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ALD of Tin Monosulfide, SnS

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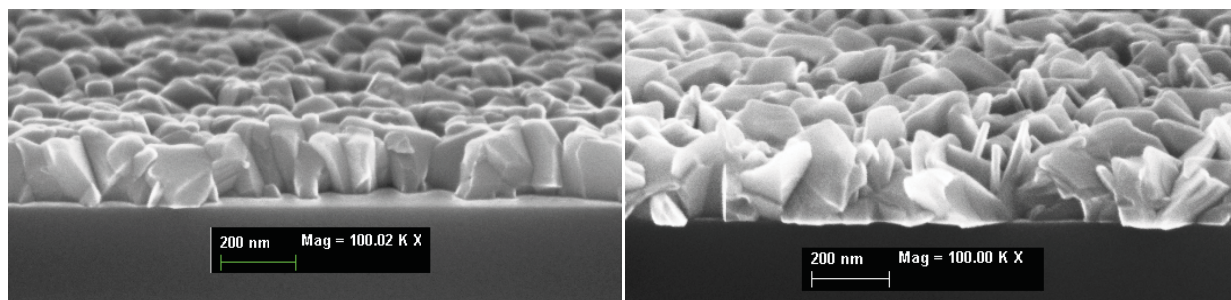
ALD of Tin Monosulfide, SnS

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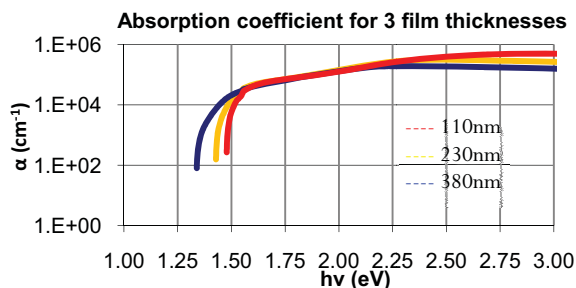
*Email: Gordon@chemistry.harvard.edu

We present a new process for ALD of tin(II) sulfide, SnS, from H₂S and a novel tin source that will be presented at the conference. The process operates at low substrate temperatures, in the range from about 100 to 250 °C. No impurities were detected in the deposited material by XPS or RBS. The films are stoichiometric to within the measuring accuracy of RBS, about $\pm 1\%$. The phase corresponds to the orthorhombic structure normally found in the bulk material (as in the mineral Herzenbergite), although under certain conditions a minor amount of a cubic phase is also detected by X-ray and electron diffraction. The morphology of the films varies from dense equiaxed columnar polycrystalline films to loosely packed plates, depending on the substrate and growth conditions. The SnS films are semiconducting with lightly p-type doping (10^{15} to 10^{16} holes cm^{-3} and hole mobility $> 6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). The films also show strong photoconductivity. Their optical band gap is about 1.3 eV, which is nearly optimum for solar cells with maximum efficiency. The optical absorption is very strong (over 10^5 cm^{-1} in the visible spectrum and over 10^4 cm^{-1} in the near infrared). Thus a very small thickness, less than 0.5 micron, is sufficient to absorb most of the solar spectrum. These properties make SnS a good candidate for the absorber material in thin-film solar cells made of earth-abundant and non-toxic materials.



equiaxed columnar grains

platelets



ALD of Tin Monosulfide, SnS

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Outline

Thin-film solar cells
the need for solar power
earth-abundant, non-toxic absorber: SnS

