CIGS Thin film solar cells.

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Summary

- Short Introduction
- CIGS solar cell structure
- Single layers + Na effect
- CdS alternatives
- Issues and challenges
- Thin cells
- Flexible cells

Thin Film PV companies

CIS

Shell Solar, CA
Global Solar Energy, AZ
Energy Photovoltaics, NJ
ISET, CA
ITN/ES, CO
NanoSolar Inc., CA
Day Star Technologies, NY/CA
MiaSole, CA
HelioVolt, Tx
Solyndra, CA

SoloPower, CA
Wurth Solar
SULFURCELL, Germany
CIS Solartechnik, Germany
Solarion, Germany
Solibro, Sweden
CISEL, France
Showa Shell, Japan
Honda, Japan

CdTe

First Solar, OH
Solar Fields, OH
AVA TECH, CO
Prime Star, CO

CANRON, NY
Antec Solar, Germany
Arendi, Italy

CIGS properties

CIGS → if $CuIn_{0.8}Ga_{0.2}Se_2$ has a band gap of 1.25eV.

Higher absorption coefficient and good diffusion length of 1μm.

1μm is enough to absorb 90% of the light .

Columnar growth and passivated grain boundaries

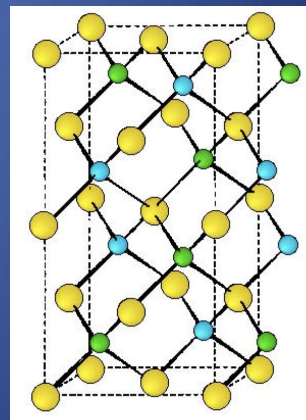
CIGS has reached 19.9% efficiency very near to Crystalline silicon

Properties

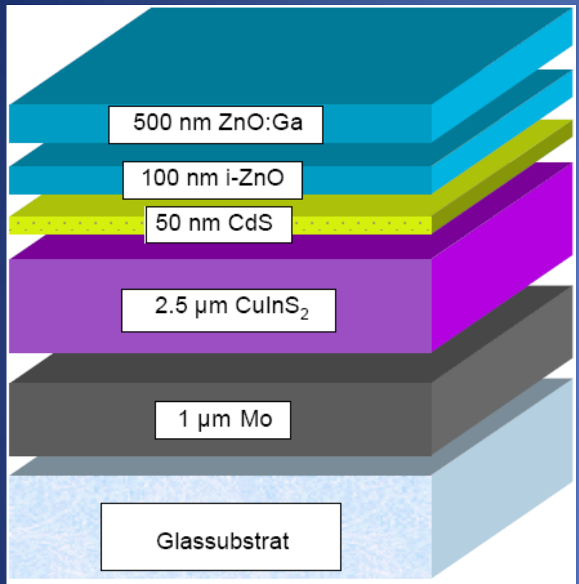
- $Cu(In,Ga,Al)(Se,S)_2$ crystallizes in chalcopyrite structure (From zinc-blend structure)
- Semiconductor of I-III-VI_2-Family have a very high absorption coefficient.
- Band gap can vary from 1,04eV ($CuInSe_2$) to 2,7eV ($CuAlS_2$)
- Principally $Cu(In,Ga)Se_2$ and $CuInS_2$ have industrial applications

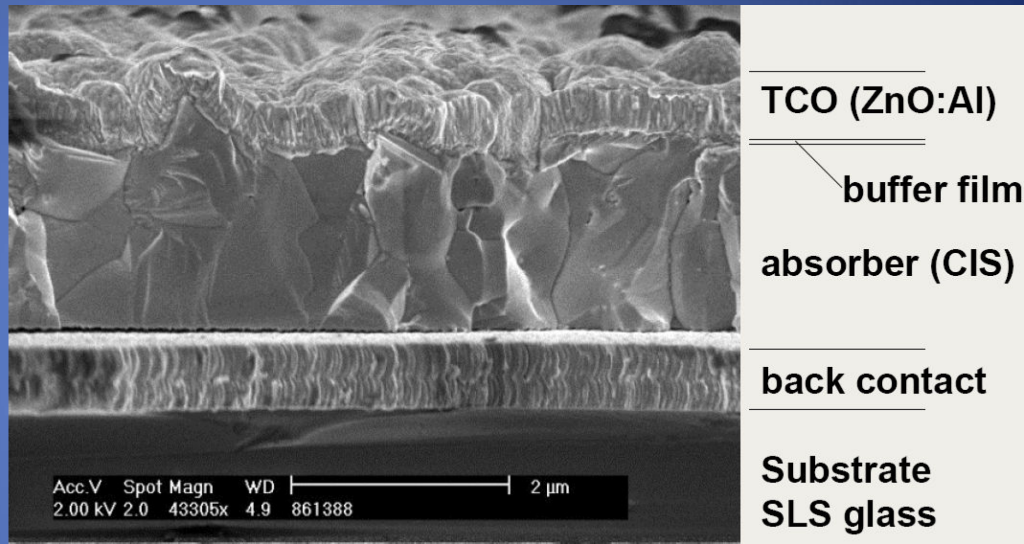
Table 1. Absorber band-gap energy E_g, efficiency η, open-circuit voltage V_{oc}, short-circuit current density j_{sc}, fill factor FF, and area A of the best $Cu(In,Ga)Se_2$, $CuInSe_2$, $CuGaSe_2$, $CuInS_2$, and the record Si solar cell

Material	E_g eV	η %	V_{oc} mV	j_{sc} mA/cm^2	FF %	A cm^2	Ref.
$Cu(In,Ga)Se_2$	1.11[a]	17.7	647	34.0	77.2	0.414	[8][b]
$CuInSe_2$	1.04	15.4	515	41.2	72.6	0.38	[30][c]
$CuGaSe_2$	1.68	8.3	861	14.2	67.9	0.471	[27][b]
$CuInS_2$	1.57	11.1	728	21.24	70.9	0.48	[28][b]
Si	1.15	24.4	696	42.0	83.6	4.00	[2][b]



CIGS solar cell scheme



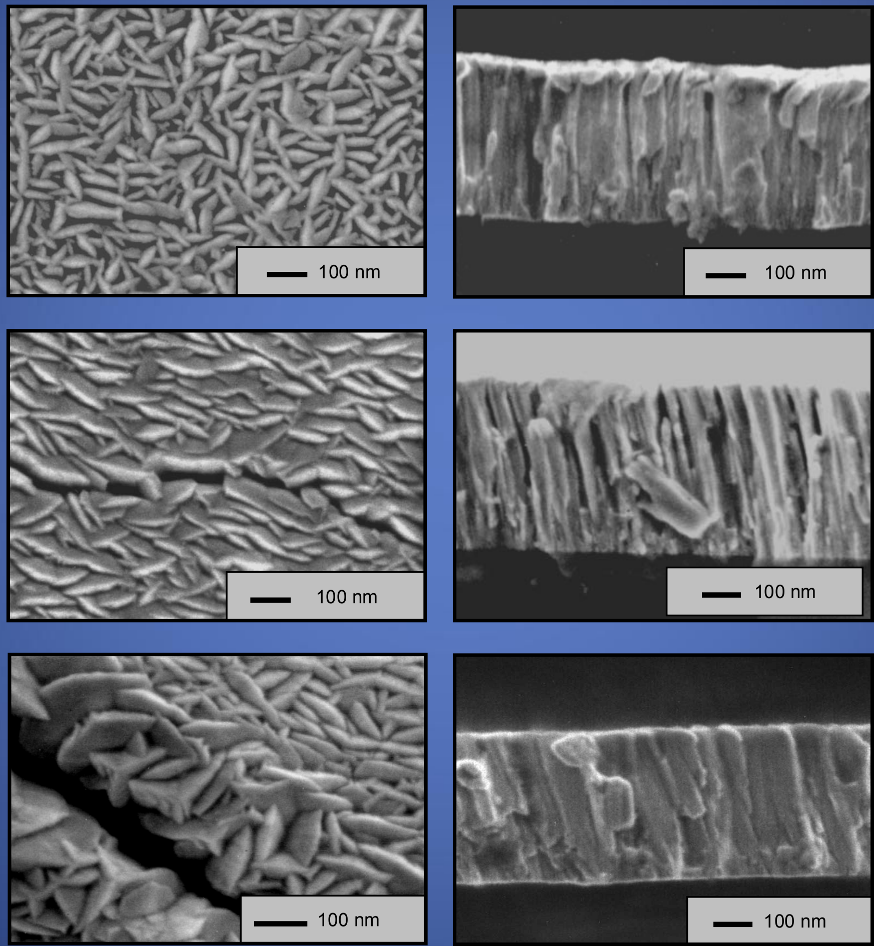


Structure of solar cells

	ZSW / Würth Solar	Avancis	Showa Shell Sekiyn	Global Solar	Sulfurcell
n-Typ Fenster ca. 1 µm	ZnO:Al	ZnO:Al	Zn:B	ZnO:Al	ZnO:Al
Puffer ca. 50 - 100 µm	CdS	CdS	$Zn(O,S,OH)_x$	CdS	CdS
p-Typ Absorber ca. 2 - 3 µm	$Cu(In,Ga)Se_2$	$Cu(In,Ga)(S,Se)_2$	$Cu(In,Ga)(Se,S)_2$ / $Cu(In,Ga)Se_2$	$Cu(In,Ga)Se_2$	$CuInS_2$
Metall-Rückelektrode ca. 0 - 5 µm	Mo	Mo	Mo	Mo / Barriere	Mo
Substrat	Fensterglas	Fensterglas	Fensterglas	Edelstahlfolie	Fensterglas

From Philipp Buchegger

Sputtered Mo Thin Films (NREL)



Pressure

5 mTorr

8 mTorr

12 mTorr

Rate: 25Å/sec.

CIGS Formation Pathways (NREL)

1. Cu + In + Ga → Cu:In:Ga intermetallic

Cu:In:Ga intermetallic + H_2Se (or Se) → $Cu(In,Ga)Se_2$

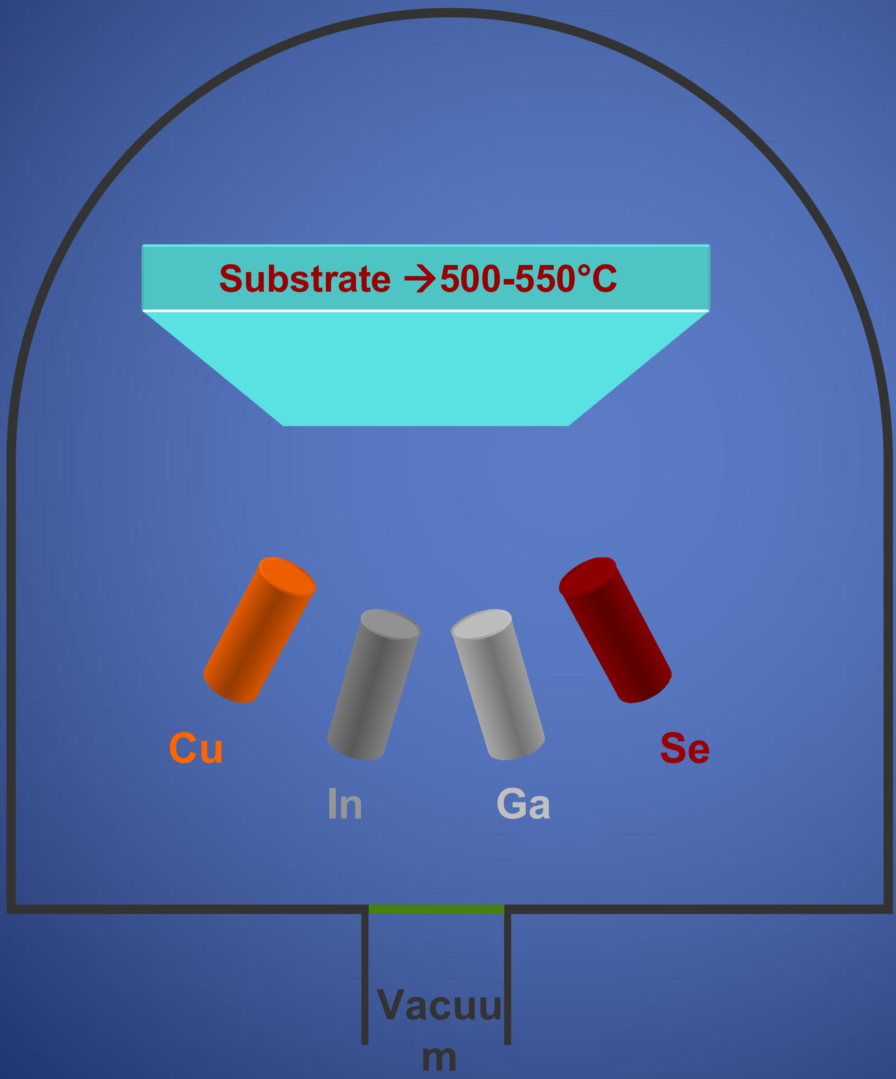
2. $Cu_2Se + (In,Ga)_2Se_3$ → $Cu(In,Ga)Se_2$

