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Status and Further Potentials of CIS and Related Solar Cells

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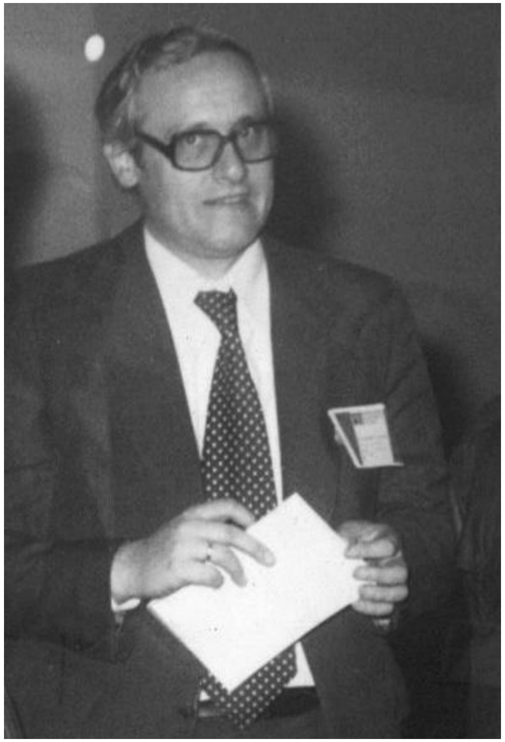
Helmholtz Centre Berlin, Division Solar Energy

WPSEC 5 - 25 EUPVSEC Valencia Spain 2010

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

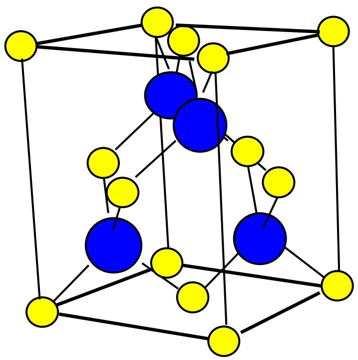
Why does it work as a PV material ?

What are the limits ?

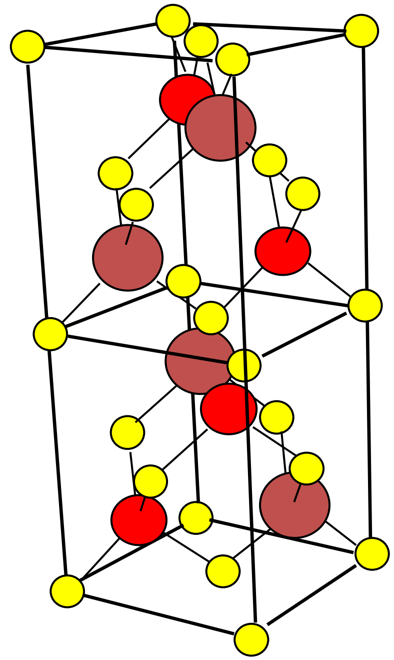
Just a diamond (silicon) like structure

From II-VI to I_2-II-IV-VI_4

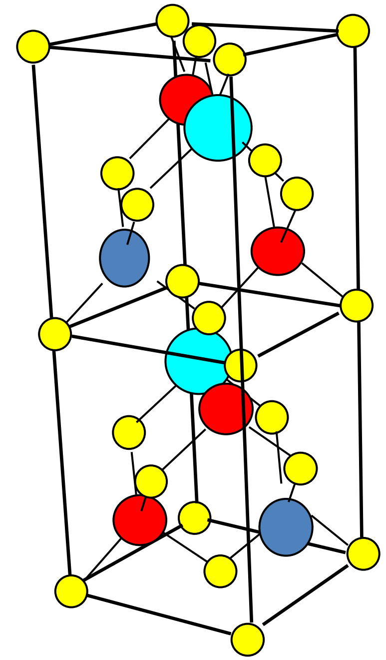
sphalerite



chalcopyrite



kesterite



II-VI	I-III-VI_2	I_2-II-IV-VI_4
easy to form	best efficiency	cheap elements

CdTe → $Cu(In,Ga)Se_2$ → Cu_2ZnSnS_4 more difficult

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

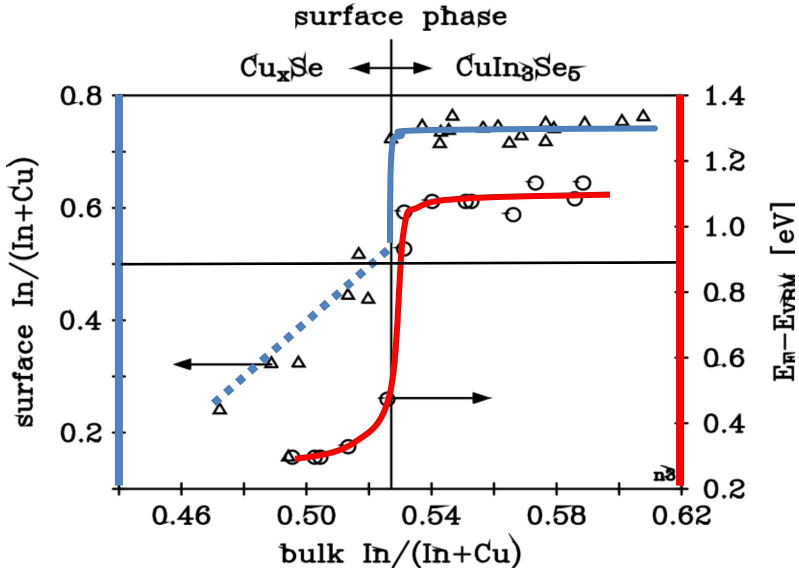
- Cu-vacancies just lower the valence band: deviations from stoichiometry i.e. Cu/In+Ga ratios form neutral defect complexes

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



Chalcopyrite/defect chalcopyrite heterojunctions on the basis of $CuInSe_2$

D. Schmid, M. Ruckh, F. Grunwald, and H. W. Schock
Institut für Physikalische Elektronik, Universität Stuttgart, Pfaffenwaldring 47, D-7000 Stuttgart 80, Germany

(Received 16 September 1992; accepted for publication 7 December 1992)

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.

