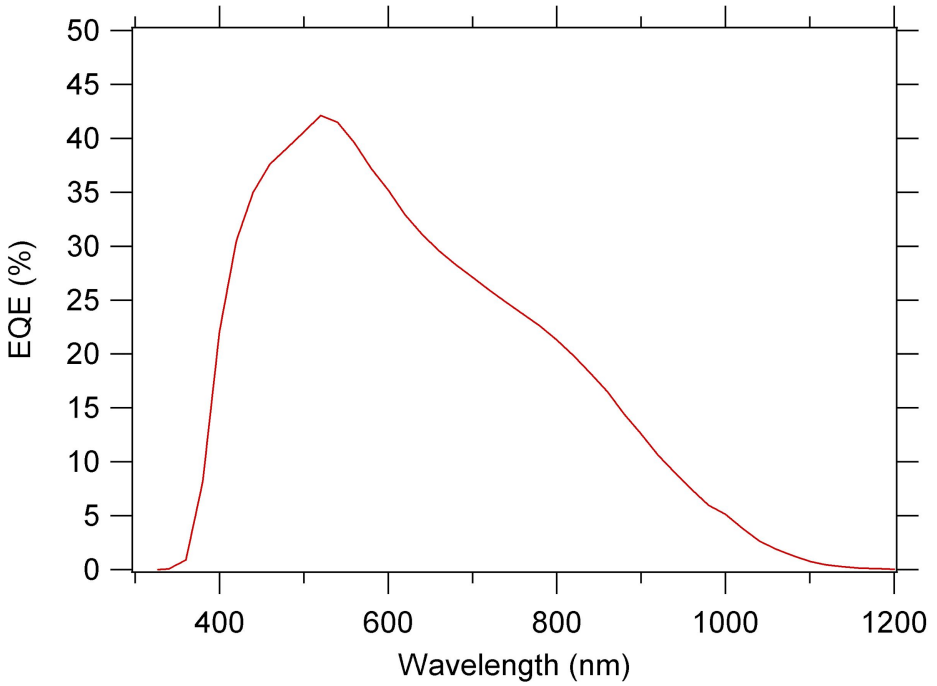
- Zn-rich films incorporated into standard CIGS device stack for testing

