# Atomic Layer Deposition of Tin(II) Sulfide

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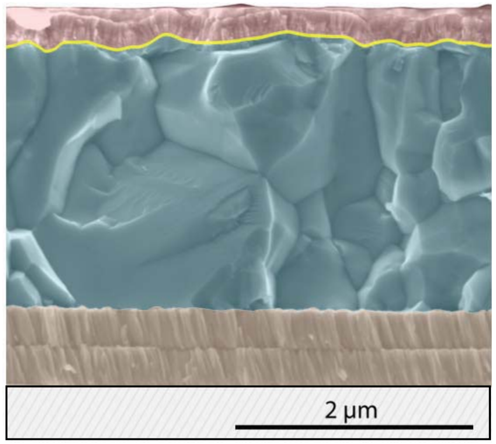
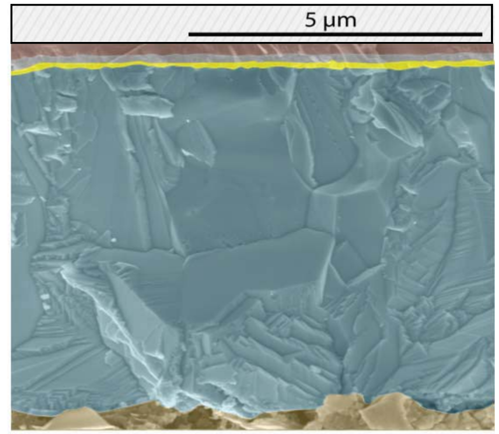
# Current Thin Film Solar Cells

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



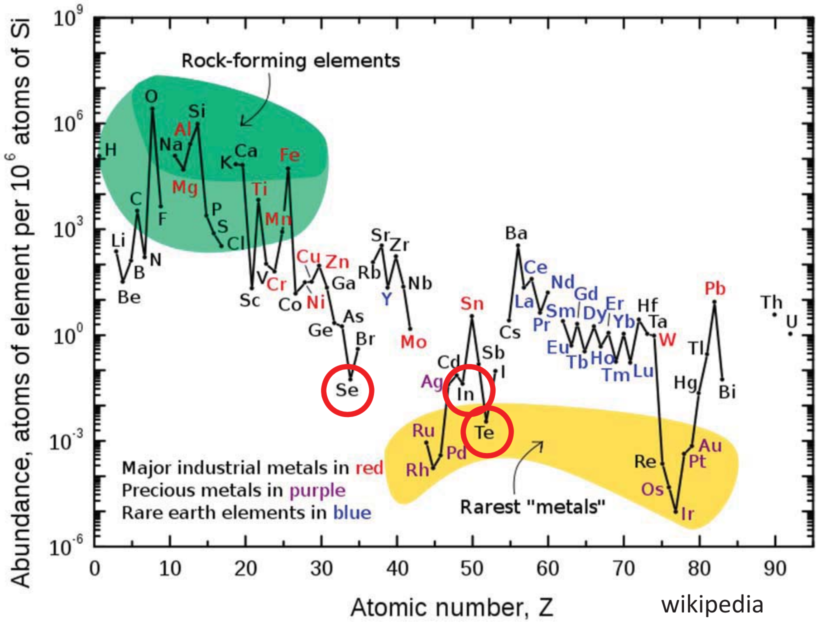

NREL

- Glass
- $SnO_2$, $Cd_2SnO_4$ - 0.2-0.5μm
- CdS - 600-2000Å
- CdTe 2-8μm
- C-Paste with Cu, or Metals

## $Cu(In,Ga)(Se,S)_2$ (CIGS)

Highest energy conversion efficiency of ~20%

## CdTe




wikipedia

## 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 ( Eg ~ 1.0-1.5 eV).
  - ✓ High optical absorption coefficient ( $10^4$- $10^5$ $cm^{-1}$).
    - → 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.