Defect-phases and stability

electronic properties not not strongly dependent on deviations from stoichiometry in $CuInSe_2$: Cu/In+Cu can range 0.8 - 0.98

Defect pair: $2V_{Cu}^{-}$ + In_{Cu}^{++}

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

➔ structure element of the defect phases with larger bandgap (lower valence band)

$Cu_2In_4Se_7$, $CuIn_3Se_5$

S.B. Zhang, S.H. Wei, A. Zunger, H. Katayama-Yoshida, Phys. Rev. B. 57, 9642, 1998

Communication

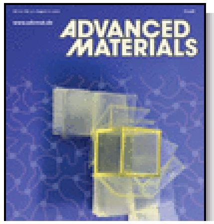
Cu(In,Ga)Se_2 Solar Cells: Device Stability Based on Chemical Flexibility

Jean-François Guillemoles[1], Uwe Rau[2], Leeor Kronik[3], Hans-Werner Schock[2], David Cahen

Article first published online: 5 AUG 1999

DOI: 10.1002/(SICI)1521-4095(199908)11:11<957::AID-ADMA957>3.0.CO;2-1

Issue

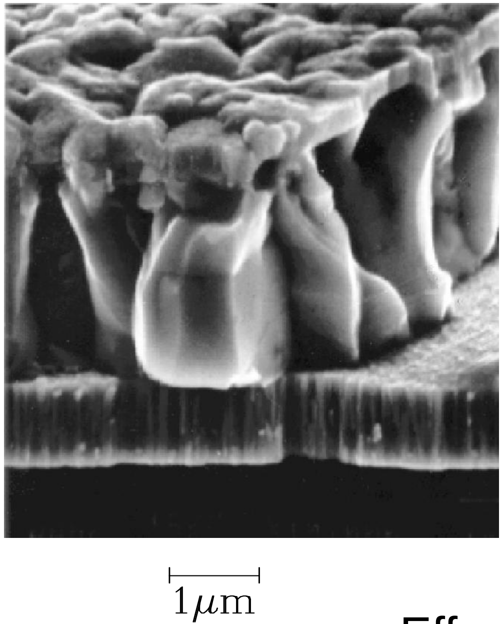


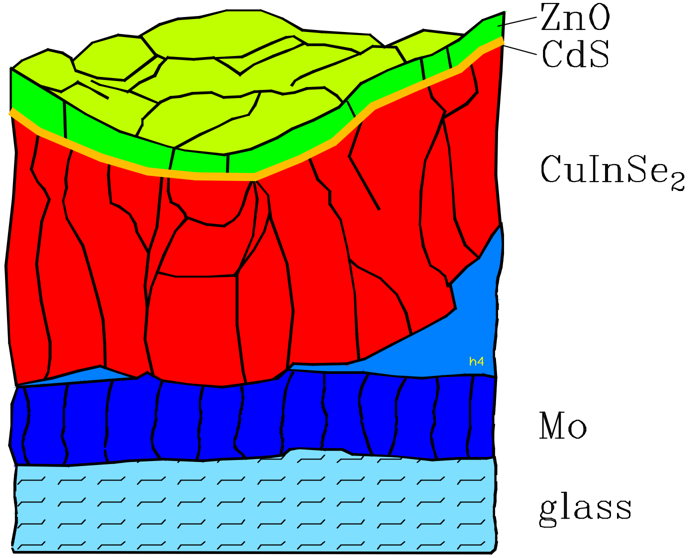
Advanced Materials

Volume 11, Issue 11, pages 957–961, August, 1999

Is "self-healing" the source of the stability of Cu(In, Ga)Se_2-based solar modules? The proven remarkable stability and radiation hardness of Cu(In,Ga)Se_2 (CIGS) solar cells stand in apparent contradiction to the fact that CIGS shows both short-range (metastable defect centers) and long-range (significant Cu migration) instabilities. The authors suggest that these instabilities may in fact be a prerequisite for CIGS's stability as they allow a degree of flexibility or "smartness" in accommodating externally imposed changes. Two self-healing cycles are proposed, in which copper species play a particularly important role.

Cross section of the first efficient $CuInSe_2$ solar cell



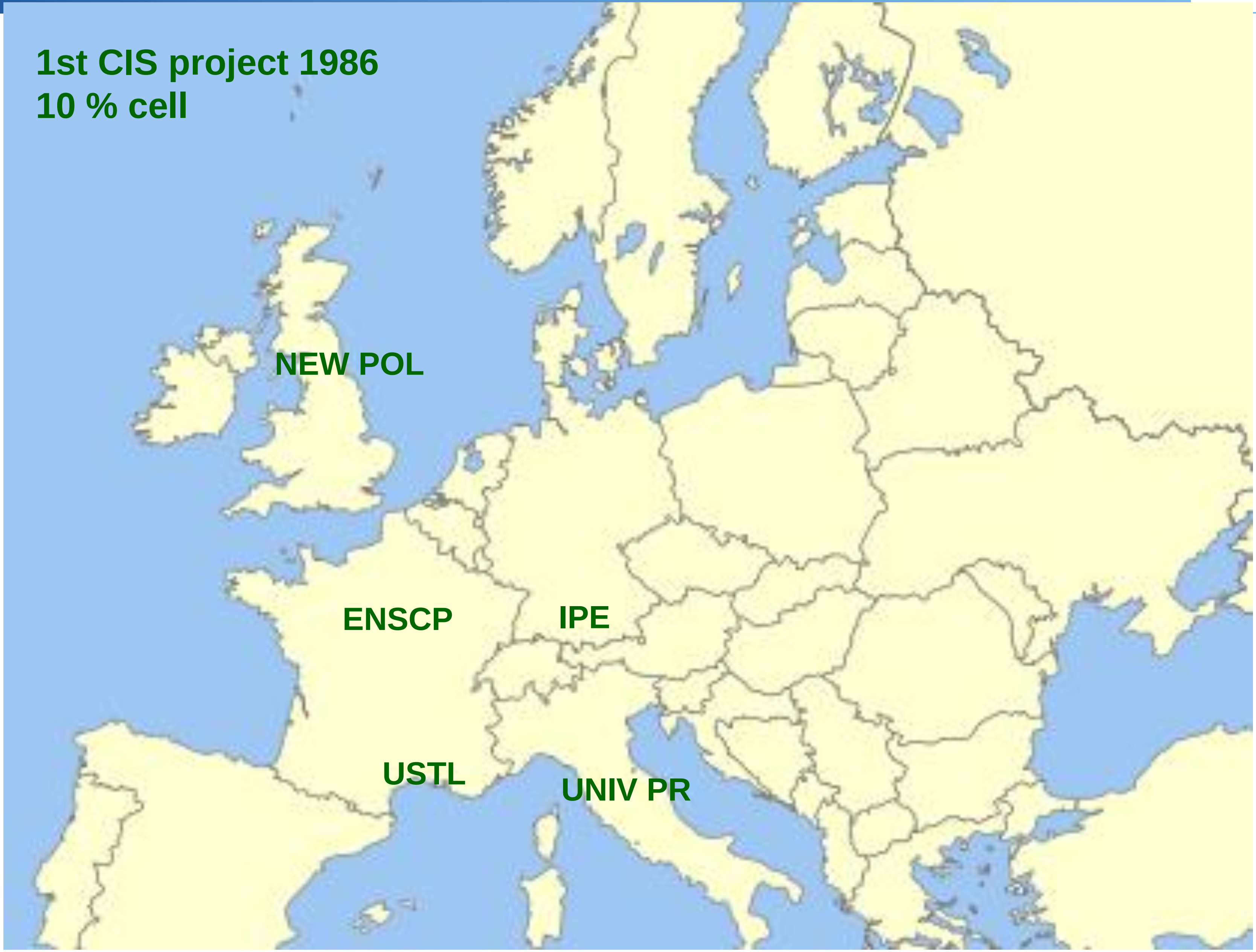


Eff. = 14.8%
Voc=513mV
FF = 0.716
Jsc = 40.4 mA/cm^2

L. Stolt, J. Hedstrom, J. Kessler, M. Ruckh, K. O. Velthaus, and H. W. Schock, "ZnO/CdS/$CuInSe_2$ THIN-FILM SOLAR-CELLS WITH IMPROVED PERFORMANCE," Applied Physics Letters 62 (6), 597-599 (1993).

