"Solar Energy" WS 2014/2015

Karlsruher Institut für Technologie

Lecture 9: CIGS and CdTe Thin Film Solar Cells

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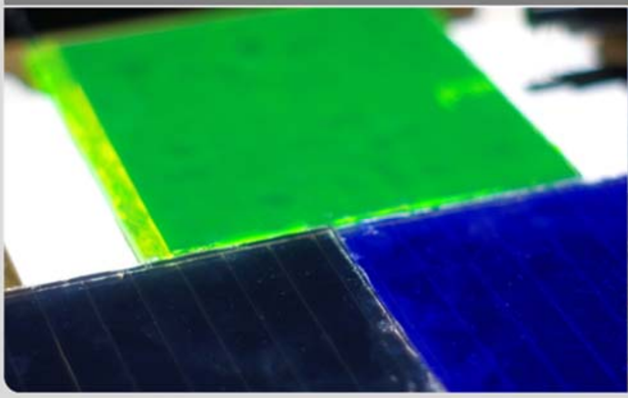
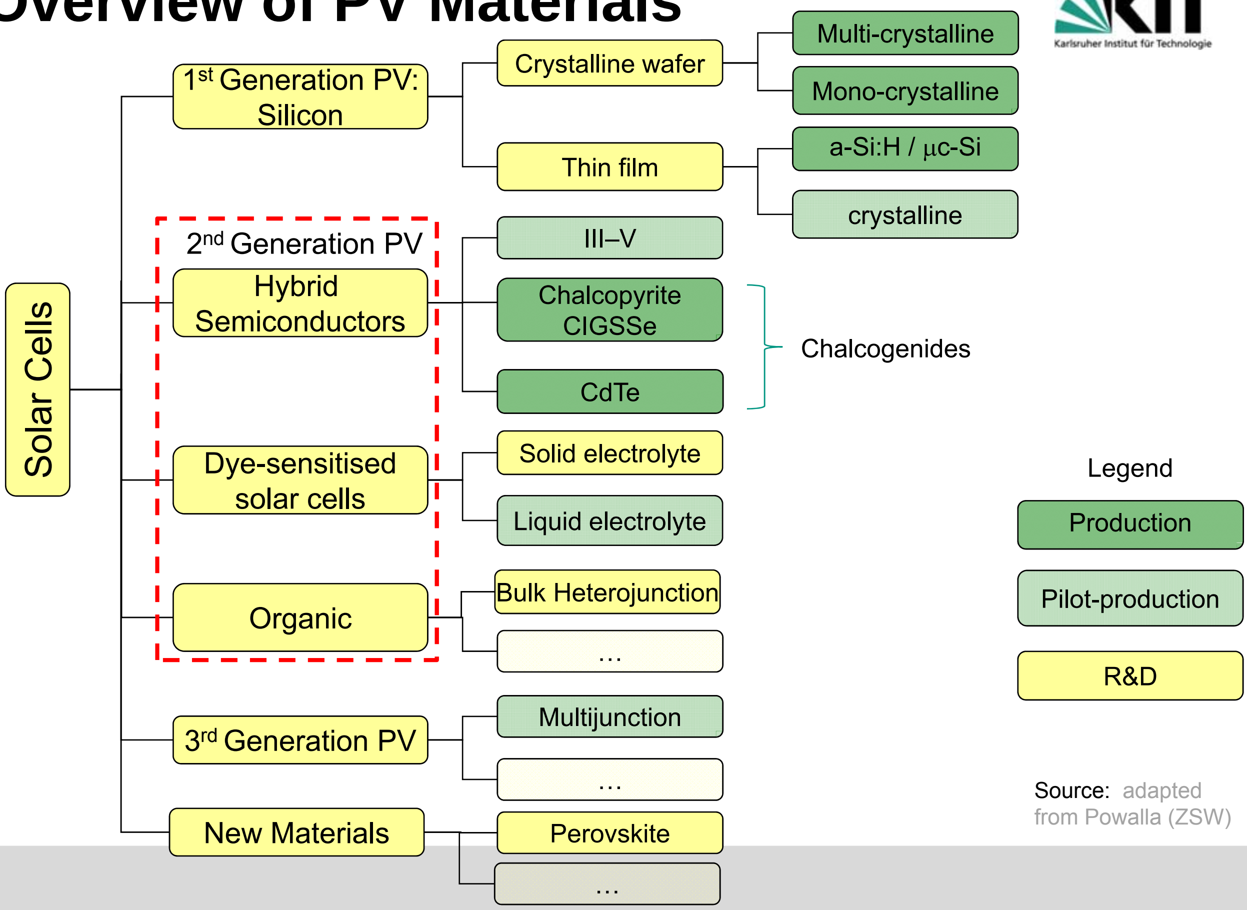
KIT Focus Optics & Photonics

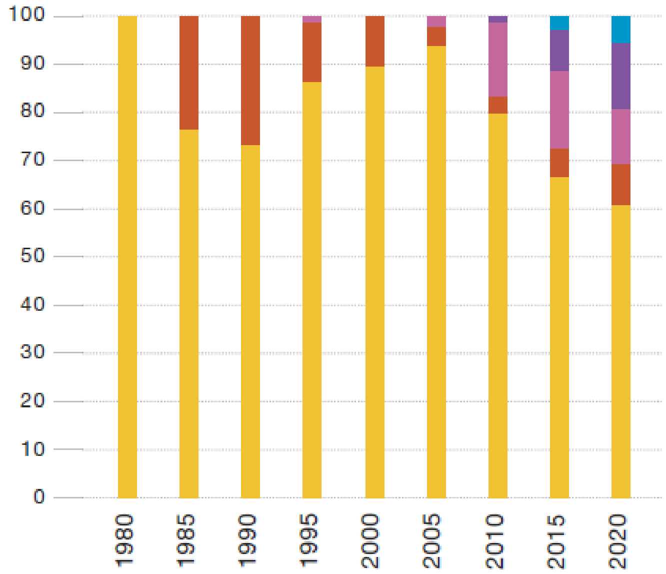


Overview of PV Materials

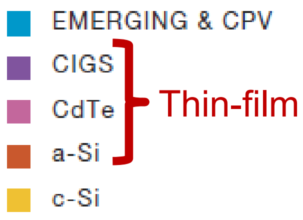


Source: adapted from Powalla (ZSW)

Market Tomorrow?



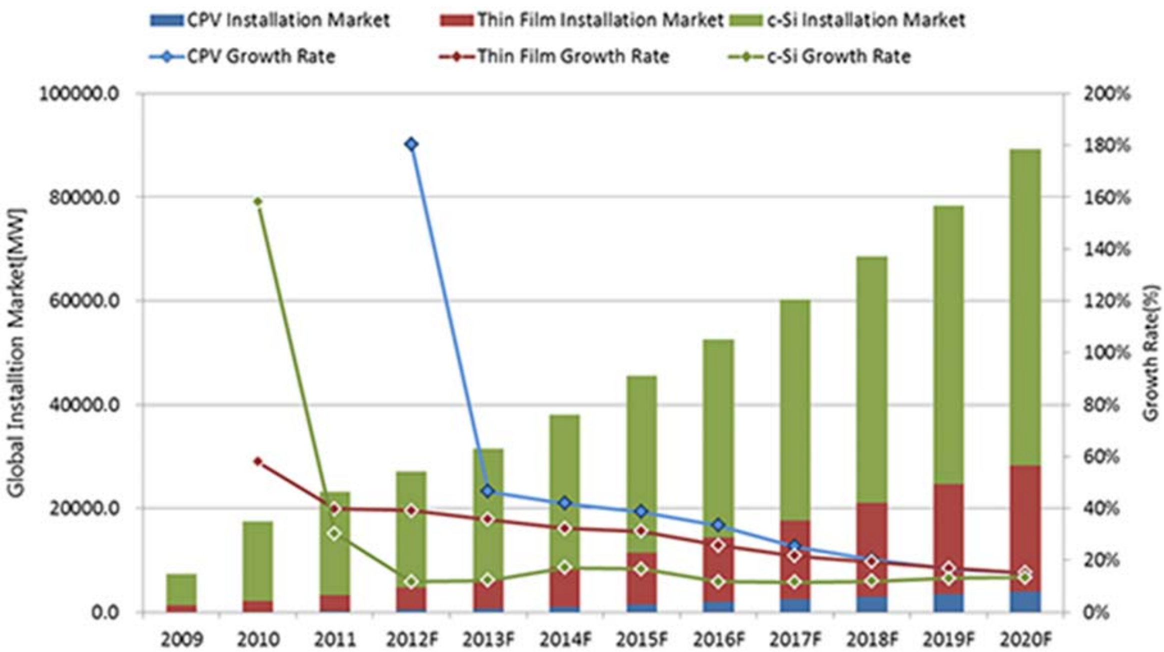
2009 prediction that CIGS market would grow significantly by 2020…



source: Historical data (until 2009) based on Navigant Consulting. Estimations based on EPIA analysis.

Market Tomorrow?

… but in this market prediction the growth is predicted to decline



Source: http://www.sino-report.com/b/nenyuan/xinnenyuan/20121031/1187.html

Market Today

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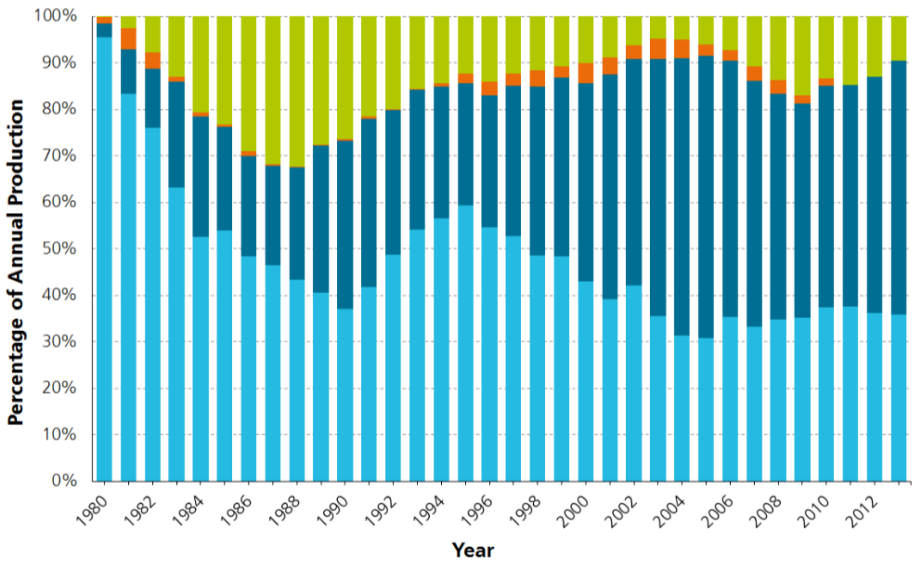
But actually the whole thin film market share has been decreasing since 2009



Production 2013 (GWp)

Thin film	3.5
Mono-Si	13.9
Multi-Si	21.3
Ribbon-Si	0

⇓

Thin film has 9% share of current PV market

Source: *http://www.ise.fraunhofer.de/de/downloads/pdf-files/aktuelles/photovoltaics-report-in-englischer-sprache.pdf*

Market Today

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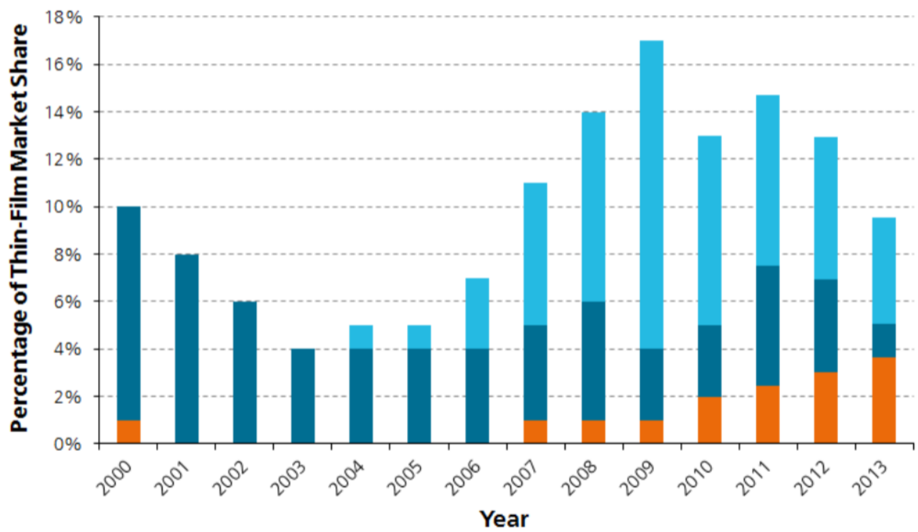
a-Si:H is the main loser in the thin film PV game:

23% market share in 2013, c.f. nearly 100% in 2000-2003



Production 2013 (GWp)

Cd-Te	1.9
a-Si	0.8
CI(G)S	0.8

⇓

CdTe & CI(G)S have ~77% share of current thin-film PV market

Source: *http://www.ise.fraunhofer.de/de/downloads/pdf-files/aktuelles/photovoltaics-report-in-englischer-sprache.pdf*

Solar Cells Design

- Recap: how do I build a solar cell? What material properties do I need?