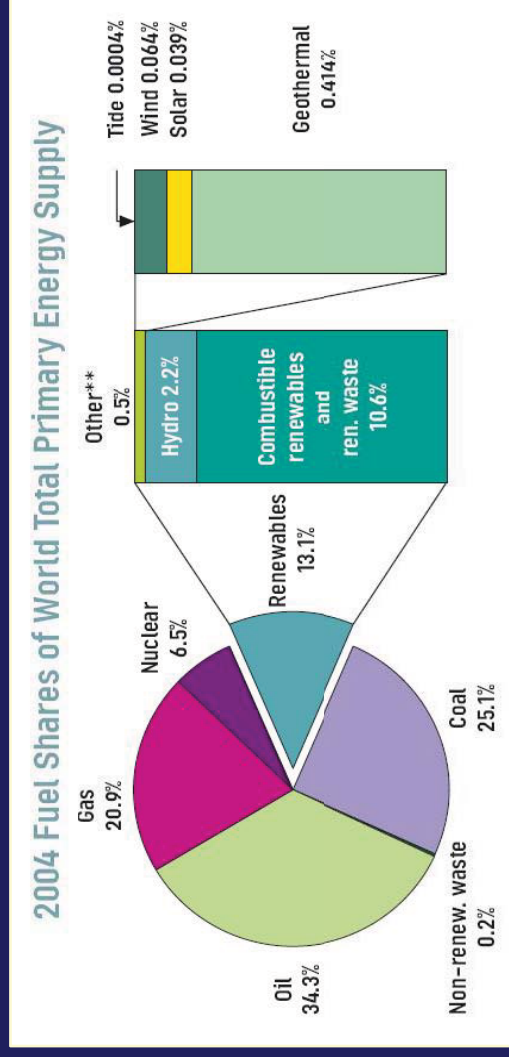
ALD process for SnS
new tin precursor
growth per cycle

SnS film properties
composition
structure
optical properties
electrical properties

Global Energy Use by Humans



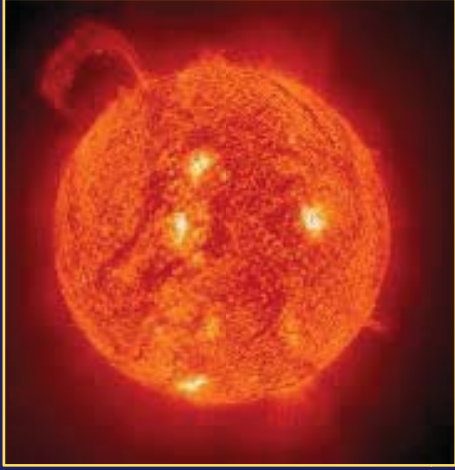
Human energy use is currently ~ 14 terawatts (14×10^{12} watts)



Source: International Energy Agency (IEA)

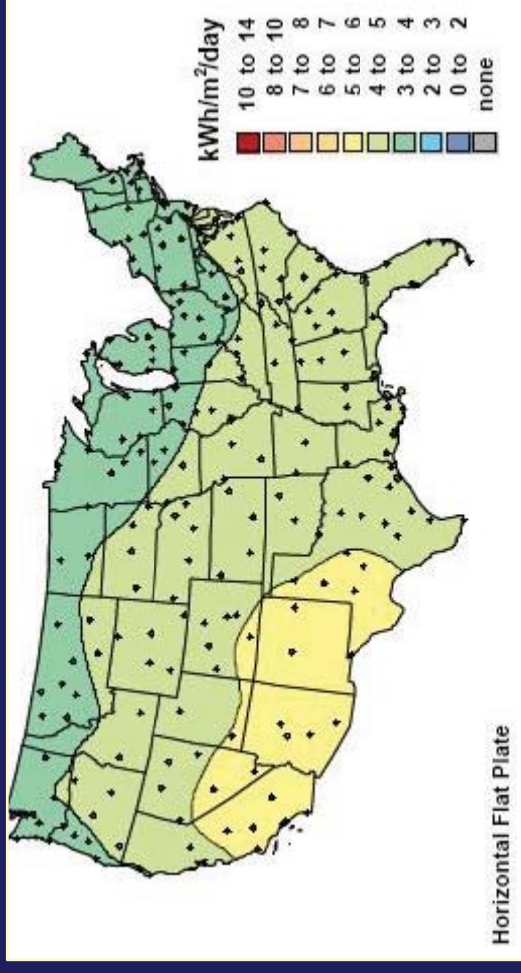
Current energy supply is unsustainable-environmentally, economically & socially

