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Atomic Layer Deposition of Tin(II) Sulfide

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Atomic Layer Deposition of Tin(II) Sulfide

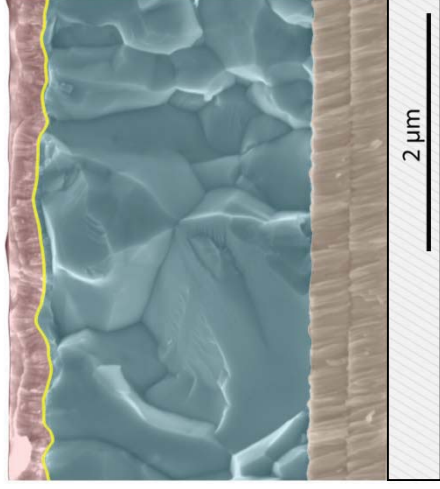
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Jaeyeong Heo, and Roy G. Gordon

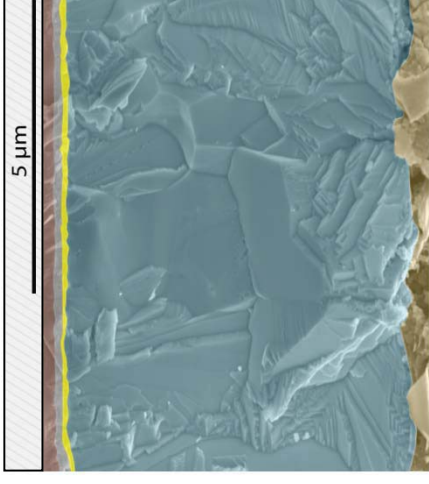
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Harvard University

Current Thin Film Solar Cells

ZnO, ITO - 2500Å
CdS - 700Å
CIGS 1-2.5µm
Mo - 0.5-1µm
Glass, Metal Foil, Plastics



Glass
SnO ₂ , Cd ₂ SnO ₄ - 0.2-0.5µm
CdS - 600-2000Å
CdTe 2-8µm
C-Paste with Cu, or Metals

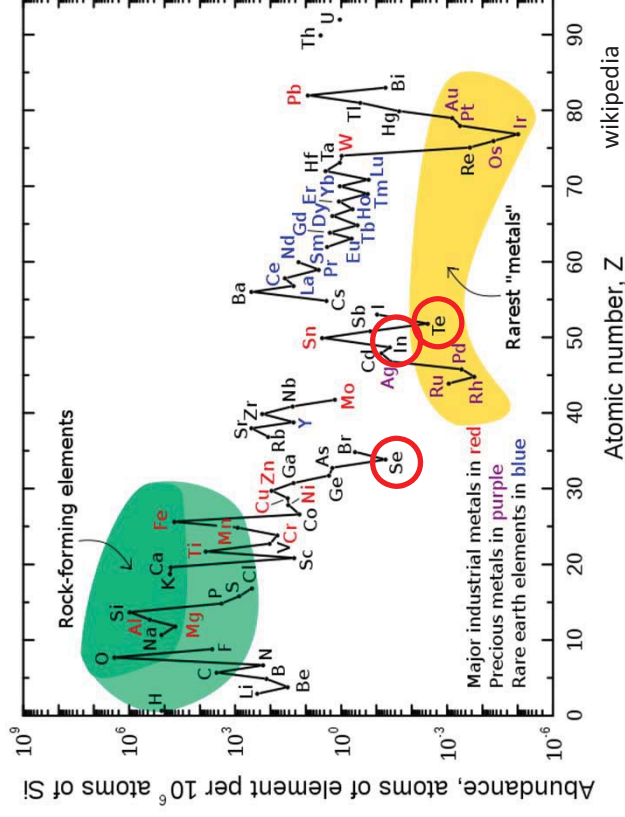


NREL

Highest energy conversion efficiency of ~20%

Cu(In,Ga)(Se,S)₂ (CIGS)

CdTe



Advantage

- Low manufacturing cost
- Moderate efficiency

Limitation

- Use rare elements (In, Te, and Se)
- Contain toxic element (Cd)

Alternate Absorber Layer in Solar PV

- ❖ Basic Criteria for the Absorber Material.
 - ✓ Suitable energy bandgap ($E_g \sim 1.0\text{-}1.5\text{ eV}$).
 - ✓ High optical absorption coefficient ($10^4\text{-} 10^5\text{ cm}^{-1}$).
 - thickness / mass of material required.
 - ? High quantum yield for the excited carriers
 - ? Long carrier diffusion length / low combination velocity
 - PV efficiency
 - ✓ The constituent elements are non-Toxic and abundant.
 - non-hazard, scalability, low cost PV.

SnS has some of these properties.

