Evidence for Cu_2SnS_3 Formation: An Important Step towards CZTS for Solar Applications

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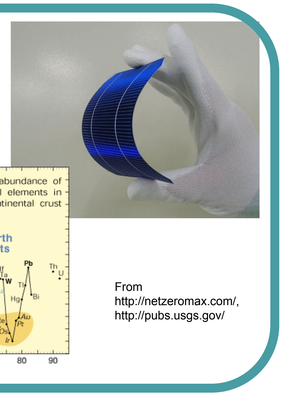
Motivation

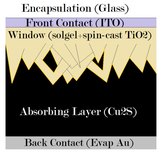
- Solar energy not yet cost-competitive with fossil fuels without subsidies
- Earth abundant materials more cost-effective and sustainable, e.g. S, Cu, Zn, Sn



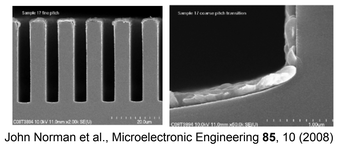
From http://netzeromax.com/, http://pubs.usgs.gov/

Experimental Aim

- Goal: Make thin film of Cu_2ZnSnS_4 (CZTS) using CVD or ALD
  - ZnS/Cu_xS multilayer/alloy stacks – unsuccessful
  - Cu_2SnS_3 – similar structure to CZTS
- CZTS could function as absorber in nanostructured solar cells, which use extremely thin absorber (ETA)
  - ETA improves charge extraction & reduces material (hence reducing cost)



- Conformal nature of ALD, CVD allows deposition into nanostructure:



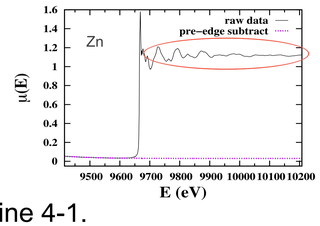
Example of CVD in high aspect ratio structure. The right picture is a zoomed-in image.

John Norman et al., Microelectronic Engineering **85**, 10 (2008)

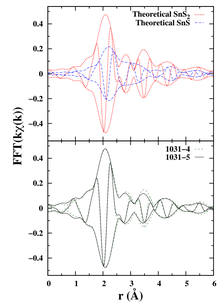
- Extended X-ray Absorption Fine Structure (EXAFS) needed to characterize the local structure [XRD inconclusive]
  - Also sensitive to type of 2nd neighbor; can look for clustering

Experimental Details

- Thin films were approximately 100 nm thick.
- EXAFS analysis was performed on the Sn and Cu K-edges of the thin films, using SSRL's Beamline 4-1.



Individual Thin Films

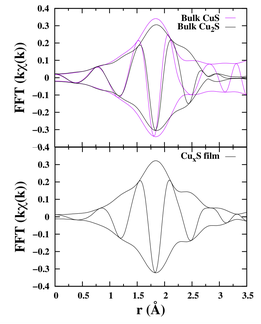


SnS_2

- Theoretical EXAFS functions for SnS and SnS_2
- SnS much more disordered structure than SnS_2
- Data for two SnS_x films match SnS_2

Cu_2S

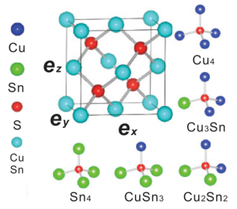
- Different shapes for CuS versus Cu_2S
- EXAFS for the thin film mostly matches bulk Cu_2S

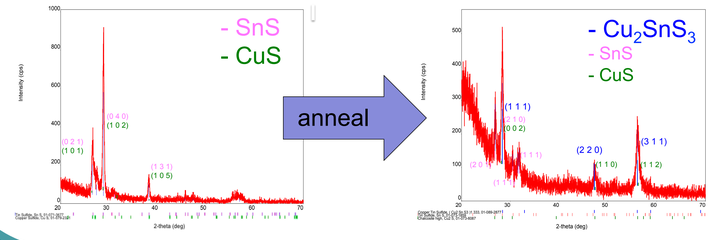


Cu_2SnS_3 Thin Films

Overview

- CVD bi-layer stack
  - Equal amounts of Cu_2S and SnS_2
  - Cu_2S first (10 min), SnS_2 (45 min)
- Successful anneal in S-environment (H_2S +N_2) at 450ºC
- EDX result ~ $Cu_{2.1}SnS_{2.9}$
- After anneal, XRD peak at ~39º disappears, new peaks appear from Cu_2SnS_3:



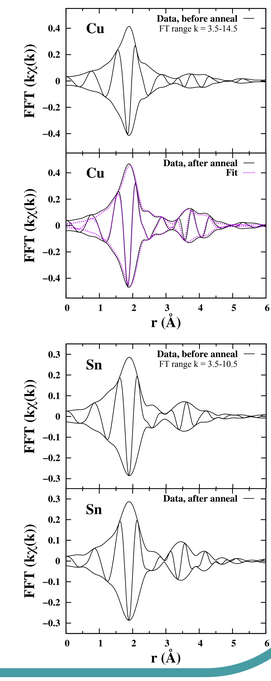


Cu EXAFS

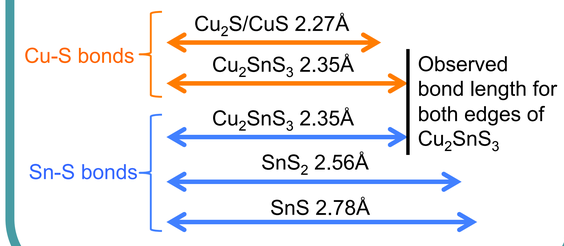
- After anneal, increase in 2nd peak's amplitude
  - Indicates formation of Cu_2SnS_3
- Fit to Cu_2SnS_3 with ~15% CuS
- Analysis of 2nd peak favors Cu-Cu bond [Should be 2/3 Cu and 1/3 Sn]

Sn EXAFS

- Sn data also has an increase in amplitude of the 2nd peak after anneal.
- While stoichiometry is Cu-rich from Cu EXAFS and EDX, preliminary Sn EXAFS analysis indicates few Cu 2nd neighbors.
  - i.e. Mostly Sn-Sn neighbors

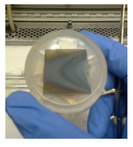


Bond Length Comparison



Conclusions

- Close to successful attempts to make Cu_2SnS_3
  - Some excess CuS
  - Bond lengths consistent with desired structure (see comparison on left)
- EXAFS suggests clustering of Cu & Sn within structure, forming mainly 2nd neighbor Cu-Cu & Sn-Sn pairs
- Progress towards CZTS
  - Next step is adding ZnS
  - EXAFS useful for secondary structures



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