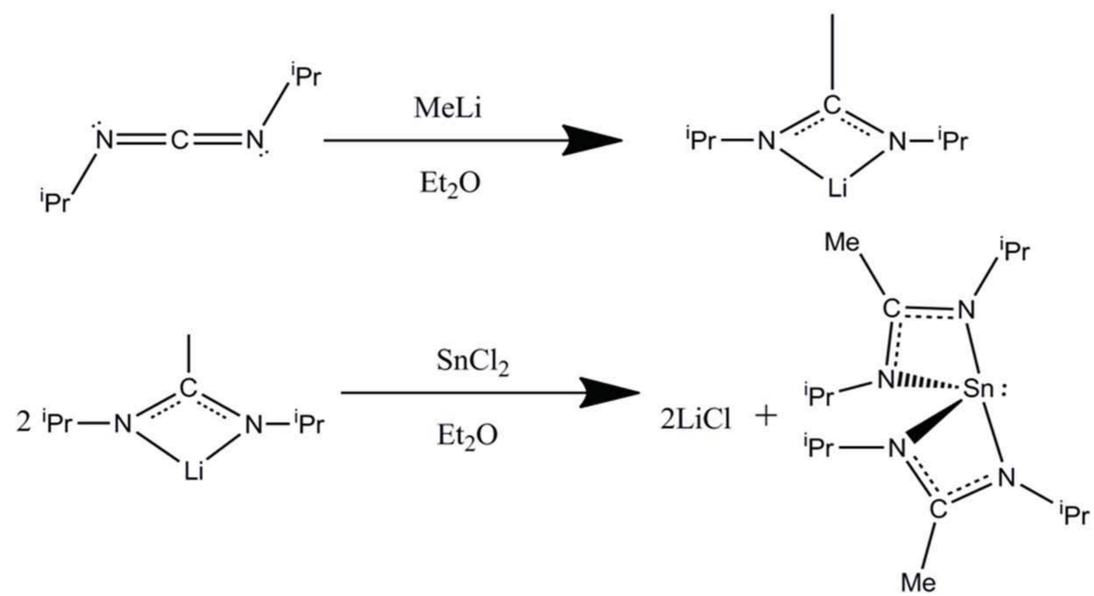
## SnS has some of these properties.

- 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 $^oC$ range @ ~ 300 $^oC$)