- ❖ Limitation from various deposition techniques
 - Contain other binary phases (SnS_2 and Sn_2S_3)
 - Contamination from oxygen (CBD) and chlorine (CVD)
 - Large deviation from ideal stoichiometric SnS (tin vacancies)
 - Narrow deposition temperature window (25-50 °C range @ ~ 300 °C)

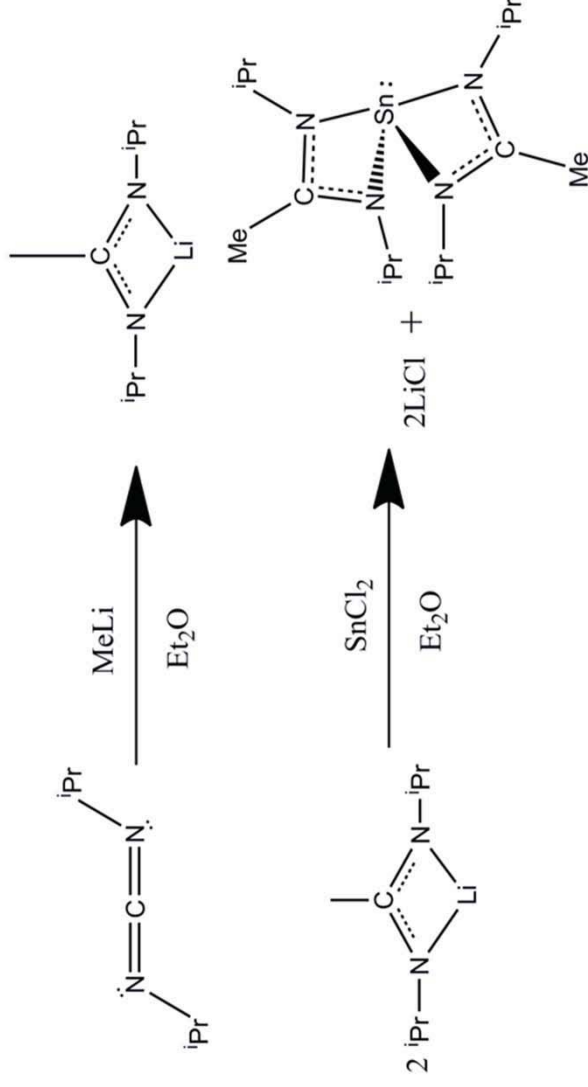
SnS Thin Film from ALD

Atomic Layer Deposition

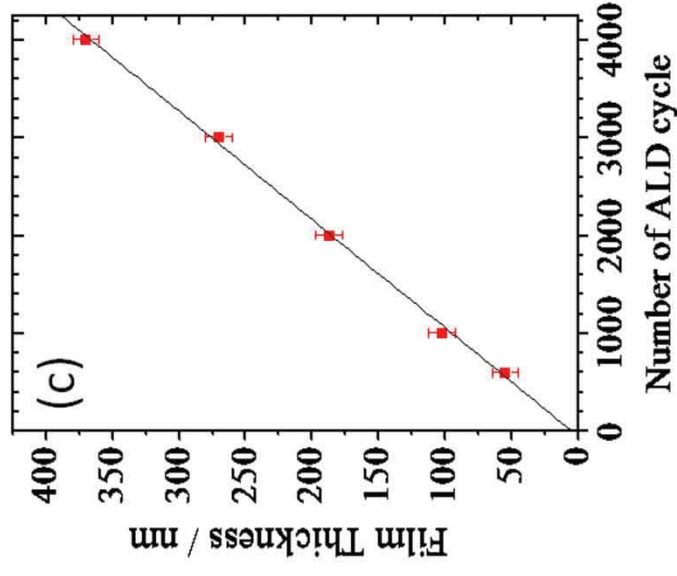
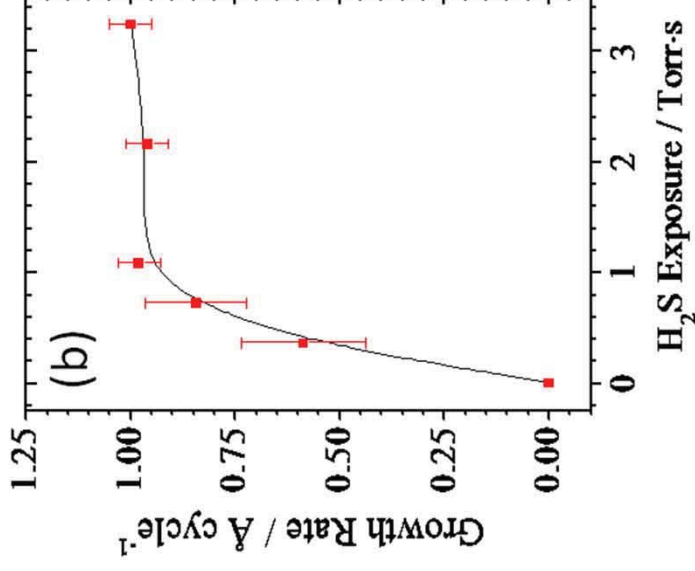
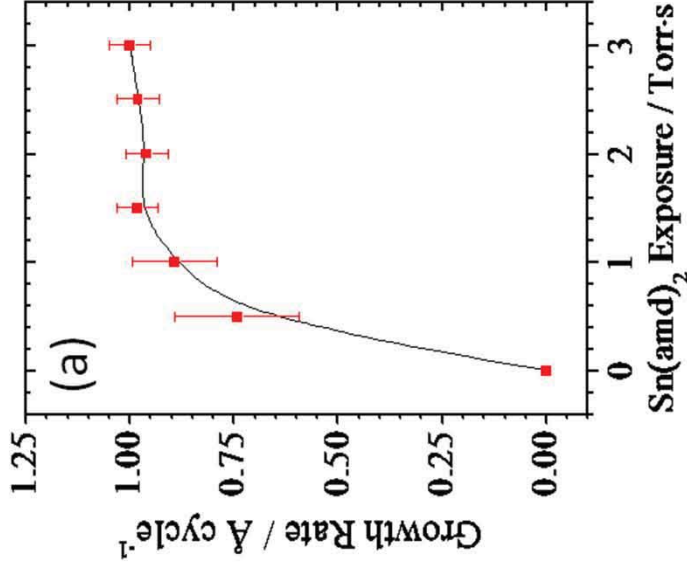
- ✓ excellent control over surface reaction
- ✓ well-controlled stoichiometry
- ✓ high density film
- ✓ low impurity
- ✓ low deposition temperature