1. Conversion from solar energy into a chemical energy
   ⇒ absorption and generation

$$d > L_\alpha = 1/\alpha$$

Cell thickness   Absorption length

2. Conversion from chemical energy into electrical energy
   ⇒ photogenerated current (lifetime)

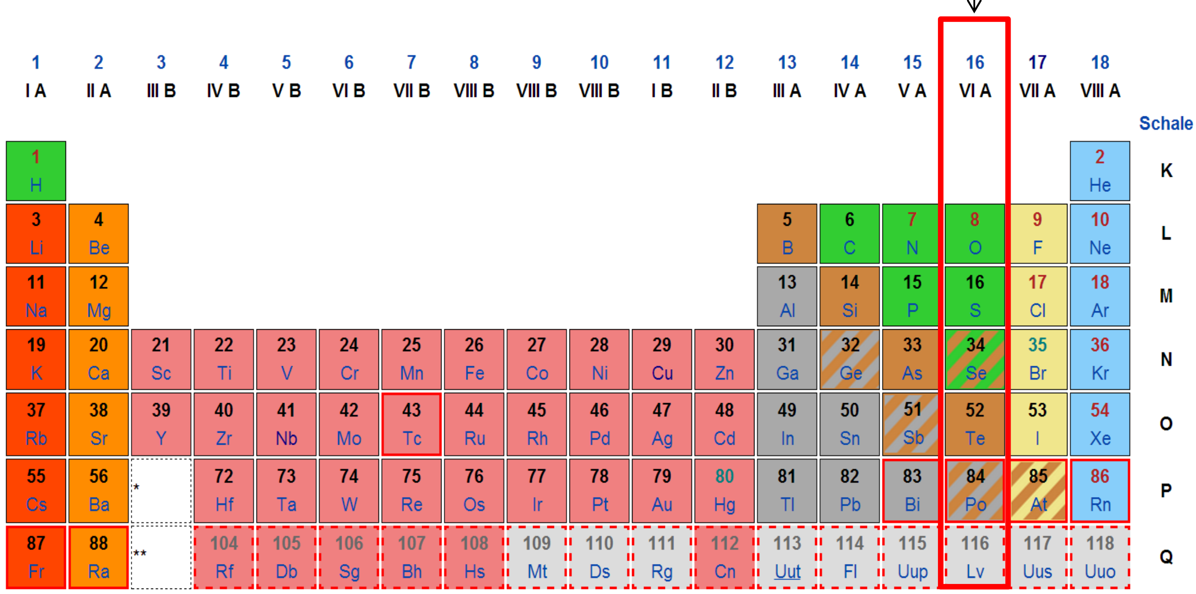
$$L_0 = \sqrt{\mu \frac{kT}{q} \cdot \tau} > d$$

Diffusion length

Chalcogenide Thin Film Solar Cells

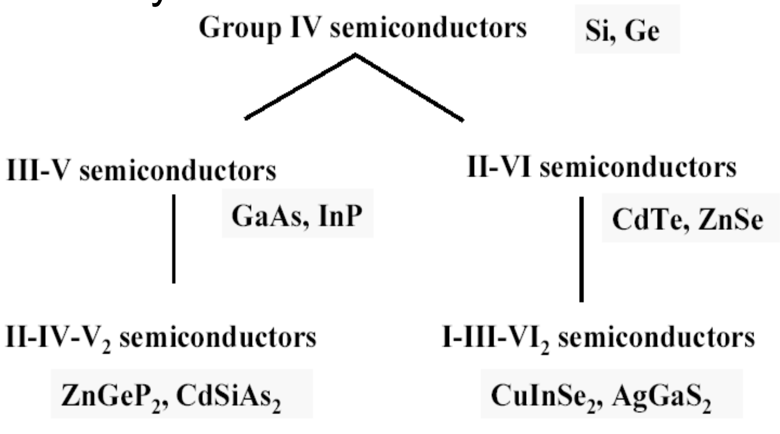
- $Cu(In,Ga)(S,Se)_2$ I-III-VI_2
- CdTe II-VI

Chalcogen elements



Hybrid Semiconductors

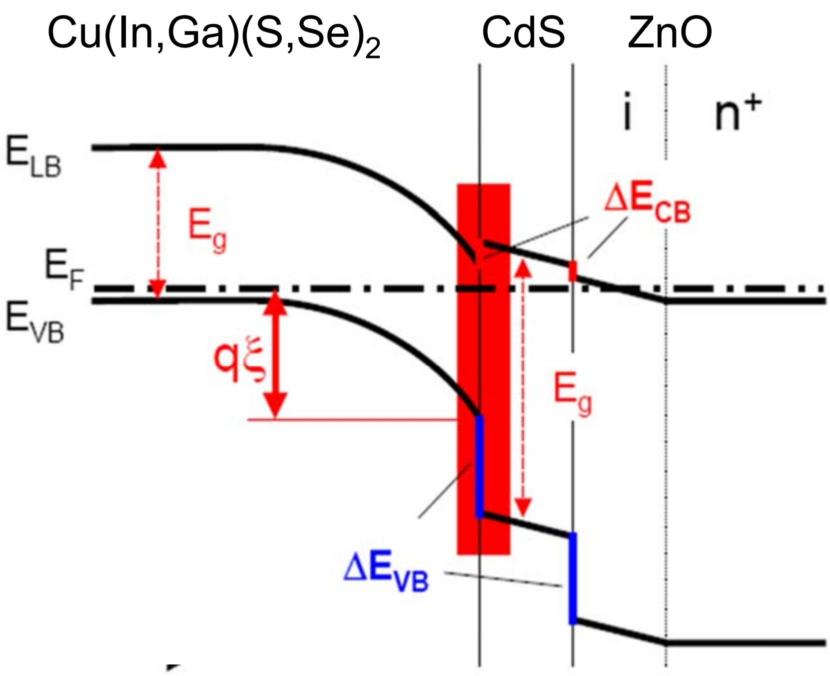
- Drift devices, like a-Si:H
- *p*-type doped material:
  - Copper indium gallium diselenide: $CuIn_xGa_{(1-x)}Se_2$ or CIGS
    - Variables: i) Ga conent and ii) sulphur (S), Se, or both
  - Cadmium telluride (CdTe)
- Both need *n*-doped “buffer” layer
- Absorption and e^--h^+ pair generation only in *p*-type layer



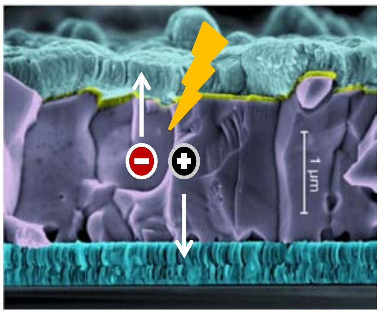
pn Heterojunctions

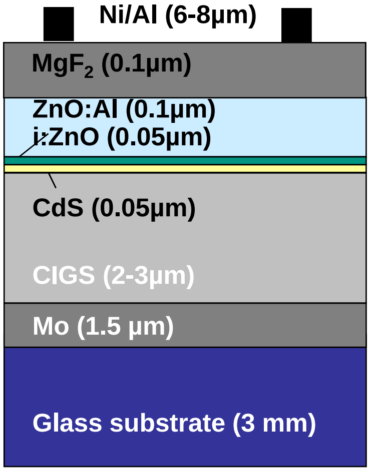
Heterojunction ≡ interface occurring between two layers or regions of dissimilar crystalline semiconductors, which have unequal bandgaps (as opposed to homojunction)

Buffer layer: e.g. *n*-type cadmium sulphide (CdS) and equivalents



Structure of CIGS solar cell





Front contact: TCO – ZnO:Al

Buffer: CdS,
Cd-free (InS, ZnS, …)

Metal back contact: Mo

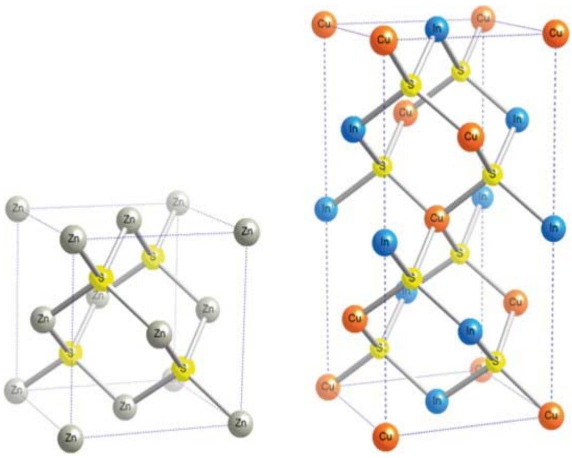
Glass oder flexible substrate
(Foils: PET, Steel, Al)

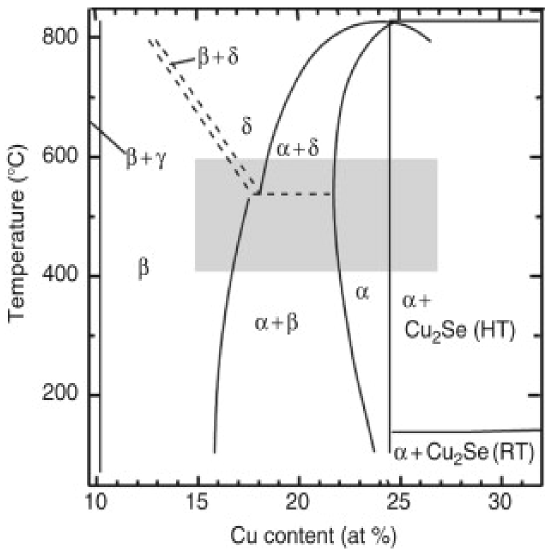
Source: ZSW Annual Report 2008

CIGS absorber material

Advantages:

- Polycrystalline structure
  (large tolerance for defects)
- Ideal bandgap
- High absorption
- Grain boundary passivation





α-Phase: **$CuInSe_2$**

β-Phase: **$CuIn_3Se_5$**

γ-Phase: **$CuIn_5Se_8$** **$Cu_{2-x}Se$**

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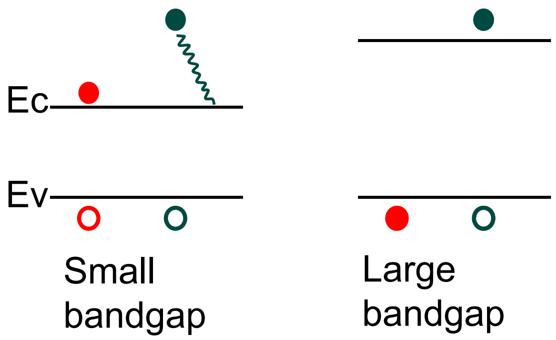

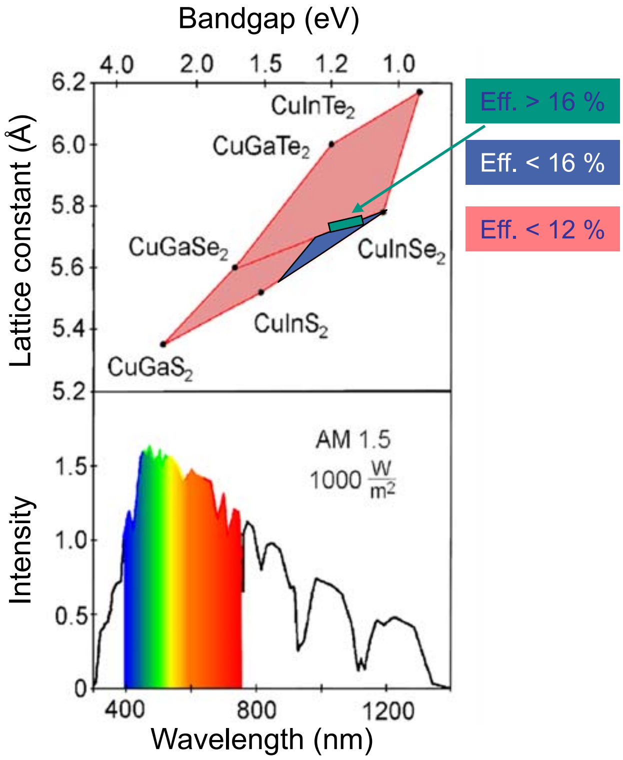

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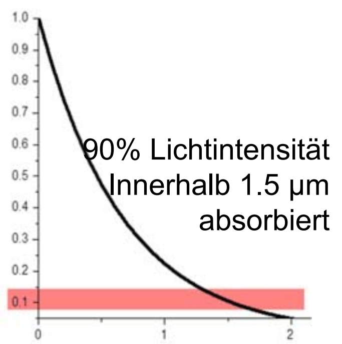
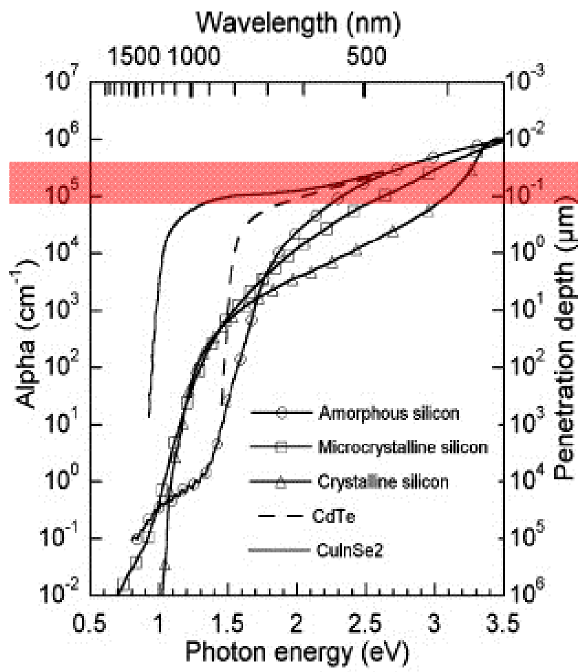




CIGS absorber material

Advantages:

- Polycrystalline structure (large tolerance for defects)
- Ideal bandgap
- High absorption
- Grain boundary passivation

Efficiency is not dependent on the crystallite size, but trade-off between:

