Atomic Layer Deposition of Chalcogenide Thin Films

PUBLICATION REVIEW ON ULTRATECH ALD SYSTEMS

09.10.2015
Highlights

- Benefits of ALD for nano-manufacturing of chalcogenides
- Atomic level thickness control
- Deposition on 3D nanostructures using Expo Mode
- Control of composition in multicomponent sulfides
- Wide range of sulfides deposited by customers: Cu₂S, Sb₂S₃, In₂S₃, SnS, ZnS, PbS, Cu₂ZnSnS₄ for PVs
- MoS₂ for 2D materials
- CNT has extensive R&D and manufacturing experience with sulfides, e.g., Zn(O,S) and handling of H₂S
Introduction

- Great interest in sulfides for photovoltaics, photonics, catalysis
- Requires H₂S
- Chalcogenide photovoltaics
  - Absorber
    - band gaps and energy levels more suitable than oxides
    - 31-34% efficiency at 1-1.6eV
    - CZTS quaternary synthesized for first time
    - Cu₂S stabilized by thin ALD oxides
  - Buffer / Emitter
    - In₂S₃, ZnS, and CdS, and Zn(O,S)
- Energy Storage
  - Cu₂S / CNT cathodes @260 mA h g⁻¹
  - Li₂S @ 800 mA h g⁻¹
- Photonics
  - ZnS for TFEL displays (first ALD industrial application)


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**Single junction efficiency limits**

**ALD sulfide absorbers**

<table>
<thead>
<tr>
<th>sulfide</th>
<th>band gap (eV)</th>
<th>majority carrier</th>
<th>type</th>
<th>power eff. (%)</th>
<th>record eff. (%) Ref(s)</th>
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</thead>
<tbody>
<tr>
<td>CuInS₂</td>
<td>1.5</td>
<td>p-type</td>
<td>ETA</td>
<td>4</td>
<td>12, 35</td>
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<tr>
<td>CZTS</td>
<td>1.5</td>
<td>p-type</td>
<td>thin film</td>
<td>—</td>
<td>12.6, 21</td>
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<tr>
<td>CuₓS</td>
<td>1.2</td>
<td>p-type</td>
<td>ETA</td>
<td>&lt;0.1</td>
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<tr>
<td>SnS</td>
<td>1.3</td>
<td>p-type</td>
<td>thin film</td>
<td>4</td>
<td>4, 37, 38</td>
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<tr>
<td>PbS</td>
<td>0.4</td>
<td>p-type</td>
<td>QDSSC</td>
<td>0.6</td>
<td>6, 39</td>
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<tr>
<td>Sb₂S₃</td>
<td>1.7</td>
<td>p-type</td>
<td>thin film</td>
<td>5.8</td>
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<tr>
<td>CdS</td>
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<td>n-type</td>
<td>QDSSC</td>
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<tr>
<td>In₂S₃</td>
<td>2.1</td>
<td>n-type</td>
<td>ETA</td>
<td>0.4</td>
<td>3, 42</td>
</tr>
</tbody>
</table>

*Bold* denotes record power efficiency for any deposition method. ETA = extremely thin absorber. QDSSC = quantum-dot-sensitized solar cell.
CIGS - Photovoltaics

- Absorber / buffer / TCO combination determines spectral capture range
- Max efficiency to date at 20%
- Complex heterojunction, where buffer and absorber interface determine band bending and ultimate efficiency
- Buffer material, composition, optical properties, and film uniformity are crucial
ZnO\(_{1-x}\)S\(_x\) composition

Composition controlled by changing the number of ZnS/ZnO cycles in order to match given CIGS composition

![Graph showing Band Gap vs. x - composition of ZnO\(_{1-x}\)S\(_x\)](image)


**TEM cross-section of a CIGS cell with ALD grown Zn(O,S) buffer layer.**

**Quantum efficiency measurement**
Cu$_2$ZnSnS$_4$ (CZST)

- **Objectives**
  - Low cost semiconductor (CZST) for photovoltaic
  - 1.4 eV band gap, conformality in 3D
  - Compositional control of quaternary materials

- **Experimental**
  - Savannah S200, Expo, H$_2$S kit, 150°C
  - Cu$_2$S: Cu$_2$DBA (Strem) @ 160°C + 1% H$_2$S
  - SnS: TDMASn + 1% H$_2$S
  - ZnS: DEZ + 1% H$_2$S
  - 2 strategies: trilayers and nanolaminates

Thimsen et al., Chemistry of Materials, 24(16), 3188–3196 (2012). doi:10.1021/cm3015463
Interface and composition profile in CZST

Cu$_2$S cathode for LIB

- **Objectives**
  - Cu$_2$S deposited on single wall carbon nanotubes

- **Experimental**
  - Savannah S200 at 135°C, expo mode
  - CuAMD (150°C) and 1% H$_2$S
  - SWCNT functionalized with 9min O$_3$

- **Results**
  - Core-shell SWCNT-n-Cu$_2$S exhibits high charge discharge/stability
  - high capacity (260mA/g)
  - >99% Coulombic efficiency

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Stabilization of Cu$_2$S for PVs

- Cu$_2$S PV absorber
  - abundant, non toxic, absorption $>1$E4 cm$^{-1}$
- Issue with Cu$_2$S/CdS junction due to Cu diffusion
- S200 for Cu$_2$S from CuAMD/H$_2$S @145°C
- TiO$_2$ ALD used as Cu diffusion barrier and n-type emitter to replace CdS
- 1-2 Al$_2$O$_3$ cycles reduce carrier concentration and stabilize film for >2 weeks

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In$_2$S$_3$ ALD

- Chalcogenide PV to replace CdS
- In(amd)$_3$ and H$_2$S in S200
- Self-limited ALD up to 225°C
- 0.89Å / cycle @ 150°C
- No detectable C, N, O halogen (RBS/AES)


Mass Gain during In(amd)$_3$ / H$_2$S cycles

Absorption coefficient at varying dep. temperatures

Impact of process temperature on n-type In$_2$S$_3$
**Sulfide work done on Ultratech CNT ALD systems**


