Kesterite, Cu$_2$ZnSn(S,Se)$_4$, for earth abundant photovoltaics: 
can we make single phase thin films, and does it matter?

- Why earth abundant photovoltaics?
- Some properties of kesterites
- Synthesis methods
- The voltage challenge
- How to overcome the $V_{oc}$ challenge?

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Assumptions:
- 14% efficiency
- 2200 kWh/m²
→ 660 x 660 km²
≡ 6.1 \cdot 10^7 football pitches

[***] slide courtesy of Diego Colombara

Photovoltaic technologies

<table>
<thead>
<tr>
<th>Material</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic</td>
<td>11%</td>
</tr>
<tr>
<td>Silicon</td>
<td>26%</td>
</tr>
<tr>
<td>Inorganic</td>
<td>22%</td>
</tr>
<tr>
<td>III-V</td>
<td>38%</td>
</tr>
<tr>
<td>Perovskite</td>
<td>15%</td>
</tr>
<tr>
<td>Dye sensitized</td>
<td>12%</td>
</tr>
<tr>
<td>Cu(In,Ga)Se$_2$</td>
<td></td>
</tr>
<tr>
<td>CdTe</td>
<td></td>
</tr>
<tr>
<td>CdTe</td>
<td></td>
</tr>
</tbody>
</table>

Transmission electron micrograph done at TDK on an LPV solar cell.
Photovoltaic technologies

Silicon – 26 %

Inorganic – 22 %

Organic – 11 %

Perovskite – 20.1 %

III - V – 38 %

Liu, Johnston and Snaith
doi:10.1038/nature12509

http://www.light.t.u-tokyo.ac.jp

- Efficient, > 15 %
- Scalable, km²
- simple & quick to produce, $$$$$
- robust, > 20 yrs lifetime

Labotatory for Energy Materials
The need for Earth Abundant Thin Film Photovoltaics

Neither Cu(In,Ga)Se$_2$ nor CdTe is abundant enough for terrawatt deployment

2 TWp would be a few percent of the world power demand

Sn, Zn are more abundant than Ga and In

Neither Cu(In,Ga)Se$_2$ nor CdTe is abundant enough for terrawatt deployment

How do Photovoltaic Devices Work?

LOAD

p n
How do Photovoltaic Devices Work?

Power output = Current (absorption co-efficient) x Voltage (band gap)

Current is the number of electrons extracted
Voltage is the difference in quasi fermi levels

0.95 ev < $E_G$ < 1.6 eV

[1] NREL website
Properties of Cu$_2$ZnSn(S,Se)$_4$ CZTS

Grimm-Sommerfeld-Rule:
4 valence electrons/atom
→ „diamond structure“
Grimm, Sommerfeld
Zeitschrift f. Physik 36, 36 (1926)

Kesterite is a suitable replacement for CIGSe and is earth abundant

Efficiency vs Cumulative Publications from first device

Kesterite efficiency is below the learning curve – why?
What is limiting device performance?

[1,2] $E_G = 1.13$ eV

$J_{sc} = J_0 \exp \left( \frac{qV}{AK_BT} \right) \frac{1}{J_{sc}}$

$V_{oc}$ is limiting the device performance – why?

What is limiting kesterite $V_{oc}$?

$V_{oc} \sim \frac{A k_B T}{q} \ln \frac{J_{sc}}{J_0}$

$J_0$ is the reverse saturation current

All devices $E_G$ 1 – 1.2 eV

$V_{oc}$ is limited by recombination at defects and surfaces?

[1] (a) Unpublished data from Yasuhiro Aida, Alex Crossay, Valérie Depredurand, Susanne Siebentritt, Stefan Haass from EMPA, and IREC are gratefully acknowledged. (b) Literature references
What is limiting kesterite $V_{oc}$?

$V_{oc}$ is limited by multiple band gaps?