Sn(amd)₂ precursor

- ✓ easily synthesized
- ✓ sufficient vapor pressure
- ✓ thermally stable



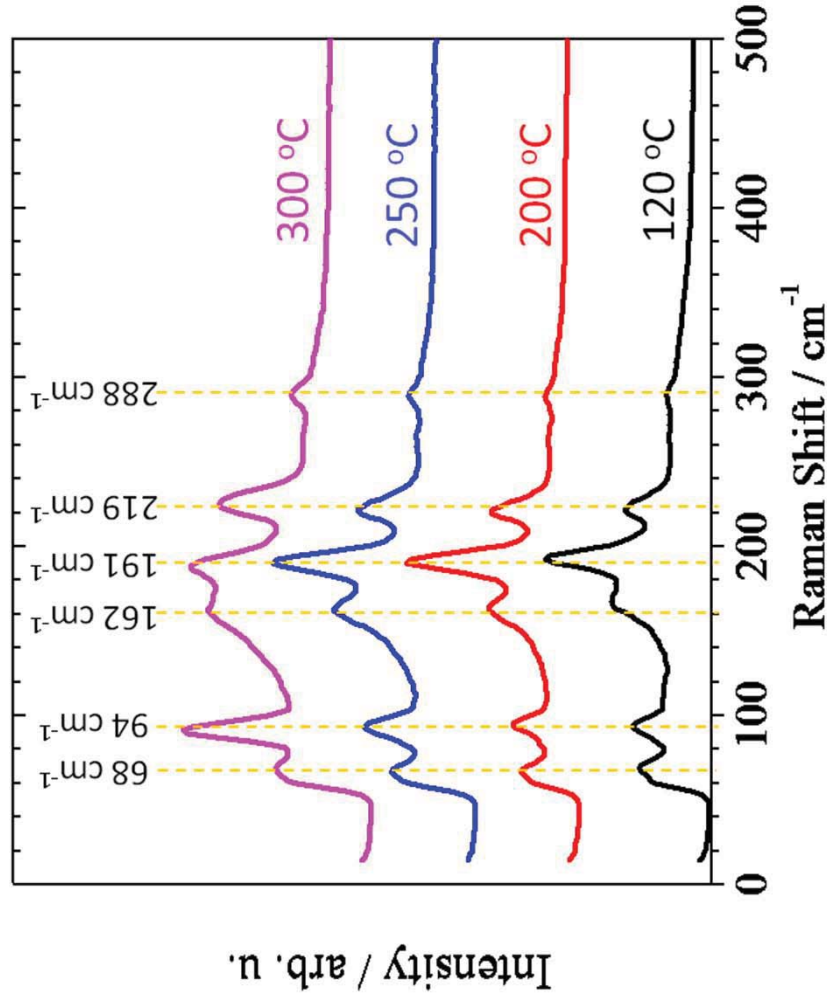
ALD Growth Behavior



- ❖ Minimum exposures of 1.5 Torr·s of Sn(amd)₂ and 1.1 Torr·s of H₂S are required to saturate the surface reactions
- ❖ Growth rate of 0.90 Å/cycle (120 °C)