# SnS Thin Film from ALD

Atomic Layer Deposition

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

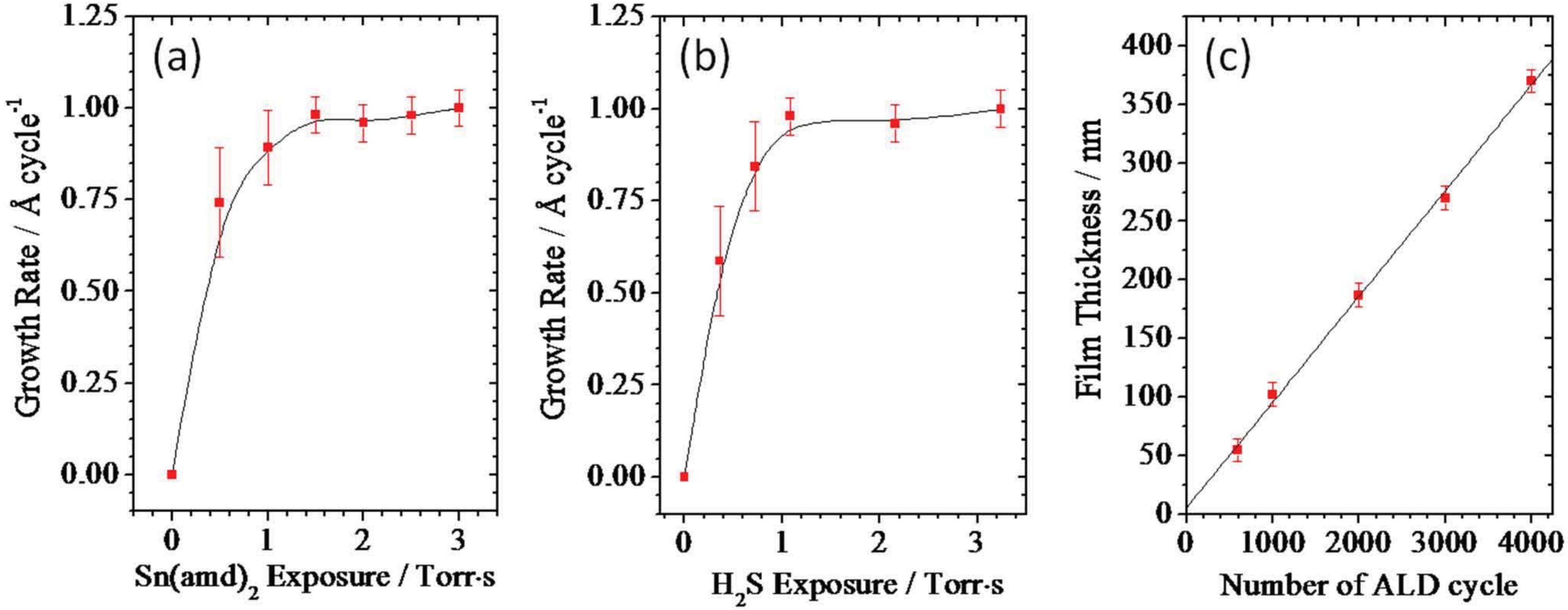



$Sn(amd)_2$ precursor

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

$Sn(amd)_2 + H_2S \rightarrow SnS$

# ALD Growth Behavior

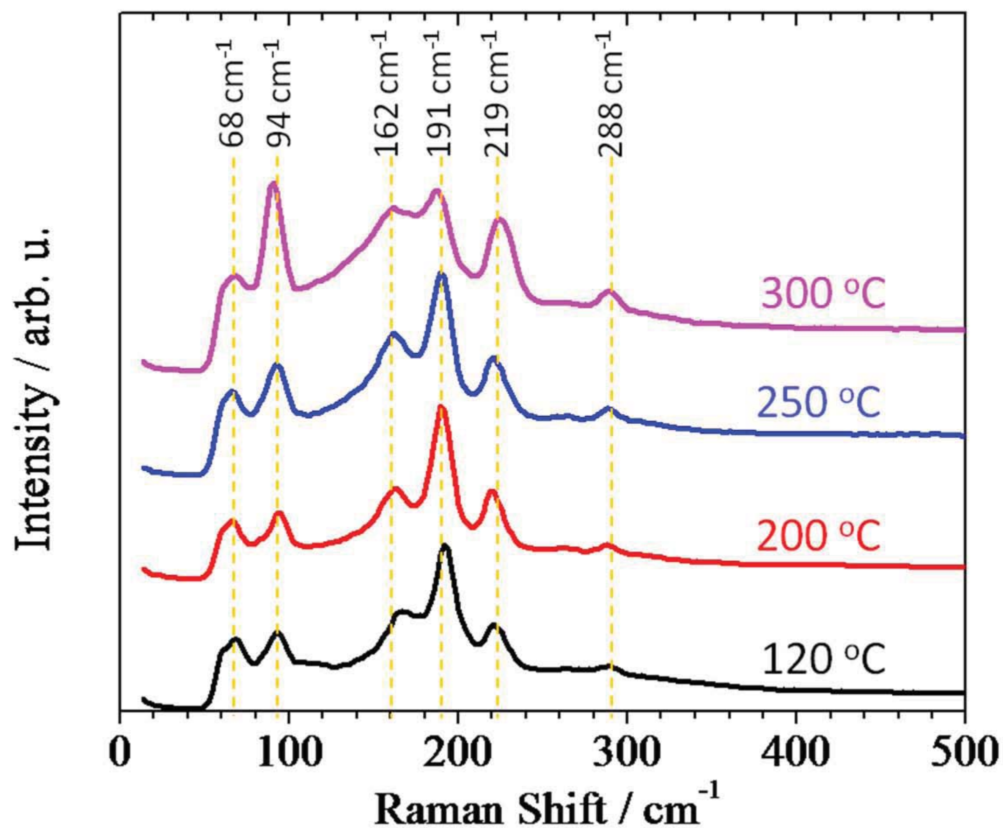



❖ Minimum exposures of 1.5 Torr·s of $Sn(amd)_2$ and 1.1 Torr·s of $H_2S$ are required to saturate the surface reactions

❖ Growth rate of 0.90 Å/cycle (120 $^oC$)