Ga content

⇳

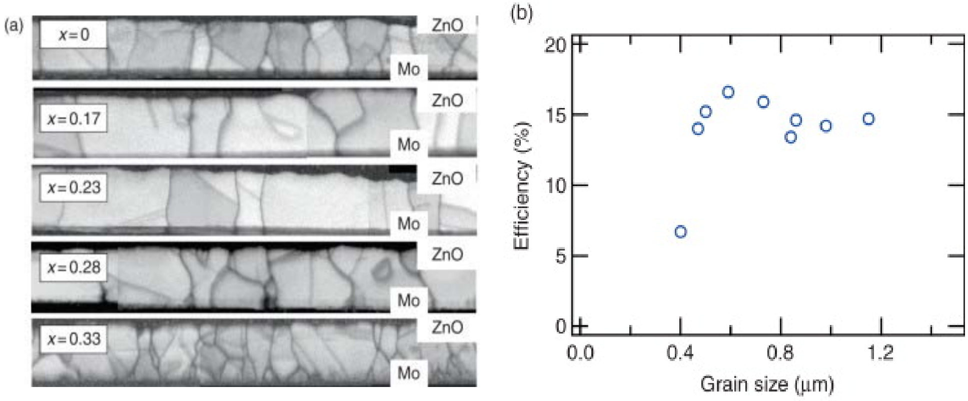
Grain size

⇳

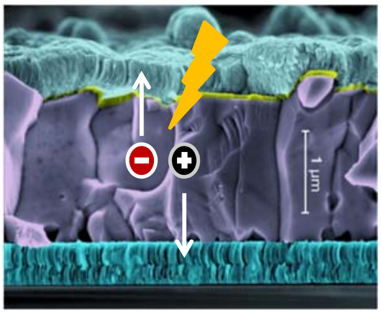
Bandgap

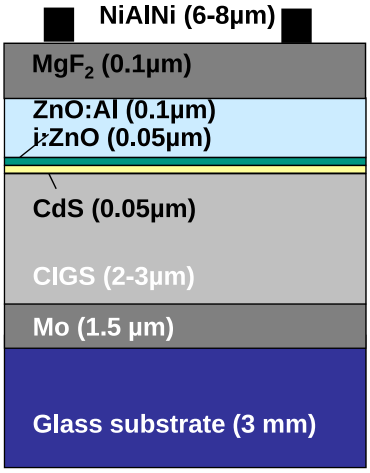
⇳

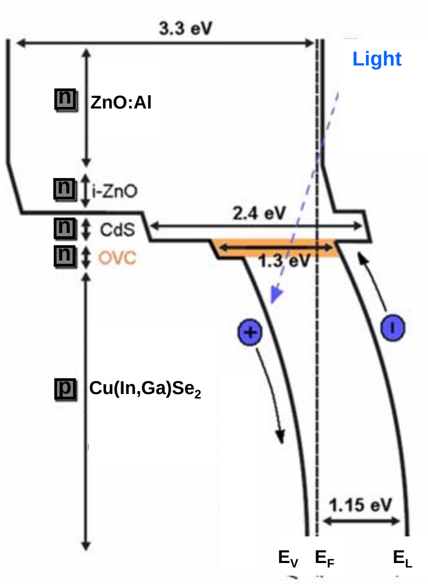
V_{oc}



CIGS solar cells



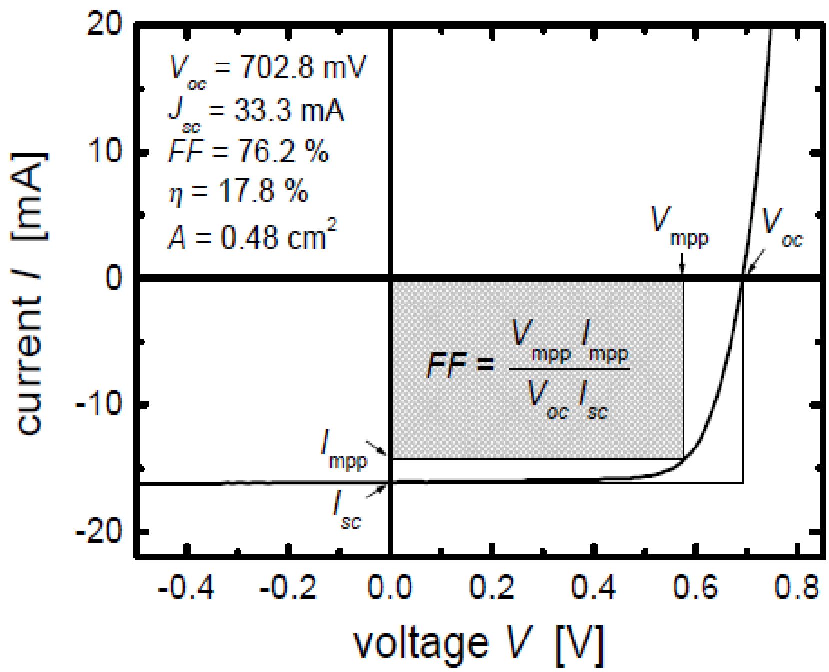




Source: ZSW Annual Report 2008

CIGS solar cells

Typical I-V curve of high-efficiency lab cell:



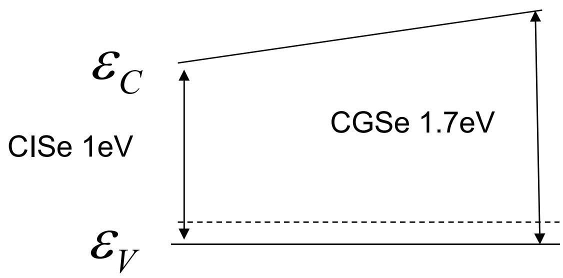
CIGS solar cells

Bandgap grading:

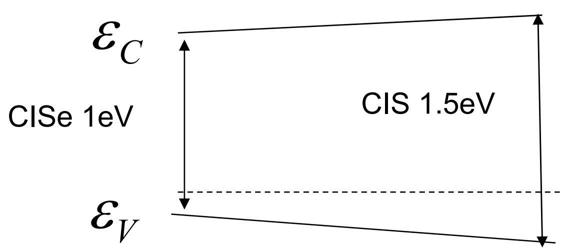
Ideal band gap grading both at

- CdS interface (hole blocker):
  - Cu-poor composition or
  - increased Ga, S content
- Mo interface (electron blocker):
  - increased Ga content

Increased Ga content



Increased S content



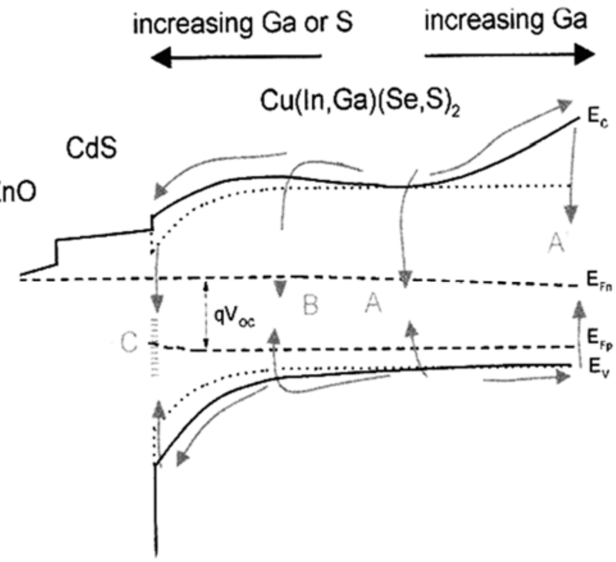
CIGS solar cells

Bandgap grading:

Ideal band gap grading both at

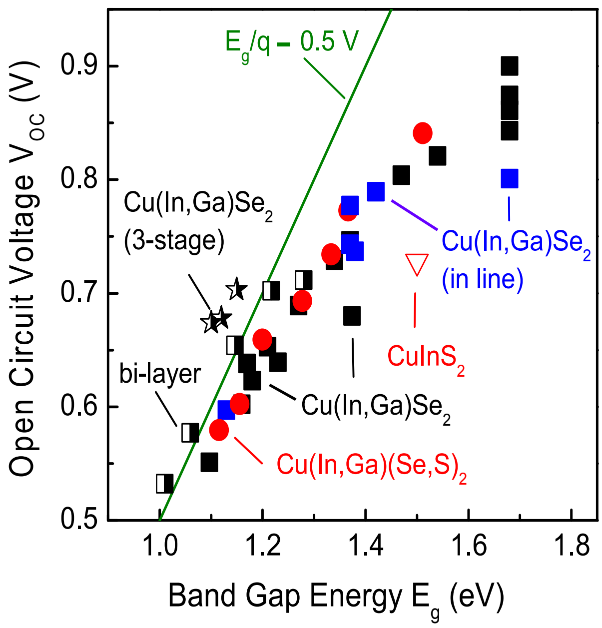
CdS interface (hole blocker):
- Cu-poor composition or
- increased Ga, S content

Mo interface (electron blocker):
- increased Ga content



Source: U. Rau in Practical Handbook of PV, Elsevier Oxford 2003

CIGS solar cells



$V_{oc,ideal}$ is material dependent:

$$V_{oc} = \frac{E_g}{q} - \frac{kT}{q}\ln(C)$$

C : Function of doping, diffusion length and photocurrent

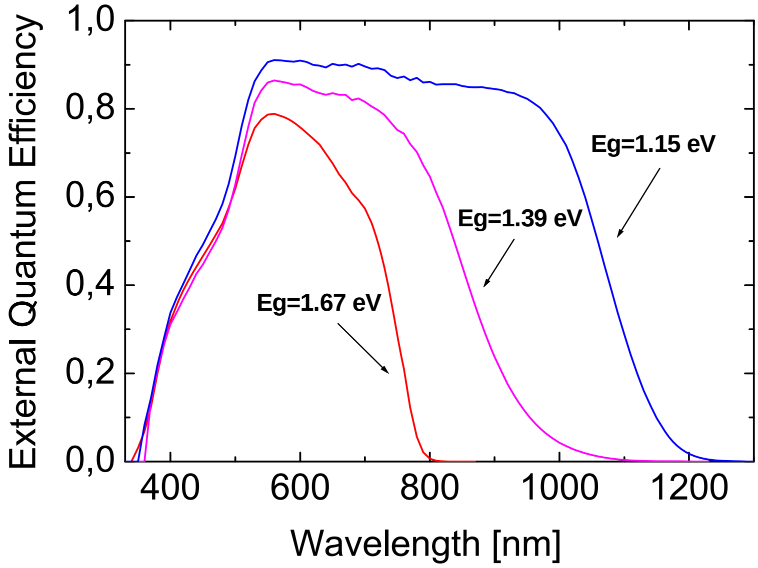
For CIS:
$V_{oc,ideal} = E_g/q - 0.5$ V

e.g. for GaAs:
$V_{oc,ideal} = E_g/q - 0.334$ V

Source: Powalla, ZSW

CIGS solar cells

EQE of $CuIn_{1-x}Ga_xSe_2$ with different bandgaps (from ZSW module line)



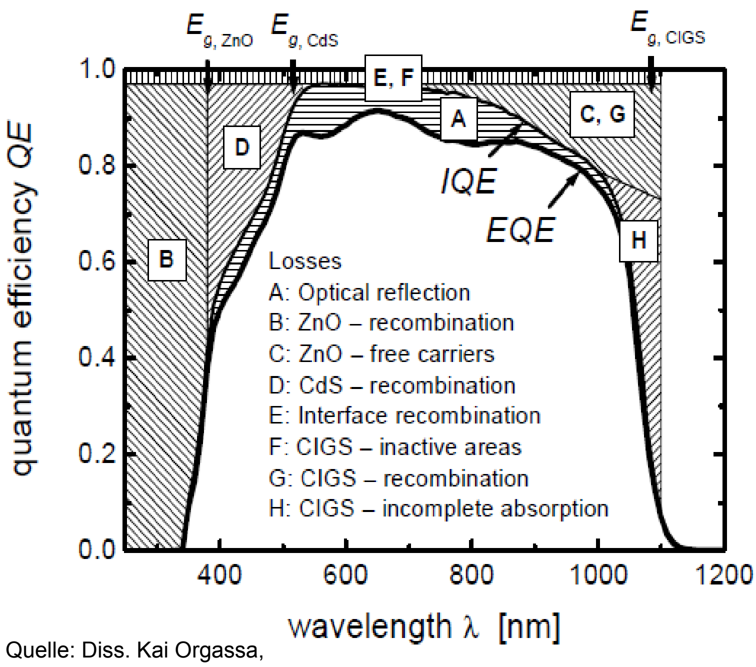
Sample	x	E_g(QE) [eV]	V_{oc} /Zelle [mV]	E_g/q-V_{oc} [mV]	j_{sc} [mA/cm^2]	FF [%]	η [%]
A	0.3	1.15	625	525	30,8	73,5	14,1
B	0.68	1.39	764	626	20,9	74,2	11,8
C	1	1.67	844	826	13,3	57	6,4

Powalla, ZSW

CIGS solar cells

Analysis of EQE and IQE curves

- origin of optical losses:



Quelle: Diss. Kai Orgassa, 2004

A: Reflection

B: Interband transitions in ZnO

C: Free-carrier absorption in ZnO

D: Parasitic absorption of photogenerated carriers in CdS

E: Photons with $\lambda > \lambda_{Eg,CdS}$ but absorbed within 100nm

F: inactive CIGS grains

G: recombination of charge carriers at back contact

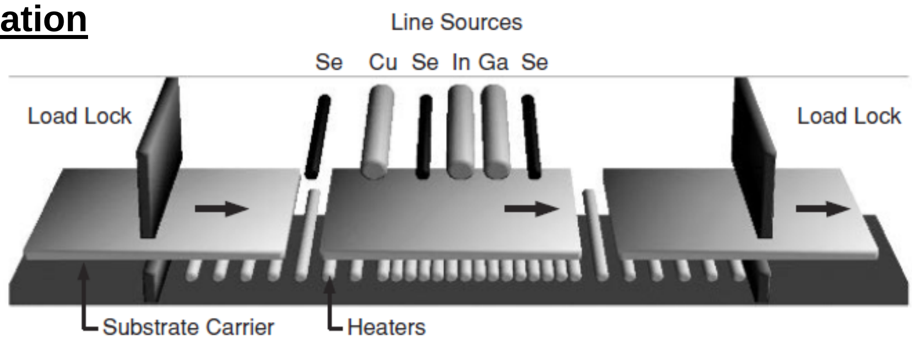
H: back contact doesn't absorb photons

CIGS solar cells

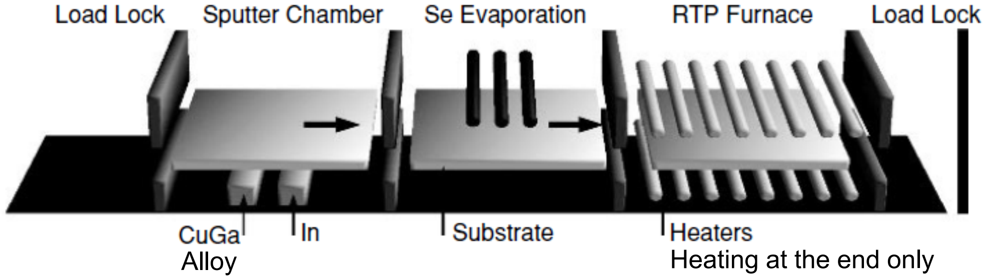
Method	Process(es)	
Co-Evaporation 1-Step-Process	Evaporation of the single elements *Cu, In, Ga, Se, S*	
2-Step-Process	<u>Precursor deposition</u> (low Temperatur) Cu, In, Ga (+ Se if req.) Substrate Metal layers	<u>**CIGS absorber formation**</u> (450 – 600 °C) **Se / H_2Se** CIGS Substrate
3-Step-Process (Sulphurisation)	CIGS Substrate Polycristalline CIGSe	S / H_2S CIGS Substrate

CIGS solar cells

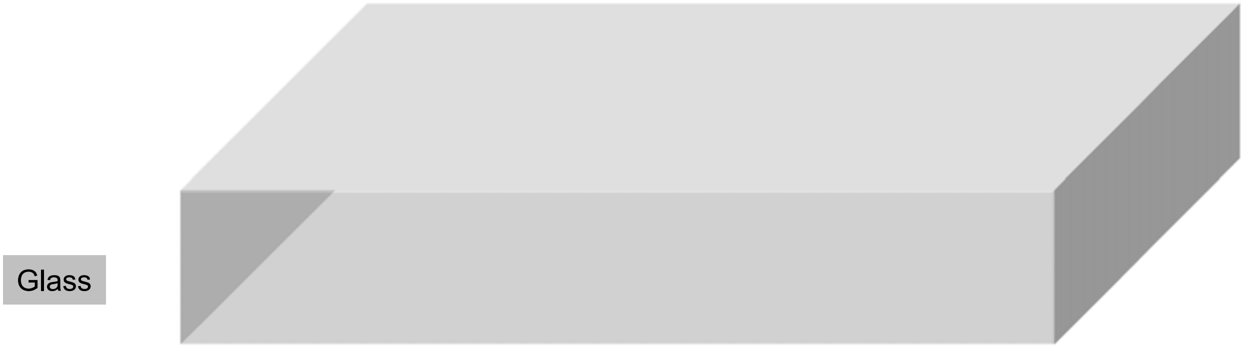
<u>Co-Evaporation</u>



<u>2-Step-Process</u>



CIGS PV modules



Step 1: Glass substrate (window glass 1 – 4 mm thick)