Device Characterization

I-V Measurement

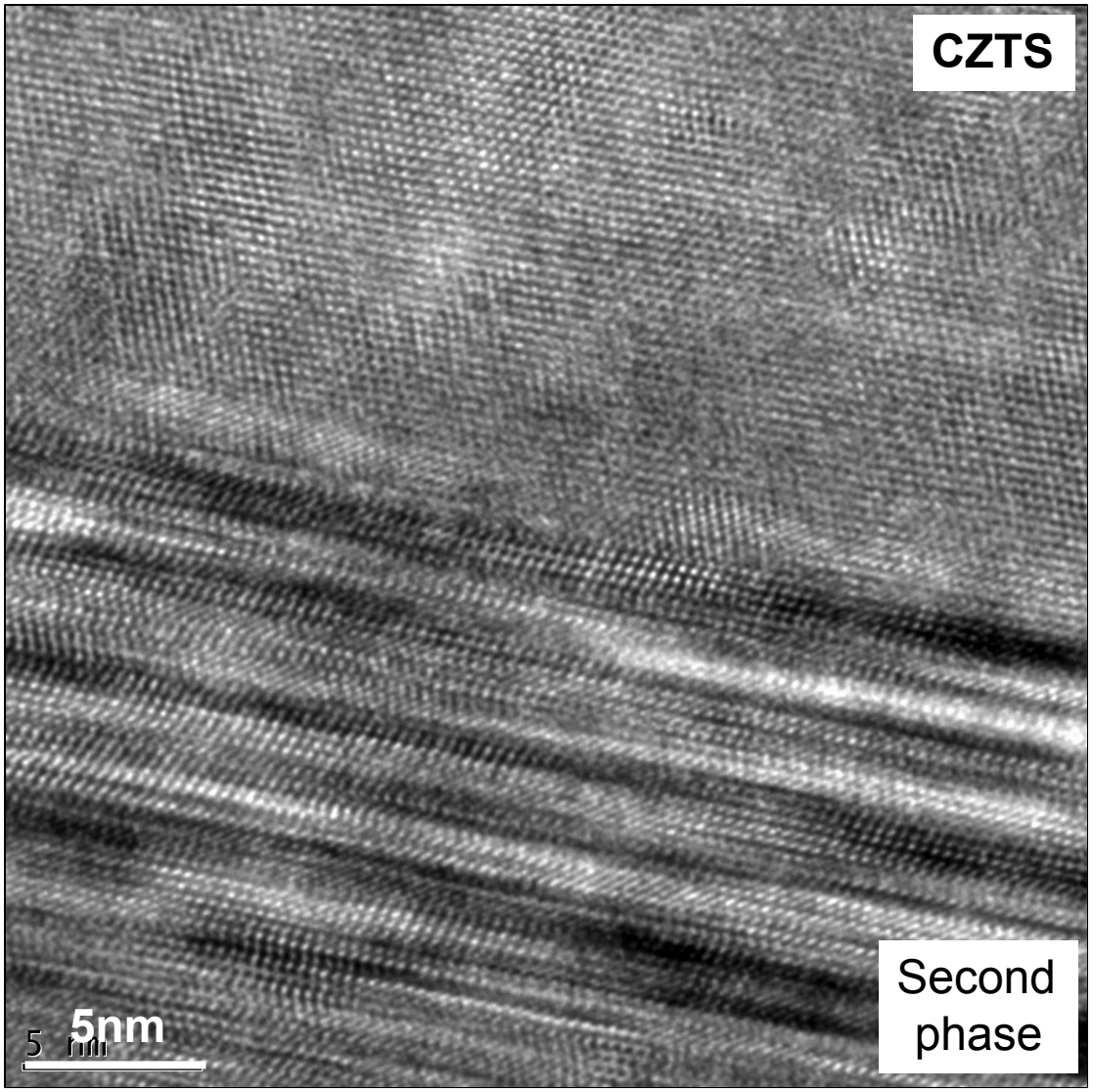


EQE Measurement



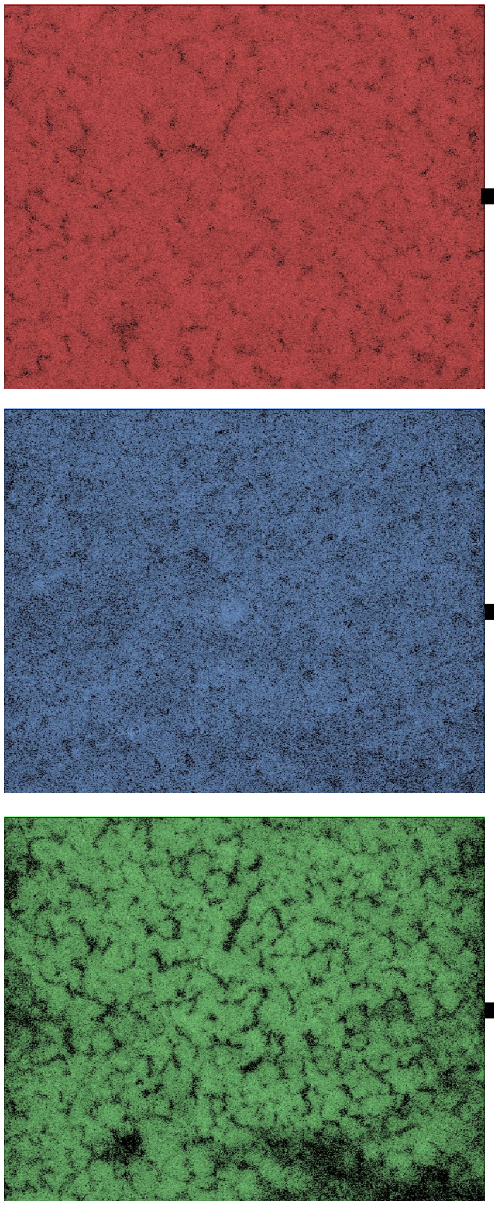
- First CZTS devices grown by a reactive sputtering process
- Efficiency = 1.35%
- **Degraded EQE clearly points to undetected defects in the absorber**