Pure SnS Phase

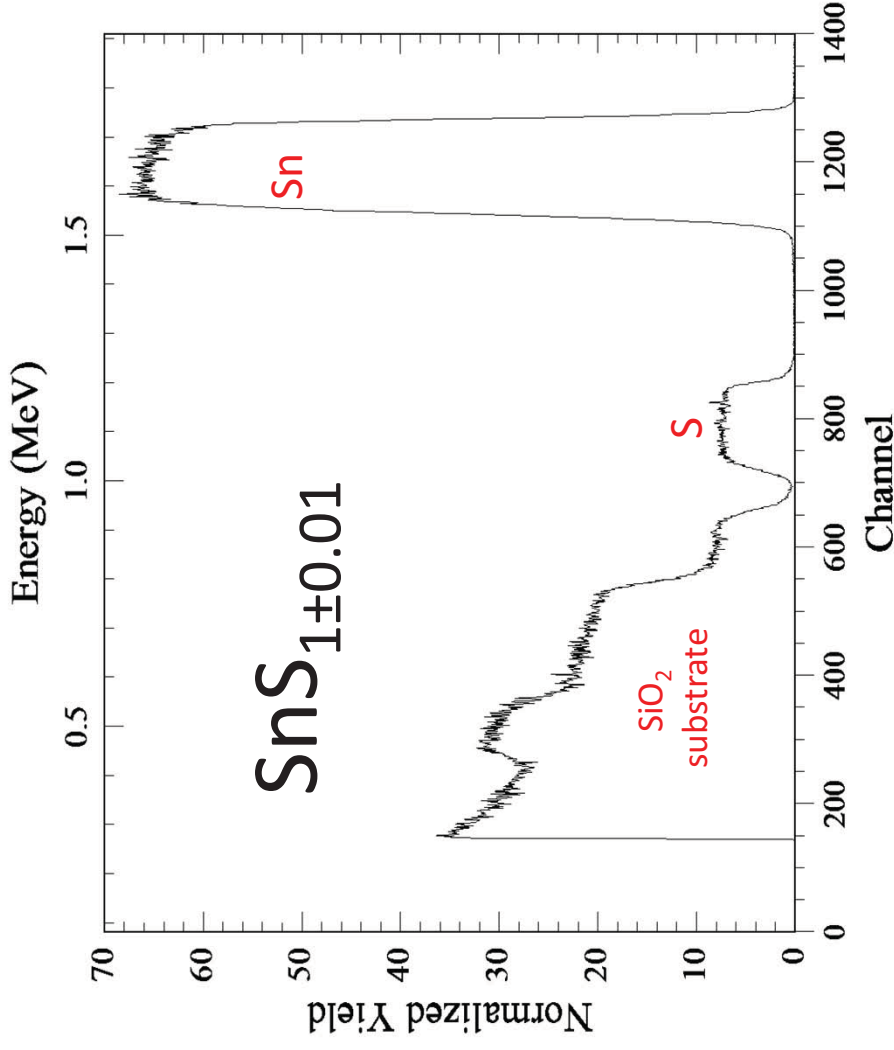
Raman Spectroscopy



- Not detect other binary phase (e.g. SnS₂ and Sn₂S₃).
- Wide deposition temperature window .