Solar Radiation on Earth



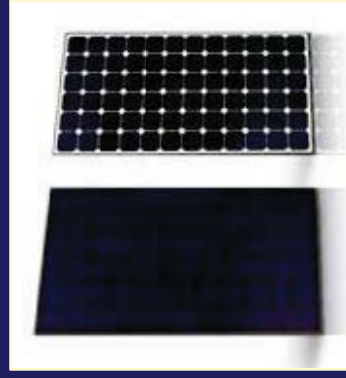
Solar power is by far our most available energy source.
average solar radiation at Earth's surface $\sim 0.2 \text{ kW/m}^2$

The Earth's land area receives
 $(1.5 \times 10^{14} \text{ m}^2) \times (0.2 \text{ kW/m}^2) \sim 3 \times 10^4 \text{ TW}$
15% efficient solar modules on 0.3%
of the Earth's total land area $\Rightarrow 14 \text{ TW}$



Flat-Panel Photovoltaic Modules

Absorber Material	Commercial PV Efficiency	Advantages	Limitations
crystalline Si	15-20%	high efficiency	high manufacturing cost
amorphous silicon, a-Si	5.3-6.3%	low cost, flexible substrates	slow deposition, low efficiency
copper indium gallium diselenide (CIGS)	8.1-11.0%	low cost, moderate efficiency	rare elements (Ga, In)
cadmium telluride, CdTe	10.4%	low cost, moderate efficiency	toxic Cd, rare element Te
Dye-sensitized cells	-	potential for lowest cost	long term instability



c-Si PV module
(SunPower Inc.)



a-Si PV module
(Uni-Solar Inc.)



CIGS PV module
(Global Solar Inc.)



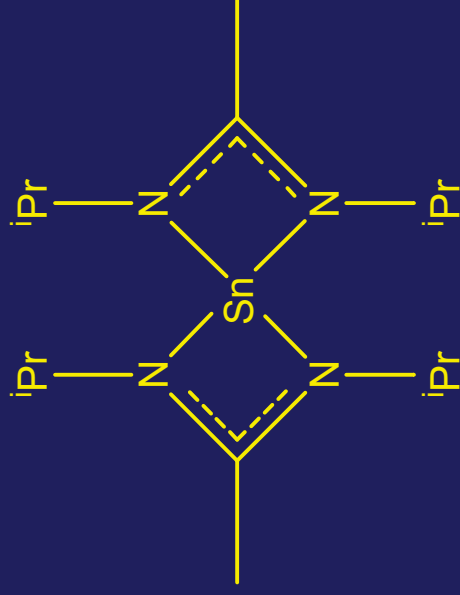
CdTe PV modules
(First Solar Inc.)

SnS: Alternate Absorber Layer in Solar PV

- ❖ Basic Criteria for the Absorber Material.
 - Suitable bandgap ($E_g \sim 1.0\text{-}1.5\text{ eV}$)
 - High quantum yield for the excited carriers
 - Long diffusion length / low combination velocity
 - PV efficiency
 - High optical absorption coefficient ($10^4\text{-} 10^5\text{ cm}^{-1}$)
 - small mass of material required
 - Constituent elements are non-toxic and abundant
 - non-hazardous, scalable, low cost PV

SnS has these properties

Tin(II) Amidinate as ALD Precursor



bis(*N,N'*-diisopropylacetamidinato)tin(II)

