Status and Further Potentials of CIS and Related Solar Cells

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In memoriam

Prof. Werner H. Bloss, winner of the Becquerel price in 1991
who was one of the most active pioneers of renewable Energy
research in Europe
What is special about Cu(In,Ga)(S,Se)$_2$?

- a multinary compound with high flexibility

Why does it work as a PV material?

What are the limits?
Just a diamond (silicon) like structure

From II-VI to $I_2$-II-IV-VI$_4$

sphalerite  

chalcopyrite

kesterite

$sphalerite$  

$chalcopyrite$  

$kesterite$

$II$-$VI$  

$I$-$III$-$VI_2$  

$I_2$-$II$-$IV$-$VI_4$

easy to form  

best efficiency  

cheap elements

CdTe $\rightarrow$ Cu(In,Ga)Se$_2$ $\rightarrow$ Cu$_2$ZnSnS$_4$

more difficult

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What is special about CIGS?

- high optical absorption

- secondary phases have commensurate structures, i.e. phase segregations do not cause severe distortion during growth

- electronic properties of CuIn(Ga)Se$_2$ extremely tolerant to defects i.e. deviations from stoichiometry, crystallographic imperfections and grain boundaries due to fortunate defect structure

- Cu-vacancies just lower the valence band: deviations from stoichiometry i.e. Cu/In+Ga ratios form neutral defect complexes

therefore:

high level of deviations from stoichiometry and impurities can be tolerated, in particular at only moderate efficiencies (< 15%).

but:

control of electronic properties by extrinsic doping is difficult or impossible - pn junctions have to rely on intrinsic defects
The favourable surface of CIS

Chalcopyrite/defect chalcopyrite heterojunctions on the basis of CuInSe$_2$

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A new model for the formation of heterojunctions in polycrystalline CuInSe$_2$ thin films on the basis of surface analysis experiments is presented. _In situ_ photoemission measurements of CuInSe$_2$ clearly show the existence of an In-rich $n$-type surface layer on samples relevant for solar-cell devices. Furthermore, this layer has been identified as an ordered vacancy compound (OVC) with a band gap of about 1.3 eV. The previous model of the CuInSe$_2$/CdS solar cell with a $p$-$n$ heterojunction between $p$-type CuInSe$_2$ and $n$-type CdS is replaced by the model of a chalcopyrite/defect chalcopyrite heterojunction between $p$-type bulk CuInSe$_2$ and the In-rich $n$-type OVC. The existence of this junction was proven directly by evaporating an ohmic metal contact onto the surface $n$-type layer and measuring the spectral quantum efficiency and electron-beam-induced current of this device. The band offsets of CuInSe$_2$-based devices have been determined.
electronic properties not strongly dependent on deviations from stoichiometry in CuInSe$_2$: Cu/In+Cu can range 0.8 - 0.98

**Defect pair:** $2V_{\text{Cu}}^- + \text{In}_{\text{Cu}}^{2+}$

- electronically neutral
- energetic position in valence- or conduction band

structure element of the defect phases with larger bandgap (lower valence band) $\text{Cu}_2\text{In}_4\text{Se}_7, \text{CuIn}_3\text{Se}_5$

Cross section of the first efficient CuInSe$_2$ solar cell

Eff. = 14.8%
Voc=513mV
FF = 0.716
Jsc = 40.4 mA/cm$^2$

EUROCIS projects

1st CIS project 1986
10 % cell

NEW POL
ENSCP
IPE
USTL
UNIV PR
EUROCIS 4/90-9/92
CIGS: 14.8 %,
EUROCIS projects

EUROCIS II 11/92-10/95,
CIGS: 17.6 %,
Module 10x10cm² - 10.2 %,
EUROCIS M 4/97-9/99, CIGS: 17.6 %,
Module 10x10 cm² - 13.9 %,
Module 30x30 cm²
EUROCIS projects

PROCIS 1/01-12/03 Technology Transfer

- ENSCP
- EDF
- IPE
- ZSW/WS
- ETH
- UU/ASC
- MC
Present developments

Efficiency

Cu(InGa)(S,Se)$_2$ - CIGS absorber layers

Heterojunctions
Development of the efficiency of thin film cells in the lab

CIGS: still continuous improvement!

CIGS is the high efficiency thin film option
Layer sequence of a CIGS solar cell

"vacuum"

sputtering/CVD

PVD, CVD/CBD

PVD, selenisation/ sulphurisation

Mo sputtering

(PVD, SiN, SiO_x)

glass/foil

substrate

"non vacuum"

APCVD, chemical?

chemical

electrodeposition/printing
selenisation/sulfurisation

PVD Mo, Cr ...
(sol gel, SiN, SiO_x, Cr, )

glass/foil

substrate structure enabling flexible cells by role-role manufacturing,
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(sol gel, SiN, SiO_x, Cr,)

glass/foil
CIGS technology quo vadis?

CIGS deposition: will it converge?