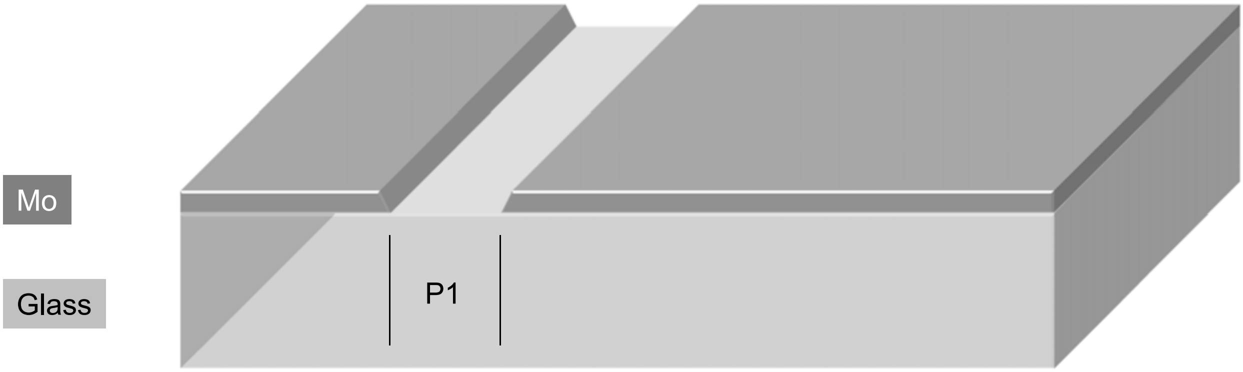
Source: Powalla, ZSW

CIGS PV modules

Step 2: DC sputtering of molybdenum back contact

Source: Powalla, ZSW

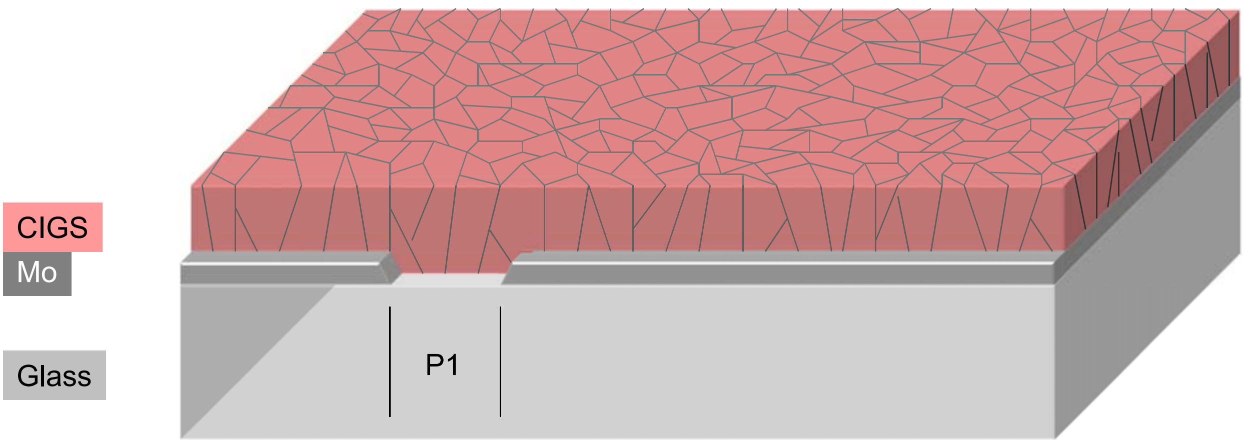
CIGS PV modules



Step 3: Laser structuring (P1)

Source: Powalla, ZSW

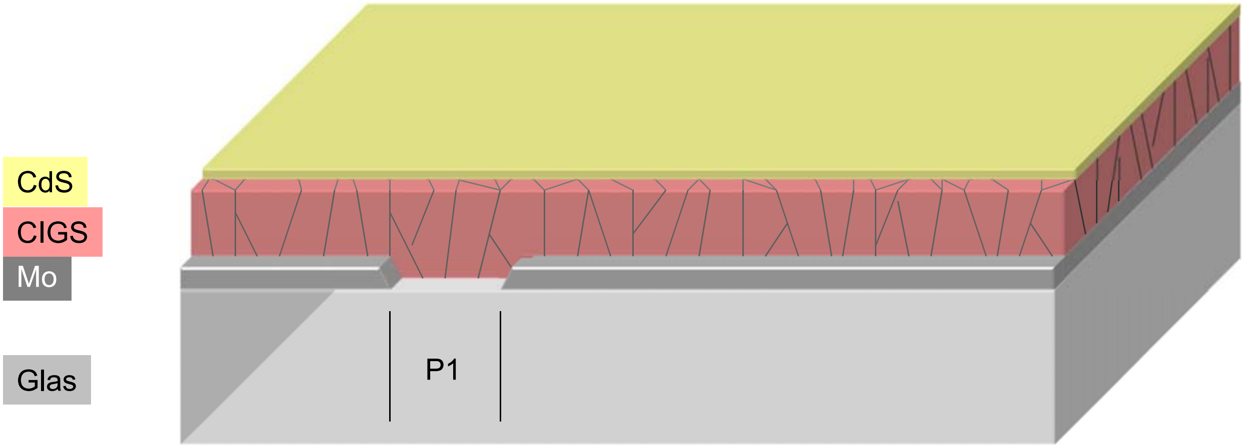
CIGS PV modules



Step 4: Evaporation of $Cu(In,Ga)Se_2$

Source: Powalla, ZSW

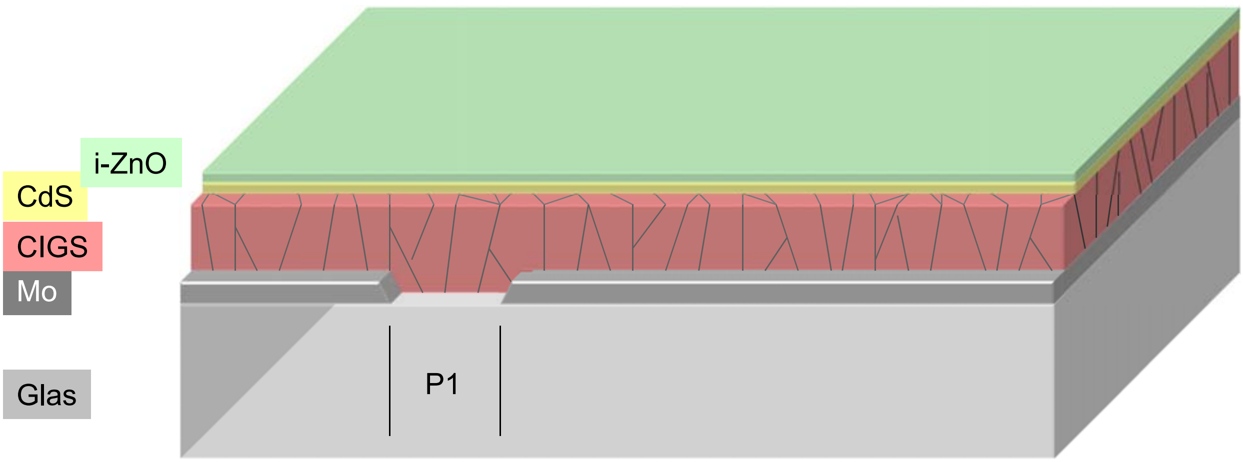
CIGS PV modules



Step 5: Chemical bath deposition of CdS

Source: Powalla, ZSW

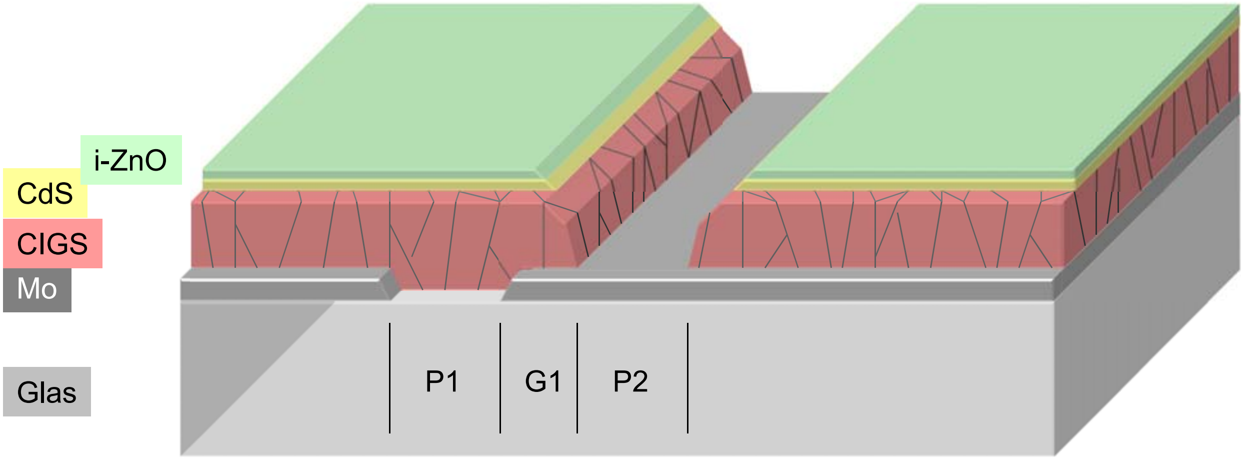
CIGS PV modules



Step 6: RF sputtering of i-ZnO

Source: Powalla, ZSW

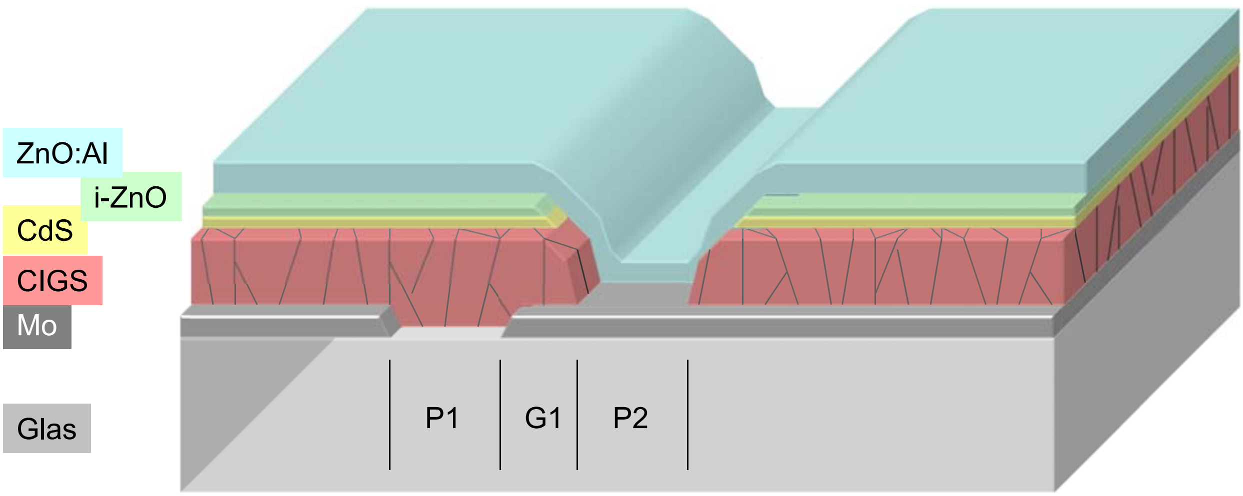
CIGS PV modules



Step 7: Mechanical structuring (P2)

Source: Powalla, ZSW

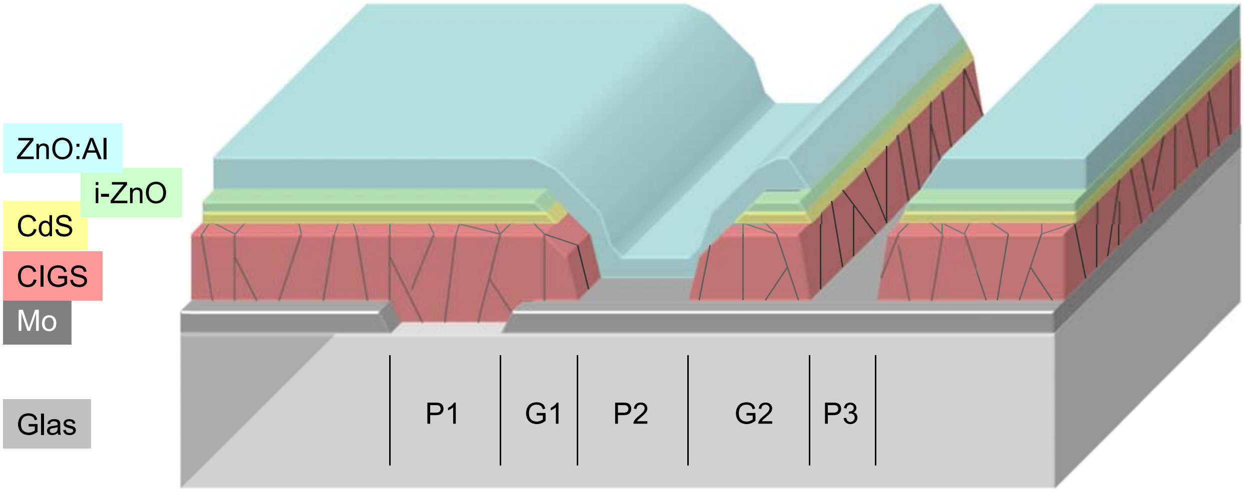
CIGS PV modules



Step 8: Sputtering of ZnO:Al (TCO)