# Pure SnS Phase

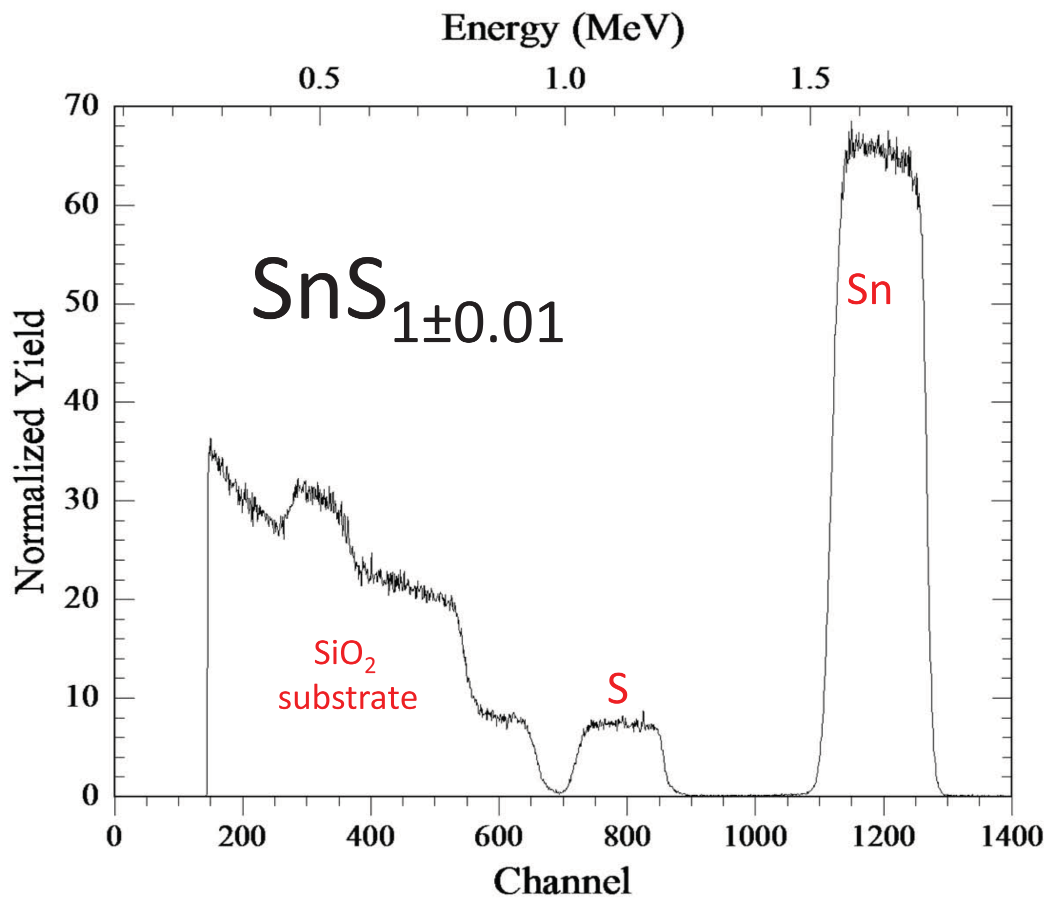
## Raman Spectroscopy




- Not detect other binary phase (*e.g.* $SnS_2$ and $Sn_2S_3$).
- Wide deposition temperature window .