- co-evaporation
- co-sputtering
- substrates: glass, metal/polymer foils
- precursor based methods: sputtering, printing, electrodepos.
- RTP of stacks and/or Se/S, H₂S/H₂Se
- new process?
- cost <0.5€/W
- 20% module efficiency
- glass or flexible

- actual production capacity 300 MW → 1000 MW
- actual production capacity 300 MW → 2000 MW


diversification of processes increases
Deposition process - Cu(In,Ga)(S,Se)$_2$ films

**Co-evaporation:**
- constant rate:
  \[ \text{Cu} \, \text{In} \, \text{Ga} \, \text{Se} \, \text{S} \]

multi stage processing

Cu-rich-In-rich
In/Ga, S/Se gradients

In$_x$Se(S)

**precursor based methods**

metal films and gas

\[ \text{Se}, \text{S} \, \text{H}_2\text{Se} \, \text{H}_2\text{S} \]

reaction of binary compounds with gas phase

\[ \text{Cu} \, \text{Se} \, \text{In} \, \text{Ga} \, \text{Se} \, \text{S} \]

Cu(In,Ga)(S)Se$_2$

**anneal**

Reaction of elemental layers

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CIGS Technology quo vadis?

CIGS junction formation: will it converge?

- CdS, (Cd,Zn)S evaporation
- buffer layer chemical bath deposition
- CdS - In,S(OH) - ZnS(OH)
- buffer layer sputtering
- TCO CVD ZnO
- TCO sputtering
- cost <0.5€/W
- 20% module efficiency
- glass or flexible

1976 1985 2010
Prospects

Efficiency potential

Wide bandgap and tandem cells

New compounds
### CIGS high efficiency thin films

<table>
<thead>
<tr>
<th></th>
<th>ZSW¹</th>
<th>NREL²</th>
<th>HZB³</th>
<th>Best values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{OC}$ (mV)</td>
<td>720.4</td>
<td>691.8</td>
<td>702.5</td>
<td>720</td>
</tr>
<tr>
<td>$J_{SC}$ (mA)</td>
<td>36.33</td>
<td>35.74</td>
<td>35.63</td>
<td>36.5</td>
</tr>
<tr>
<td>FF (%)</td>
<td>76.78</td>
<td>81.03</td>
<td>77.52</td>
<td>81.2</td>
</tr>
<tr>
<td>$\eta$ (%)</td>
<td>20.3</td>
<td>20.0</td>
<td>19.4</td>
<td>21.3</td>
</tr>
</tbody>
</table>

like crystalline wafer cells, just planar structures!

¹ ZSW Press release 2010
³ HZB, 24th PVSEC Hamburg 2010 and this conference
Wide-gap chalcopyrites

>20% device efficiency has been reached only for low bandgap (<1.2 eV)

- **Cu(In,Ga)Se$_2$**
  - single layer
  - bilayer
- **Cu(In,Ga)(Se,S)$_2$**
- **CuGaSe$_2$**

recent results on
- **Cu(In,Ga)S$_2$**
- S. Merdes et. al.

High Efficiency, High Voltage Solar Cells by Band Gap and Defect Engineering in Cu(In,Ga)(S,Se)$_2$
High efficiency concepts

Tandem structures?

> 25% efficiency

1.7 eV

1.0 eV

highly efficient wide gap cell needed tunnel heterojunction

The challenge of monolithic tandem structures:
- solve the problem of wide gap cells
- self organizing structure and interfaces

substrate or superstrate?
Kesterite compounds - Progress in efficiency

1989

Kesterites make slow but steady progress


Monograins, E. Mellikov et al

Kesterite publications
Conclusions

Chalcopyrite semiconductors

- Favourable properties facilitate realisation of efficient photovoltaic devices
- High efficiency devices in the laboratory do not differ significantly from devices in commercial modules.

- CIGS is very tolerant to deviations from stoichiometry

- By proper choice of reaction path for the formation of thin films high quality material can be realized with easy control of processes.

- In spite (or because) of apparent complexity there many ways for upscaling of production
Acknowledgements

Becquerel Committee

all my former colleagues at IPE

the colleagues who participated in the EUROCIS consortia

the colleagues at ZSW and Würth Solar who pushed for production

the colleagues at the Helmholtz Centre who made my new start in Berlin most convenient

all the colleagues and friends of the international PV community

My Wife and my Children who always provide me a very stable mental background in demanding times in the amphitheater of PV
CIGS Technology quo vadis?

- Custom equipment engineering solutions for perfect process control coevaporation
- Adapting process to high throughput standard equipment sequential processes

The compromise:
- Adapted standard equipment
- High throughput high quality
High efficiency concepts

Intermediate band absorber materials

would be an ideal solution for simple high efficiency devices
new material science - needs proof of concept

![Graph showing efficiency vs. bandgap](image)

**CuGaS$_2$:M film**

$M = \text{Sn, Fe, Ti}$

First experiments show photocurrent from impurities - but $V_{oc}$ gets lower


**Modeling suggests optimum host bandgap 2.4 eV.**

Cu(Ind,Ga)S$_2$ system covers bandgap range 1.5-2.5 eV.