Film Composition

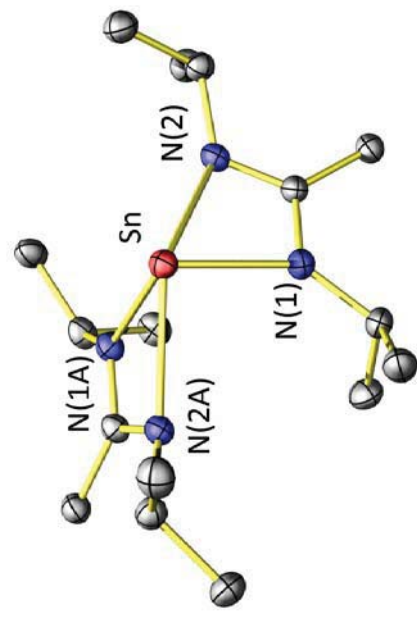
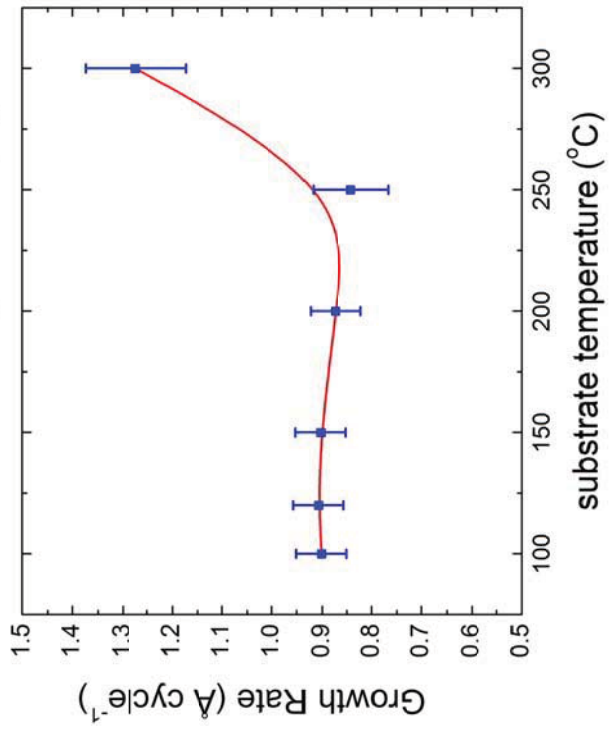
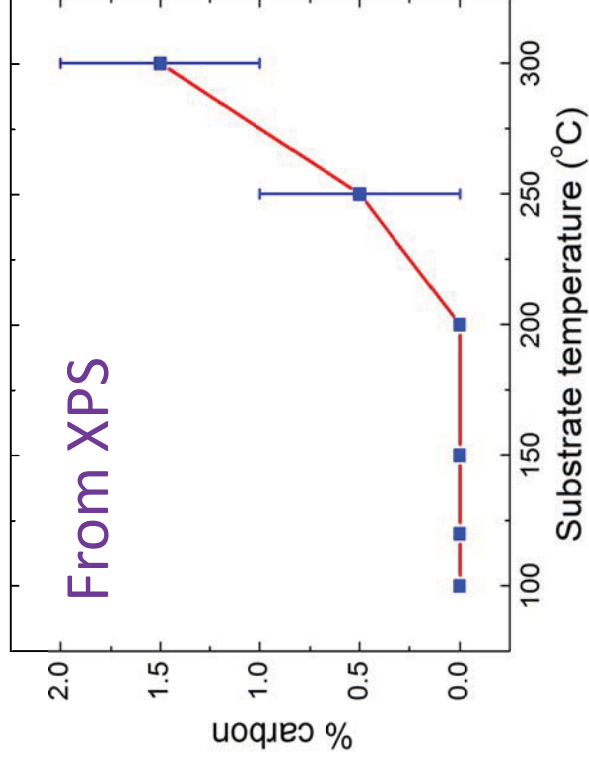
Rutherford Backscattering Spectroscopy (RBS)



- Stoichiometric SnS (Low Sn⁺² vacancy) below 200 °C
- Density ~ 4.6 g/cm³ (~ 90% of bulk value)