3. Cu + In + Ga + Se → $Cu(In,Ga)Se_2$

Deposition Methods

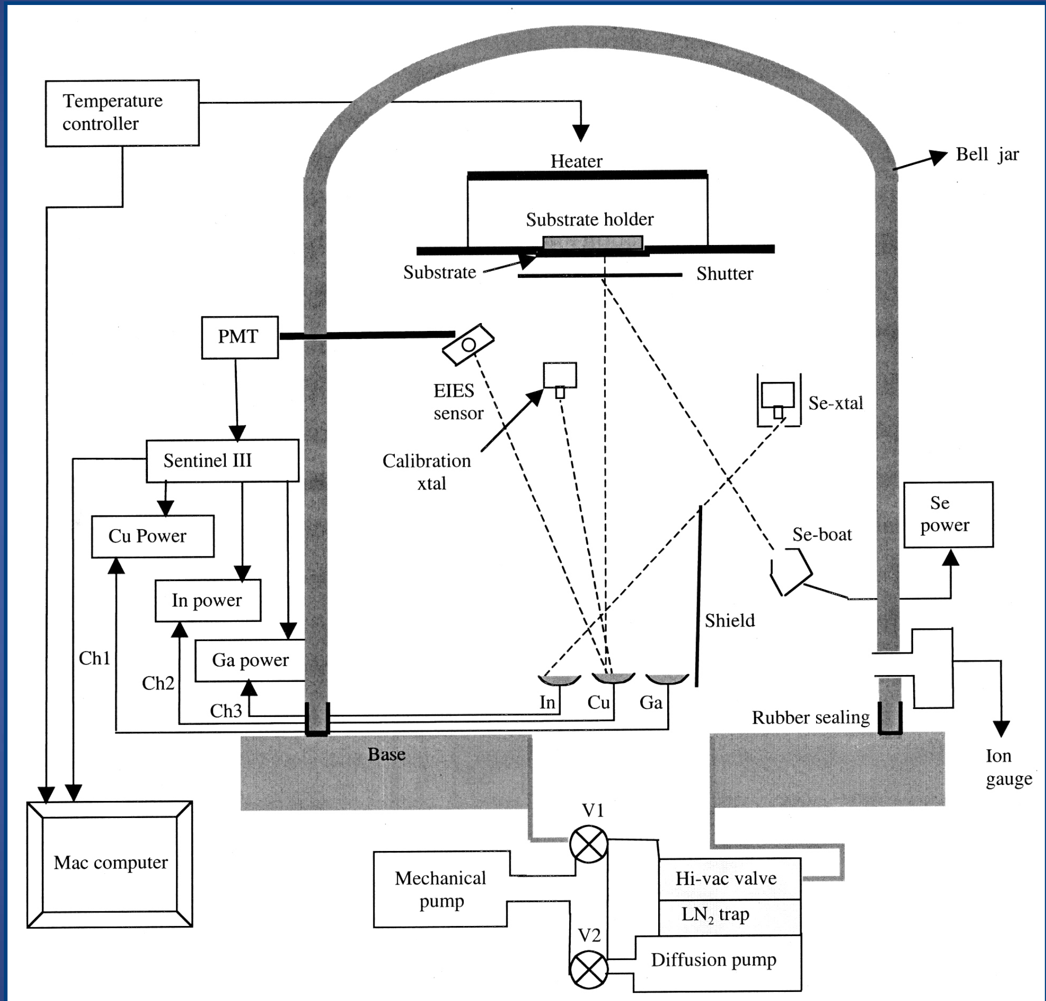
Evaporation of the Elements	Vacuum
Sputtering of the Elements	Vacuum
Nanotechnology/Nano-particles-(Inks)	Printing
CVD-based (lab. R&D)	Low Vacuum