EUROCIS projects

1st CIS project 1986
10 % cell



EUROCIS projects

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EUROCIS projects

EUROCIS II 11/92-10/95,
CIGS: 17.6 %,
Module 10x10cm^2 - 10.2 %,

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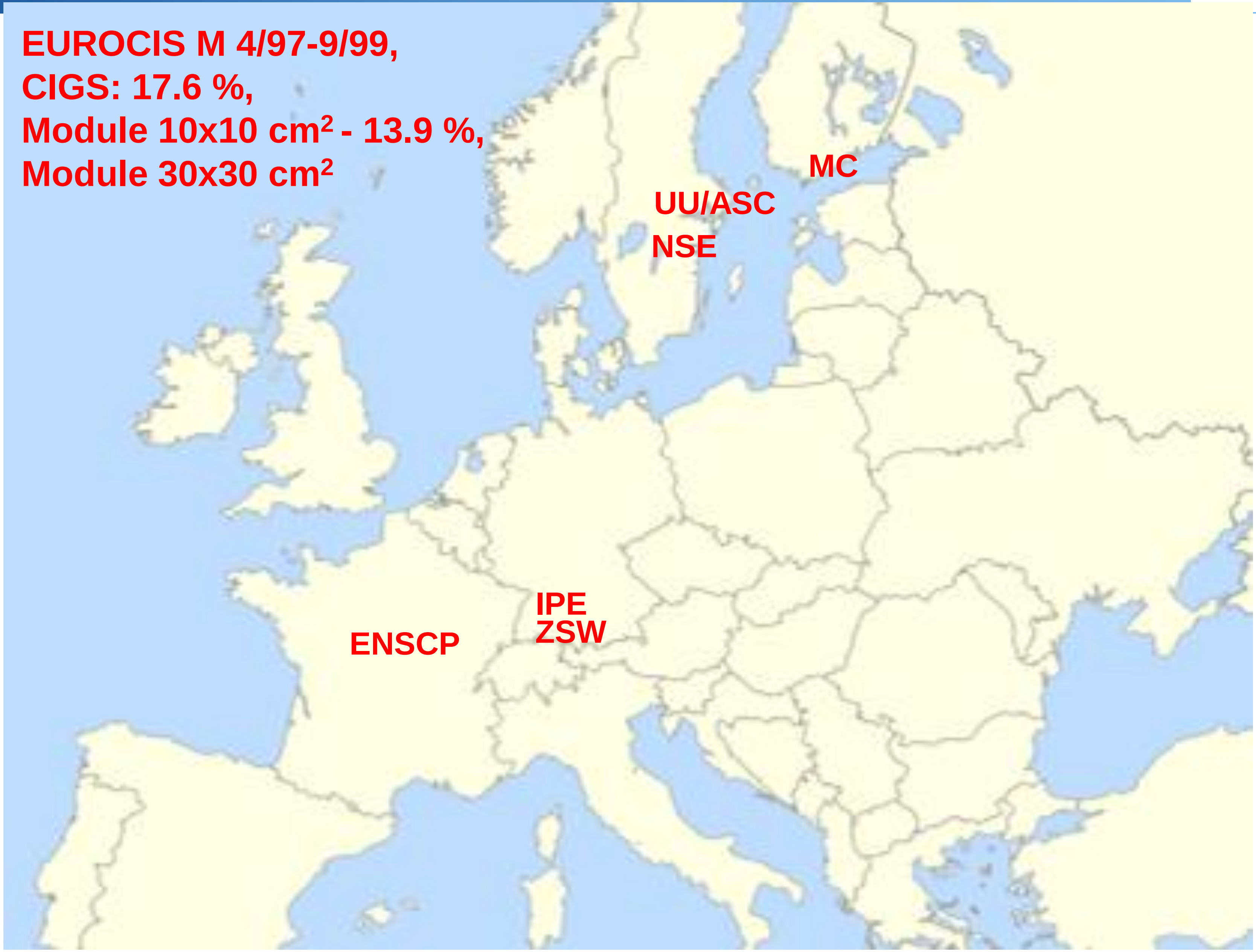
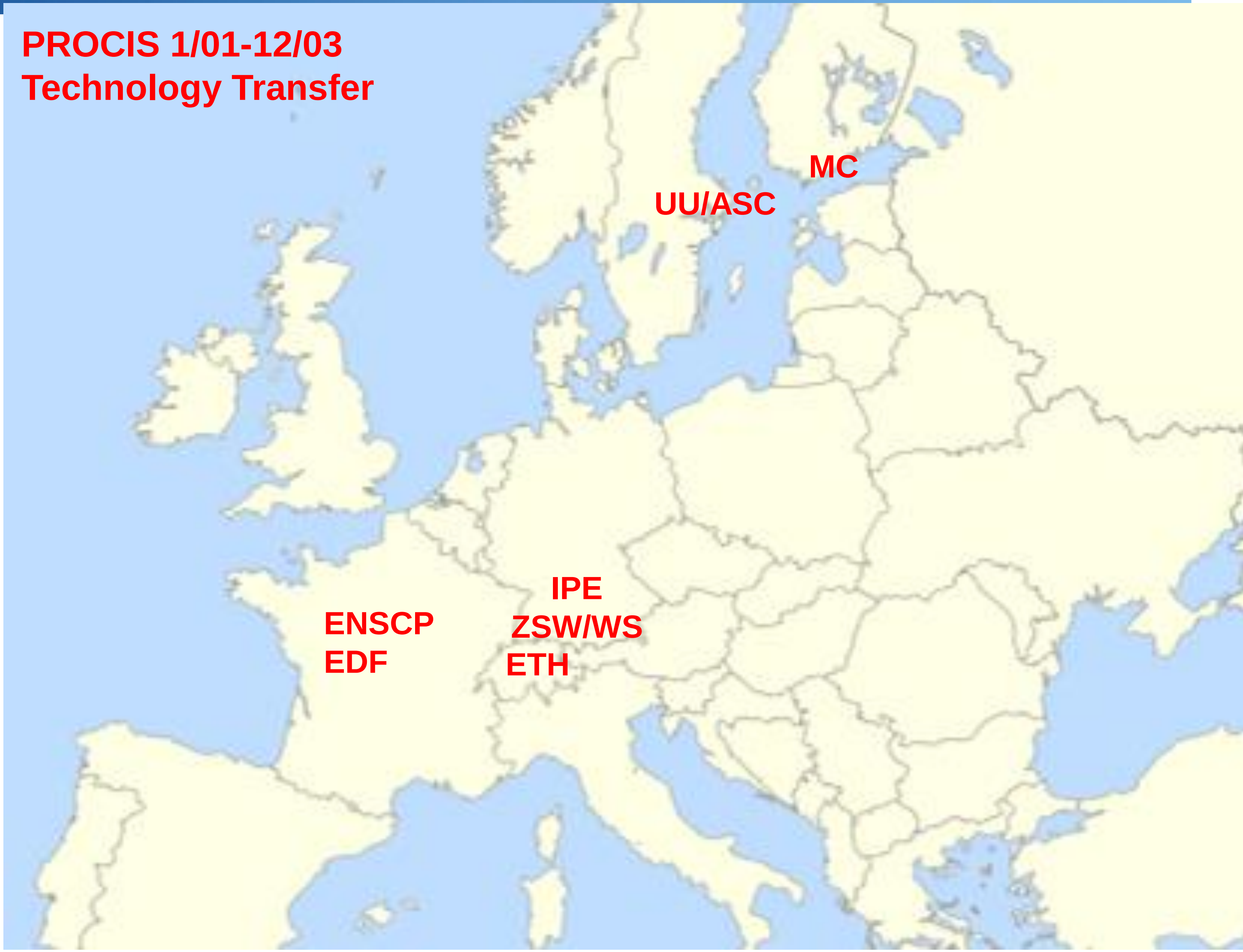
EUROCIS M 4/97-9/99,
CIGS: 17.6 %,
Module 10x10 cm² - 13.9 %,
Module 30x30 cm²