[1] Rau, Werner, Appl. Phys. Lett 84, 3735 (2004);
Composition and homogeneity are the key?

- Recombination in the bulk
- Secondary phases
- Differences in band gap
What makes the highest quality absorber? One step or two?
### Methodologies pursued

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Kesterite in</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metals + Chalcogen</td>
<td>1 step</td>
<td>co-evaporation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>monograin</td>
</tr>
</tbody>
</table>

Best process is two stage – all elements intimately mixed in precursor, no carbon residue

[1] Contains unpublished data from IREC and EMPA, IMRA – this conference
Best devices are not in the single phase region

Secondary phases can reduce short circuit current, and voltage.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Band gap (eV)</th>
<th>Effect on solar cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_{2-x}$Se</td>
<td>semi-metallic</td>
<td>shunting</td>
</tr>
<tr>
<td>ZnSe</td>
<td>2.7</td>
<td>reduces current</td>
</tr>
<tr>
<td>SnSe</td>
<td>0.95</td>
<td>reduces voltage</td>
</tr>
<tr>
<td>Cu$_2$SnSe$_3$</td>
<td>0.5 [3]</td>
<td>reduces voltage</td>
</tr>
</tbody>
</table>

Secondary phase formation due to CZTSe instability with gas phase

\[\text{Cu}_2\text{ZnSnSe}_4(s) \leftrightarrow \text{Cu}_2\text{Se}(s) + \text{ZnSe}(s) + \text{SnSe}(s) + 0.5\text{Se}_2(g)\]  

[1,2]

[adapted from 3]

Cu = red  
Zn = green  
Sn = blue

Secondary phase formation due to CZTSe instability with substrate

\[ 2\text{Cu}_2\text{ZnSnSe}_4 + \text{Mo} \rightarrow 2\text{Cu}_2\text{Se} + 2\text{ZnSe} + 2\text{SnSe} + \text{MoSe}_2 \]  

How to deal with secondary phases?

[1] Top surface – chemical etching


2Cu$_2$ZnSnSe$_4$ + Mo $\rightarrow$ 2Cu$_2$Se + 2ZnSe + 2SnSe + MoSe$_2$

Chemical etching removes secondary phases, barrier layers reduce formation

Composition and homogeneity are the key?

recombination in the bulk

Secondary phases

Differences in band gap

Cu$_2$ZnSnSe$_4$(s) ⇌ Cu$_2$Se$_{(s)}$ + ZnSe$_{(s)}$ + SnSe$_{(s)}$ + 0.5Se$_2$(g)
Defect states in the bulk

Sn heavily implicated for deep defects and thus high recombination

Composition and homogeneity are the key?

recombination in the bulk

Secondary phases

Differences in band gap

\[ \text{Cu}_2\text{ZnSnSe}_4(s) \rightleftharpoons \text{Cu}_2\text{Se}_{(s)} + \text{ZnSe}_{(s)} + \text{SnSe}_{(s)} + 0.5\text{Se}_2(g) \]
Voc deficit problem due to mixed band gaps

Three possible reasons for multiple band gaps at least!

1. Disordering of lattice
2. Chemical substitution
3. Chemical defects

Kesterite Summary on voltage loss mechanisms

\( J_0 \) is the reverse saturation current

\[ \text{Cu}_2\text{ZnSnSe}_4(s) \rightleftharpoons \text{Cu}_2\text{Se}(s) + \text{ZnSe}(s) + \text{SnSe}(s) + 0.5\text{Se}_2(g) \]
Time to panic? Not yet

- Uniform precursor deposition essential on a sub-micron scale
- Back contact is thermodynamically inert and provide ohmic contact
- Annealing atmosphere is controlled to avoid changes in composition
- Secondary phases only nucleate on the surface to be etched away
- Band gap grading is implemented like in Cu(In,Ga)Se$_2$
- Buffer and window layer optimization (more transparent in the IR)

role of grain boundaries and alkali dopants