Sn-N bonds => reactive to H_2S

Chelate structure => thermal stability

Hydrocarbon ligands => volatility

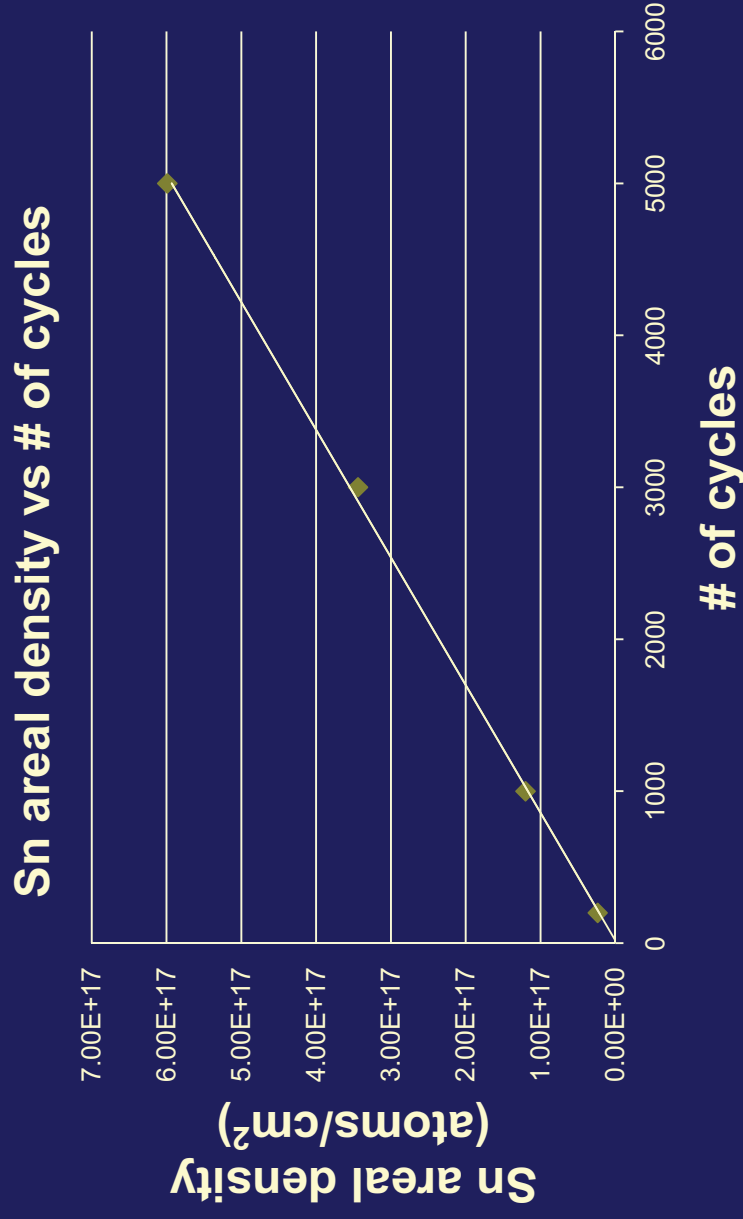
ALD Process for SnS

Source temperature: 90 °C

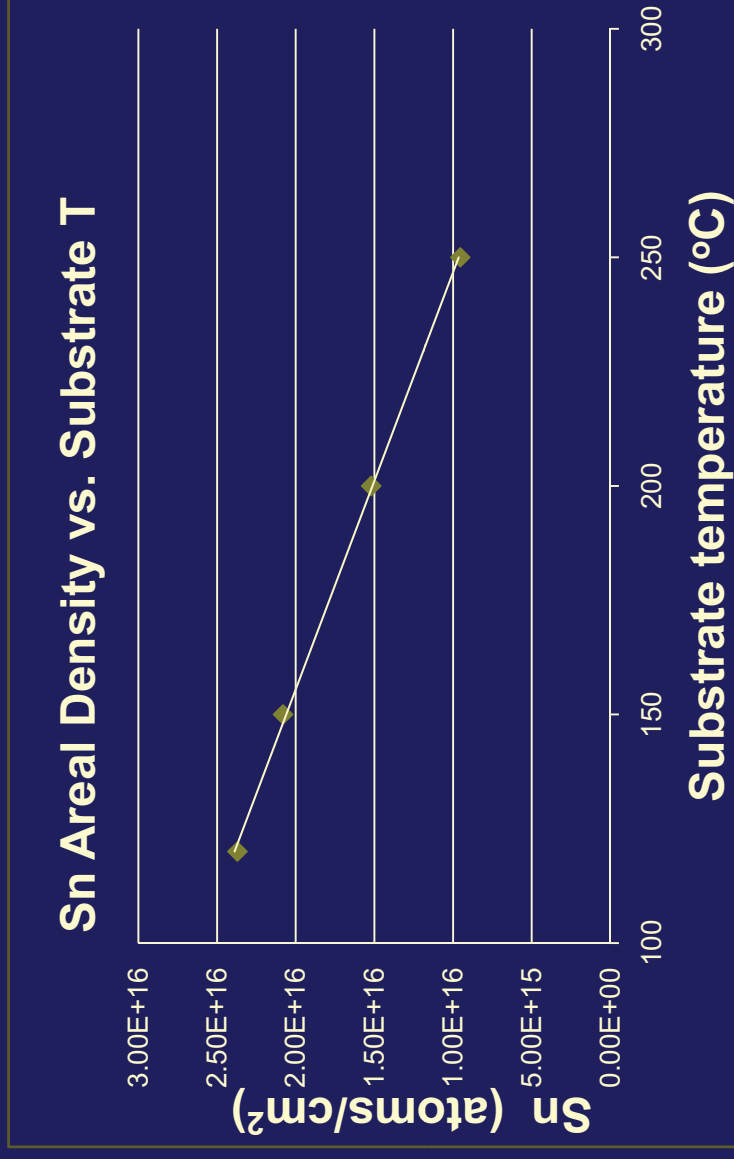