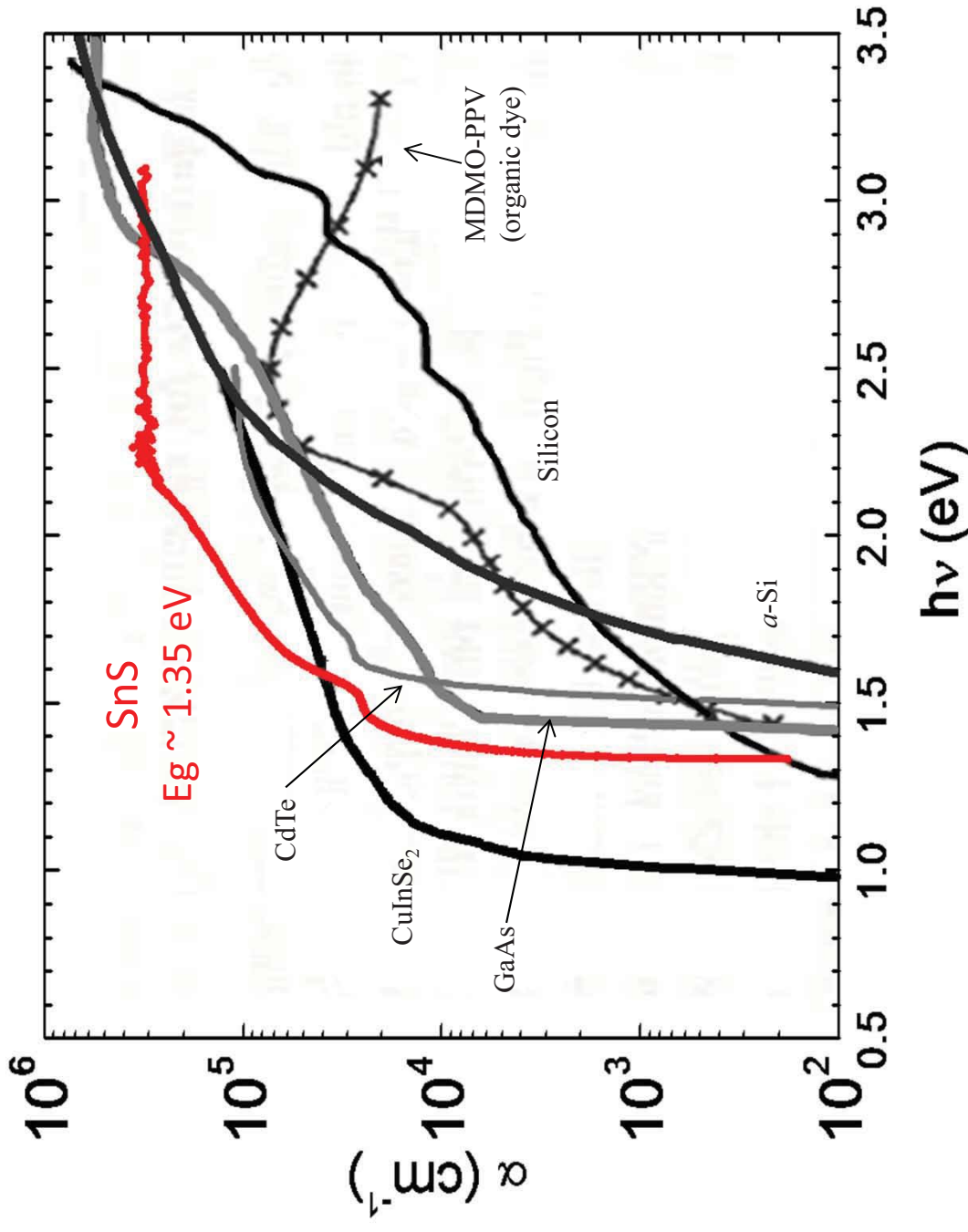
Impurity

- No carbon, nitrogen, or oxygen detected on SnS film deposited below 200 °C. (SIM)
- ~ 1-2% carbon contamination on film deposited above 250 °C.



Sn(amd)₂ starts to decompose above 250 °C.

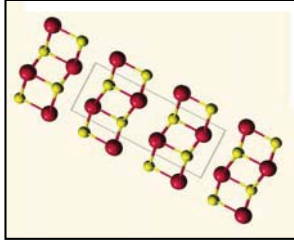
Optical Property



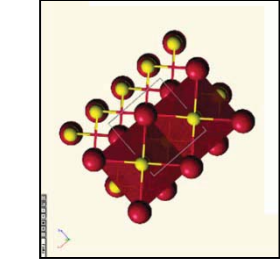
$\alpha \sim 10^5 \text{ cm}^{-1} \rightarrow$ Need $\sim 500 \text{ nm}$ for 95% absorption

Crystal Structure

Orthorhombic Structure ($a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$)

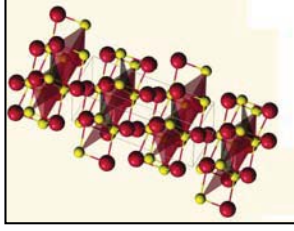


Side view



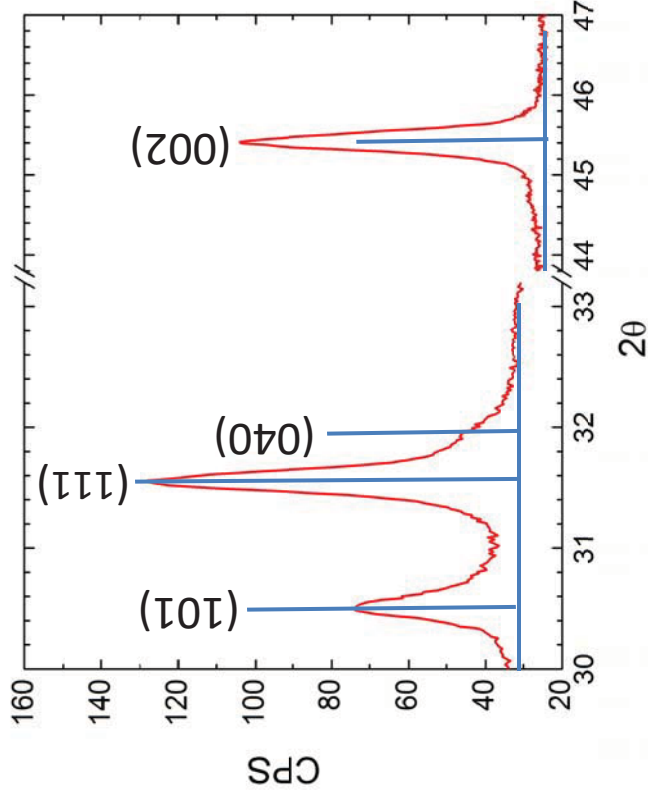
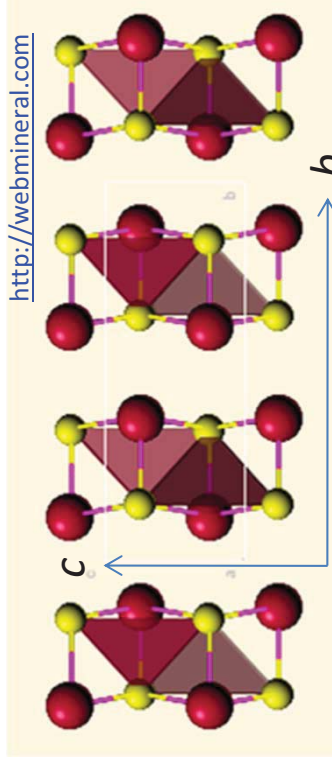
Top view along b axis