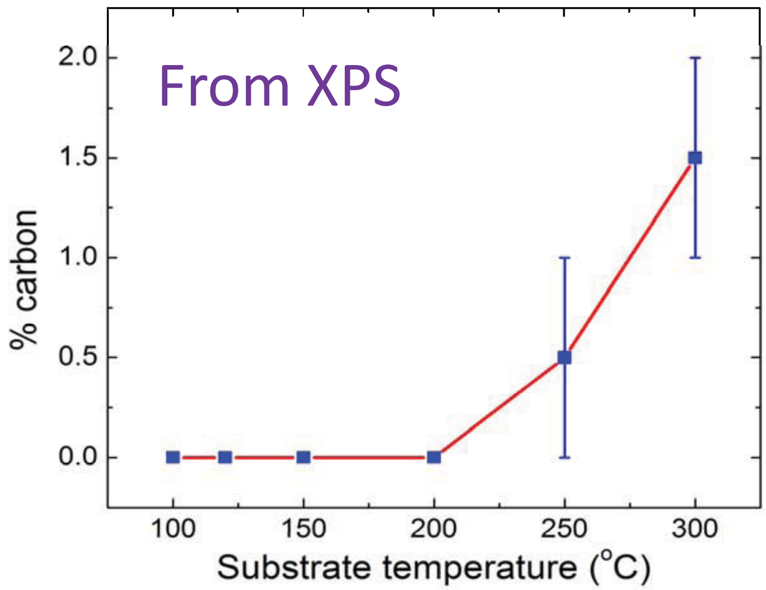
# Film Composition

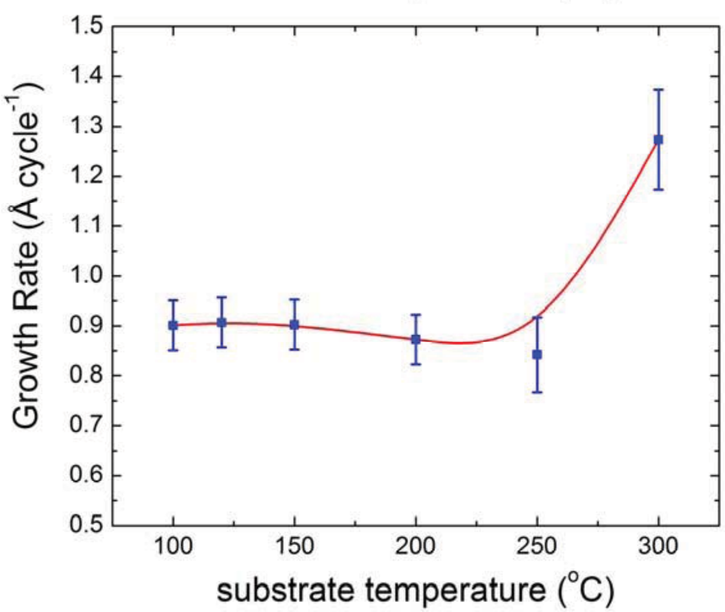
## Rutherford  Backscattering Spectroscopy (RBS)



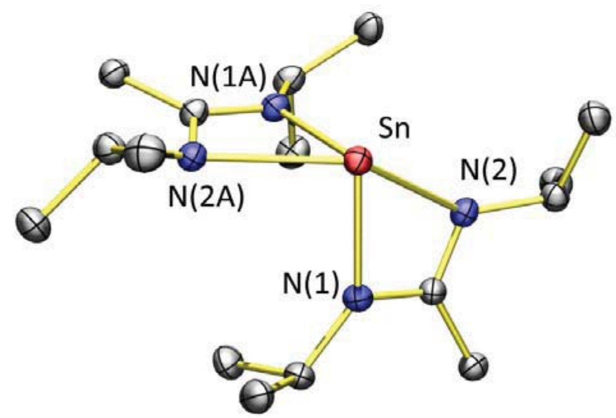

- Stoichiometric SnS (Low $Sn^{+2}$ vacancy) below 200 $^{o}C$
- Density ~ 4.6 $g/cm^3$ (~ 90% of bulk value)