EUROCIS projects




LARCIS 11/2005 - 10/2009
Large Area Technology
Transfer
UU/ASC
Solibro
HZB
ENSCP
EDF
SGR
ZSW/WS
ETH
UB-EME

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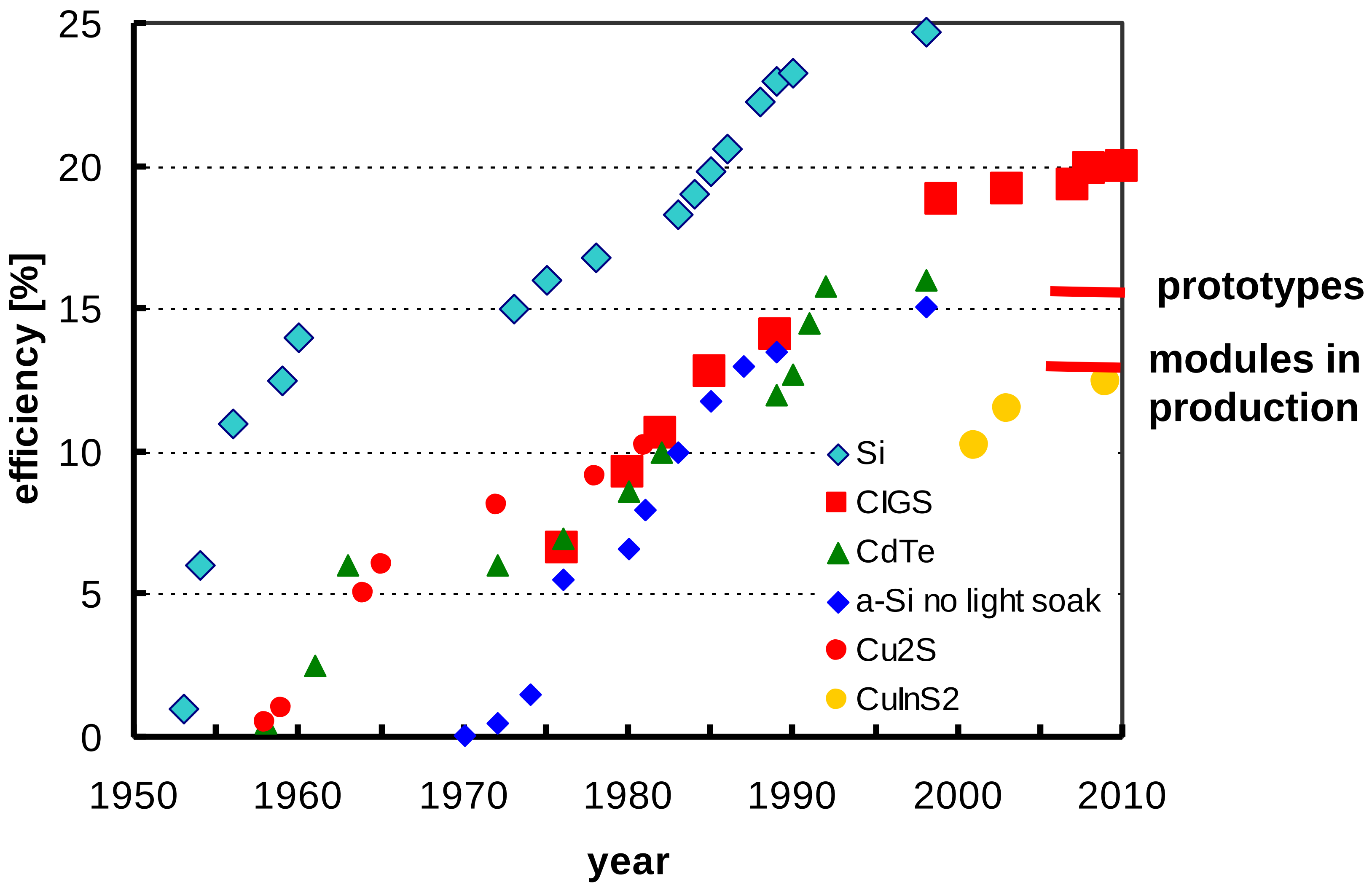
Efficiency