$a = 4.28$, $b = 11.20$, $c = 3.99 \text{ \AA}$



- double layer distorted NaCl structure.
- highly anisotropic material.

crystal preferred orientation



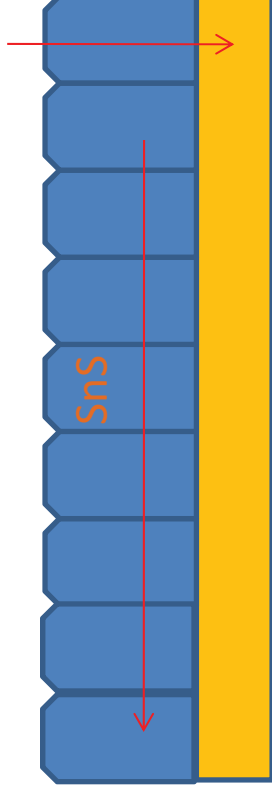
- Desirable crystal orientation.
 - ❖ higher mobility through the film.
(Single crystal: $\mu_{//} / \mu_{\perp} \sim 10$.)*
 - ❖ carrier transport along defect-tolerant layer plane

*Nassary, M.M., Journal of Alloys and Compounds, 2005. 398(1-2): p. 21-25.

Electrical Property

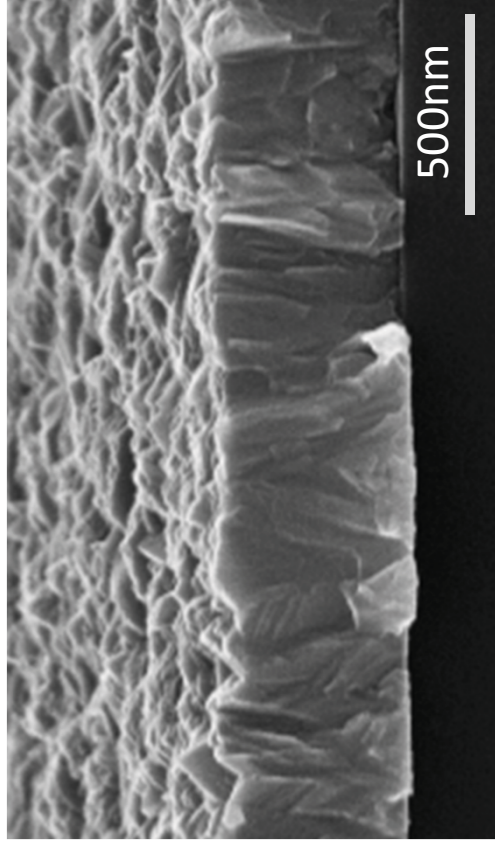
- ❖ Hall measurement
 - lateral resistivity $\rho \sim 10 - 900 \Omega \cdot \text{cm}$
 - low hole concentration $\sim 10^{16} \text{ cm}^{-3}$
 - few Sn^{+2} vacancies
 - wide depletion region in p-n junction
 - lateral hole mobility $\sim 1-4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$

