Atomic Layer Deposition of Tin(II) Sulfide

Prasert Sinsermsuksakul,
Jaeyeong Heo, and Roy G. Gordon

Department of Chemistry and Chemical Biology
Harvard University
Current Thin Film Solar Cells

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

Cu(In,Ga)(Se,S)₂ (CIGS)  
Highest energy conversion efficiency of ~20%

CdTe 2-8μm

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td></td>
</tr>
<tr>
<td>SnO₂Cd₂SnO₄</td>
<td>0.2-0.5μm</td>
</tr>
<tr>
<td>CdS</td>
<td>600-2000Å</td>
</tr>
<tr>
<td>CdTe</td>
<td>2-8μm</td>
</tr>
<tr>
<td>C-Paste with Cu, or Metals</td>
<td></td>
</tr>
</tbody>
</table>

Advantage
- Low manufacturing cost
- Moderate efficiency

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

NREL
wikipedia
Alternate Absorber Layer in Solar PV

- Basic Criteria for the Absorber Material.
  - Suitable energy bandgap (\(\text{E}_g \sim 1.0-1.5\) eV).
  - High optical absorption coefficient (\(10^4-10^5\) \(\text{cm}^{-1}\)).
    → 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 (\(\text{SnS}_2\) and \(\text{Sn}_2\text{S}_3\))
  - Contamination from oxygen (CBD) and chlorine (CVD)
  - Large deviation from ideal stoichiometric SnS (tin vacancies)
  - Narrow deposition temperature window (25-50 °C range @ \(\sim 300\) °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

\[
\text{Sn(amd)₂} + \text{H}_2\text{S} \rightarrow \text{SnS}
\]
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)
Not detect other binary phase (e.g. SnS$_2$ and Sn$_2$S$_3$).
Wide deposition temperature window.
Film Composition

Rutherford Backscattering Spectroscopy (RBS)

- Stoichiometric SnS (Low Sn$^{+2}$ vacancy) below 200 °C
- Density ~ 4.6 g/cm$^3$ (~ 90% of bulk value)
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)\textsubscript{2} starts to decompose above 250 °C.
Optical Property

SnS
$E_g \sim 1.35$ eV

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

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

Orthorhombic Structure (a ≠ b ≠ c and α = β = γ = 90°)

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

Desirable crystal orientation.
- higher mobility through the film.
  (Single crystal: μ∥ / μ⊥ ~ 10.)*
- carrier transport along defect-tolerant layer plane

Electrically 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

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

Temperature Dependence

- $T_{\text{sub}} = 120 \, ^{\circ} \text{C}$
- $T_{\text{sub}} = 200 \, ^{\circ} \text{C}$
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$_2$S.
  - 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 $\mu_p \sim 1 - 4$ cm$^2$V$^{-1}$s$^{-1}$
  - $\sim 3x$ higher mobility through the film due to columnar structure and crystal orientation
  - long minority carrier lifetime ($\sim 90$ ns)
Acknowledgement

Prof. Roy G. Gordon

Precursor: Adam S. Hock and Wontae Noh

Reactor: Sheng Xu and Harish Bhandari

Colleagues: Jaeyeong Heo, Leizhi Sun, and Helen Park

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