$Cu(InGa)(S,Se)_2$ - 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

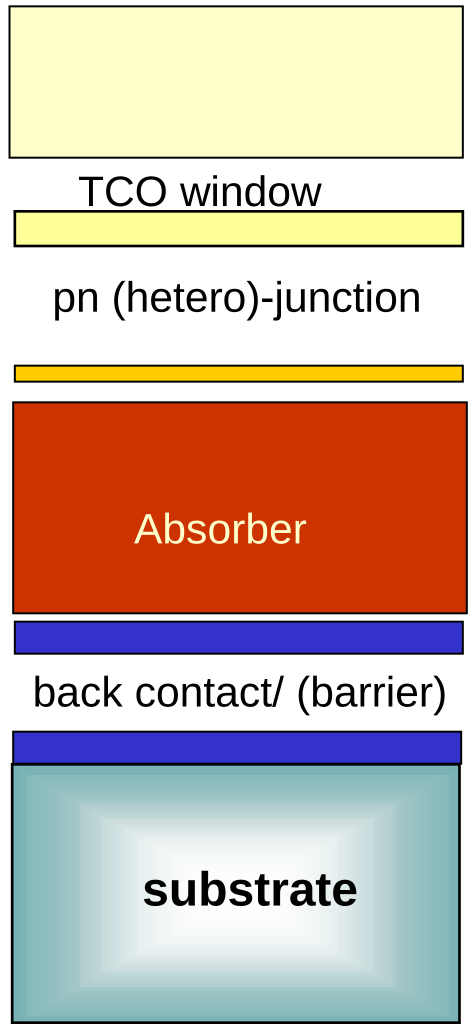
PVD,
CVD/CBD

PVD, selenisation/
sulfurisation

Mo sputtering

(PVD, SiN, SiO_x)

glass/foil



"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,

Layer sequence of a CIGS solar cell

"vacuum"

sputtering/CVD

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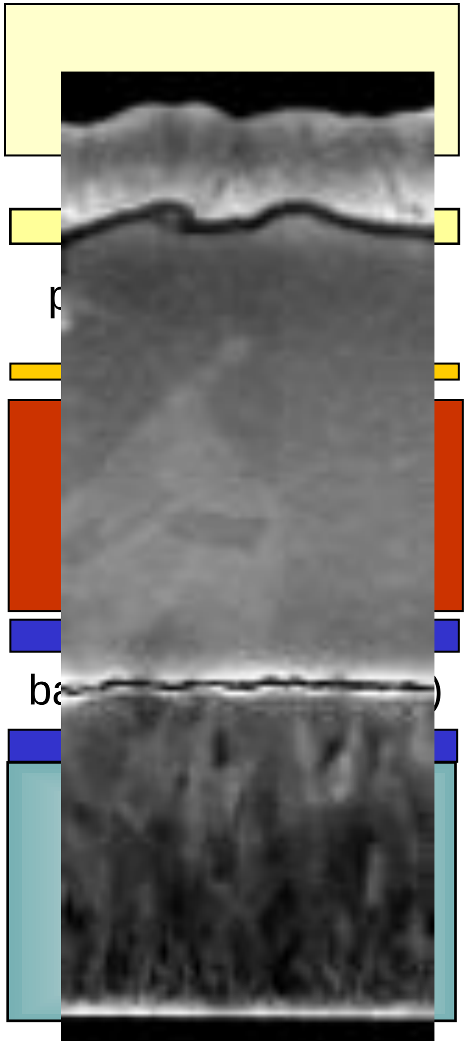
PVD, selenisation/
sulfurisation

Mo sputtering

(PVD, SiN, SiO_x)

glass/foil



"non vacuum"

APCVD, chemical?

chemical

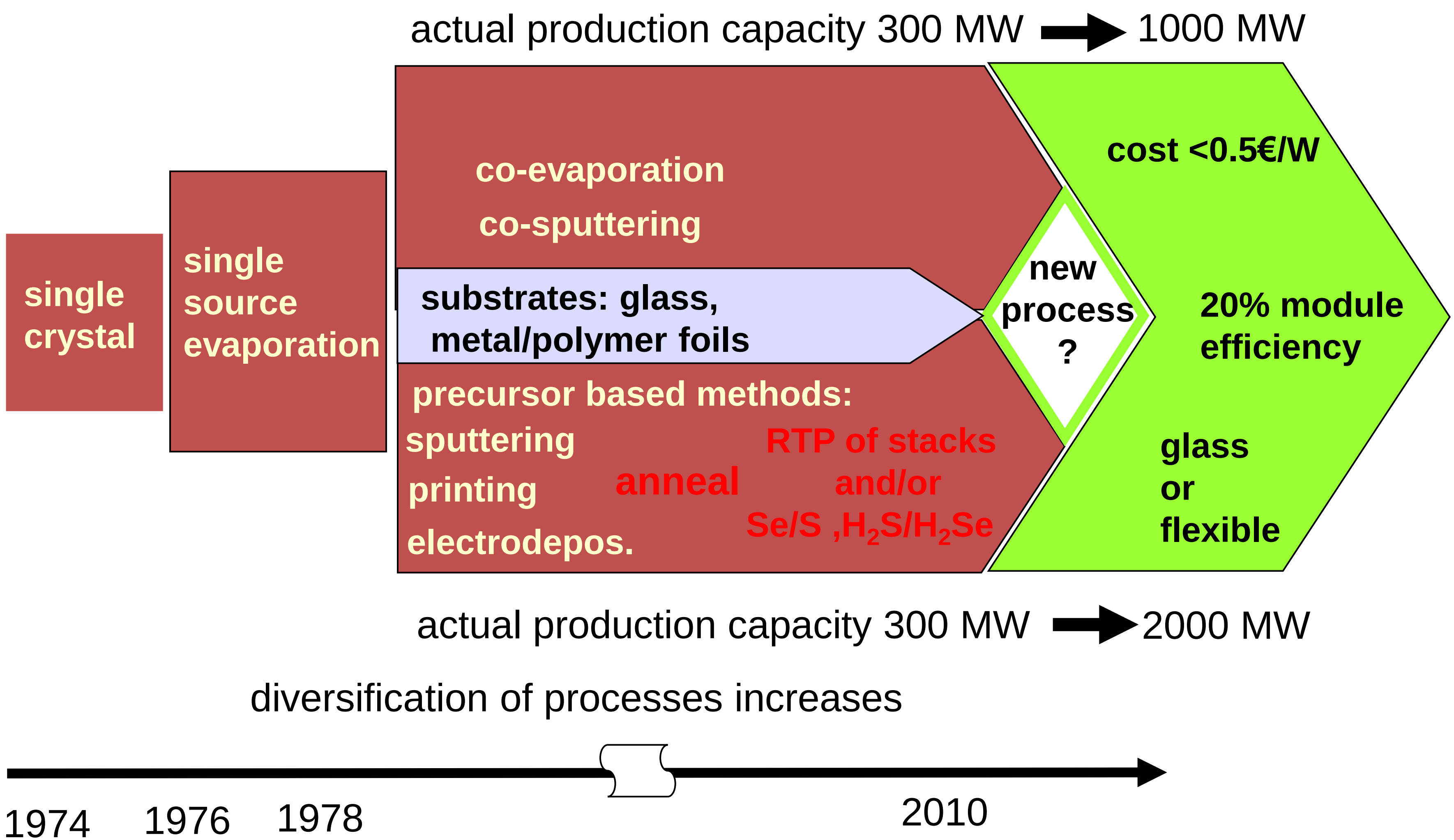
electrodeposition/printing
selenisation/sulfurisation

PVD Mo, Cr ...