# Impurity



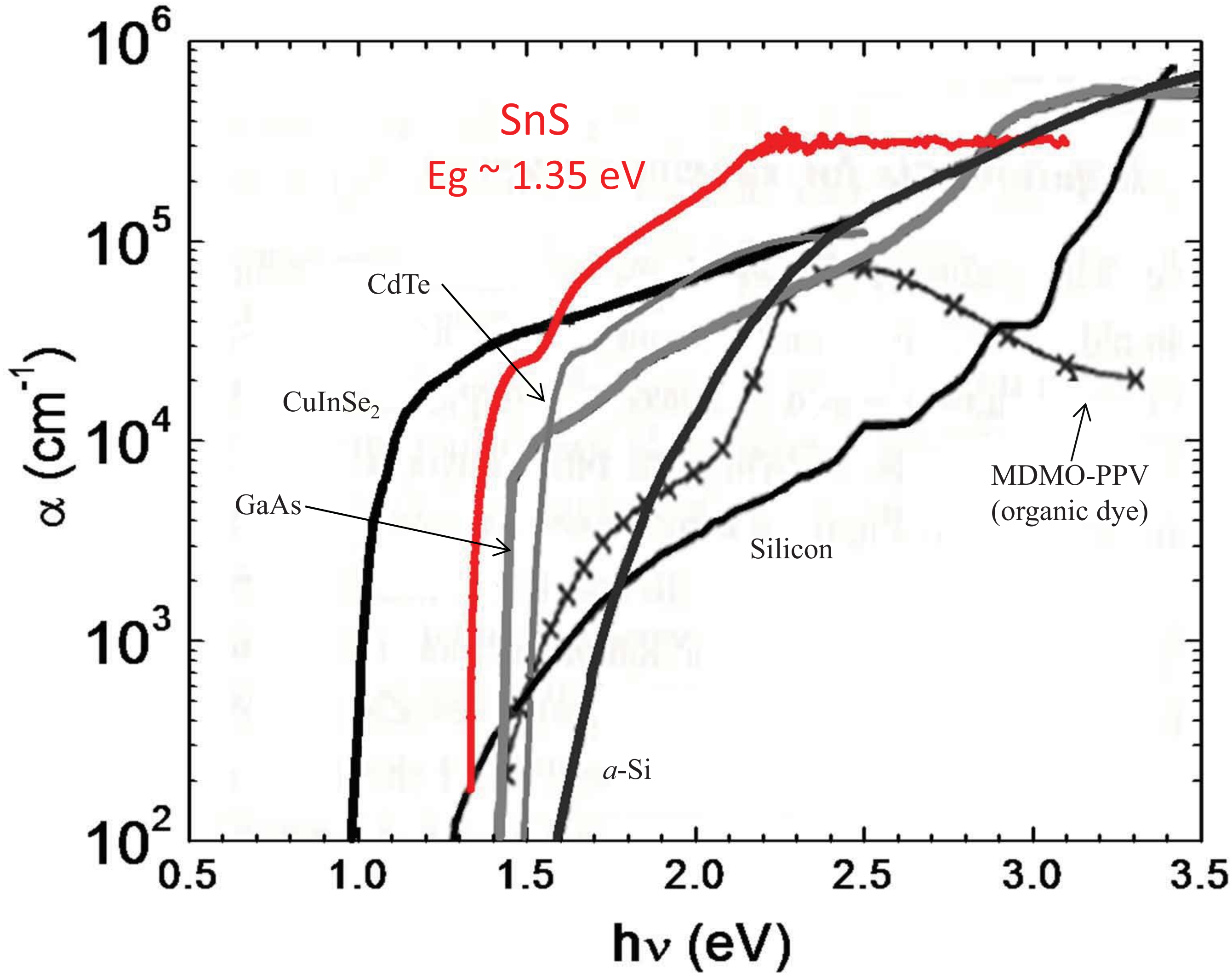




- No carbon, nitrogen, or oxygen detected on SnS film deposited below 200 °C. (SIM)
- ~ 1-2% carbon contamination on film deposited above 250 °C.




$Sn(amd)_2$ starts to decompose above 250 °C.

# Optical Property



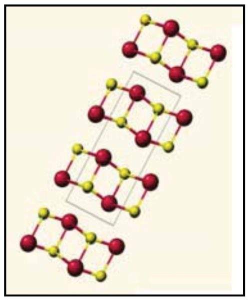

$\alpha \sim 10^5\ cm^{-1} \rightarrow$ Need ~ 500 nm for 95% absorption



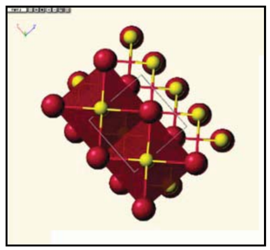
Nelson, J. The Physics of Solar Cells; Imperial College Press

# Crystal Structure

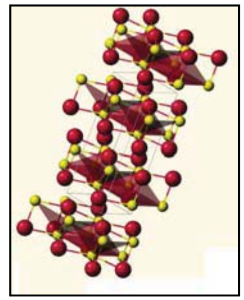
Orthorhombic Structure ( $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^o$ )



