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 ± 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 (10¹⁵ to 10¹⁶ holes cm⁻³ and hole mobility > 6 cm² V⁻¹ 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 10⁵ cm⁻¹ in the visible spectrum and over 10⁴ 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.
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 x 10^{12} watts)

Current energy supply is unsustainable-environmentally, economically & socially

Source: International Energy Agency (IEA)

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Solar Radiation on Earth

Solar power is by far our most available energy source.
average solar radiation at Earth’s surface ~ 0.2 kW/m²

The Earth’s land area receives

\( (1.5 \times 10^{14} \text{ m}^2) \times (0.2 \text{ kW/m}^2) \approx 3 \times 10^{14} \text{ TW} \)

15% efficient solar modules on 0.3%
of the Earth’s total land area => 14 TW
# Flat-Panel Photovoltaic Modules

## Absorber Material

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

## Commercial PV Modules

- 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 (Eg ~ 1.0-1.5 eV)
  - High quantum yield for the excited carriers
  - Long diffusion length / low combination velocity
  - PV efficiency
  - High optical absorption coefficient (10^4-10^5 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

\[
\text{bis}(N,N’\text{-diisopropylacetamidinato})\text{tin}(\text{II})
\]

Sn-N bonds => reactive to \( \text{H}_2\text{S} \)

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

Sn areal density vs # of cycles

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Temperature Dependence of Growth

Sn Areal Density vs. Substrate T

- Sn (atoms/cm²)
- Substrate temperature (°C)

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SnS Composition

Rutherford Backscattering Spectroscopy (RBS)

![Graph showing energy (MeV) versus normalized yield, with peaks for SnS and Cl.]

SnS$_{1+0.01}$
SEM of SnS Films Deposited at 120 °C

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Distorted NaCl Structure of SnS Films

TEM (+electron diffraction)

<table>
<thead>
<tr>
<th>Literature</th>
<th>XRD</th>
<th>TEM</th>
<th>Miller indices</th>
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</table>

X-Ray Diffraction (XRD)

Orthorhombic Structure: a ≠ b ≠ c and α = β = γ = 90°
SnS has Very Strong Optical Absorption

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

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

\[ \Rightarrow \text{ Solar cell } < 1 \text{ \( \mu \)m thick} \]

\[ \Rightarrow \text{ little material needed} \]

Band gap for thicker films ~ 1.3 eV, optimum for solar cells

Band gap decreases with increasing film thickness

=> large exciton diameter, small effective mass, high mobility

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Electrical Properties

Undoped P-type by Hall measurements

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

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

Properties similar to CdTe and CuInSe$_2$ 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 H$_2$S $\Rightarrow$ 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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