Atomic layer deposited Indium oxy-sulfide on CZT(S,Se) absorbers

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Outline

- Motivation
- ALD of In$_2$S$_3$ thin films
- Band alignment studies and need for In$_2$(O,S)$_3$
- ALD of In$_2$O$_3$ thin films
- Tuning S:O ratio in In$_2$(O,S)$_3$
- Summary
Relative progress of CZTS Solar Cell Efficiency

Strategies for higher efficiency:

- More stable buffer layer than CdS to avoid interdiffusion
- More reflective back contact to increase current
- Lower recombination at back contact to increase voltage
Why Replace CdS buffer with $\text{In}_2(\text{O,S})_3$?

Problems with Chemical bath deposited (CBD) CdS

- Toxicity of Cadmium
- Presence of uncontrolled oxygen content
- In a superstrate configuration Cd$^{2+}$ ions diffuse during high-temperature anneal

Solution: Atomic Layer Deposited (ALD) S:O tunable $\text{In}_2(\text{O,S})_3$

- Non-toxic $\text{In}_2(\text{O,S})_3$ can have good band alignment with CZTS$^1$
- Control over in-situ Oxygen content => tunable conduction band offset
- Diffusion of In$^{3+}$ is slower than Cd$^{2+}$, enabling a superstrate configuration with a more efficient back contact made as the last step

A new indium formamidinate precursor with $\text{H}_2\text{S}$ provides **low-temperature, carbon-free** ALD of $\text{In}_2\text{S}_3$

Newly synthesized tris($N,N'$-diisopropylformamidinato)indium precursor vaporized at 130 °C

ALD $\text{In}_2\text{S}_3$ films grow at 0.65 Å/cycle on substrates at 150 °C have negligible contamination by carbon, nitrogen or oxygen
ALD provides In(S,O)$_3$ with good band alignment (oxygen results from post-ALD diffusion)

CZTS, Se

0.15 eV Spike

In$_x$(S,O)$_y$

0.6 eV

E$_F$

0.5 eV

B.B = 0.375 eV

1.2 eV

C.B.

1.95 eV

V.B.

In$_x$(S,O)$_y$ / CZT(S,Se)

BB = 375 meV

1.2 eV

Counts

Binding Energy (eV)

Ultraviolet Photoelectron Spec

UV-VIS Spec Photometry
ALD In$_2$O$_3$ from indium formamidinate and H$_2$O

Indium oxide ALD growth window using a newly synthesized, highly volatile indium formamidinate precursor (1).

- Low carbon (which contaminated In$_2$(acac)$_3$ films), no oxygen or nitrogen contamination
- Reduced copper diffusion during ALD (in substrate configuration), because deposition time is shorter than with In$_2$(acac)$_3$
ALD of ternary $\text{In}_2(\text{O},\text{S})_3$ with tunable S:O

ALD at 210 °C substrate temperature
Indium Formamidinate-$\text{H}_2\text{S}$ cycle followed by Indium Formamidinate-$\text{H}_2\text{O}$
Reactivity of Indium Formamidinate with $\text{H}_2\text{S}$ roughly twice that of $\text{H}_2\text{O}$

X-Ray Photoelectron Spectroscopy Results

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic % after ~ 120 sec Ar etch</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1:1 In-$\text{H}_2\text{S}$ to In-\text{H}_2\text{O} Ratio</td>
</tr>
<tr>
<td>In</td>
<td>43.2</td>
</tr>
<tr>
<td>S</td>
<td>36.2</td>
</tr>
<tr>
<td>O</td>
<td>20.6</td>
</tr>
<tr>
<td>C</td>
<td>&lt; 1%</td>
</tr>
<tr>
<td>N</td>
<td>&lt; 1%</td>
</tr>
</tbody>
</table>
Motivation to target Superstrate v/s the Substrate Configuration for CZT(S,Se) Cells

Substrate
- Ni/Al
- ITO
- ZnO shunt protector
- CdS (0 - 25 nm, CBD)
> 2 μm CZT(S,Se)
- Mo coated glass

Superstrate
- Reflective Back Contact => higher current
- Selective Hole transport layer => higher voltage
- Thinner CZT(S,Se)
- CZT(S,Se) anneal temperature stable- In$_2$(O,S)$_3$ buffer
- CZT(S,Se) anneal temperature stable- shunt protector
- FTO coated glass

Wang et al. – Advanced energy Materials 2014, 4, 1301465
Summary

- ALD process conditions for pure, stoichiometric In$_2$S$_3$, In$_2$O$_3$ and In$_2$(O,S)$_3$
- In$_2$(O,S)$_3$ with high sulfur content identified as a promising choice for non-toxic buffer on CZTS,Se absorber with ideal conduction band offset
- ALD process for tunable S:O in In$_2$(O,S)$_3$ established
Thanks for your attention!

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Blowup of band edge region
CZTS, Se

Zn 3d
BB = -170 meV

S-3p

Cu-3d