Co-Evaporation



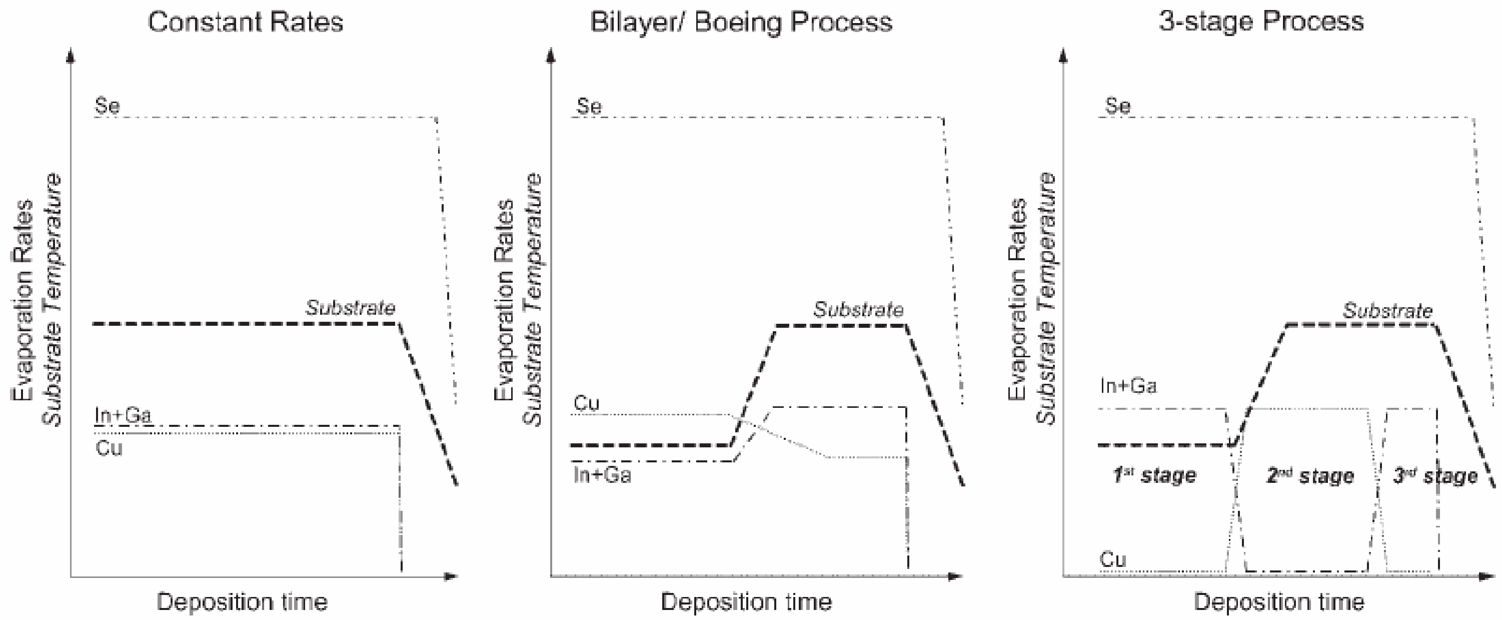
$\eta = 19.9\%$

CIGS Deposition System



From Philipp Buchegger

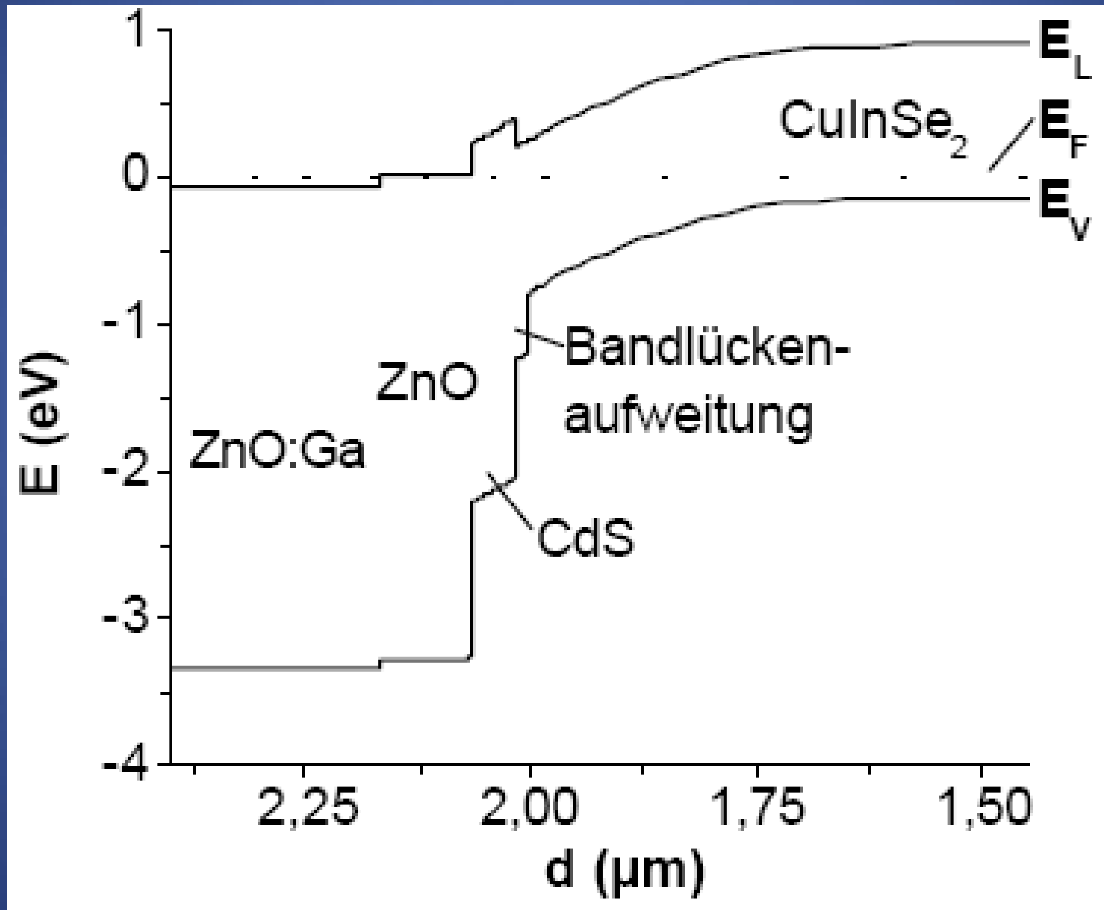
Different preparation processes



Highest efficiency

A.Romeo et al. Prog. Photovolt: Res. Appl. 2004

Band grading



From Philipp Buchegger

Incorporation of sodium

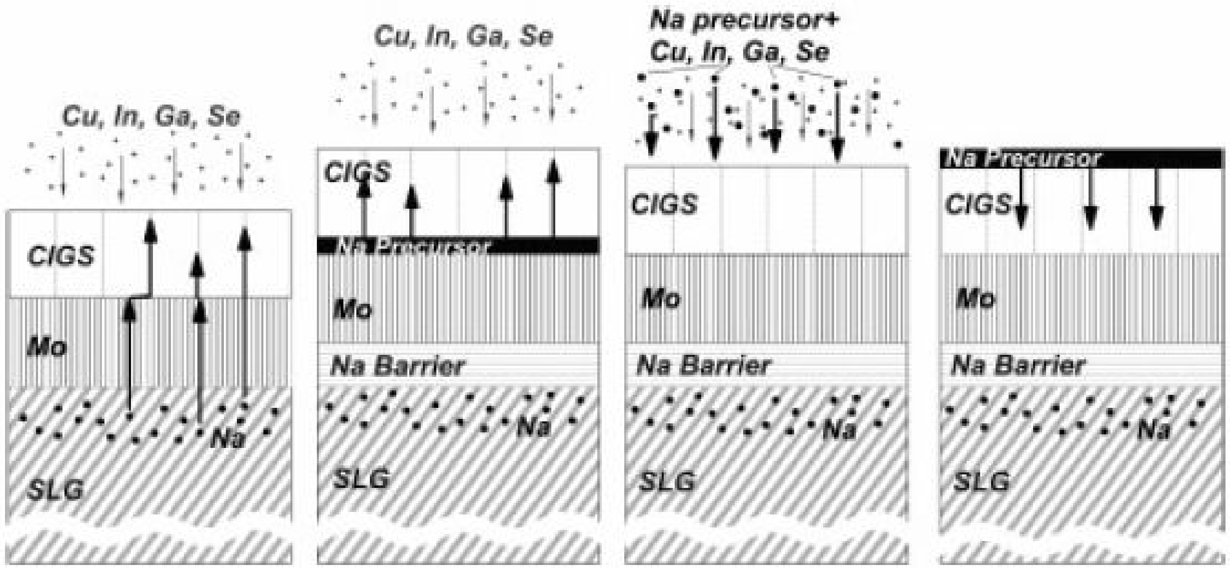


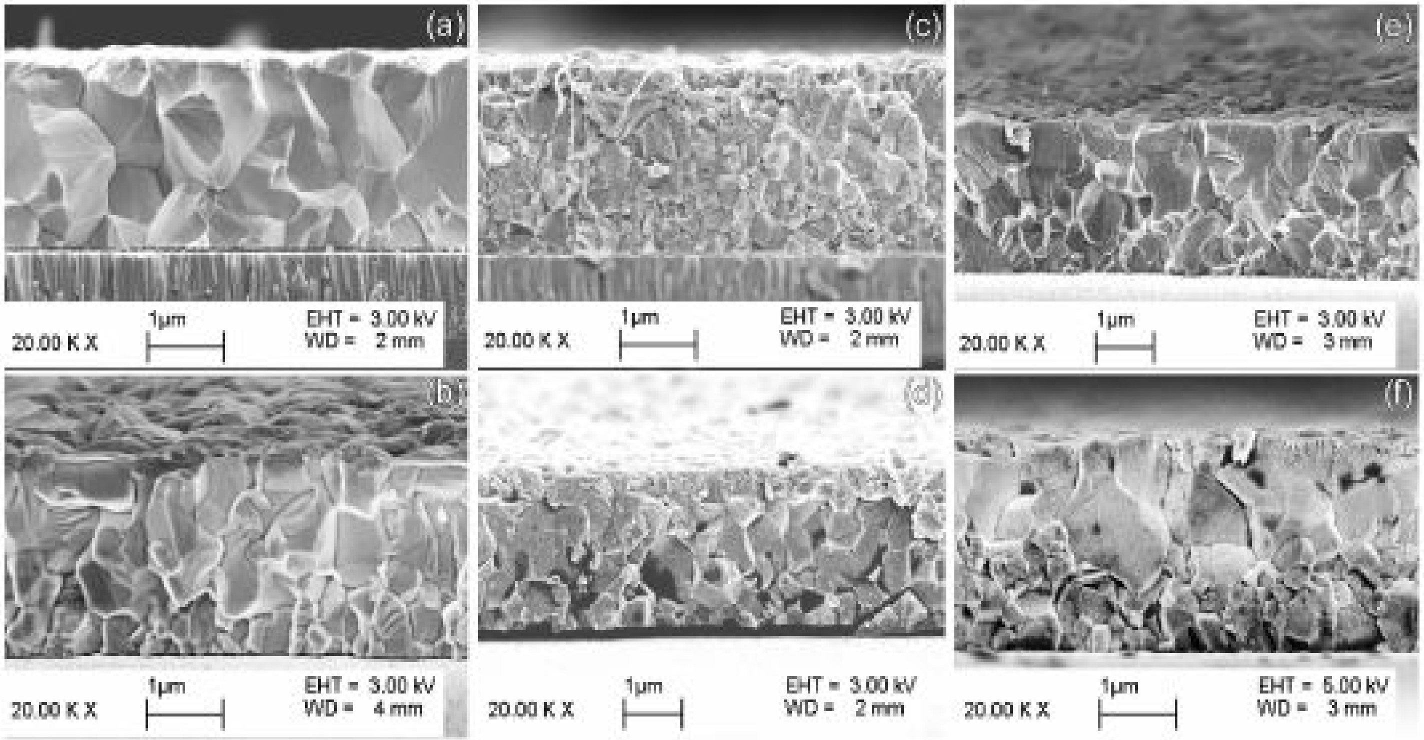
Figure 6. Schematics of different Na incorporation methods into the CIGS absorber

Sodium is beneficial but some effects are depending on the deposition process

Sodium is doping the CIGS material

A.Romeo et al. Prog. Photovolt: Res. Appl. 2004

Incorporation of Na by various methods



(a) CIGS without Na

(b) Coevaporated NaF (20 nm, 1st stage)

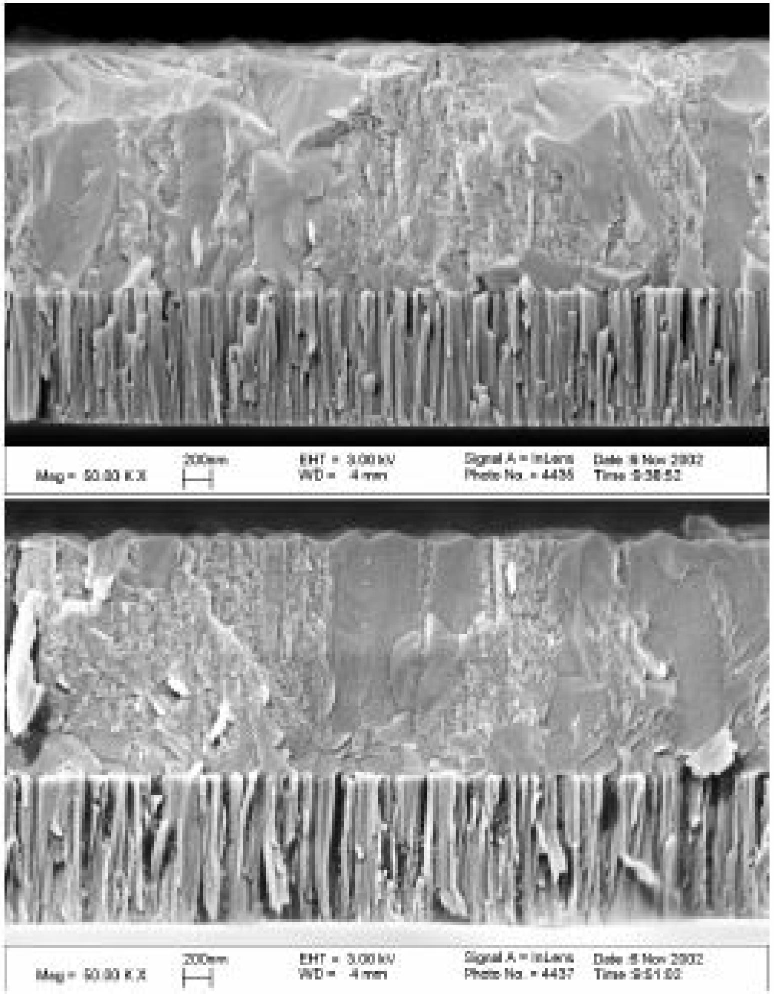
(c) Coevaporated NaF (40 nm, 1st stage)

(d) Coevaporated NaF (40 nm, 2nd stage)

(e) NaF precursor (40 nm)

(f) Diffusion from SLG (no barrier)