Side view

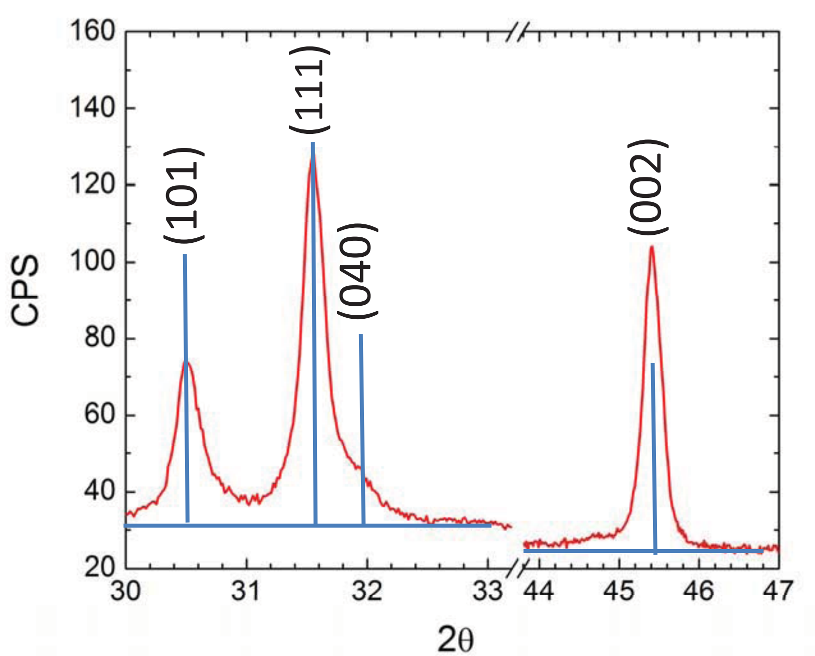


Top view along b axis



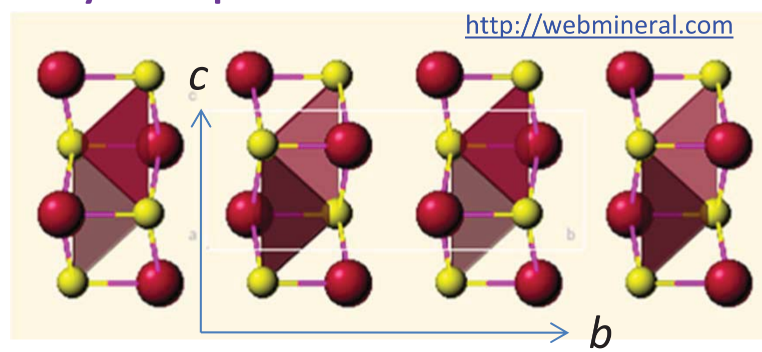
a = 4.28, b = 11.20, c = 3.99 Å

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




## crystal preferred orientation

http://webmineral.com




➢ Desirable crystal orientation.

❖ higher mobility through the film.
(Single crystal: $\mu_{//} / \mu_{\perp} \sim 10.$)*

❖ carrier transport along defect-tolerant layer plane

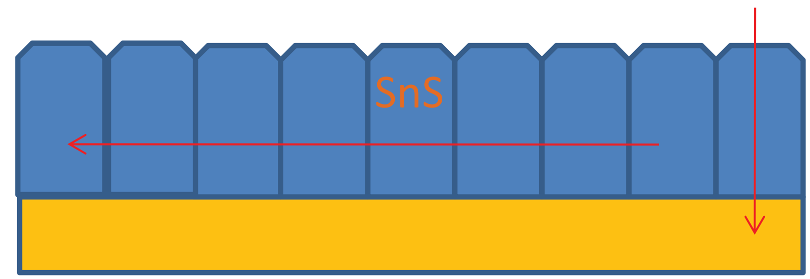


*Nassary, M.M., Journal of Alloys and Compounds, 2005. **398**(1-2): p. 21-25.

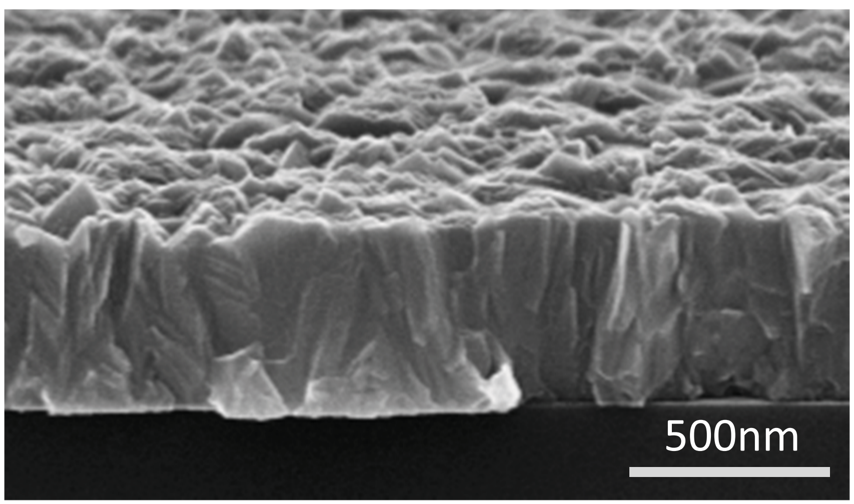
# Electrical Property

- Hall measurement
  - lateral resistivity ρ ~ 10 – 900 Ω•cm
  - low hole concentration ~ $10^{16}$ $cm^{-3}$
    - few $Sn^{+2}$ vacancies
    - wide depletion region in p-n junction
  - lateral hole mobility ~ 1-4 $cm^2$ $V^{-1}$ $s^{-1}$