Substrate temperature: 120 °C

Growth per cycle: 0.08 nm

No induction period

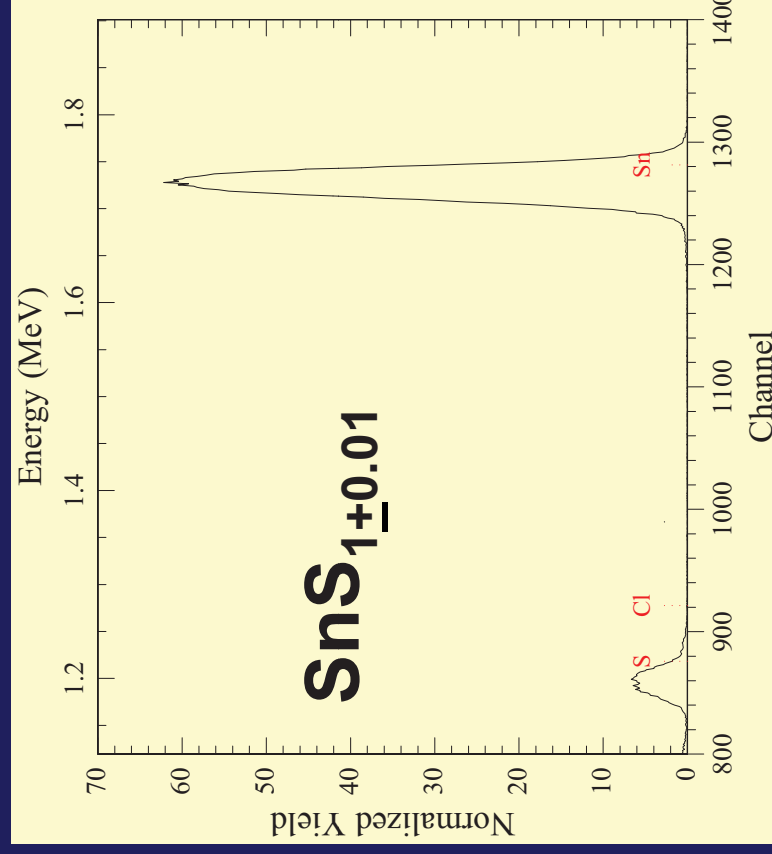


Temperature Dependence of Growth



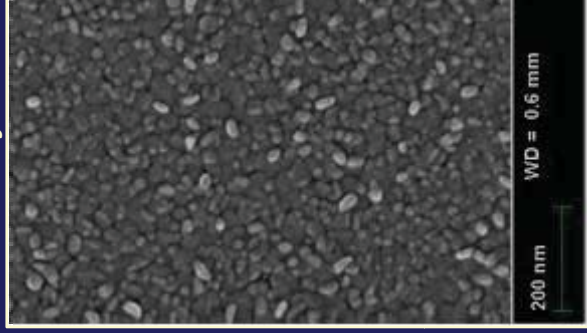
SnS Composition

Rutherford Backscattering Spectroscopy (RBS)