From Dominik Rudmann ETH Zurich



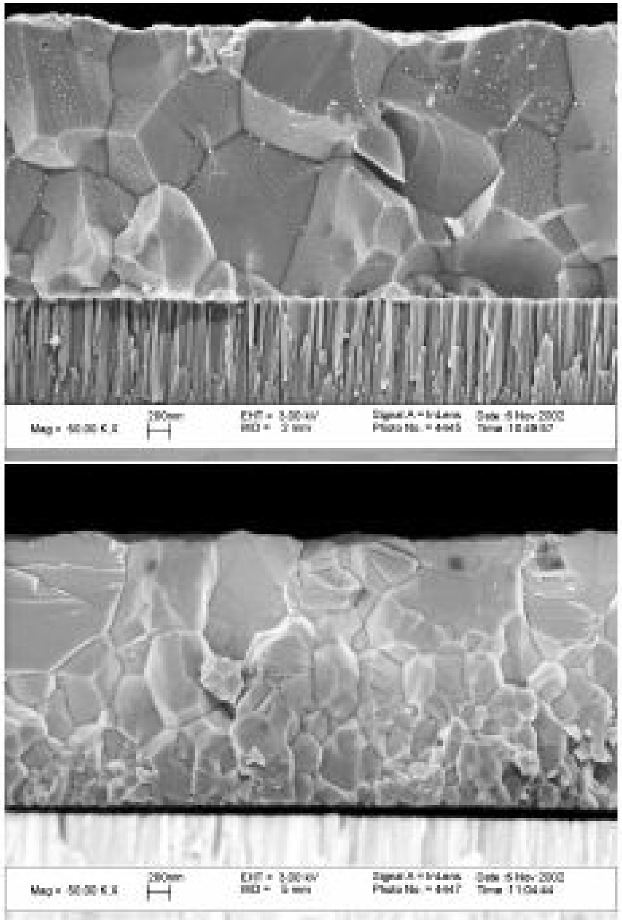
"CIGS growth" stopped after 1st stage

=> $(In,Ga)_xSe_y$

with Na barrier

without Na barrier

From Dominik Rudmann ETH Zurich



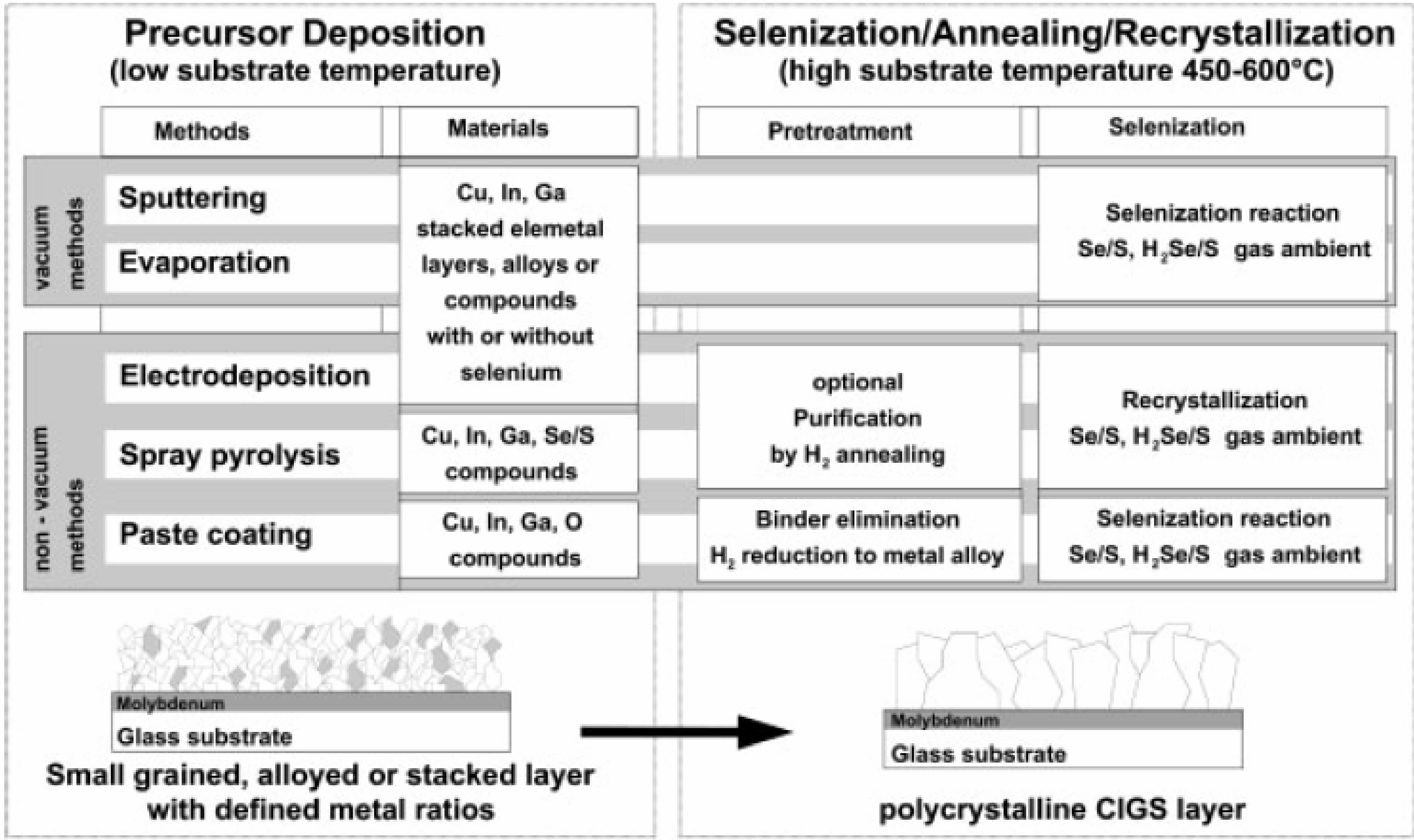
CIGS growth stopped after 2nd stage

=> Cu-rich CIGS

with Na barrier

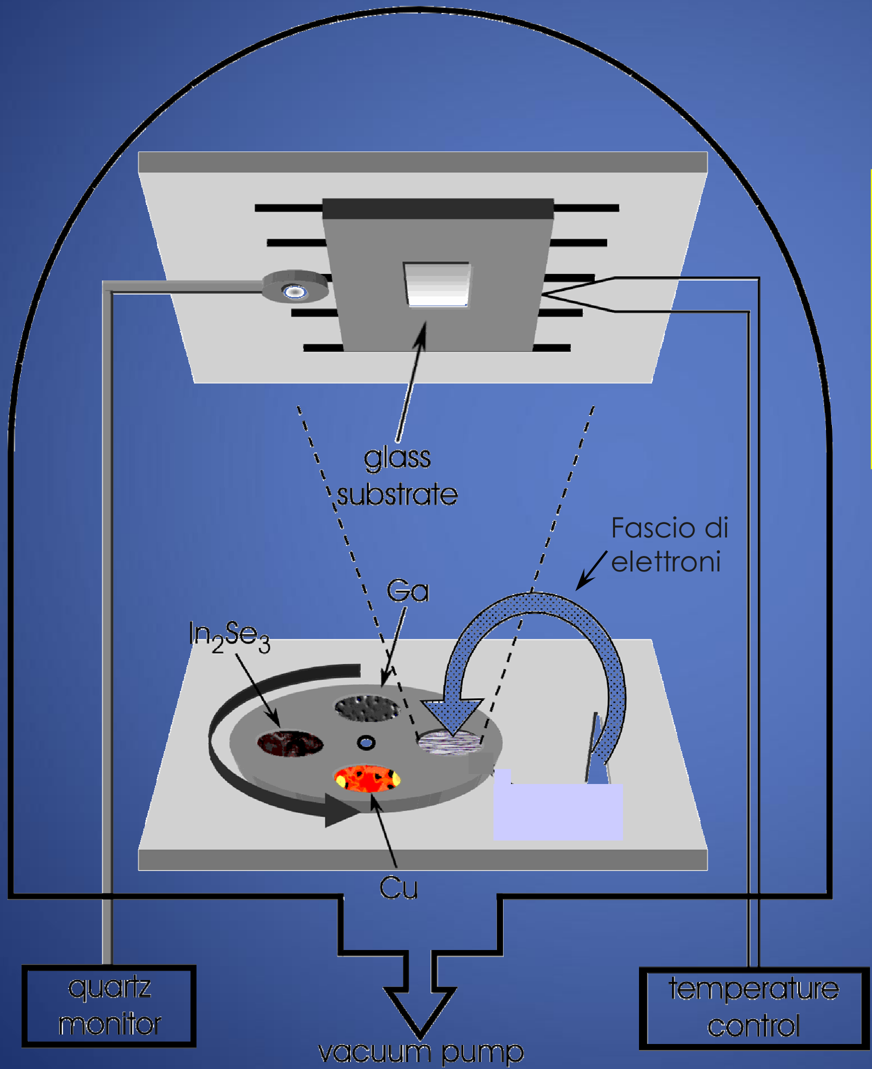
without Na barrier

CIGS preparation by precursors



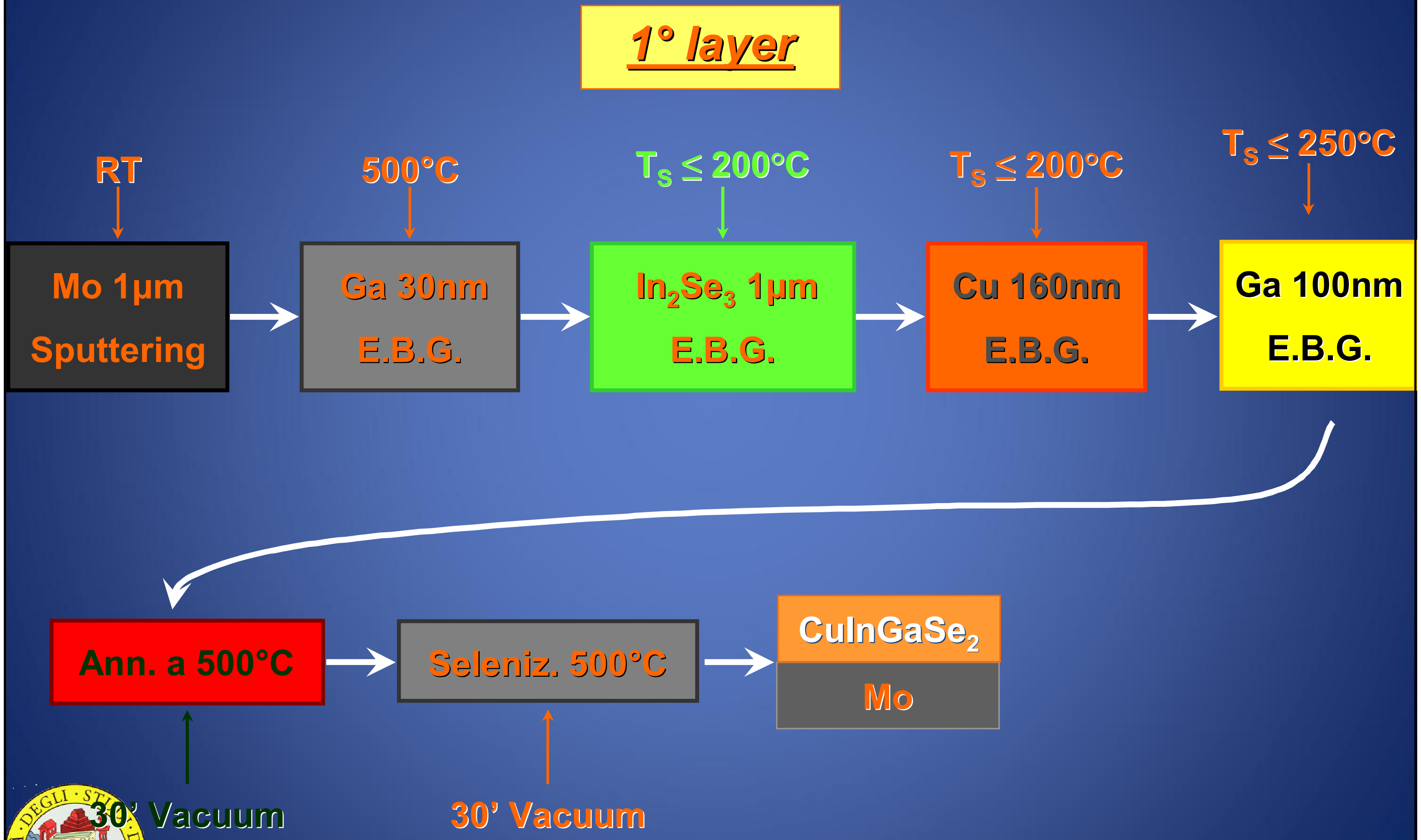
A.Romeo et al. Prog. Photovolt: Res. Appl. 2004

Electron Beam Gun (UniPR)