Columnar structure

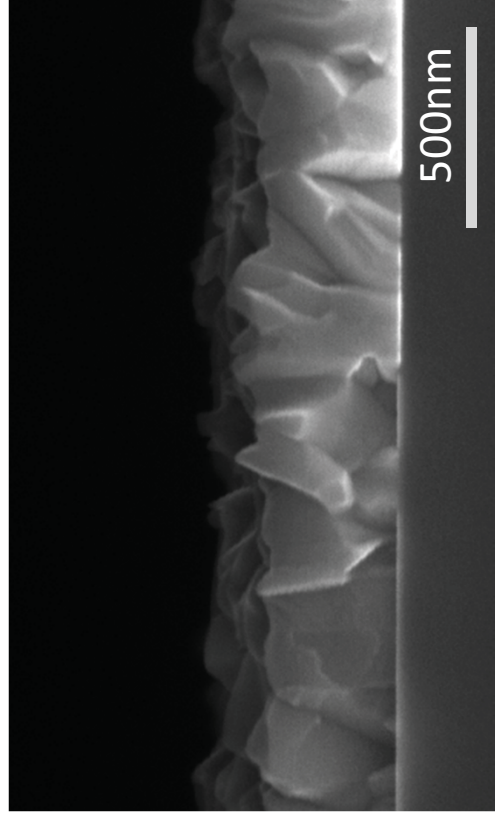


$$\diamond \sigma_{\text{vertical}} / \sigma_{\text{lateral}} \sim 3$$

- lower scattering from grain boundary
- higher mobility along crystal planes



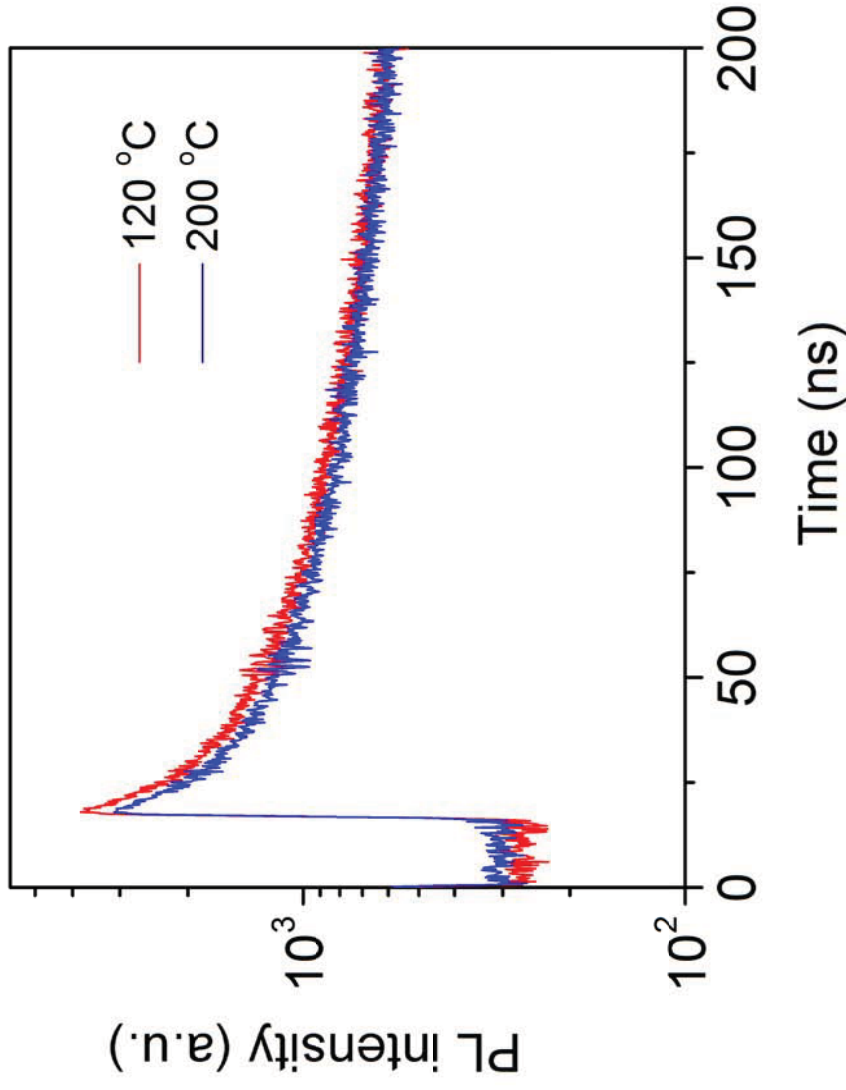
Tsub = 120 °C



Tsub = 200 °C

Minority Carrier Lifetime

Time-Resolved Photoluminescence



- Minority carrier lifetime ~ 90 ns
- Estimated minority carrier diffusion length $\sim 1.5 \mu\text{m}$

Summary

- ❖ SnS is a promising absorber material for earth-abundant, non-toxic thin film solar cells.
- ❖ ALD of SnS from the reaction of tin(II) amidinate and H₂S.
 - ✓ pure SnS phase over wide temperature range.
 - ✓ stoichiometric SnS
 - ✓ no impurity from other elements.
 - ✓ low deposition temperature.
- ❖ Optical and electrical properties suitable for thin film solar cells.
 - ✓ $E_g = 1.35$ eV with $\alpha > 10^5$ cm⁻¹
 - ✓ $[p] \sim 10^{16}$ cm⁻³ with $\mu_p \sim 1 - 4$ cm²V⁻¹s⁻¹
 - ✓ ~ 3 x higher mobility through the film due to columnar structure and crystal orientation
 - ✓ long minority carrier lifetime (~ 90 ns)

Acknowledgement

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Hall measurement: Mark Winkler, Renee Sher, and Prof. Eric Mazur

