Ge incorporated $\text{Cu}_2\text{ZnSnSe}_4$ thin-film solar cells

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Introduction – Kesterite solar cells

CZT(S)Se

- In, Ga → Zn, Sn
- High absorption coefficient
  - $\alpha > 10^4 \text{ cm}^{-1}$
- Using the earth abundant materials
- Production cost down
Introduction – Band gap tuning of kesterite thin films

Band gap tuning with S incorporation

Problems of S incorporation

- The control of $S/(S+Se)$ ratio is difficult due to the high volatility of the anionic components.
- Large $V_{OC}$ deficit ($E_g/q-V_{OC}$) with S incorporation
  - $CZTSe \approx 0.577 \text{ mV} \rightarrow CZTSSe \approx 0.647$, (at champion cells respectively)
  - Ex) CIGSe $\approx 0.5$
- Low FF
  - Low $V_{OC}$ and high ideality factor ($A$)
  - Secondary phase problems

$\sim 1.0 < E_g(CZT(S_xSe_{x-1})) < \sim 1.5 \text{ eV}$

Ge incorporated CZTSe (CZTGSe)

- Tunable band-gap using cationic element
  \[ \sim 1.0 < E_g(CZTGSe) < \sim 1.5 \text{eV} \] controlled by Ge/(Sn+Ge) ratio.
- Reduced \( V_{OC} \) deficit
- Large grain growth caused by GeSe\(_2\) liquid phase

![Graph showing the relationship between energy and (d\(\alpha/d\theta\))^2 \(\times 10^8 \text{(eV/cm)}^2\) for different Ge/(Sn+Ge) ratios.](image)

![SEM image of Ge incorporated CZTSe film with a scale bar of 1 \(\mu\)m.](image)
# I-V Results of Ge incorporated Cells

<table>
<thead>
<tr>
<th>Cell</th>
<th>Eff. (%)</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>$E_g$ (eV)</th>
<th>$E_g/q-V_{OC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZTGSSe Perdue Univ. (2013)</td>
<td>9.40</td>
<td>0.460</td>
<td>31.9</td>
<td>63.8</td>
<td>1.19</td>
<td>0.730</td>
</tr>
<tr>
<td>CZTGSSe AIST (2015)</td>
<td>10.03</td>
<td>0.543</td>
<td>29.5</td>
<td>62.7</td>
<td>1.19</td>
<td>0.647</td>
</tr>
<tr>
<td>CZTSe IREC (2015)</td>
<td>10.60</td>
<td>0.473</td>
<td>34.3</td>
<td>65.1</td>
<td>1.03</td>
<td>0.550</td>
</tr>
<tr>
<td>CZTGSSe Univ. of Washington (2016)</td>
<td>11.00</td>
<td>0.583</td>
<td>33.6</td>
<td>55.9</td>
<td>1.30</td>
<td>0.717</td>
</tr>
</tbody>
</table>

Experimental Procedure

Co-evaporation

As grown CZTGSe deposited by co-evaporation method.
Composition Control

Annealing

Sample

Internal gases flow

Annealing using two zone furnace

Grain Growth

CZTGSe solar cell structure

Al
AZO
i-ZnO
CdS
CZTGSe
Mo
SLG
New efficiency of Ge incorporated kesterite solar cell

- The highest efficiency of Ge incorporated kesterite solar cell greater than 12%
## Device parameters

<table>
<thead>
<tr>
<th>Cell</th>
<th>Eff. (%)</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>$R_s$ (Ω·cm$^2$)</th>
<th>$R_{sh}$ (Ω·cm$^2$)</th>
<th>$A$</th>
<th>$J_0$ (A/cm$^2$)</th>
<th>$E_g$ (eV)</th>
<th>$E_g/q$-$V_{OC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZTSSe IBM (2013)</td>
<td>12.60</td>
<td>0.513</td>
<td>35.2</td>
<td>0.698</td>
<td>0.72</td>
<td>621</td>
<td>1.45</td>
<td>7.0E-8</td>
<td>1.13</td>
<td>0.617</td>
</tr>
<tr>
<td>CZTGS Se AIST (2015)</td>
<td>10.03</td>
<td>0.543</td>
<td>29.5</td>
<td>0.627</td>
<td>0.20</td>
<td>694</td>
<td>2.49</td>
<td>6.3E-6</td>
<td>1.19</td>
<td>0.647</td>
</tr>
<tr>
<td>CZTGS Se AIST (2016)</td>
<td>12.32</td>
<td>0.527</td>
<td>32.2</td>
<td>0.727</td>
<td>0.36</td>
<td>1111</td>
<td>1.47</td>
<td>3.6E-8</td>
<td>1.11</td>
<td>0.583</td>
</tr>
</tbody>
</table>

- Highly improved fill factor over 0.7
- Reduced device parameters – $A$, $J_0$ and $V_{OC}$ deficit
  → Improved junction quality and reduced carrier recombination in SCR
Atomic ratio of CZTGSe thin films (EPMA)

Efficiency shows similar tendency with FF.

Optimized surface conditions are observed at Cu/Zn=1.9 and Zn/IV=1.2.
LifeTime measurement by TRPL

- Improved carrier life time
- PL peak is closed to the band edge position (≈0.03) – it may be beneficial effect in reducing $V_{OC}$ deficit

<table>
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<tr>
<th>Cell</th>
<th>Eff. (%)</th>
<th>Lifetime (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZTSSe IBM (2013)</td>
<td>12.60</td>
<td>6.7</td>
</tr>
<tr>
<td>CZTGSe AIST (2015)</td>
<td>10.03</td>
<td>2.5</td>
</tr>
<tr>
<td>CZTGSe AIST (2016)</td>
<td>12.32</td>
<td>5.6</td>
</tr>
</tbody>
</table>

$E_g = 1.1 \text{ eV}$

$E_{opt} = 1.08 \text{ eV}$
Summary

• We demonstrate new results of Ge incorporated kesterite thin-film solar cell.
  – High efficiency greater than 12%
  – Large improvement in FF over 0.7
  – Improved junction quality and reduced carrier recombination in SCR
    – $A$, $J_0$ and $V_{OC}$ deficit
  – Increased carrier life time
Thank you for your attention!