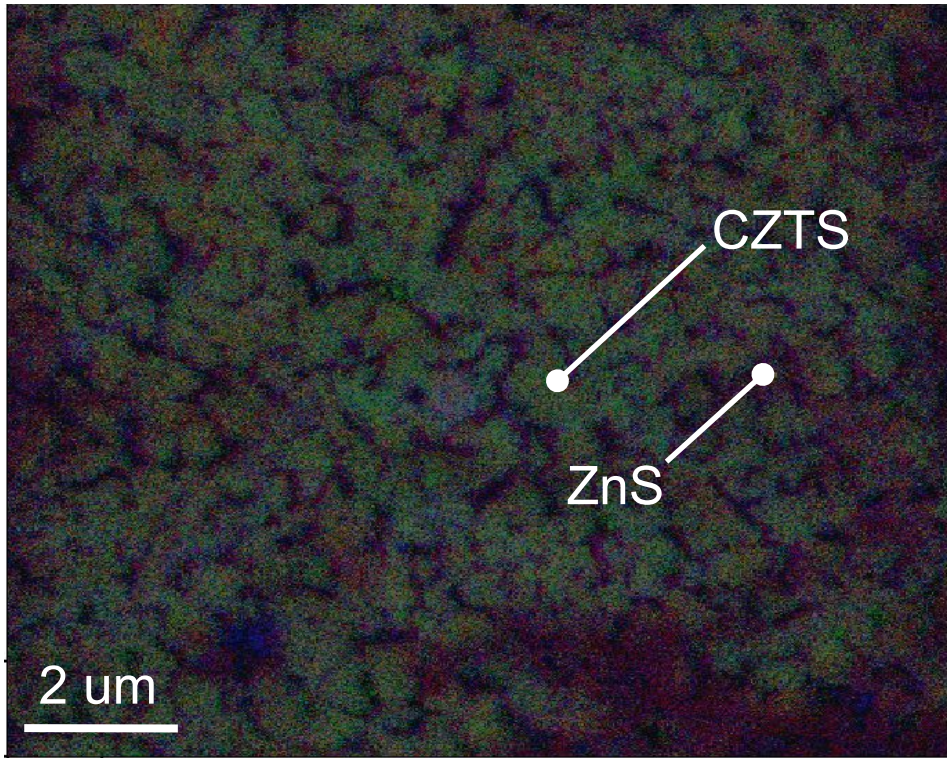
Characterization - TEM



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

Characterization - Auger

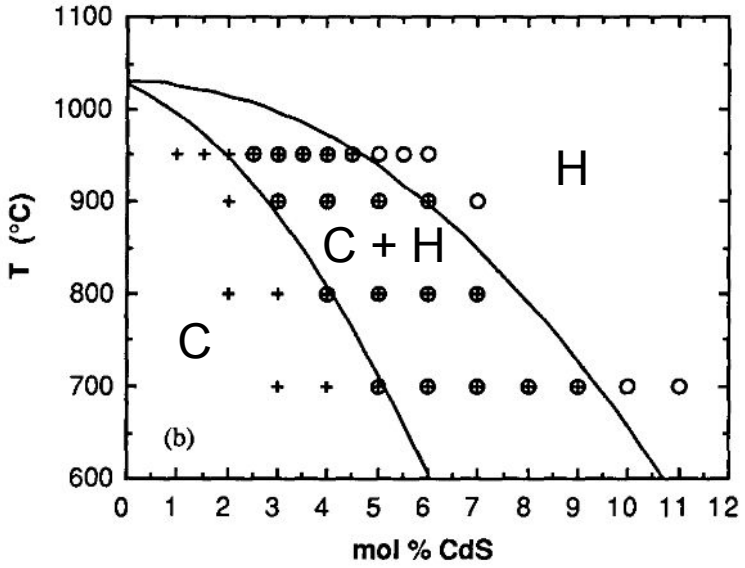




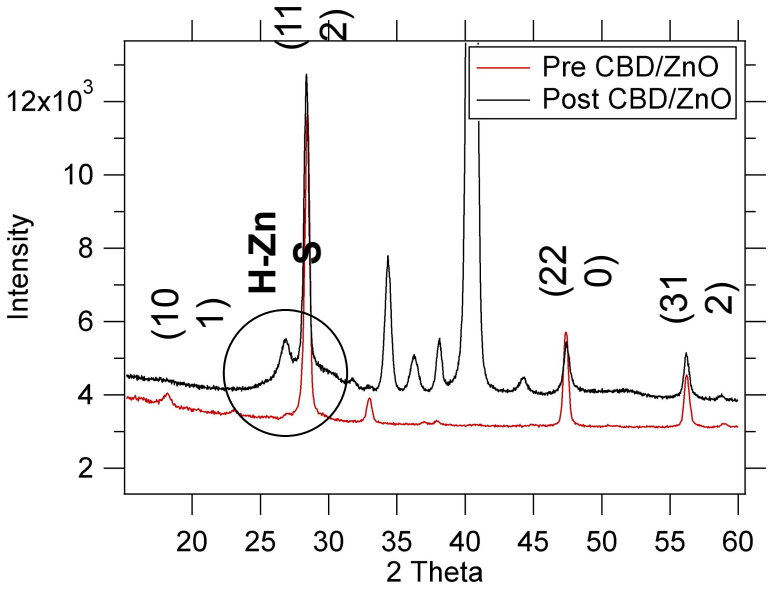
- Raster beam over sputtered surface of sample and scan for Cu, Zn, Sn
- Overlay Cu, Zn, Sn signal
- Composition variation points to CZTS / ZnS (Zn-rich)