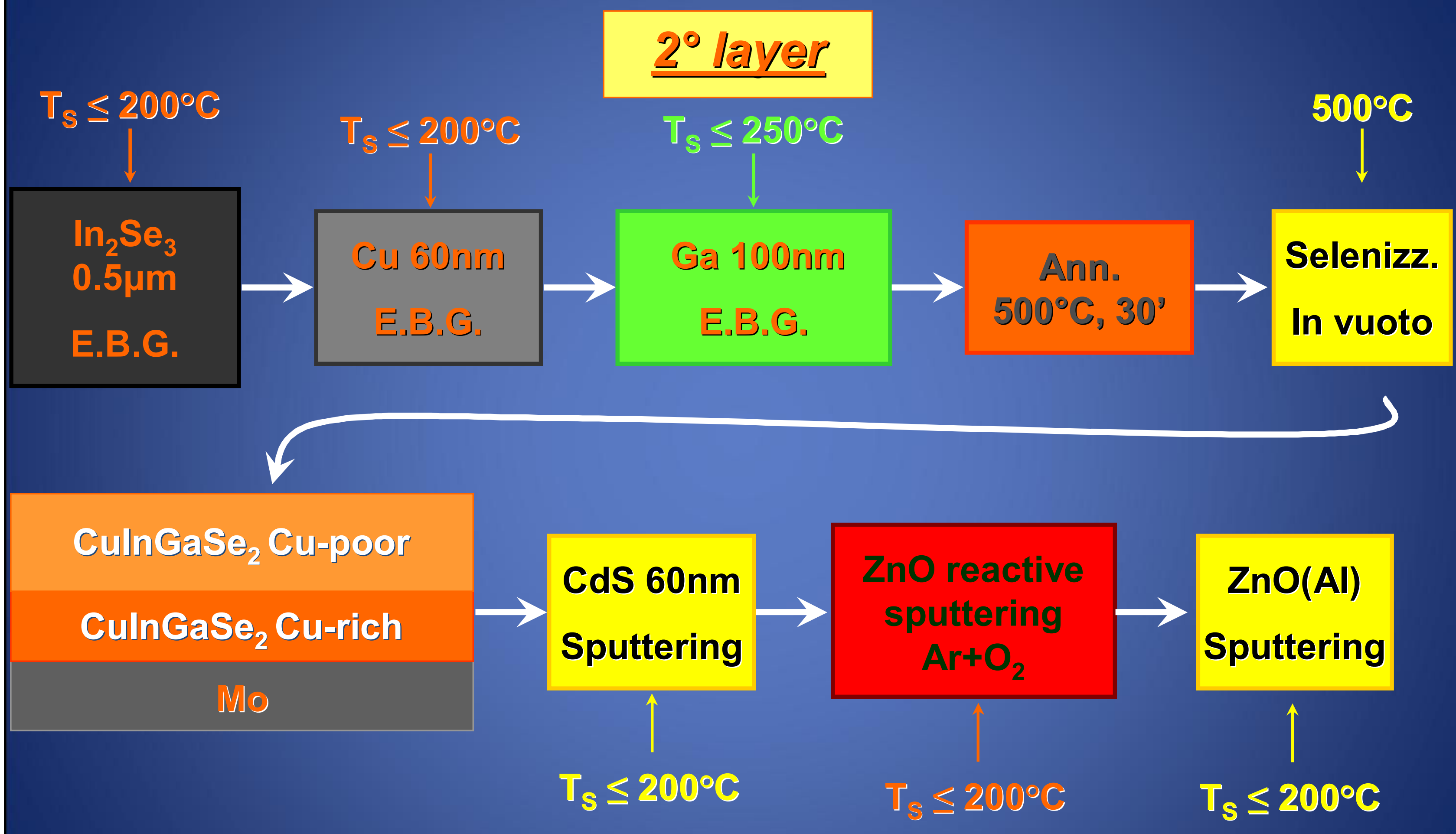


Sequence evaporation E.B.G. (Electron Beam Gun)

Preparation by precursors (UniPR)



Preparation by precursors (UniPR)



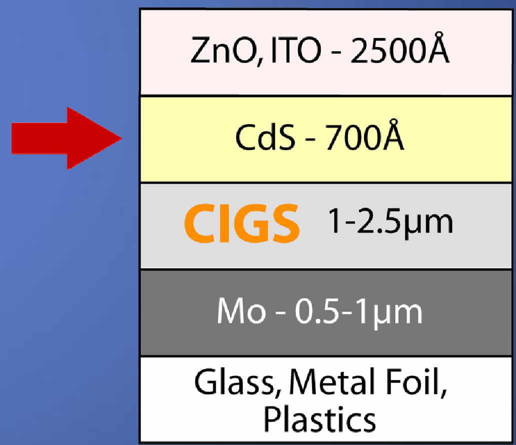
Deposition of CdS

Chemical Bath Deposition:

Solution (CBD): $CdSO_4$, NH_4OH, N_2H_4CS (Thiorea), H_2O

Temperature: 60°C to 85°C

Time: 4 to 20 min.



Sputtered CdS

Ts 150-200°C: more difficult to have a thin layer

Possible Reasons for CdS Alternatives

(1) Basic Performance.

Higher current from improved blue photon collection (generally realized), while maintaining equal voltage (generally not realized).

(2) Conduction-Band Offset Considerations

(a) Better match to CIS, especially when no blue photons present (current issue). (b) Better match to wide band-gap CIGS (voltage issue).

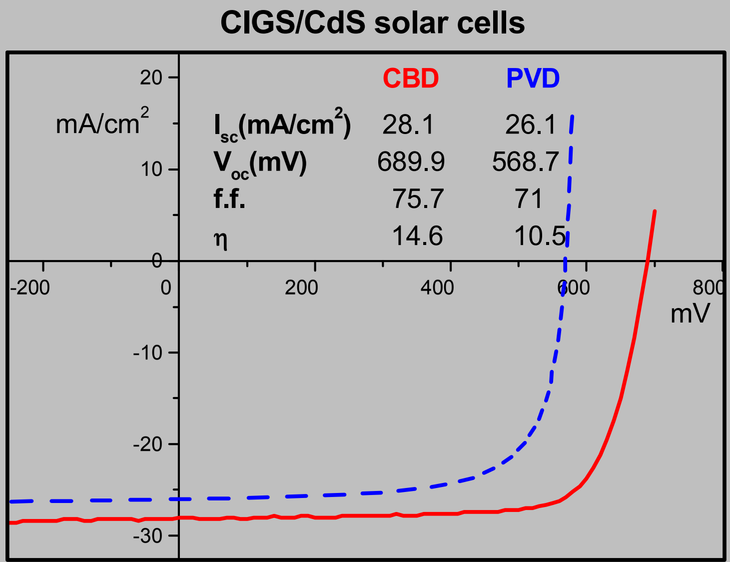
(3) Other Considerations

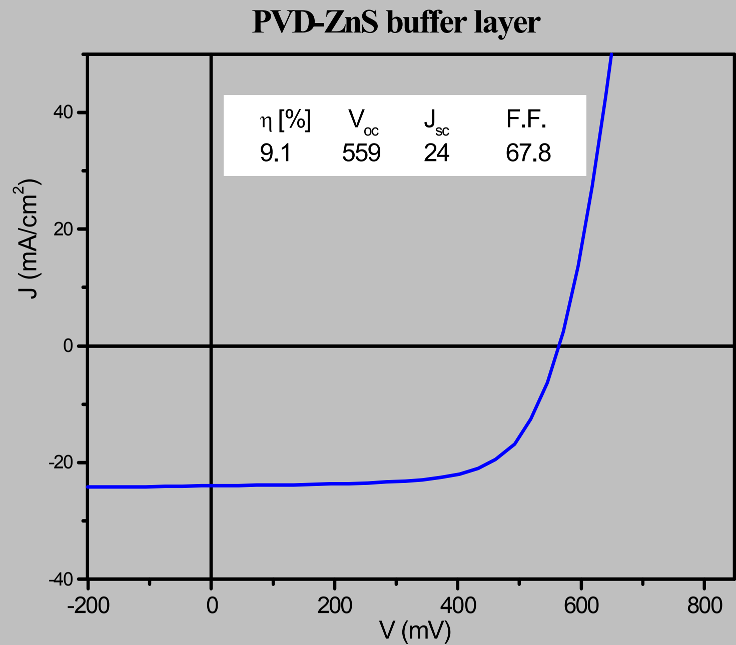
(a) More robust junction when front contact deposition requires elevated temperature. (b) "Cadmium-free" could assist marketing.

Best CIGS Performance

Buffer Layer	Efficiency
CBD-CdS	19.9% (2008)
CBD- ZnS(O,OH)	18.6% (2003)
CBD- InS(O,OH)	16.2% (2003)
ALD-In_2Se_3	16.4% (2003)
Cd-PE	15.7% (2003)
ZnO	15.0% (1999)
$ZnIn_2Se_4$	14.5% (1998)
ZnSe	14.2% (2000)

CIGS solar cells with different buffer layers (ETHZ-ARomeo)



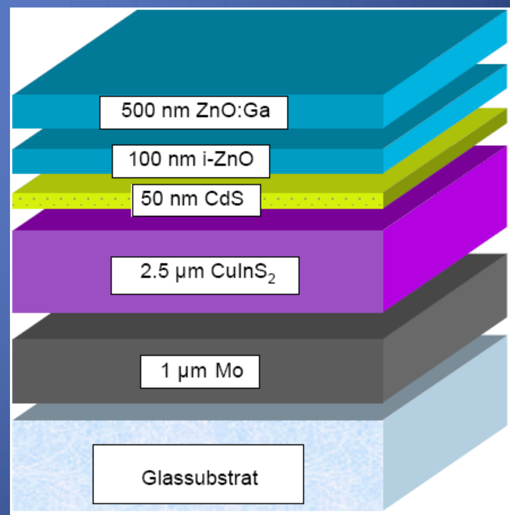


Efficiency with PVD-buffers: 9 to 12%

Buffer layer

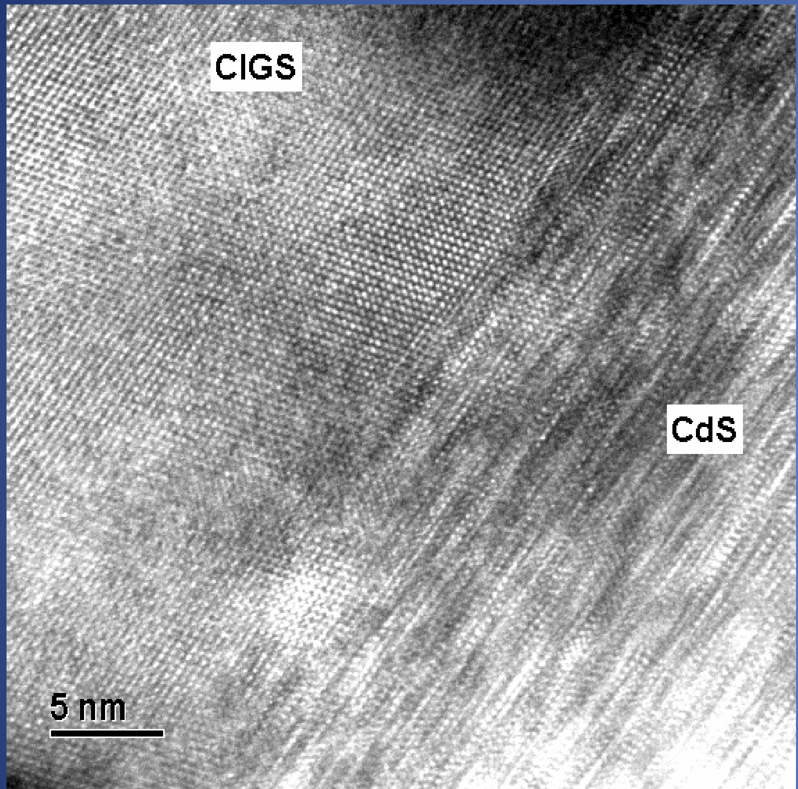
- Protection from sputtering of ZnO
- CdS (ZnS, ZnSe) buffer layer is deposited with a temperature of 60°C in a chemical bath on the CIGS
- In_2S_3 buffer layer with PVD or ALD (0.5nm/min) or sputtering (20nm/min)

Puffer	η [%]	VOC/Zelle [V]	FF [%]	jSC [mA/cm²]	Zellen	Fläche [cm²]
RF-In_2S_3	11,2	632	63,6	27,9	12	68,9
CBD-CdS	12,3	661	66,1	28,0	12	68,9