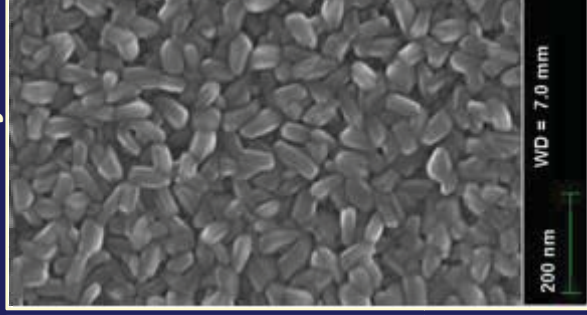


SEM of SnS Films Deposited at 120 °C

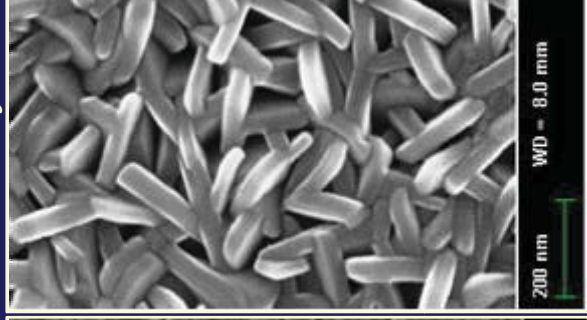
200 cycles



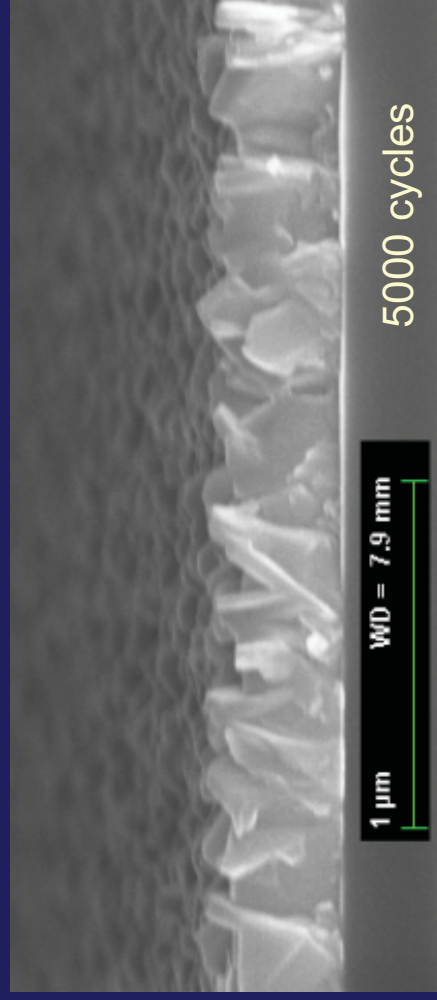
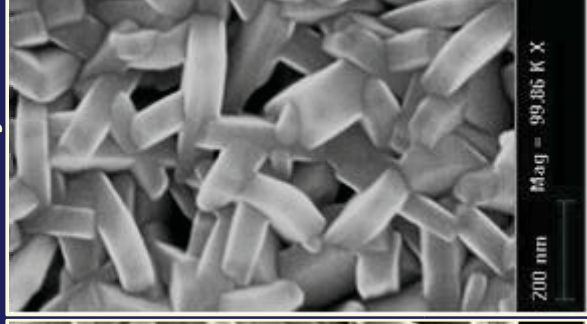
1000 cycles