Source: Powalla, ZSW

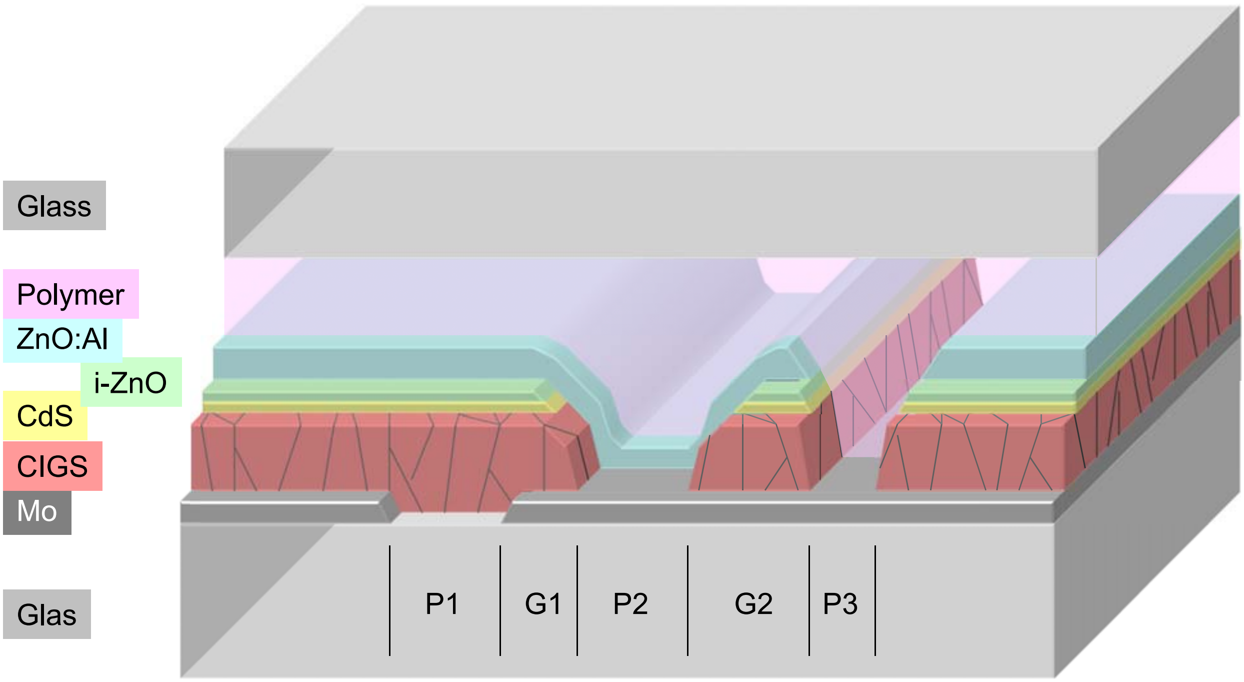
CIGS PV modules



Step 9: Mechanical structuring (P3)

Source: Powalla, ZSW

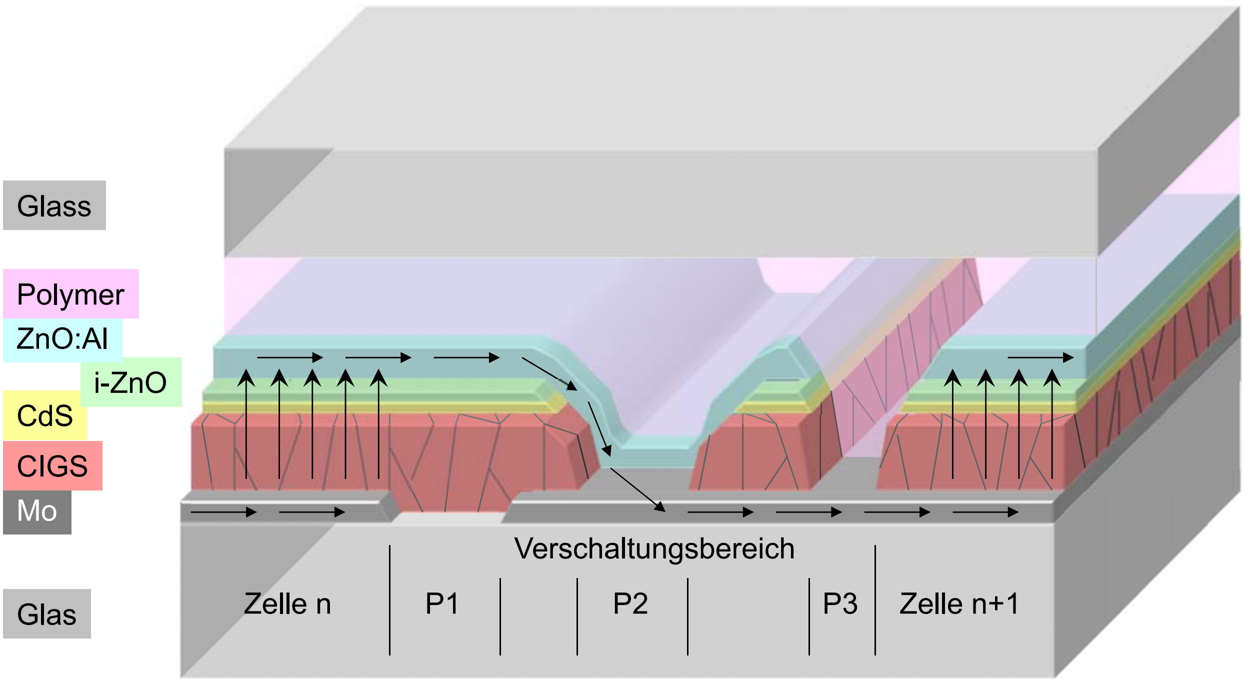
CIGS PV modules



Step 10: Encapsulation with polymer foil and glass

Source: Powalla, ZSW

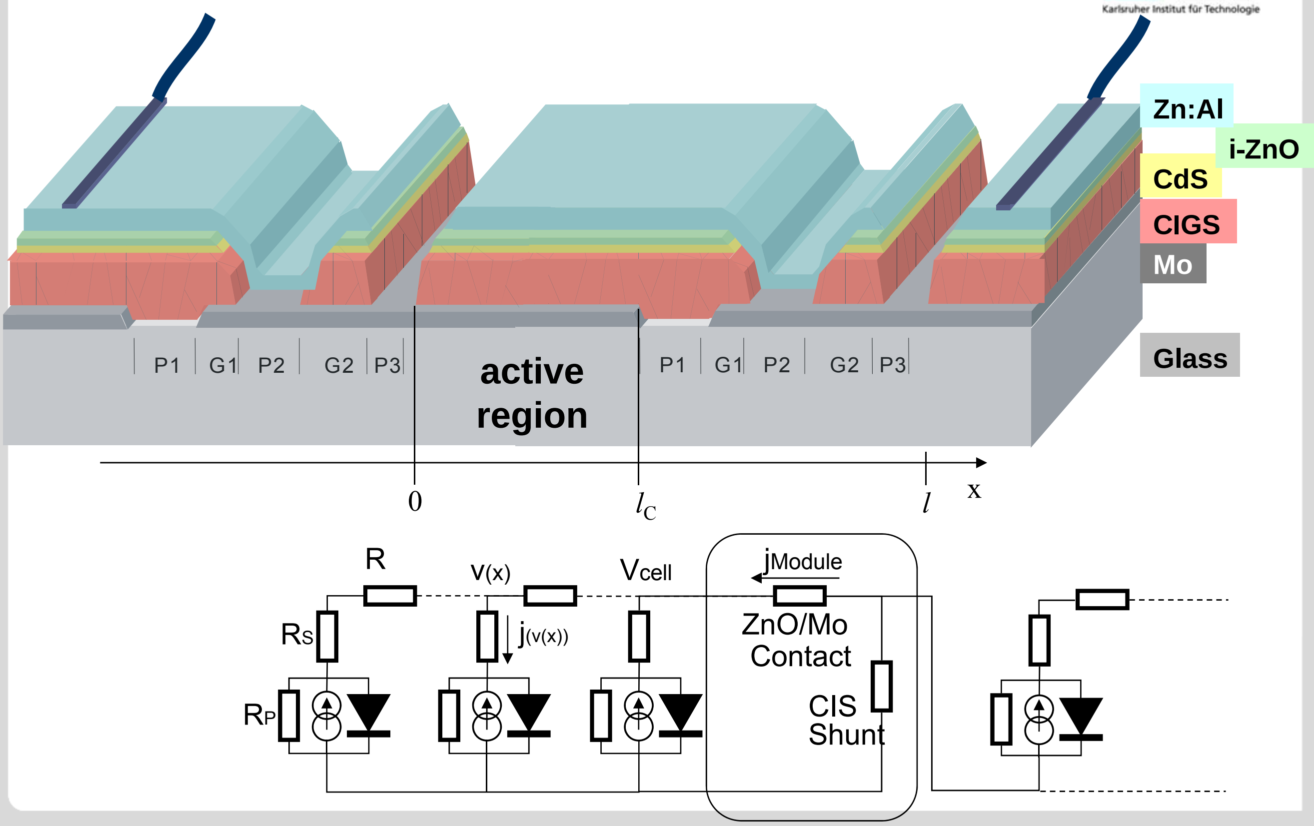
CIGS PV modules



Flow of current in PV module

Source: Powalla, ZSW

CIGS PV modules



Series connection

Source: Powalla, ZSW

CIGS PV modules

Commercial implementations of CIGS PV technology

Layer	ZSW / Manz	Avancis	Solar Frontier	Global Solar	Soltecture
n-type Window ~1 µm	ZnO:Al	ZnO:B	Zn:B	ZnO:Al	ZnO:Al
n-type Buffer 50 – 100 nm	CdS	CdS	$Zn(S,OH)_X$	CdS	CdS
p-type Absorber ~ 2 – 3 µm	$Cu(In,Ga)Se_2$	$Cu(In,Ga)(S,Se)_2$	$Cu(In,Ga)(Se,S)_2$ / $Cu(In,Ga)Se_2$	$Cu(In,Ga)Se_2$	$CuInS_2$
Metal back contact ~ 0.5 – 1 µm	Mo	Mo / Barriere	Mo / Barriere	Mo / Barriere	Mo
Substrate	Window glass	Window glass	Window glass	Stainless steel foil	Window glass

Source: Powalla, ZSW

CIGS PV modules

Method | Process(es)

Co-Evaporation

1-step process

Evaporation of single elements *Cu, In, Ga & Se*

Vacuum based technologies = expensive

2-step process

<u>Precursor deposition</u>
(low temperature)
Cu, In, Ga (+ Se if req.)

<u>CIGS-Absorber-Bildung</u>
(450 – 600 °C)
Se / H_2Se

Substratd

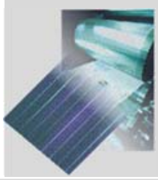
Metal layers

CIGS

Substrate

Substrate

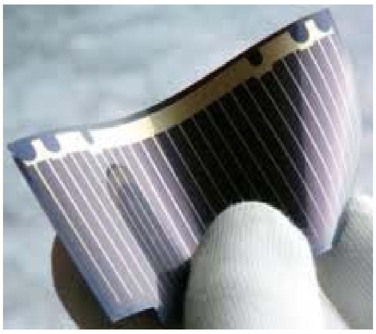
Precursor ink film



CIGS Druck

CIGS PV modules

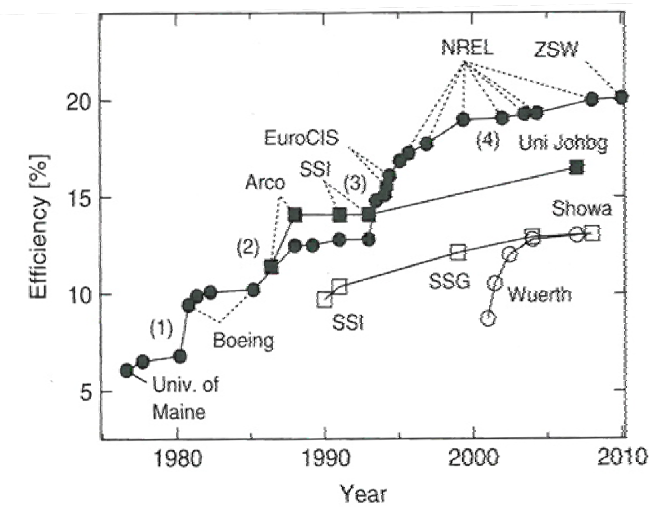


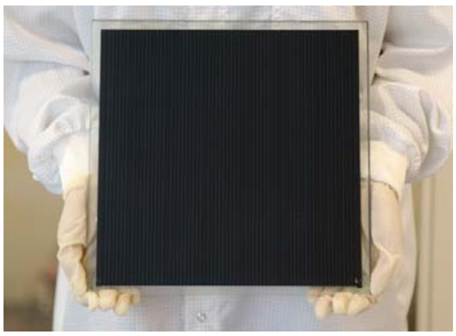



CIGS PV modules

Keys to high efficiency:

1) Triple source evaporation ⇒ Cu/In rate control
2) CBD for CdS
3) Gallium
4) 3-stage co-evaporation
   ⇒ composition grading



CIGS PV modules

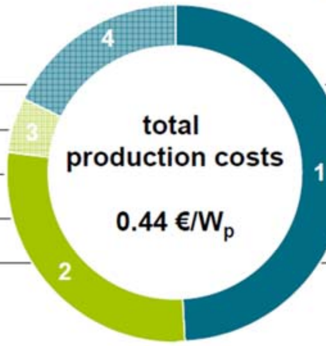
CIGSfab
COST STRUCTURE, where are the potentials ?

manz
passion for efficiency

COST STRUCTURE CIGSfab (214 MW/a)

TODAY

BASED ON MANUFACTURING SITE IN ASIA
and start of production in 2014



1 I	0.20 €	Material
2 I	0.13 €	Depreciation
3 I	0.02 €	Labor
4 I	0.09 €	Others (facility, maintenance, energy)

In comparison:
European site
smaller fab size:
= 0.54 €/W_p

FUTURE

Further cost reduction is major target of Manz R&D efforts!
cost reduction —► < 0.4 €/W_p within the next years

CIGS world record

Press Release 12/2014

Stuttgart, September 22, 2014

Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW)

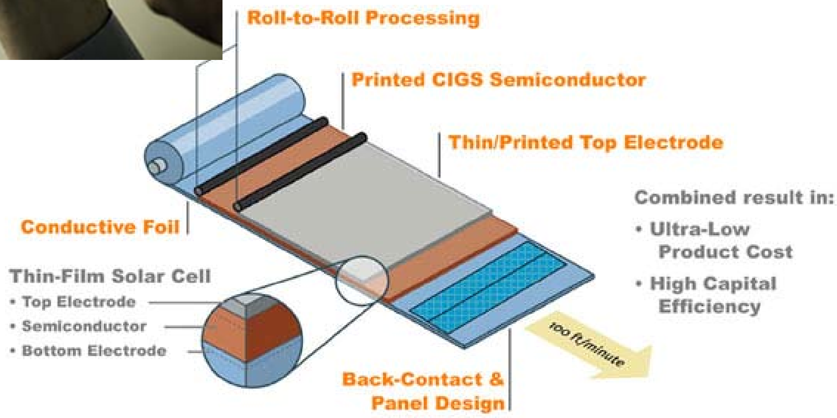
Standort Stuttgart:
Industriestr. 6, 70565 Stuttgart

ZSW Brings World Record Back to Stuttgart

New best mark in thin-film solar performance with 21.7 percent efficiency

The Centre for Solar Energy and Hydrogen Research Baden-Württemberg (ZSW) has set a new world record in thin-film photovoltaics. Scientists in Stuttgart achieved 21.7 percent efficiency with a solar cell made of copper indium gallium diselenide (CIGS). ZSW succeeded in bringing the record back to the institute with this cell's performance. Swedish researchers achieved a new best mark in June, which has now been surpassed by 0.7 percentage points. The progress underway in the southwest of Germany is helping to make solar power more affordable.