Nakada et al. CIGS/ZnS → 18.6%

CIGS/buffer layer interface

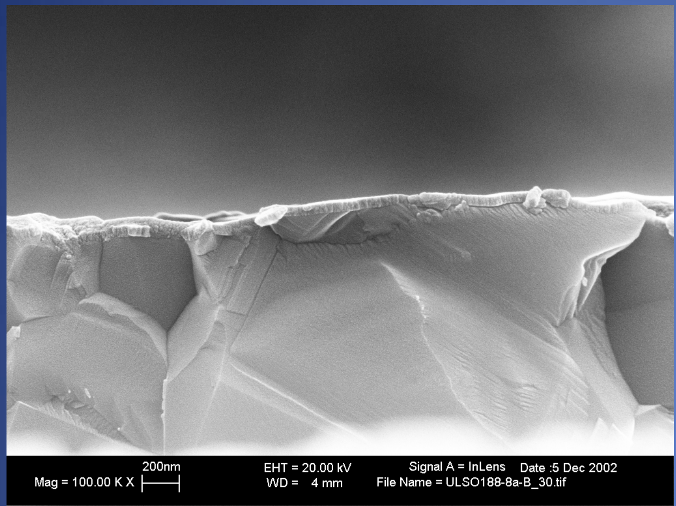


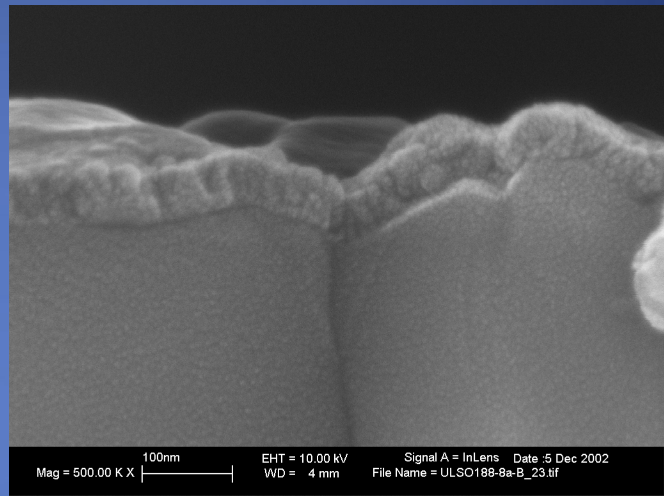
CIGS/CdS

CIGS/In_2S_3

Interface characterization with TEM

ZnSe buffer layer

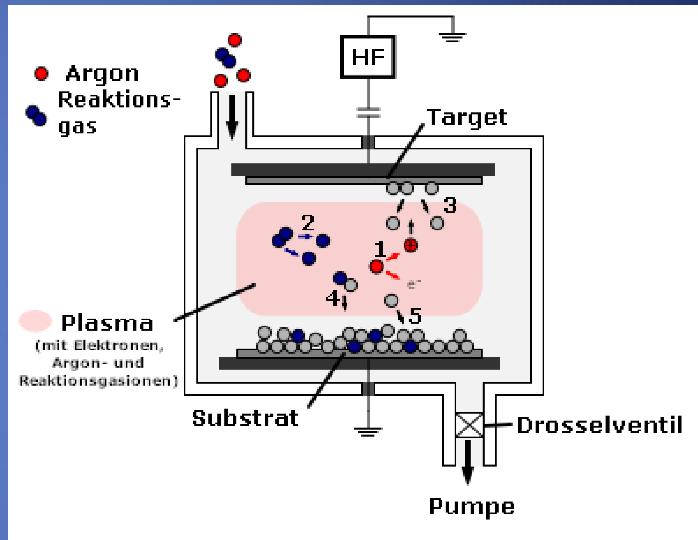




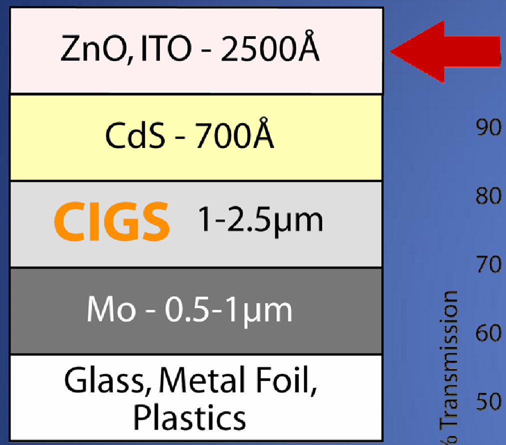
Cross-section SEM images of CIGS covered with 50 nm thin ZnSe buffer layer shows a uniform coverage.

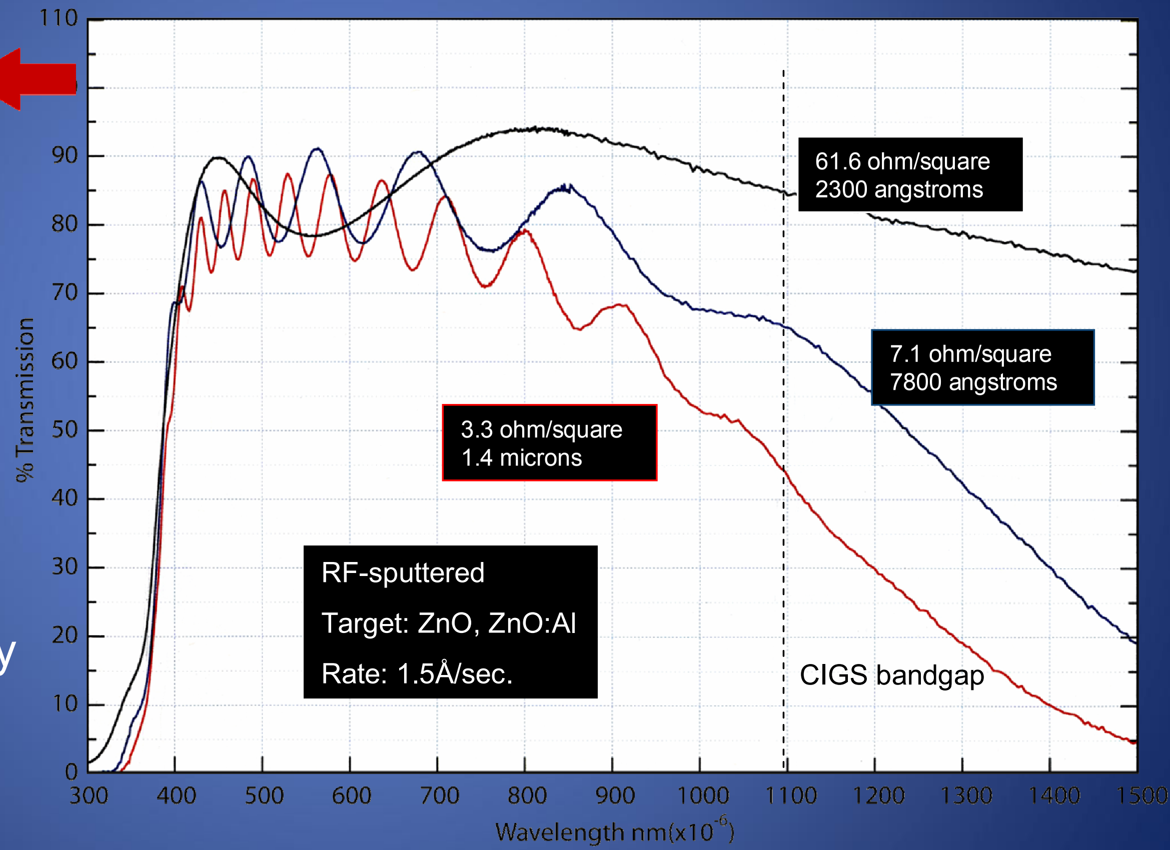
Front contact

- Contact layers: Mo und ZnO:
  - Sputtering
    - Argon atmosphere
    - ZnO with RF-Plasma
    - ZnO:Al with DC-Plasma 70nm/s
    - Substrate temperature 20-400°C



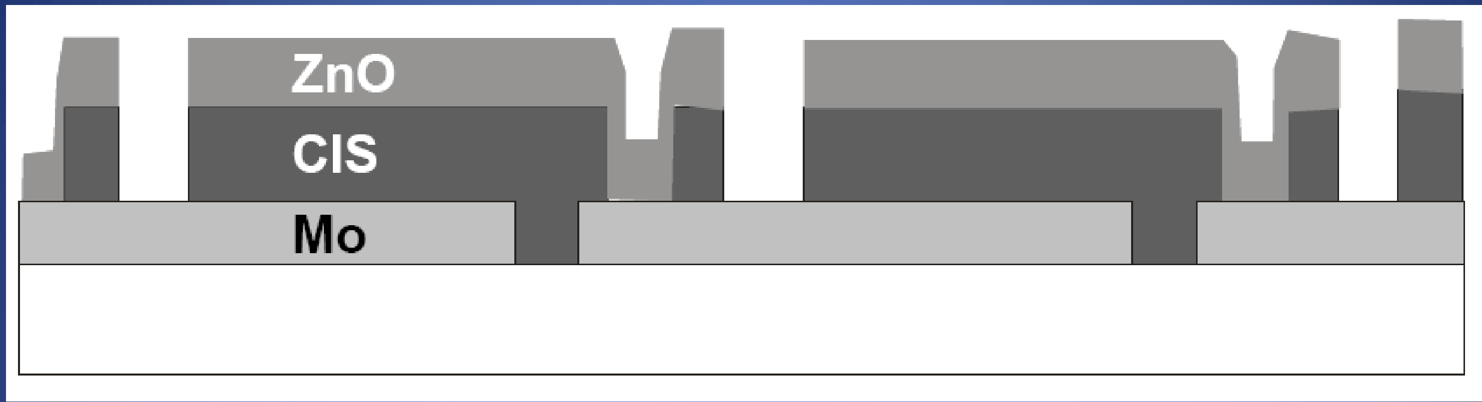
Optical Transmission - ZnO





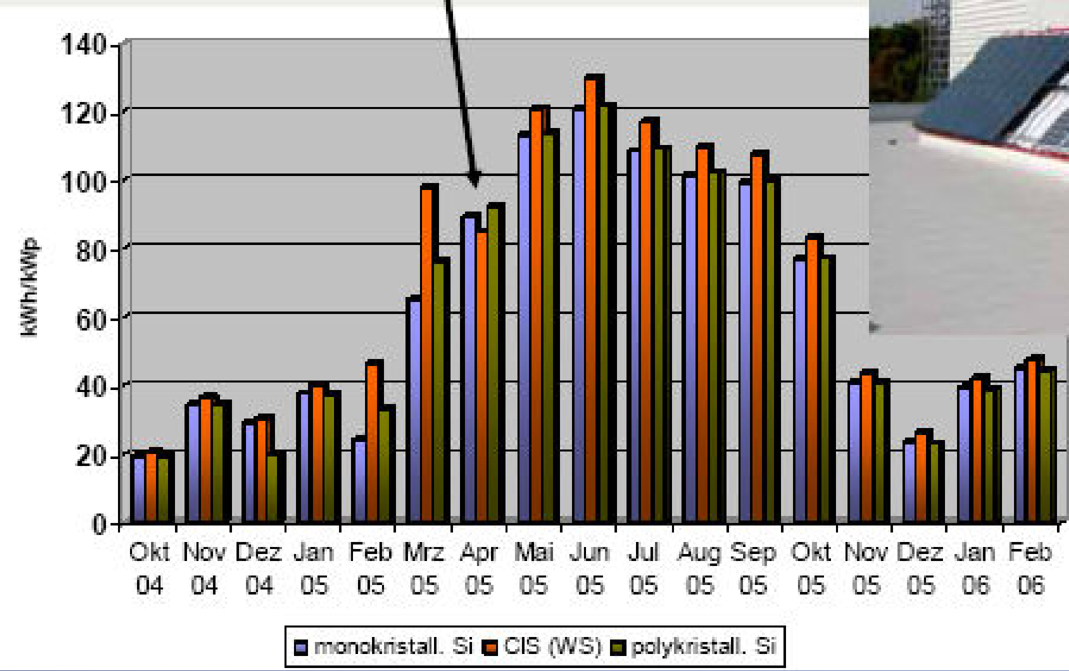
ZnO:B deposited by CVD (industry)

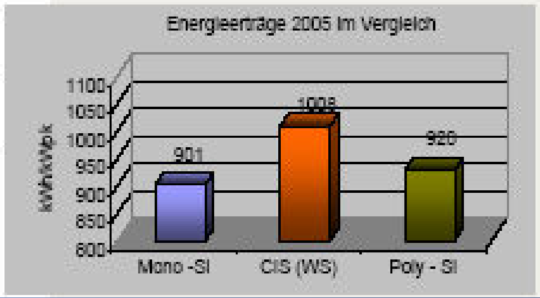
Monolithic integration



Generally TCO is laser scribed and absorber and Mo are mechanically scribed.