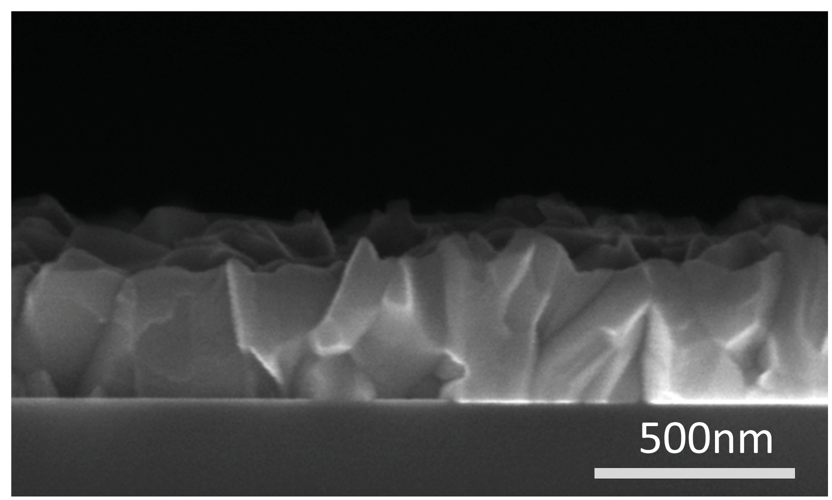
Columnar structure




- $\sigma_{vertical}$ / $\sigma_{lateral}$ ~ 3
  - lower scattering from grain boundary
  - higher mobility along crystal layer planes



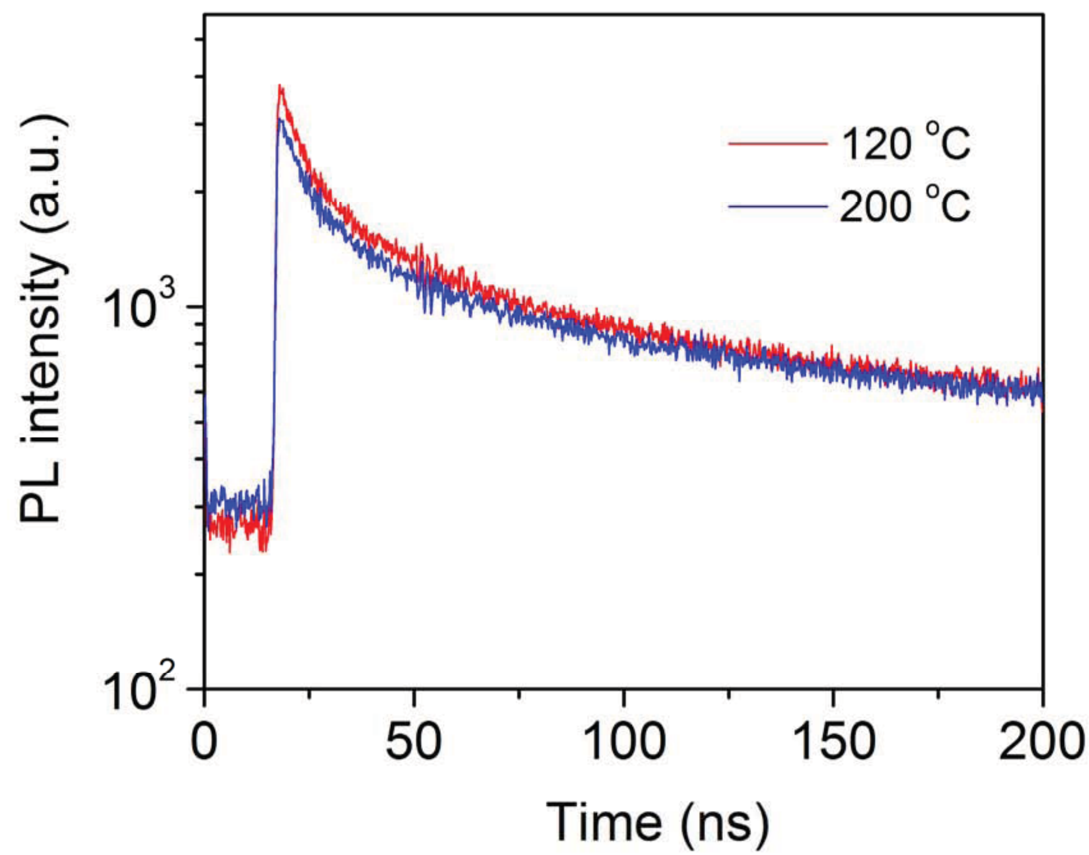

Tsub = 120 °C




Tsub = 200 °C

# Minority Carrier Lifetime

## Time-Resolved Photoluminescence




- Minority carrier lifetime ~ 90 ns
- Estimated minority carrier diffusion length ~ 1.5 μm

# 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 $H_2S$.

- ✓ 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.

- ✓ Eg = 1.35 eV with $\alpha > 10^5$ cm-1
- ✓ [p] ~ $10^{16}$ $cm^{-3}$ with $\mu_p$ ~ 1 - 4 $cm^2V^{-1}s^{-1}$
- ✓ ~ 3x higher mobility through the film due to columnar structure and crystal orientation
- ✓ long minority carrier lifetime (~ 90 ns)

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