CIGS technology – vacuum-free



CIGS technology – vacuum-free

Source: https://www.youtube.com/watch?v=FTiSIZIA3YA

CIGS technology – vacuum-free

Nanosolar

From Wikipedia, the free encyclopedia

Nanosolar was a developer of solar power technology. Based in San Jose, CA, Nanosolar developed and briefly commercialized a low-cost printable solar cell manufacturing process. The company started selling thin-film CIGS panels mid-December 2007, and planned to sell them at 99 cents per watt, much below the market at the time. However, prices for solar panels made of crystalline silicon declined significantly during the following years, reducing most of Nanosolar's cost advantage.[2][3][4] By February of 2013 Nanosolar had laid-off 75% of its work force.[5] Nanosolar began auctioning off its equipment in August of 2013.[6] Co-Founder of Nanosolar Martin Roscheisen stated on his personal blog that nanosolar "ultimately failed commercially." and that he would not enter this industry again because of slow-development cycle, complex production problems and the impact of cheap Chinese solar power production.[7] Nanosolar ultimately produced less than 50 MW of solar power capacity despite having raised more than $400 million in investment.[8]

Nanosolar, Inc.

nanosolar

Type	Private
Industry	Solar Energy
Founded	2002
Founders	Martin Roscheisen Brian Sager
Headquarters	San Jose, California, U.S.
Key people	Eugenia Corrales (CEO) Dave Jackrel John McAdoo Becky Baybrook John Bender
Products	Solar panels
Revenue	US$3,100,000 (2007)[1]

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Financial backers and manufacturing [edit]

Nanosolar was started in 2002 and is headquartered in San Jose, California. The company has received financing from a number of technology investors including Benchmark Capital, Mohr Davidow Ventures, and Larry Page and Sergey Brin, the founders of Google. Nanosolar received the largest amount in a round of Venture Capital technology funding amongst United States companies during Q2 2006, with 100 million USD of new funding secured.[9] It also received the largest amount of financing of any private company in 2008 (USD 300 million in Q1).

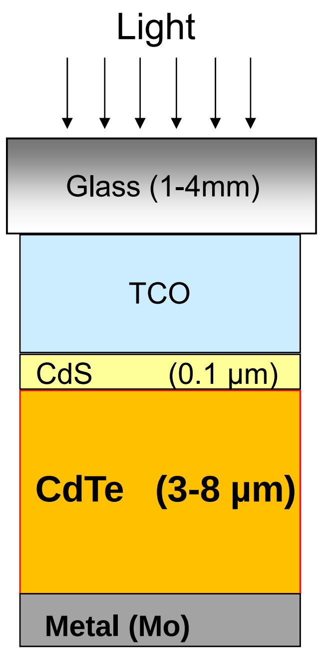
Nanosolar planned to build a large production facility in San Jose, and in Germany at Luckenwalde (Berlin),[10] with an annual capacity of 430 megawatts. Several German energy and venture capital companies have heavily invested in this company as a consequence of the favourable economics for solar energy in Germany due to government subsidies.[11]

CdTe solar cells

History:

1956	Suggested for PV by Loferski
1963	first *p*-$Cd_{2-x}Te$/CdS solar cells from Cusano, General Electric
1967	Large area PV modules with η = 3%
1969	Large *p*-CdTe/*n*-CdS solar cells from Adirovitch with η = 1%
1972	η = 5% (Bonnet and Rabenhorst)
ab 1980	several groups with η > 10%

CdTe Solar Cells



<u>Deposition of CdS</u>

- Chemical bath deposition
- Vapour deposition
- Spray deposition

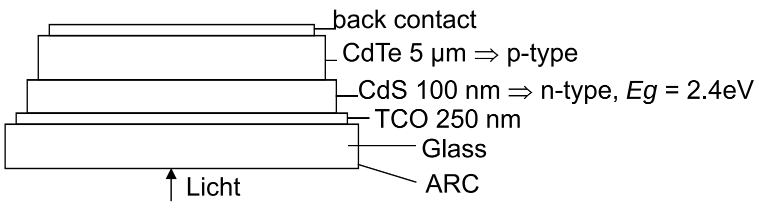
<u>Deposition of CdTe</u>

- Spray deposition
- Electrodeposition
- Screen printing + sintering at 700°C
- Metallorganic chemical vapour deposition (MOCVD) on a substrate 400°C

N.B. Relative thick absorber and no texturing or light trapping

CdTe Solar Cells

Principal construction and fabrication methods:

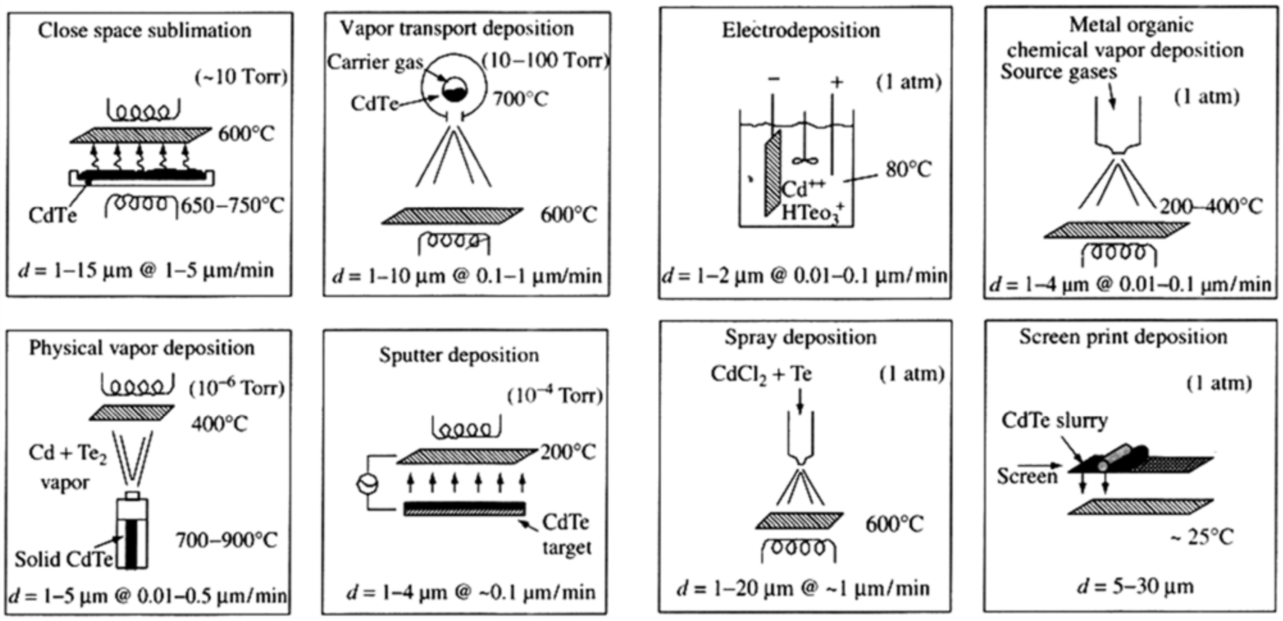


CdTe: E_g = 1.45 eV, α = 5 x 10^4 /cm (at 0.2eV above E_g)

Above 449°C CdTe grows stoichiometrically

- Closed spaced sublimation CSS ⇒ CdTe granules @ 770°C and glass substrate @ 500°C
- Electrodeposition: from water-based solutions of $CdSO_4$ und TeO_3 @ 90°C
- Screen printing process (Matsushita) ⇒ CdS powder, $CdCl_2$, propylene glycol
  drying and sintering @ 690°C, (or sintering of Cd + Te powder @ 620°C)

CdTe Solar Cells



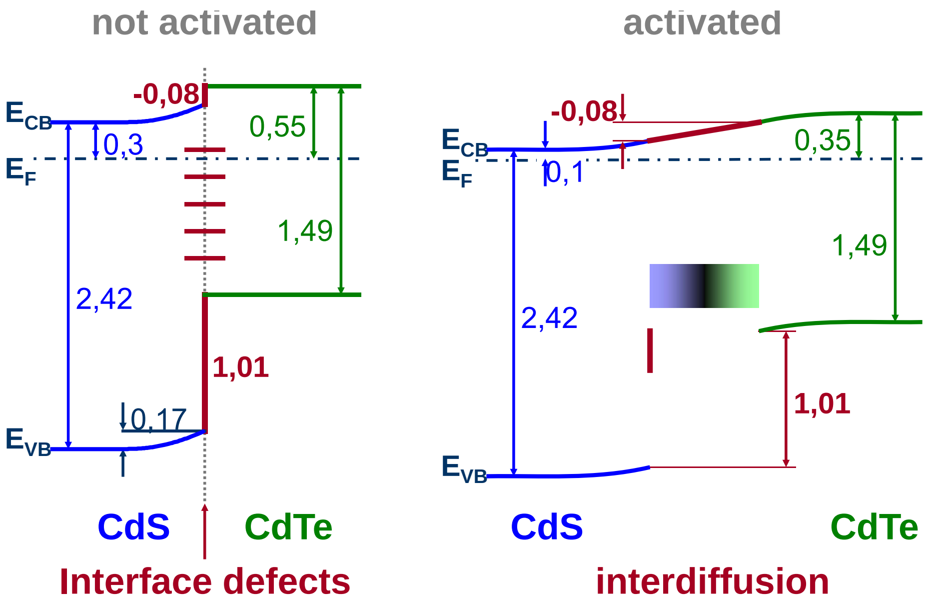
Source: Luque, Handbook of PV

CdTe Solar Cells

Advantages and disadvantages of CdTe:

- Advantage: very fast deposition @ 10 µm/min
  Disadvantage: public acceptance of Cd, environmental concerns
- Efficiency of lab-devices up to 20.4%
- Problem: back contact
    - For an ohmic contact one needs a metal with work function $\Phi_M > \Phi_{semi}$
    - But there isn't one: therefore doping of surface required
- Activation with $CdCl_2$ (next slide)

CdTe Solar Cells



After CdTe/CdS deposition ⇒ material “activated” with $CdCl_2$:
- change in morphology ⇒ coarsely crystalline material
- inter-diffusion of CdTe and CdS at the interface
- reduction of interface states
- change in dopant gradient (mainly *n*-type side)

CdTe Solar Cells

Cross-sectional image - scanning electron microscope

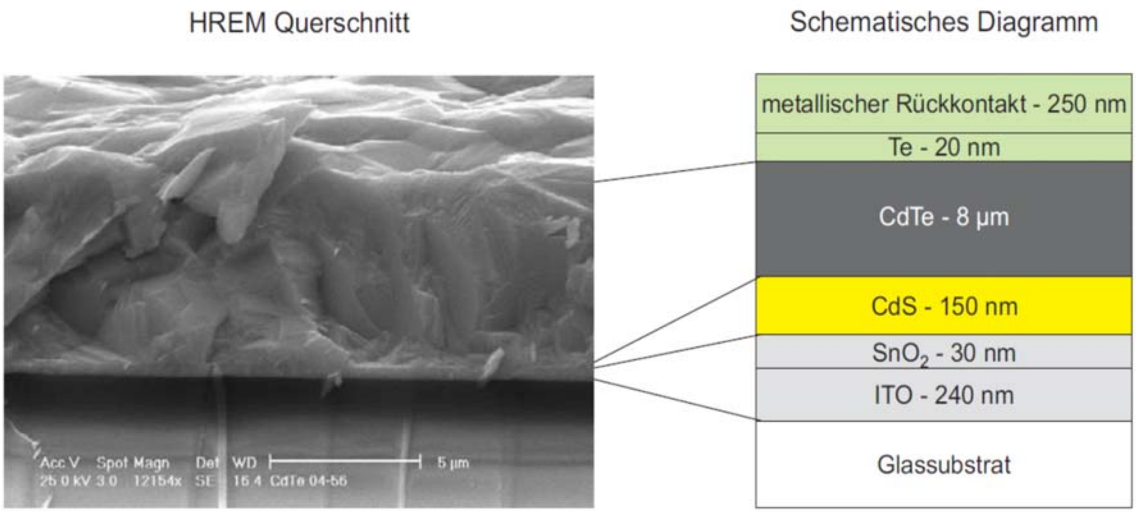


Abbildung 1.6: Querschnitt einer polykristallinen CdTe-Dünnschichtsolarzelle in der Superstrat-Konfiguration: **(rechts)** Schematische Darstellung der Teilschichten; **(links)** Rasterelektronenmikroskopische Aufnahme einer CdTe-Dünnschichtsolarzelle der Firma ANTEC (ohne Rückkontakt) .

Source: Diss. Fritsche, TU Darmstadt 2003

CdTe Solar Cells

Energy band diagram

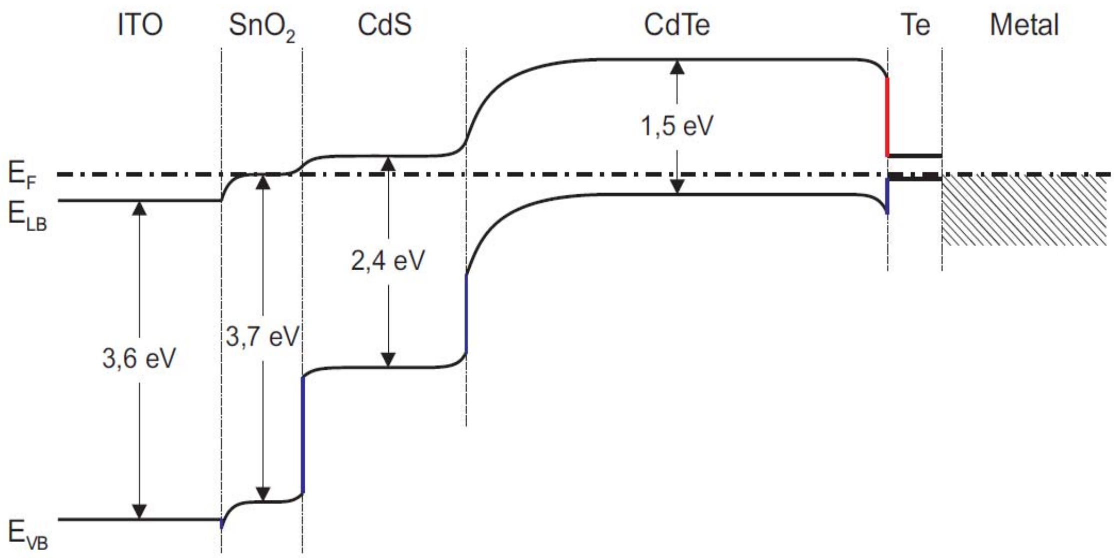
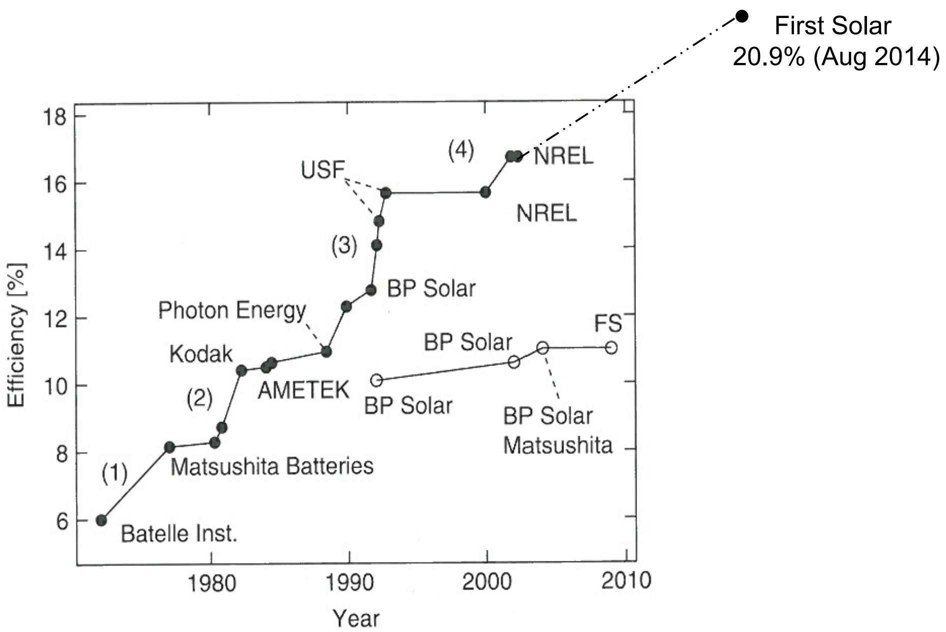


Abbildung 2.3: Vorläufiges schematisches Bandenergiediagramm der CdTe/CdS-Dünnschichtsolarzelle.