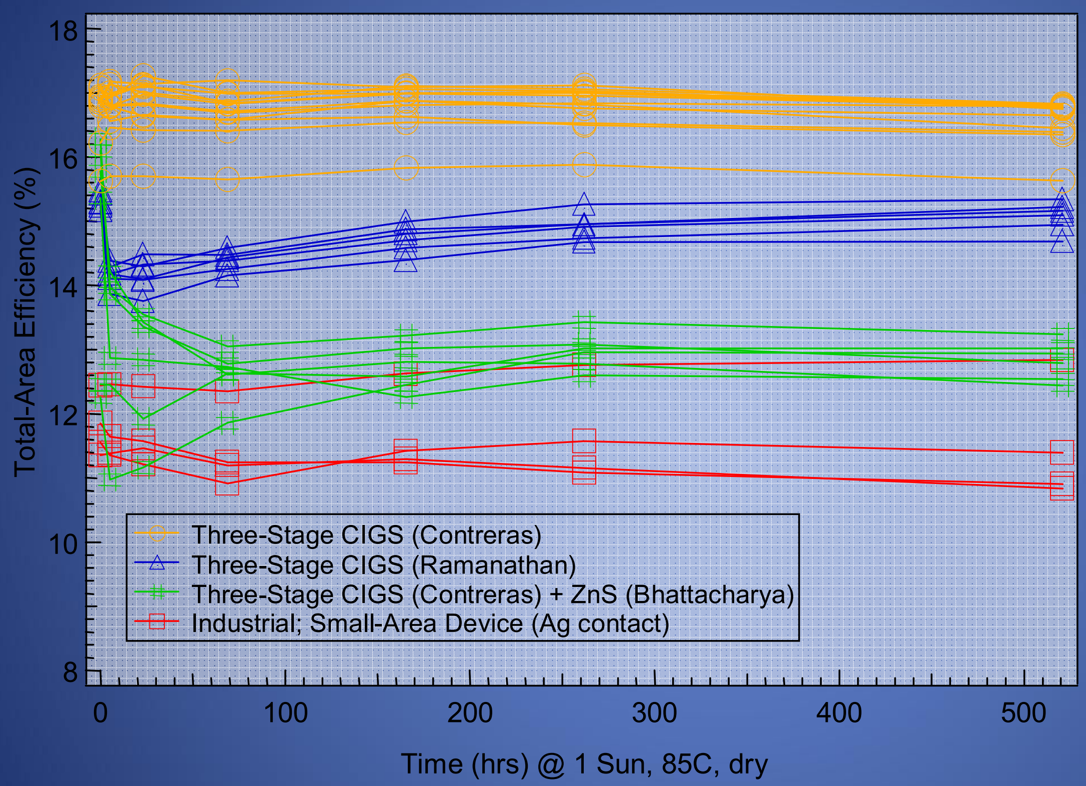
Comparison with Si technology





Source: Würth Solar

CIGS Stability Dry/1-Sun/85° (Nrel)



Identical 3-stage process; yet very different transient recovery behavior; distinguishing difference = Mo

Modified "ZnS" junction; different characteristics on the same substrate

"Industrial" samples showed biggest spread in light-soak behavior

After some initial "equilibration", CIGS devices show excellent stability (dry/1-Sun/85°C/Voc bias)

Future for CIGS-Technology

Substitution of indium →CZTS: Cu_2ZnSnS_4→ 6.7 % Katagiri et Al.

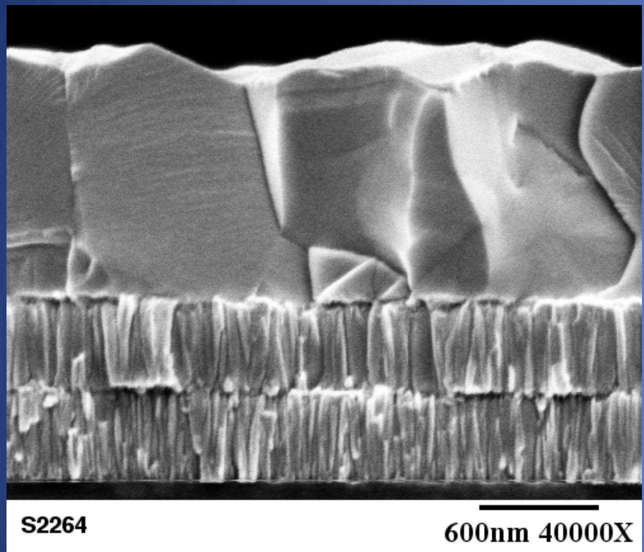
http://www.goldseiten.de/bilder/artikel/mueller-1308_3.jpg

Thinner CIGS Absorbers

- **Indium availability and price are concerns for CIS PV.**
- **Began work to fabricate solar cells on thinner (≤1 µm) absorbers grown by modified 3-stage process.**
- **Thin absorbers also fabricated using co-deposition of all elements.**

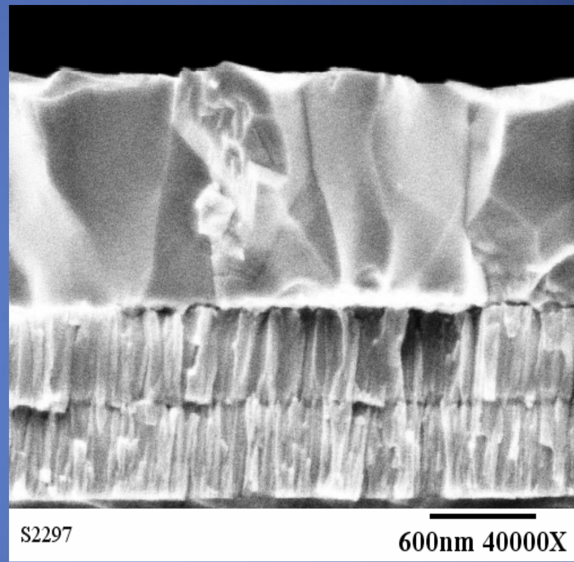
Thick absorbers 1-μm (NREL)

3-stage



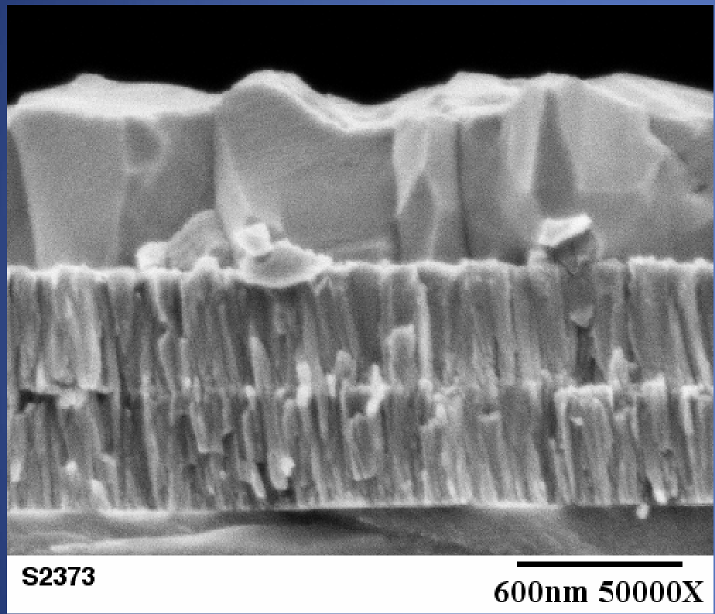
V_{oc}= 0.654 V;
J_{sc}= 31.6 mA/cm²
FF= 78.3%; Eff = 16.2%

Co-deposition

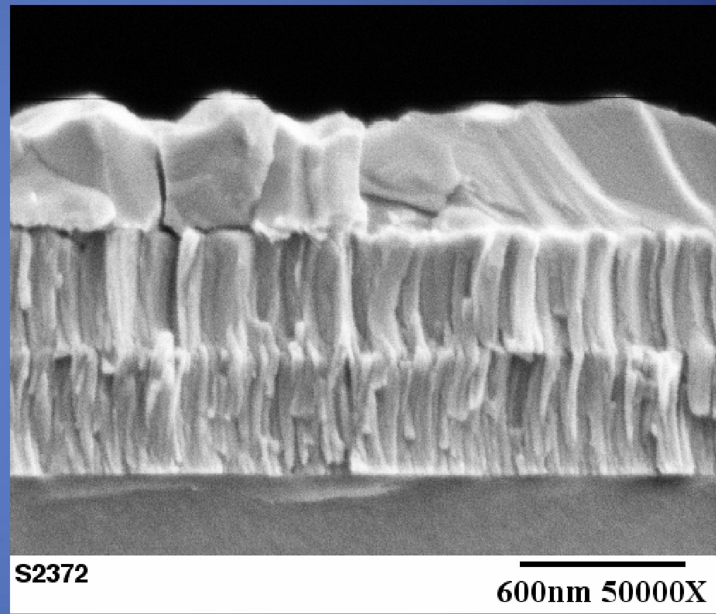


V_{oc}= 0.699 V;
J_{sc}= 30.6 mA/cm²
FF= 75.4%; Eff = 16.1%

Thinner CIGS Absorbers (NREL)



0.75 µm (12.5%)

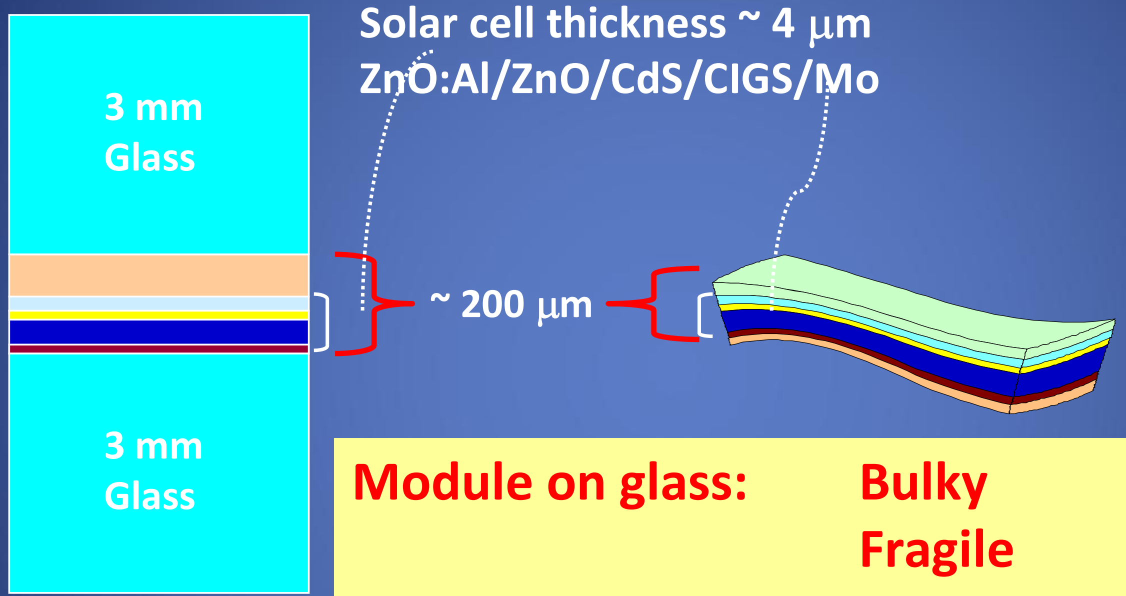


0.4 µm (9.1%)

Thin CIGS Cells Summary (NREL)

t (µm)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	Eff (%)
1.0 (3 stg)	0.678	31.9	79.2	17.15
1.0 (codep)	0.699	30.6	75.4	16.0
0.75	0.652	26.0	74.0	12.5
0.40	0.565	21.3	75.7	9.1
1.4 (450˚C)	0.585	31.1	70.6	12.9