3000 cycles

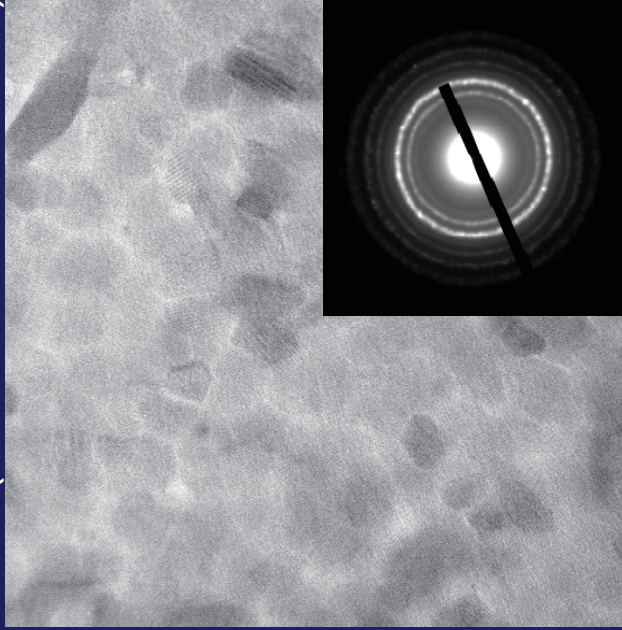


5000 cycles



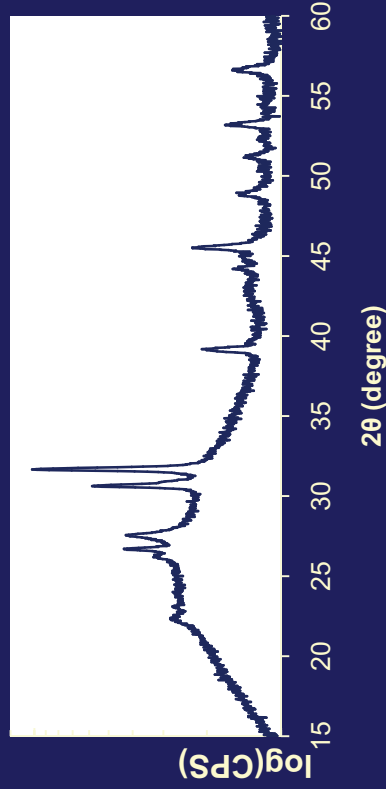
Distorted NaCl Structure of SnS Films

TEM (+electron diffraction)

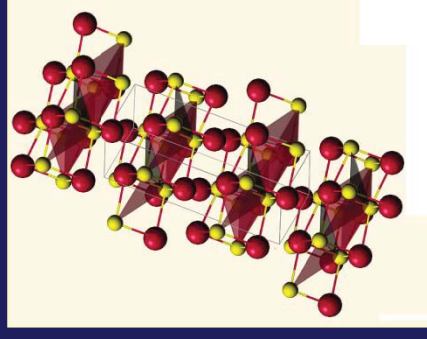
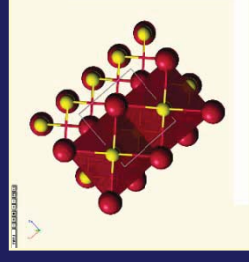
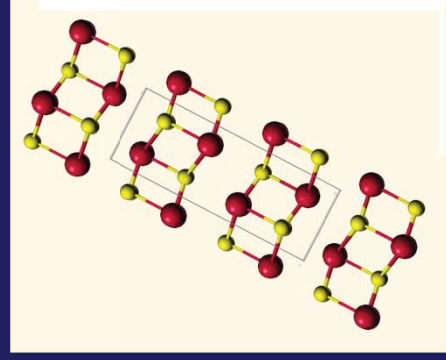


literature		XRD		TEM		Miller indices	
θ	d_{SnS} (Å)	d_{XRD} (Å)	d_{TEM} (Å)	d_{TEM} (Å)	hkl	hkl	hkl
22.01	4.035	4.001	3.87	3.87	110	110	
26.01	3.423	3.404	3.33	3.33	120	120	
27.47	3.244	3.243	-	-	021	021	
30.47	2.931	2.919	-	-	101	101	
31.53	2.835	2.823	2.84	2.84	111	111	
-	2.597	-	2.53	2.53	121	121	
39.05	2.305	2.302	2.29	2.29	131	131	
44.73	2.024	2.021	2.02	2.02	141	141	
45.49	1.9921	1.999	-	-	002	002	
51.31	1.7791	-	1.78	1.78	151	151	
53.15	1.7219	1.722	-	-	122	122	
56.67	1.6228	1.626	1.62	1.62	042	042	