Source: Diss. Fritsche, TU Darmstadt 2003

CdTe Solar Cells



CdTe Solar Cells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First Solar sets new world record for thin film solar PV at 21%

05. AUGUST 2014 | INDUSTRY & SUPPLIERS, GLOBAL PV MARKETS, MARKETS & TRENDS | BY: CHRISTIAN ROSELUND

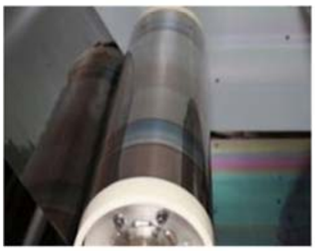
The U.S. PV maker's new cadmium telluride (CdTe) solar cell narrowly beats Solar Frontier's 20.9% record for copper indium gallium diselenide (CIGS) solar PV.

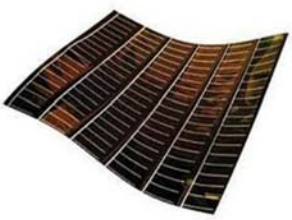
First Solar has produced a 21% efficient solar PV cell at its research and development (R&D) center in the U.S. state of Ohio. This efficiency has been certified by Newport Corporation's Technology and Applications Center PV Lab.

First Solar produced the record cell at its Ohio R&D facility.

CdTe PV Modules

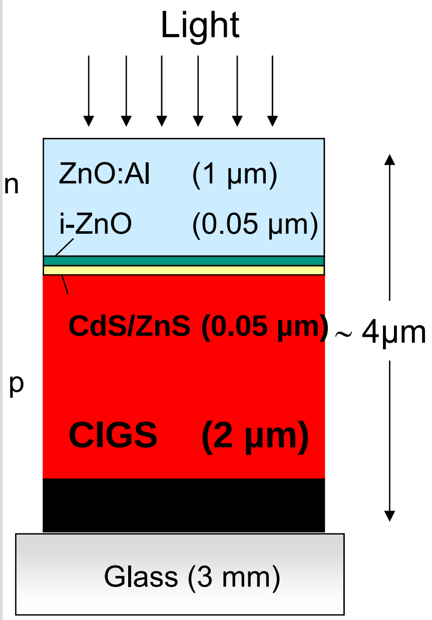
S. Ölting (ANTEC)

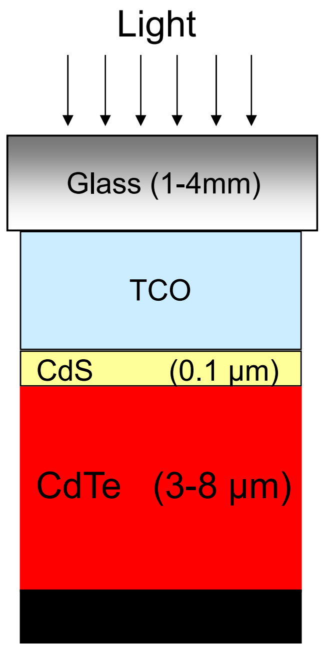


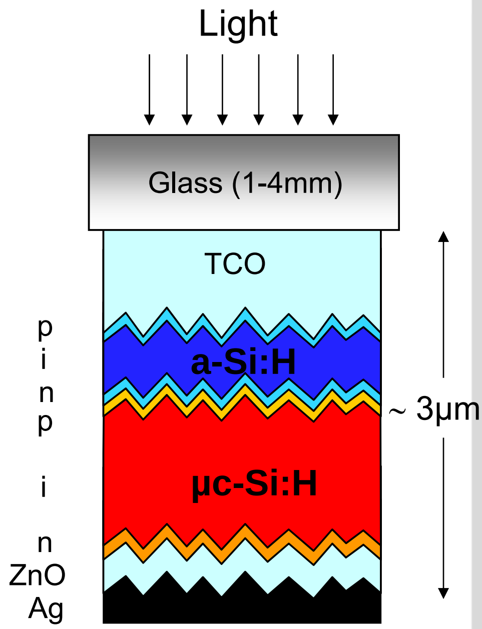


Thin Film Solar Cells

CIGS | **CdTe** | **a-Si/µc-Si tandem**







$CuIn_{1-x}Ga_xSe_{1-y}S_y$

CdTe

a-Si, a-Si/a-Si a-Si/µc-Si
a-Si/a-$SiGe_x$/a-$SiGe_x$

Thin Film PV Modules

Photo: Würth Solar/Manz

Photo: First Solar

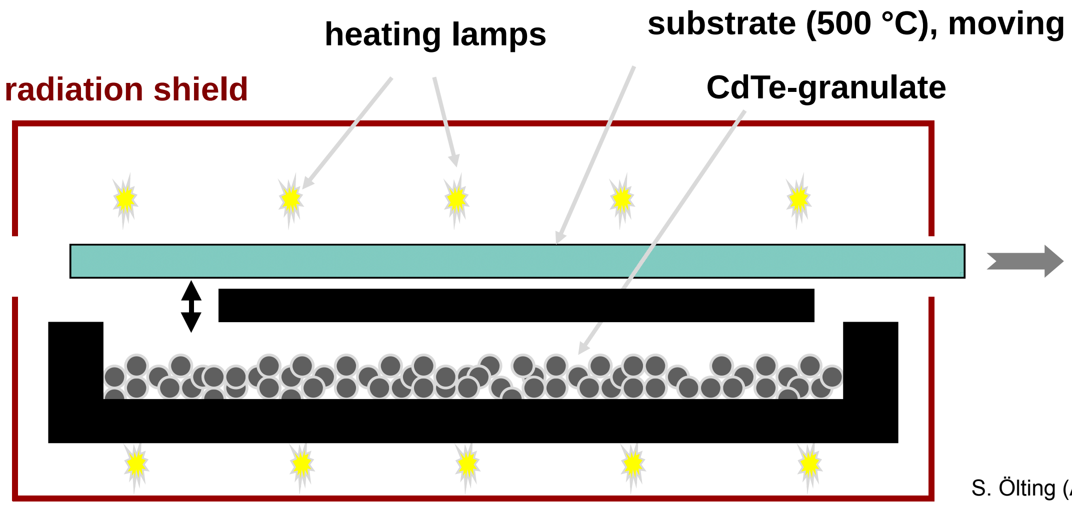
Photo: Schott Solar

CdTe PV Modules

Antec Solar (Germany)

- 130.000 modules/year (60x120 cm^2)
- 7 days, 24 hours
- module efficiency 9-10%

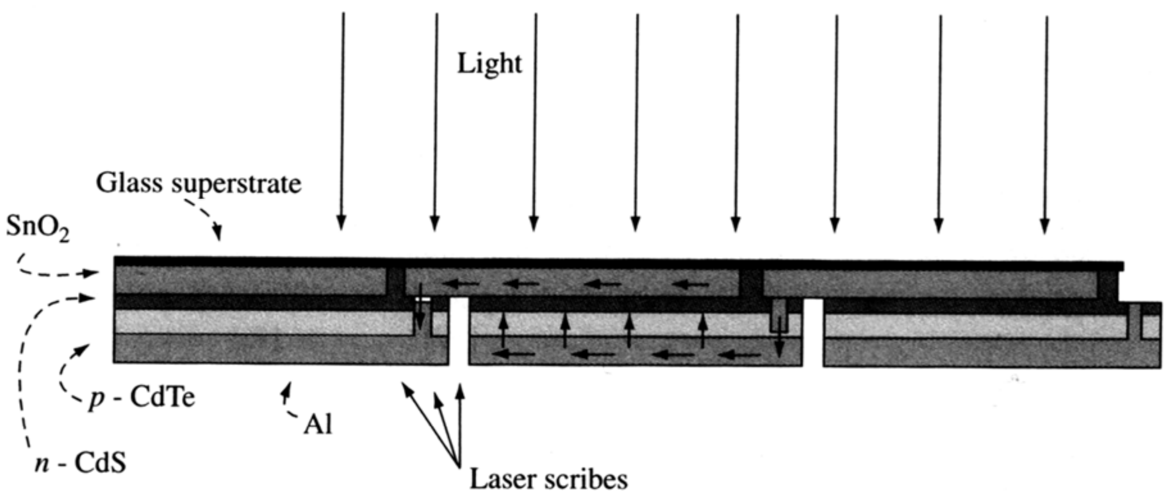
Industrially-implemented "Close spaced sublimation"



S. Ölting (ANTEC)

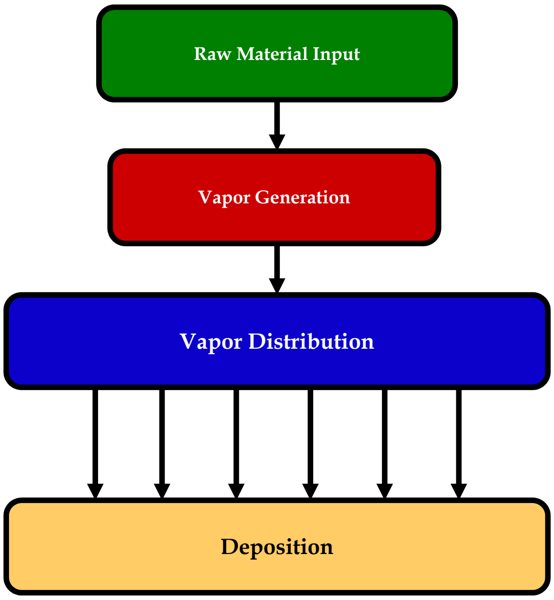
CdTe PV Modules

Monolithically interconnected modules



Schematic of a series-connected integrated CdTe module having three laser scribes

