Identification of Defects and Secondary Phases in Reactively Sputtered Cu<sub>2</sub>ZnSnS<sub>4</sub> 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







- CZTS is a line compound between Cu<sub>2</sub>SnS<sub>3</sub> 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.





**Theoretical XRD Patterns of CZTS, Cu<sub>2</sub>SnS<sub>3</sub>, 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 H<sub>2</sub>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<sub>x</sub>S phases can be seen
- Cu<sub>x</sub>S can be removed with KCN etch



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- Raman spectra show only minor changes even though composition is varied dramatically
- No evidence of the Cu<sub>x</sub>S phase shown by other groups at growth temperatures higher than 500C



## **Device Fabrication**



#### Aluminum Grid 340 nm **ZnO:Al** ZnO:Al (n-type) ZnO 85 nm ZnO CdS 55 nm CdS (n-type) CZTS Absorber (p-type) 1.75 µm **CZTS** Molybdenum Layer 1 µm 3000 µm **Glass Substrate** 500nm Mo

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

#### CZTS Device Stack

#### SEM Image







- 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**



CZTS





Characterization - CdZnS





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



Sn

Cd

## **Characterization - Auger**





 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





- 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?