X-Ray Diffraction (XRD)



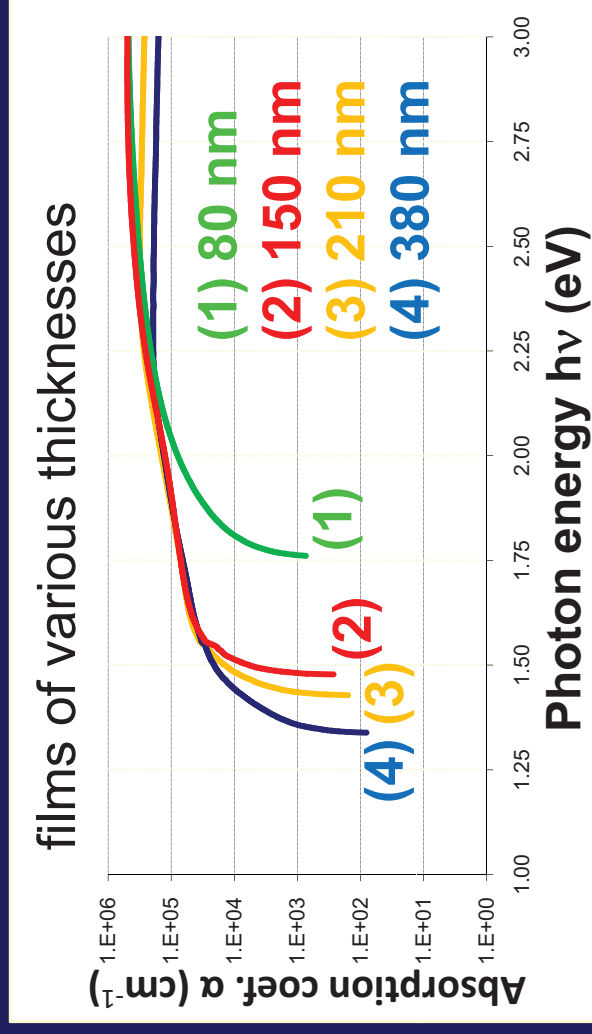
Orthorhombic Structure: $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$



Side view

Top view along b axis

SnS has Very Strong Optical Absorption



$\alpha > 10^4 \text{ cm}^{-1}$ for $> 1.4 \text{ eV}$

$\alpha > 10^5 \text{ cm}^{-1}$ for $> 2.0 \text{ eV}$

\Rightarrow Solar cell $< 1 \mu\text{m}$ thick

\Rightarrow little material needed

Band gap for thicker films $\sim 1.3 \text{ eV}$, optimum for solar cells

Band gap decreases with increasing film thickness

\Rightarrow large exciton diameter, small effective mass, high mobility

Electrical Properties

Undoped P-type by Hall measurements

hole concentration $\sim 10^{17} \text{ cm}^{-3}$

hole mobility $\sim 5\text{-}10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$

Properties similar to CdTe and CuInSe₂
currently used in thin-film solar cells

Summary

SnS is an absorber for earth-abundant, non-toxic solar cells

ALD from tin(II) amidinate and $\text{H}_2\text{S} \Rightarrow \text{SnS}$

pure, stoichiometric, polycrystalline SnS

optical and electrical properties suitable for thin solar cells

**ALD suitable for prototype deposition of solar cells
(well-controlled composition and structure)**

another possible application: thin-film transistors on plastic

Acknowledgements

Hall measurements done with Mark Winkler and Eric Mazur

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