First Solar – VTD process

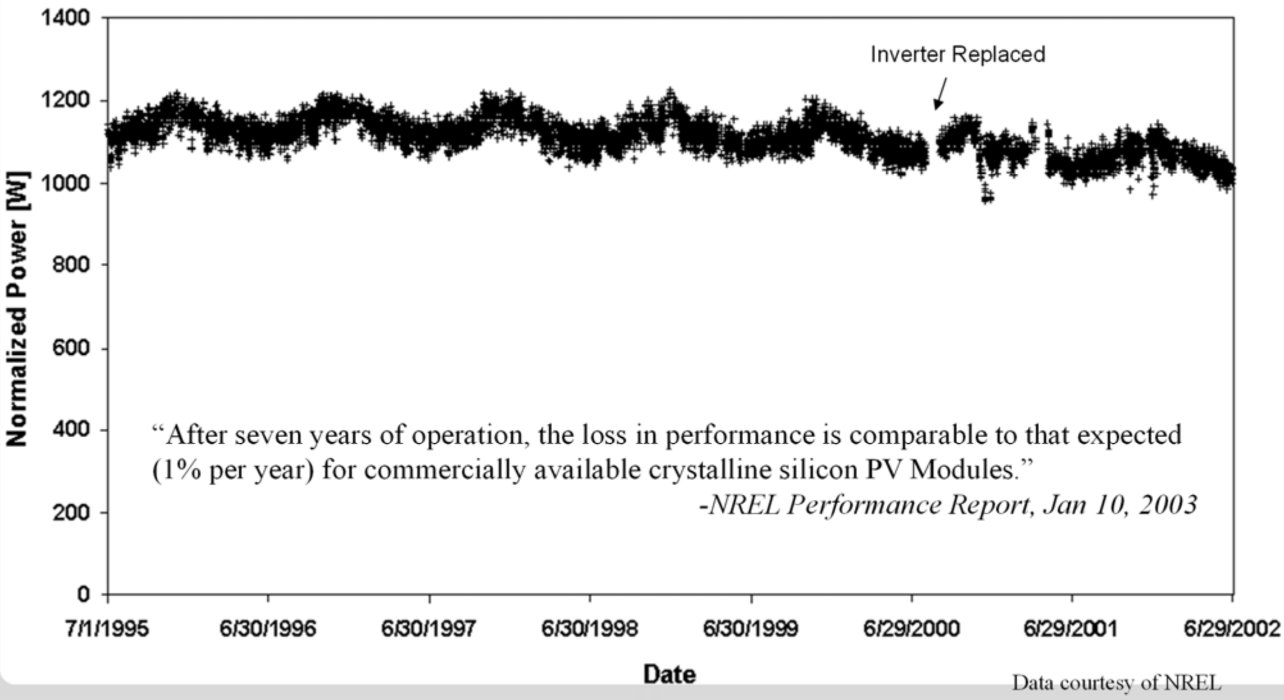


Semiconductor Deposition System

CdTe PV Modules

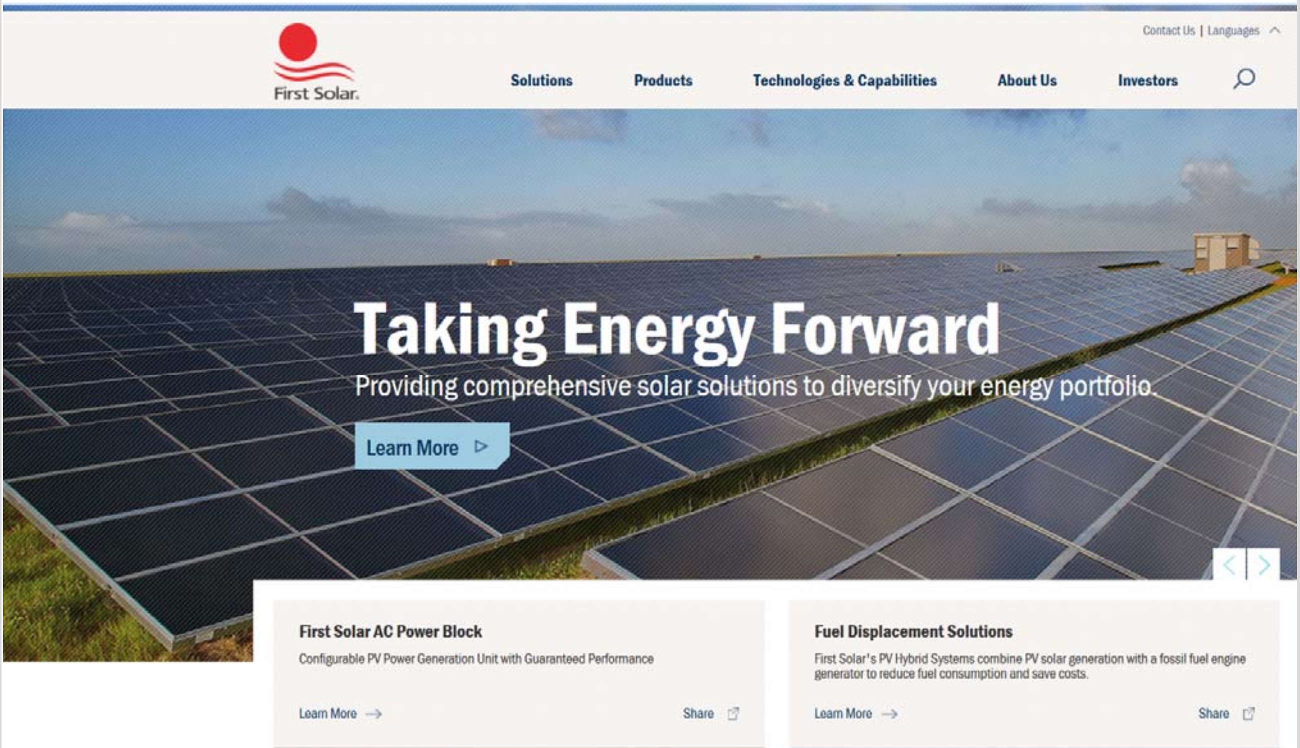
NREL OTF Results

First Solar 1kW Array at NREL OTF



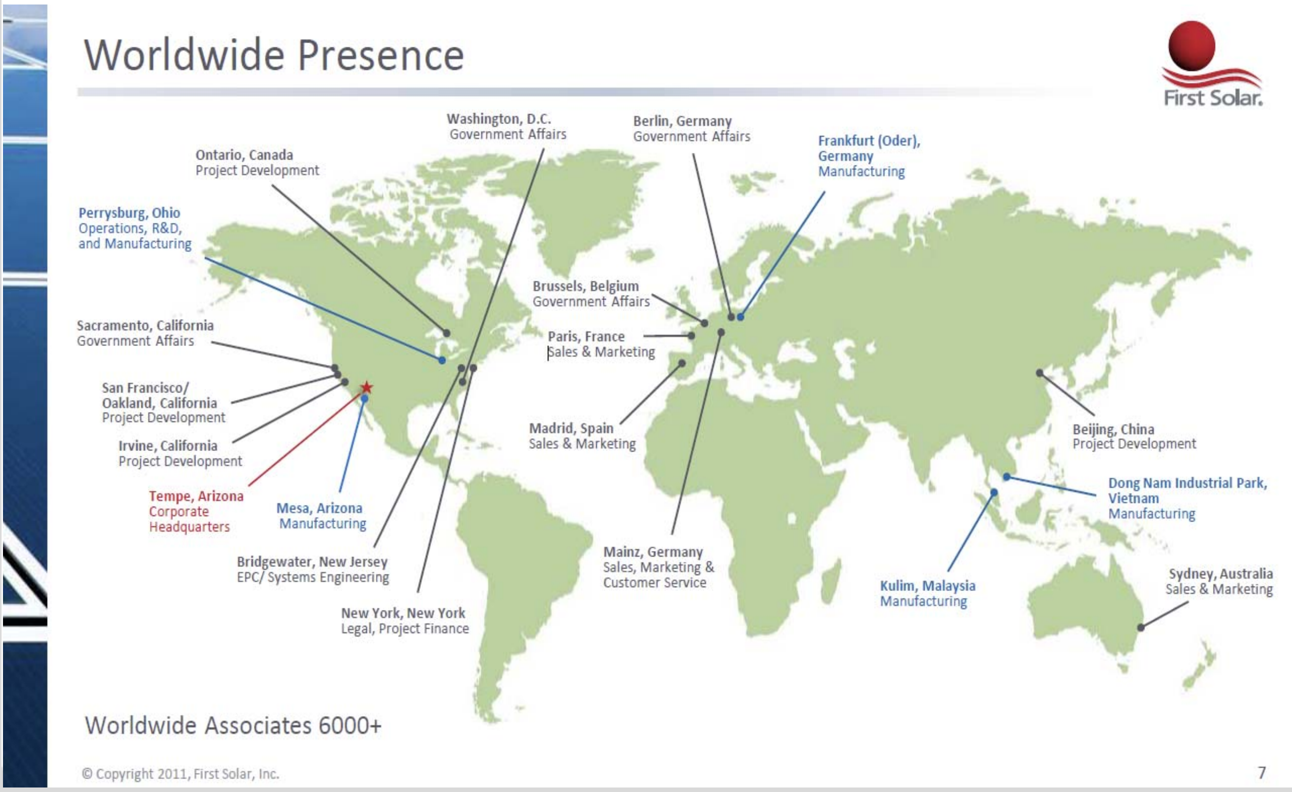
Data courtesy of NREL

Example company: First Solar

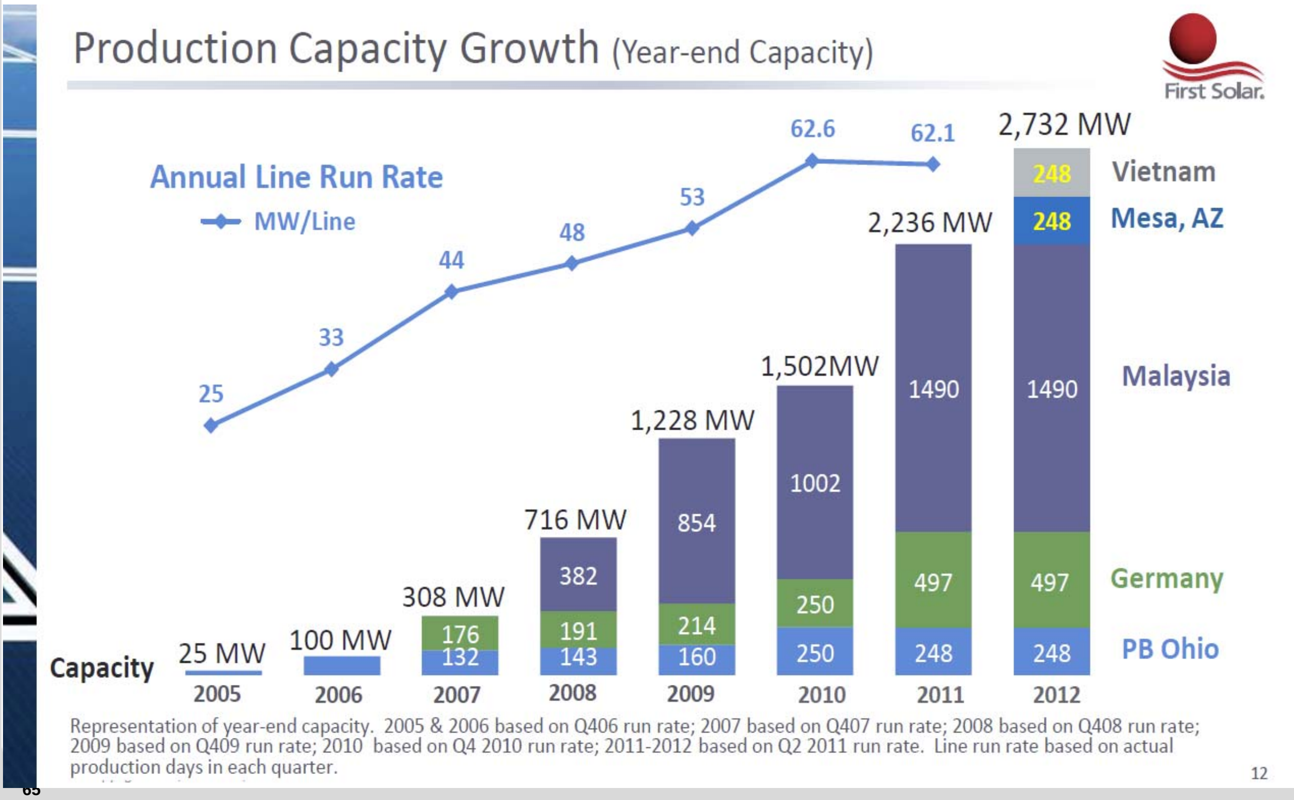


www.firstsolar.com

Example company: First Solar



Example company: First Solar



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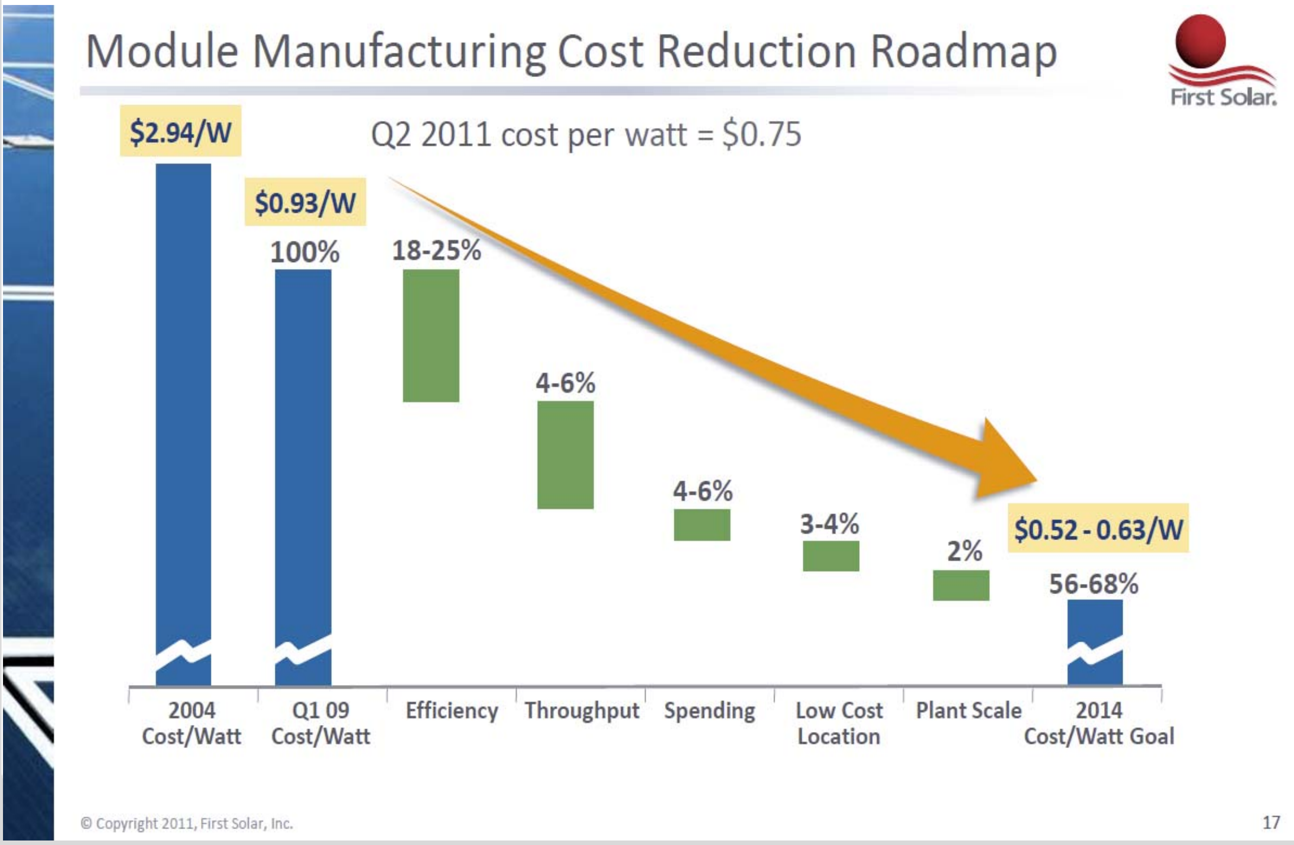

Example company: First Solar (25Nov14)

FIRST SOLAR STATISTICS

~40,000
GLOBAL SUPPLY CHAIN JOBS

4,850
FIRST SOLAR ASSOCIATES

~$9 Billion
FIRST SOLAR PROJECTS FINANCED

100M+
MODULES MANUFACTURED

5,464,823.3
HOMES POWERED*

19,798,616.6
DISPLACED H_2O CONSUMPTION*

1999
COMPANY FOUNDED

8 GIGAWATTS
INSTALLED WORLDWIDE

2.6 GIGAWATTS+
CONTRACTED AC PIPELINE

17.0%
CDTE MODULE EFFICIENCY WORLD RECORD

2GW+
ENGINEERED

1.6GW+
CONSTRUCTED

2GW+
DC UNDER OPERATION

7,249,568.0
DISPLACED CO_2 EMISSIONS*

1,455,737.00
EQUIVALENT CARS REMOVED*

185,886,371
EQUIVALENT TREES PLANTED

** Based on worldwide averages*

Gescher-Estern
Entsorgungs-Gesellschaft Westmünsterland (EGW),
put in operation August 2006.
One of the biggest roof-top installations
(1.4 MWp, CdTe, First Solar) 23 430 thin-film modules on an area of ca. 17 000 m² and an investment of € 5.6 Mio.

Source: Reinecke + Pohl Sun Energy AG

BELECTRIC connected the largest First Solar thin film solar power plant in Europe (128 MWp capacity) in Brandenburg to the grid (21 April 2013)

- Over 1.5 million CdTe PV modules from First Solar
- 114 centralised inverters from SMA
- 120 million kWh electricity (~36000 households)
- Displaces ~90000 tonnes of CO_2

Source: http://blog.belectric.com/2013/04/belectric-schliest-das-groste-first-solar-dunnschicht-solarkraftwerk-europas-mit-128-mwp-leistung-in-brandenburg-ans-netz-an/