(sol gel, SiN, SiO_x, Cr,)

glass /foil

CIGS deposition: will it converge?



Deposition process - Cu(In,Ga)(S,Se)$_2$ films

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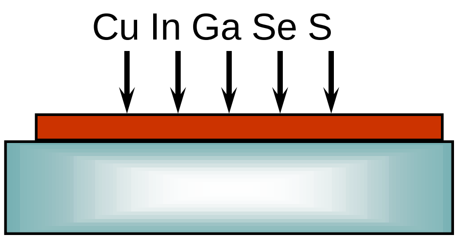
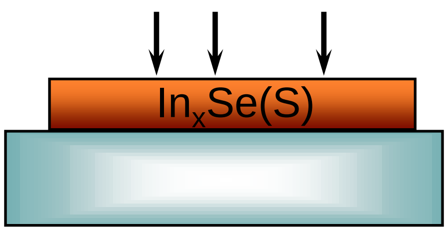
Co-evaporation:

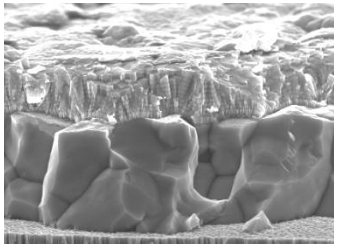
- constant rate:



multi stage processing

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

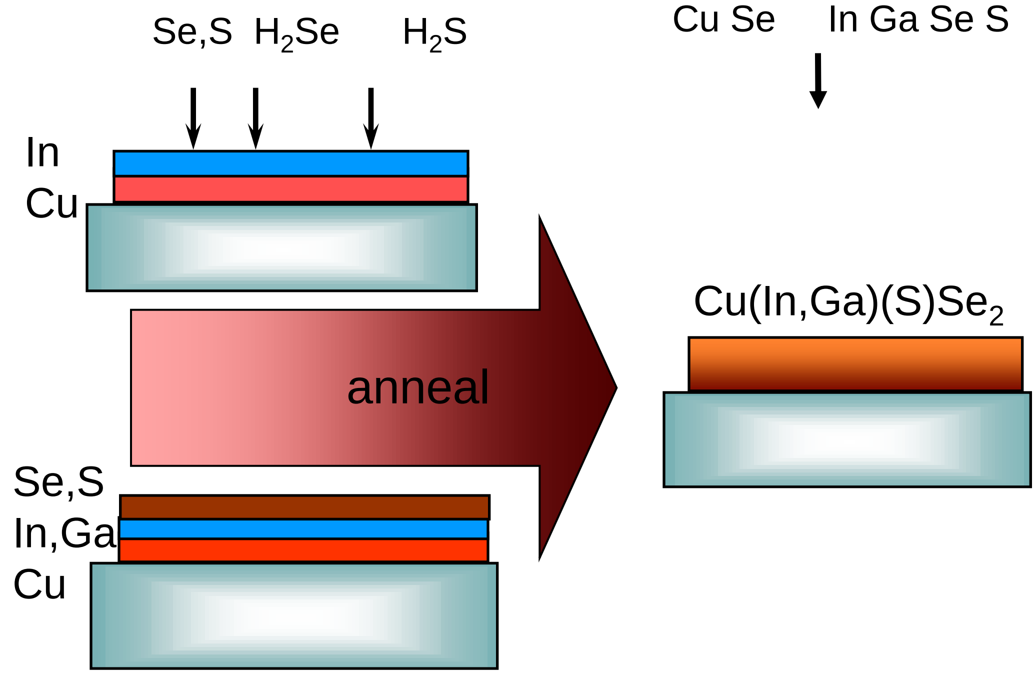




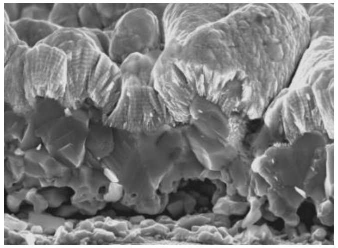
precursor based methods

metal films and gas

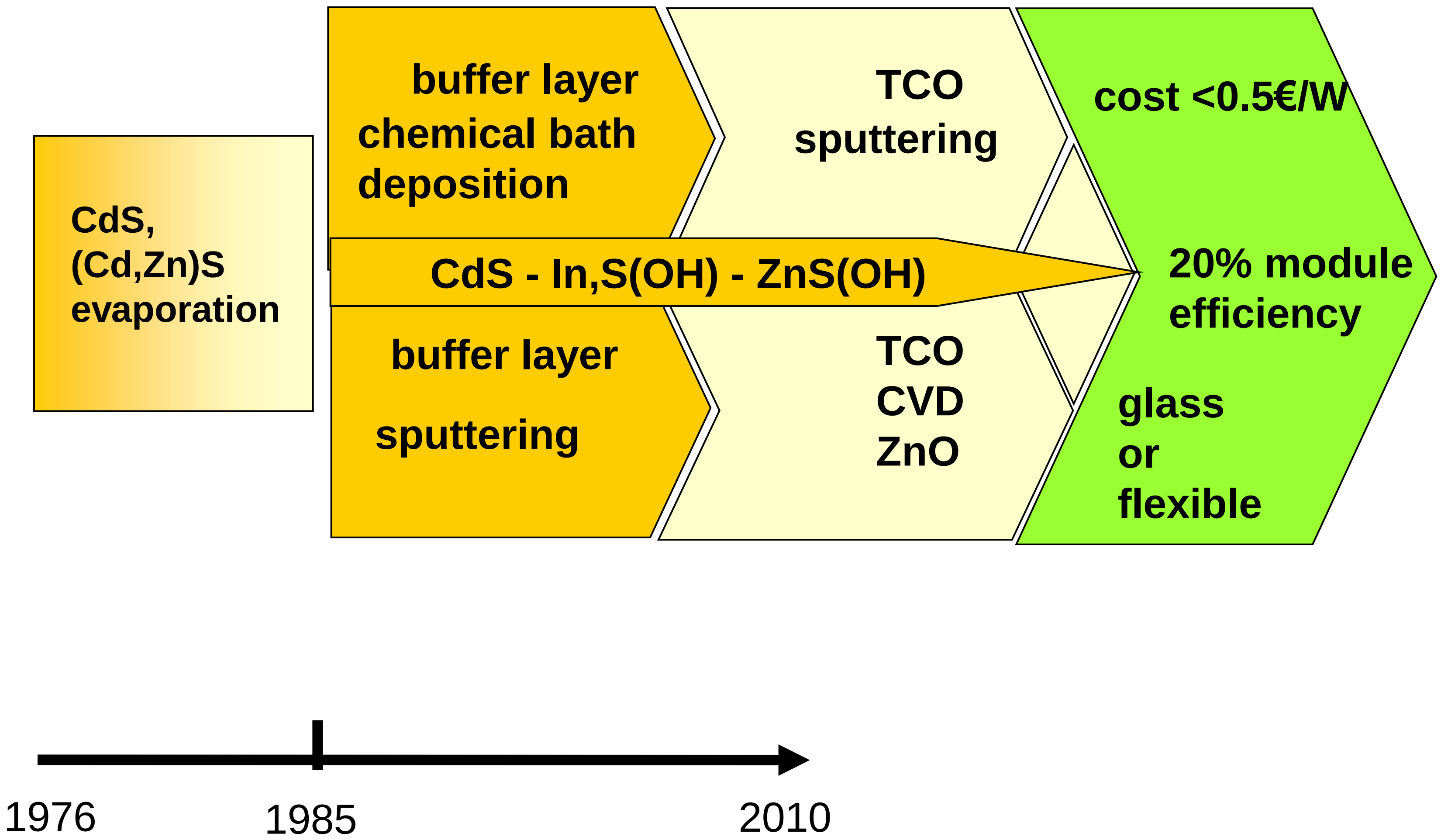
reaction of binary compounds with gas phase



