A steady rise of kesterite Solar Cells

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CIGS solar cell market

Light weight
Flexible /rigid
Better performance in weak light
Stable: serving long lifetime

Hanergy “Hantile”
Miasole: lightweight CIGS on factory rooftop
Miasole: lightweight CIGS on boat
Helios

Cut and fit into tiny shapes
Earth abundant and non-toxic kesterite CZTS
The manufacturing of CZTS solar cells

Current commercialized manufacturing for CIGS

Future up-scalable industrial scale for CZTS

From https://www.greentechmediwesoff
INNOVATION HIGHWAY: breakthrough milestones and key developments in CIGS

- NREL-certified 11% CZTS cell

- Cu2S is not stable!

- Power pack failure, substrate overheating!

- Running out of Boronsilicate glass!

- Accidental surprise!

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INNOVATION HIGHWAY: breakthrough milestones and key developments in CIGS and kesterite (CZTSSe and CZTS)
Challenges of CZTS solar cells: absorber

CIGS vs. CZTS

CIGS

Defect transition energy level

$V_{\text{Cu}}$ has a shallow acceptor level

Formamtion energy of $V_{\text{Cu}}$ is low

CZTS

Defect formation energy vs. Fermi energy

Formation energy of $V_{\text{Cu}}$ & In$_{\text{Cu}}$ are negative

Interfaces of CZTS solar cells

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

- ZnO, ITO - 2500Å
- CdS - 700Å
- CZTS - 1μm
- Mo - 0.5-1μm
- Glass, Metal Foil, Plastics
CZTS/Mo(S)_2 interface engineering


Accidental surprise!
CZTS/CdS interface
-sulfurization in a combined S and SnS atmosphere

- Suppress the Sn loss and remove the tens-nm sized small CZTS grains at the surface of CZTS absorber

- Realise localised “hetero-epitaxy” along the interface
  - (111)CdS II (112) CZTS & (002)CdS II (200) CZTS

• Crystalline defective hetero-interface (CdS side )
  - small size grains (a); extensive stacking faults and twins (b);

Interfaces of CZTS solar cells

Major losses/problems of CZTS solar cells (baseline efficiency >8%)

- Interfaces: Interface recombination
  - Back contact/bottom CZTS issue (UNSW, Liu F., Hao X., NPG Asia Materials (2017) 9, e401; doi:10.1038/am.2017.103)

- Bulk:
CZTS/CdS heterojunction interface engineering

UNSW, Kaiwen Sun, Xiaojing Hao et al., *Advanced Energy Materials* 6 (12), 1600046

- **Alternative ZnCdS buffer layer**

  - CdS
  - ZnCdS

  - Undesirable band alignment between CZTS/CdS;
  - Tunable band gap of ZnCdS;
  - Form favorable band alignment with CZTS.
Heterojunction heat treatment mainly affect Voc and FF

- Heat treatment at 270°C boosts the efficiency from ~8% up to 11%

CZTS/CdS heterojunction-heat treatment

- Heterojunction heat treatment mainly affect heterojunction region

<table>
<thead>
<tr>
<th>CZTS device</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>Eff(%)</th>
<th>$R_{S,L}$ (Ω cm$^2$)</th>
<th>$G_{s,L}$ (mS cm$^{-2}$)</th>
<th>A</th>
<th>$J_0$ (A/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W/o HT</td>
<td>672.5</td>
<td>20.65</td>
<td>56.29</td>
<td>7.82</td>
<td>4.40</td>
<td>0.56</td>
<td>2.61</td>
<td>$9.0 \times 10^{-7}$</td>
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<tr>
<td>With HT</td>
<td>730.6</td>
<td>21.74</td>
<td>69.27</td>
<td>11.01</td>
<td>2.58</td>
<td>0.98</td>
<td>1.44</td>
<td>$6.8 \times 10^{-11}$</td>
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</table>

Graphs showing $J_0$ and $J_{oc}$ values with and without heat treatment.

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CZTS/CdS heterojunction-heat treatment

- Reduced non-radiative recombination is mainly located at heterojunction region.
CZTS/CdS heterojunction-heat treatment

- Element inter-diffusion between CdS and CZTS: mainly Zn and Cd
CZTS/CdS heterojunction-heat treatment

- Buffer side: Zn diffusion into CdS- ZnxCd1-xS

Absorber side: possible Cu2ZnxCd1-xSnS4 phase

First principle calculations confirm the thermal-dynamical favorable formation of $\text{Cu}_2\text{Na}_{2-x}\text{ZnSnS}_4$ with low Na concentration ($X<0.4$).

Band alignment

- After HT, the Fermi Level gets closer to VBM.
- The CBO changed from (-0.13 eV) before HT to (-0.04 eV) after HT assuming Eg of CdS and CZTS unchanged.

Demonstrated 11% record efficiency sulphide kestertite CZTS solar cells.

What's next? - Innovation highway of kesterite

- Low conductivity

- Other deep level defects / defects clusters?

- $V_{Cu}$ or $Cu_{Zn}$

- $Sn$-related? $S$-related?

- $Cu_{Zn}$ disorder

- Benign grain boundary?
  - Passivation?

- $Cu_{Zn}$ disorder pinned Fermi level

- Defect Control

- Wrong bonds, dangling bonds
What's next? - Innovation highway of kesterite

Welcome more accidental surprise

 ultra thin Buffer & Window

<table>
<thead>
<tr>
<th>Material</th>
<th>η (%)</th>
<th>V_{OC} (mV)</th>
<th>J_{SC} (mA/cm^2)</th>
<th>FF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSnO</td>
<td>9.3</td>
<td>720</td>
<td>20.5</td>
<td>63.5</td>
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<tr>
<td>Al_{2}O_{3}</td>
<td>10.2</td>
<td>736</td>
<td>21.0</td>
<td>65.8</td>
</tr>
</tbody>
</table>

(Full Area)

Current density (mA/cm^2)
Voltage (V)

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UNSW
Fruitful exchange of ideas between labs globally

First Asia Pacific-European Kesterite workshop in 2017
(22 different countries in 5 continents)

First Asia-Pacific Kesterite workshop in 2018

Global competition & collaboration will make the kesterite to keep rising!

Continue on
2019, Xi’an, China
2020, Korea
2021, Sydney

China Nov 2018
What we learn here?

• Kesterite: high promise (earth-abundant & non-toxic & stable), challenging but full of fun.

• Demonstrated 11% efficiency CZTS solar cells

• Still a lot of unknowns about CZTS absorber materials & devices
  -interesting fundamentals
  -Never stand still!

• We are on the innovation highway!

• Global competition & collaboration will make the kesterite to keep rising
Acknowledgment

Collaborators:
Dr Steve Johnston, Dr Glenn Teeter at NREL
Dr Oki Gunawan at IBM
Prof Hong Lin at Tsinghua Uni
A/Prof Lydia Wong at NTU
Prof Brain Gorman at Colorado School of Mines
Prof Julie Kairney at University of Sydney
Prof Shiyou Chen at East Chine Normal University
Questions and Thank You!
• Reduced non-radiative recombination is mainly located at heterojunction region.
CZTS/CdS heterojunction-heat treatment

Buffer side: Zn diffusion into CdS- ZnxCd1-xS