Substrate for CIGS solar modules: Glass *vs* foil

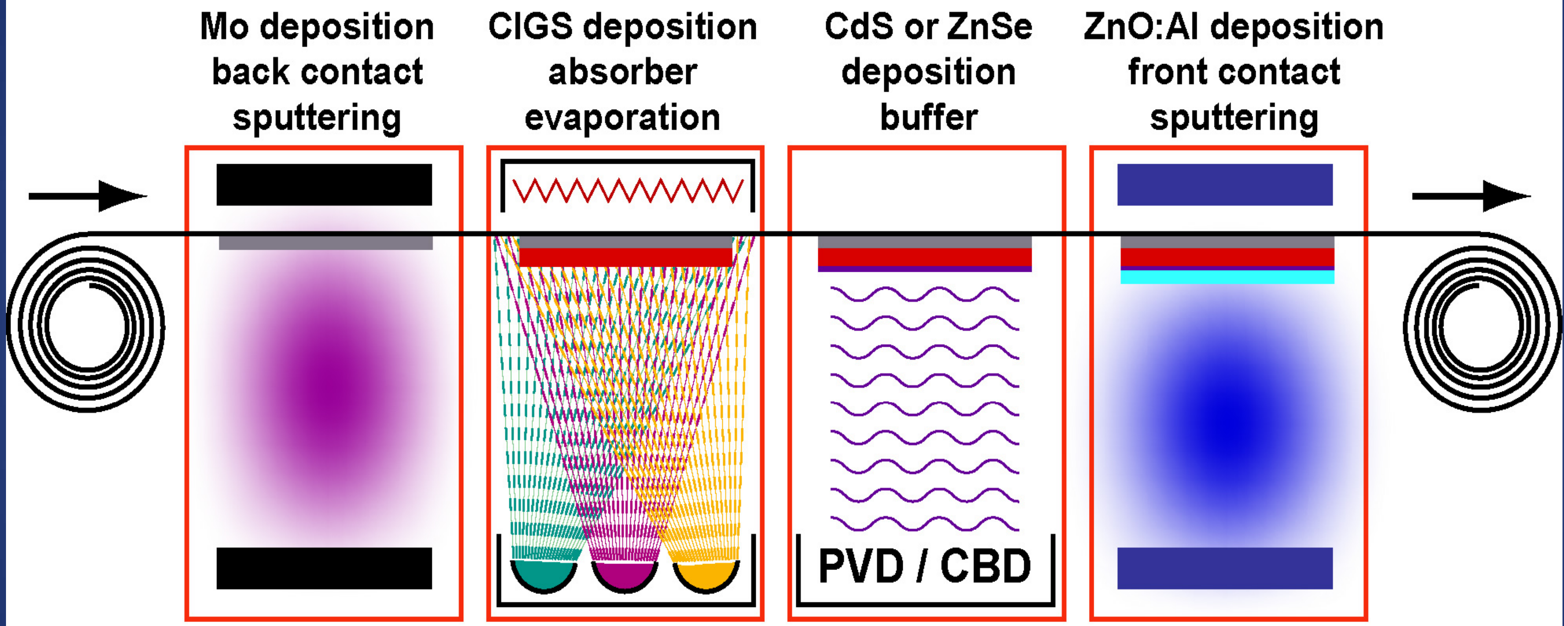


Module on glass: Bulky
Fragile
Heavy

Flexible solar modules offer several advantages

Roll-to-roll deposition on metal or polyimide foil

Next generation of production technology



Modules -> Need scribing and patterning for interconnections

But not yet developed for PV !

General problems !!

Why solar cells on flexible substrates ?

Manufacturing advantages:

Roll-to-roll deposition methods for industrial production

Lower costs of equipment and infrastructure

- 10-30 times smaller size of R-R equipment for foil than for in-line glass substrates
- No need of robotics for handling of heavy and fragile glass

High speed of deposition (food packaging industry trends)

Lower cost of solar modules (< 0.60 €/W)

→ **Lower energy pay back time**

CIGS flexible solar cells and modules

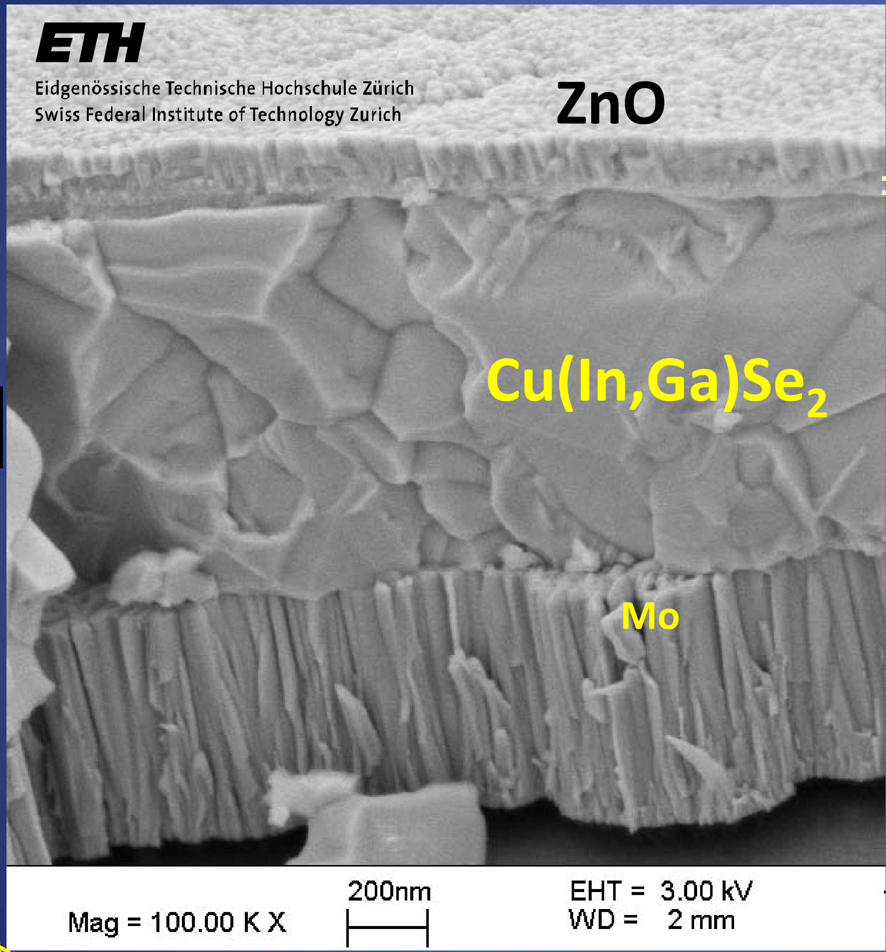
Choice of substrate is very important

Metal or polymer foil ?

Polymer suitable for monolithic integration

but low deposition temperature process required

CIGS solar cell on polyimide



1-2 µm

50nm CdS

Sputtering
Chemical Bath

Co-Evaporation

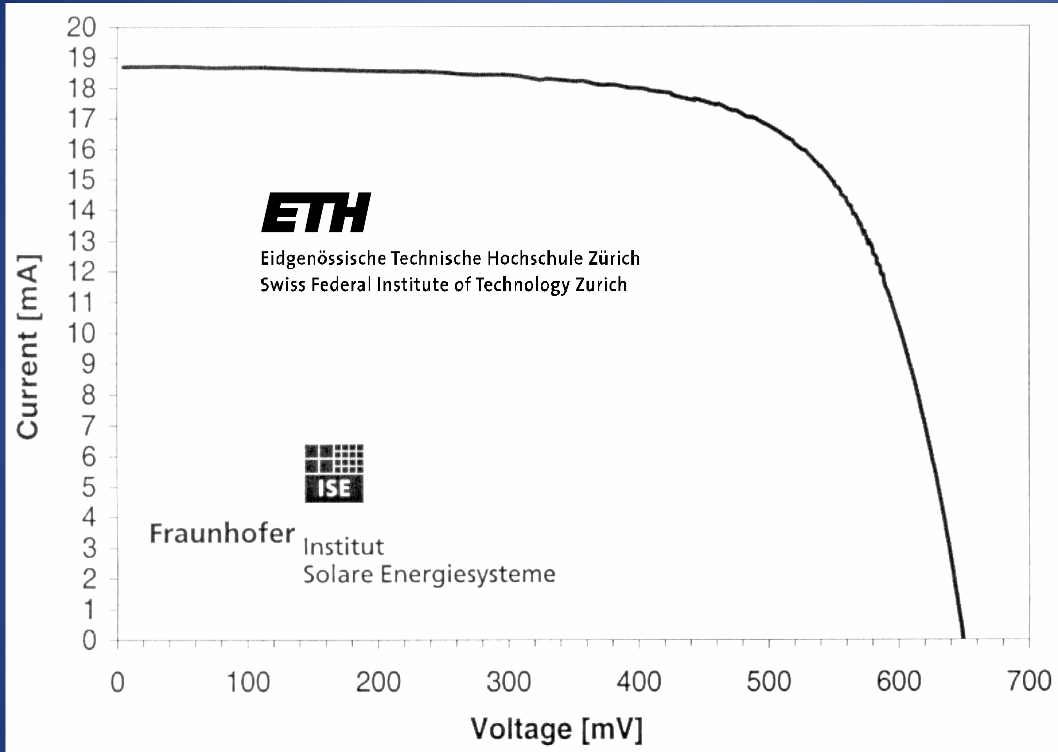
Sputtering

Substrate
(Polyimide)

FLEXIBLE

Highest efficiency record

Flexible and lightweight CIGS solar cells on polymer foil



V_{oc} = 649.4 mV

J_{sc} = 31.48 mA/cm^2

FF = 69.1%

η = 14.1%

Certified efficiency: Total area, AM1.5 illumination, no AR coating

FLEXIBLE

Power output from solar module*

12% efficiency means 120 watt from 1 m^2 surface area exposed to sun

Lower efficiency means larger area needed

Efficiency*	Area need for 20 W
12% (CIGS)	0.166 m^2 (0.3 X 0.55 m^2)
6% (a-Si)	0.332 m^2 (0.3 X 1.1 m^2)
3%	0.664 m^2 (0.3 X 2.2 m^2)

*- Under AM1.5 illumination

Conclusions

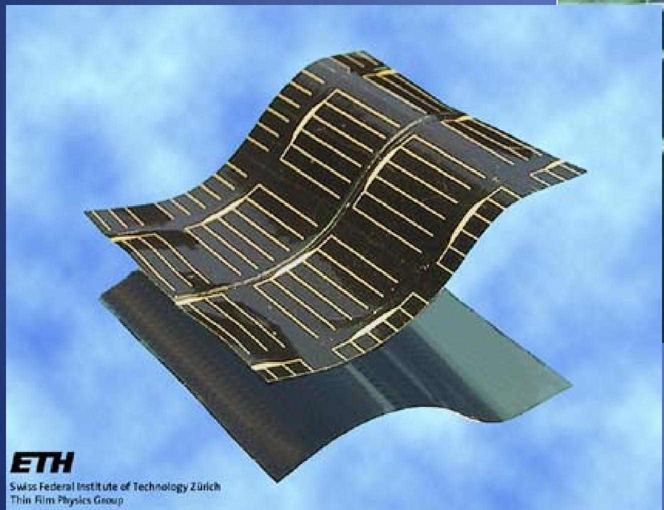
CIGS solar cell can give very high efficiency

Despite a less scalable process than CdTe the higher efficiency promises a low cost production.

Alternative buffer layers have been provided with success

High efficiency CIGS flexible solar cells have been achieved

Thank you for your attention !!!



Rotbäumesfeld, Ludwigsburg