Reaction of elemental layers



CIGS junction formation: will it converge?



Prospects

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Efficiency potential

Wide bandgap and tandem cells

New compounds

CIGS high efficiency thin films

	ZSW[1]	NREL[2]	HZB[3]	Best values	
V_{OC} (mV)	720.4	691.8	702.5	720	
J_{SC} (mA)	36.33	35.74	35.63	36.5	
FF (%)	76.78	81.03	77.52	81.2	
η (%)	20.3	20.0	19.4	21.3 →	25 ?

like crystalline wafer cells, just planar structures!

[1]ZSW Press release 2010
[2] I.Repins et al. in Progress in Photovoltaics: Research and Applications 16(3):235–239, 2008
[3] HZB, 24th PVSEC Hamburg 2010 and this conference

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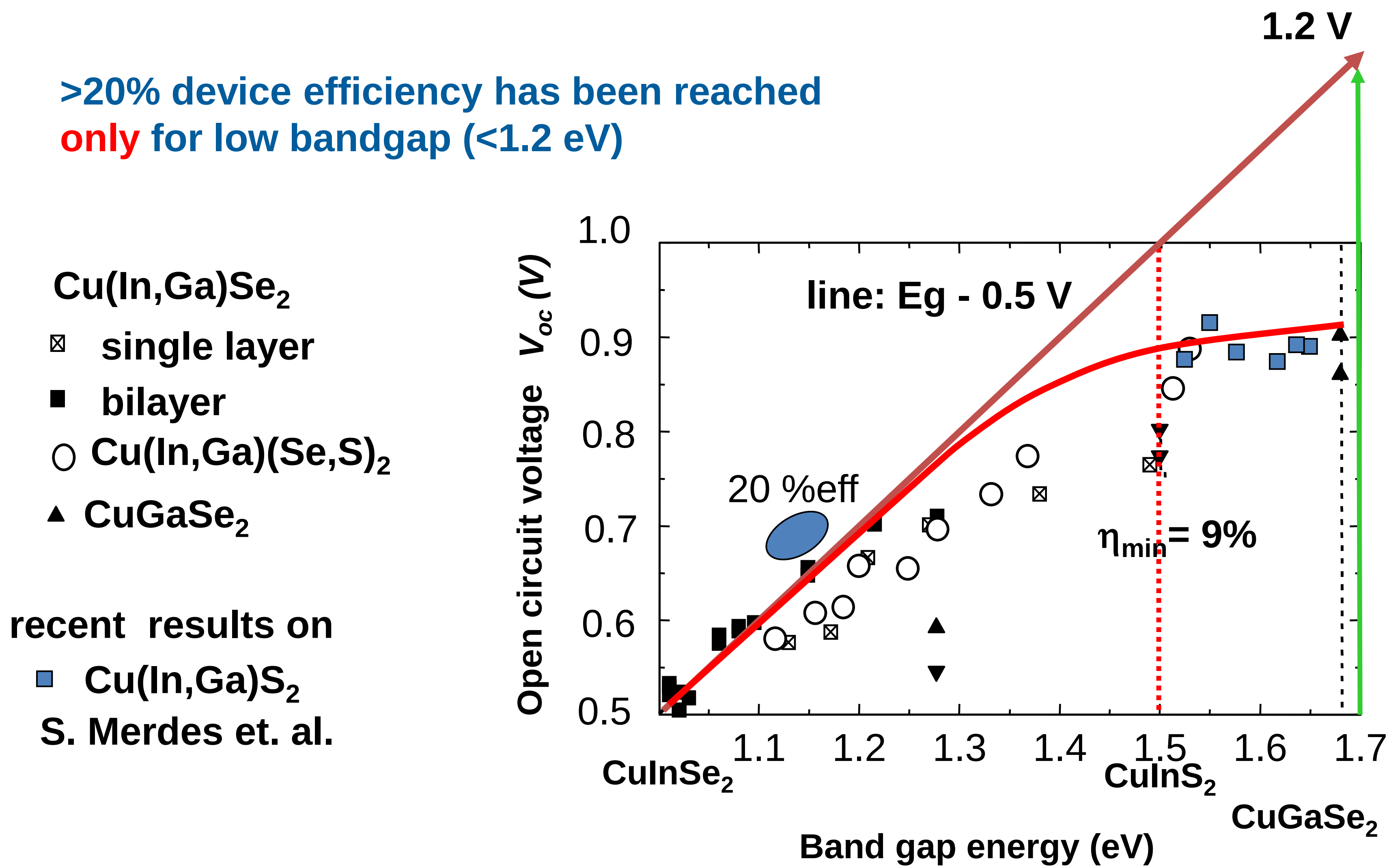
>20% device efficiency has been reached
only for low bandgap (<1.2 eV)

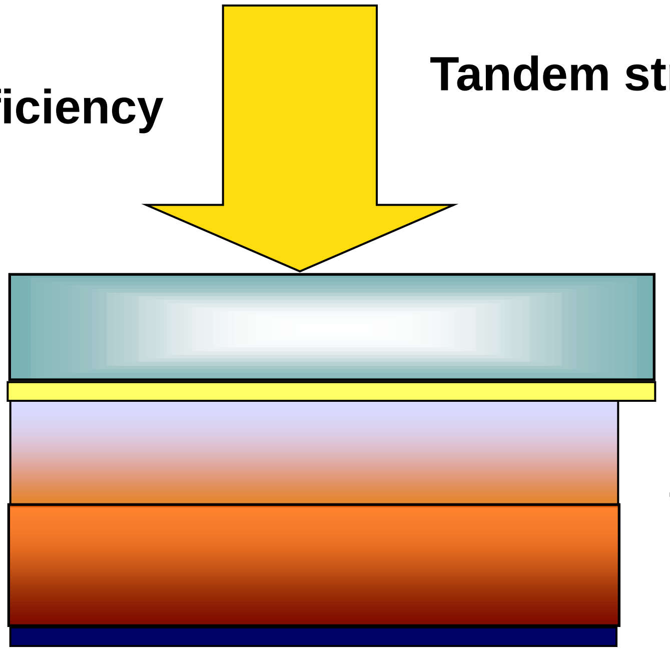


High Efficiency, High Voltage Solar Cells by Band Gap and Defect Engineering in Cu(In,Ga)(S,Se)2 Chalcopyrite Semiconductors, H. W. Schock, et al, Proc. 16th Europ. PV Solar En. Conf, Glasgow, 2000

High efficiency concepts

→ **> 25% efficiency**

Tandem structures?