Characterization - CdZnS

CdS – ZnS Phase Diagram



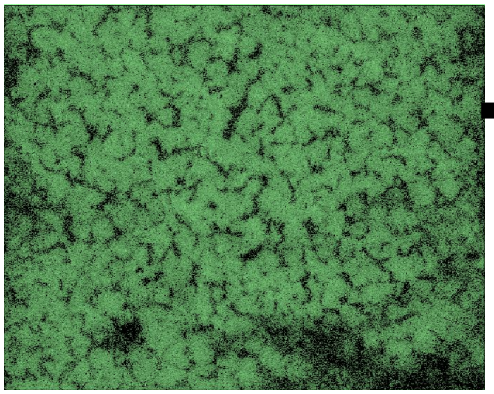
XRD before and after CBD



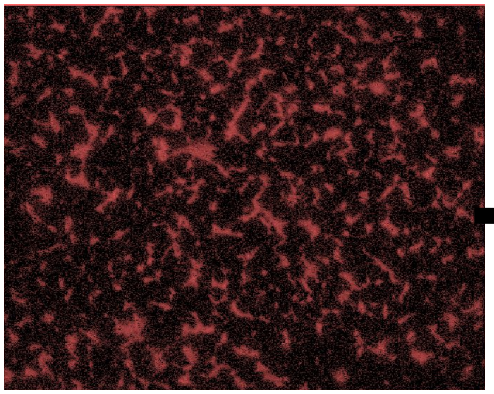
- Cd penetration into ZnS lowers the cubic-hexagonal transition temperature
- Stacking faults in TEM images are created during CBD of CdS layer

Chen et al."Solid State Phase Equilibria in the ZnS-CdS System." *Materials Research Bulletin*. 23. (1988): 1667-1673. Print.

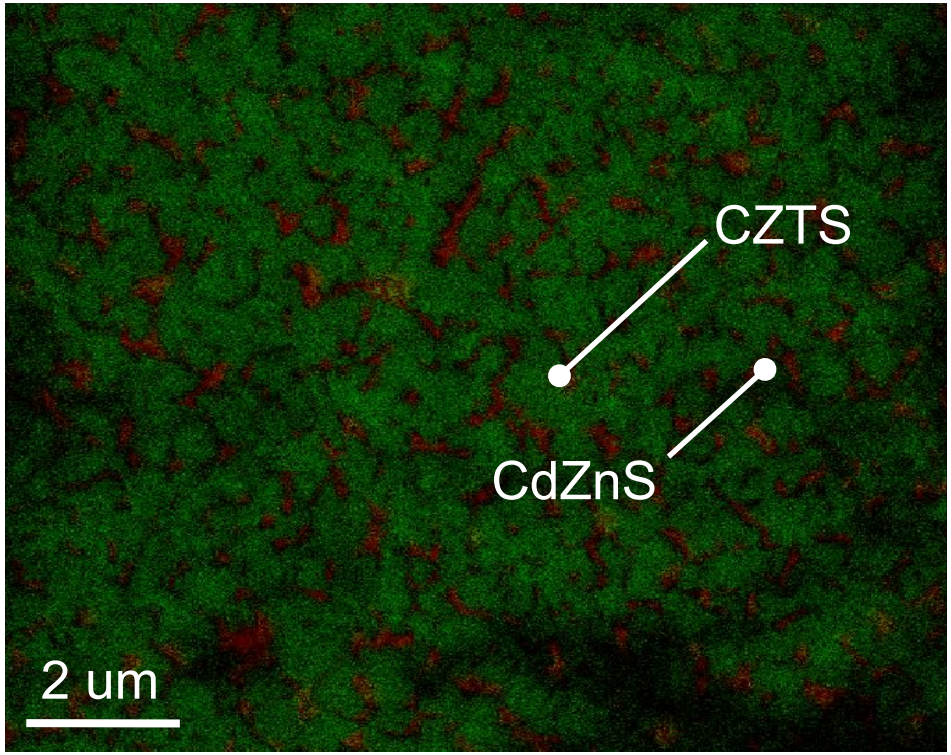
Characterization - Auger



Sn



Cd



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

Summary

- 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

- 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

Questions?