1.7 eV

1.0 eV

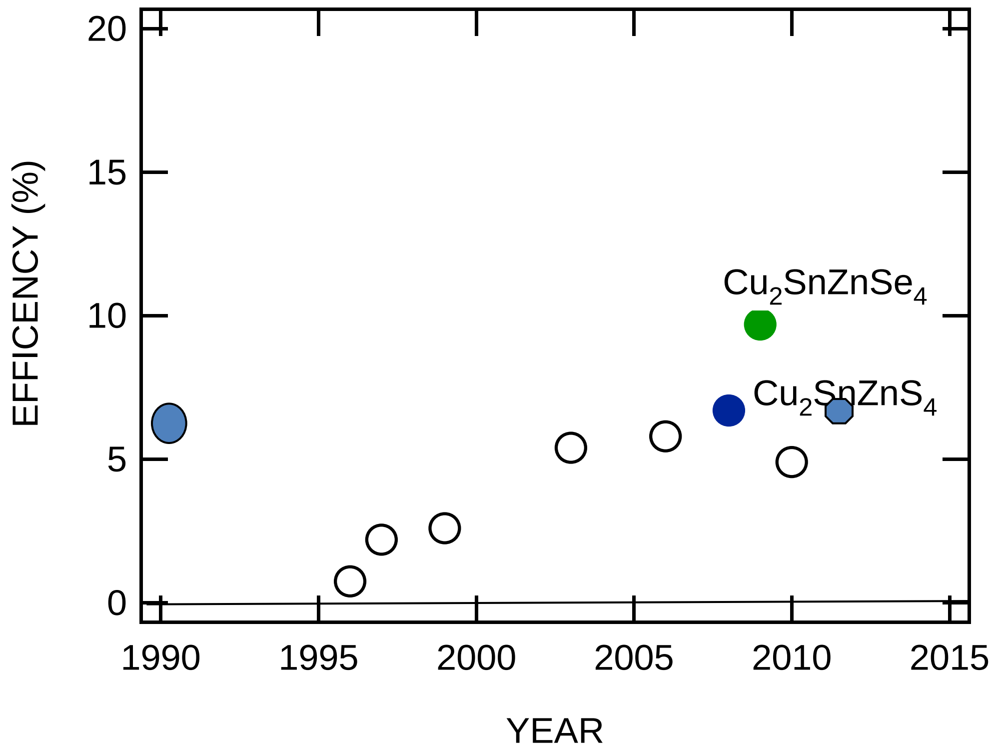
highly efficient wide gap cell needed

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



T: K. Todorov, K: B. Reuter, D. B. Mitzi, Adv. Mat., 22, p E156 - E159, Published Online: 8 Feb 2010

Monograins,
E. Mellikov et al

HZB

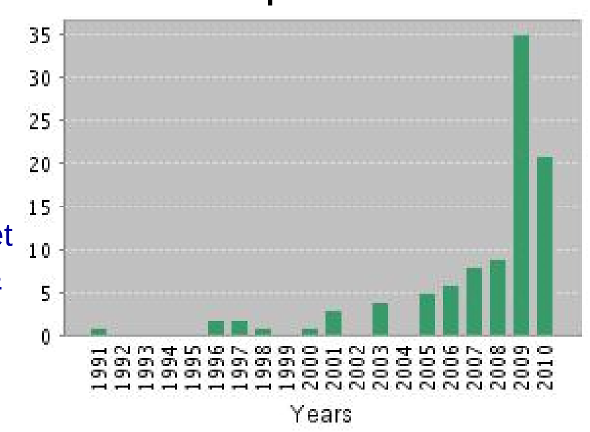
1989

K. Ito and T. Nakazawa. In: *Proc. 4th Int. PVSEC* (1989), pp. 341–346

Friedlmeier, T. M., H. Dittrich, et al. (1998). Iop Publ.,Ltd. **152:** 345-348.

Katagiri, H., K. Jimbo, et (2008). Applied Physics Express **1**(4).

Kesterite publications



Kesterites make slow but steady progress

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

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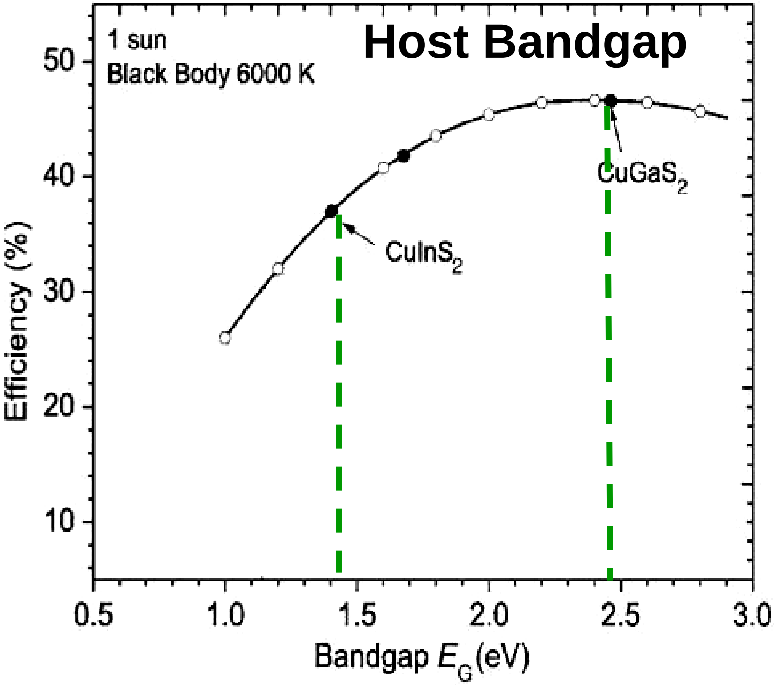
Intermediate band absorber materials

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



Martí, D. Fuertes Marrón, and A. Luque,
J. Appl. Phys. **103**, 073706 (2008).

$CuGaS_2$:M film
M = Sn, Fe, Ti

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

Modeling suggests optimum host bandgap 2.4 eV.
$Cu(In,Ga)S_2$ system covers bandgap range 1.5-2.5 eV.