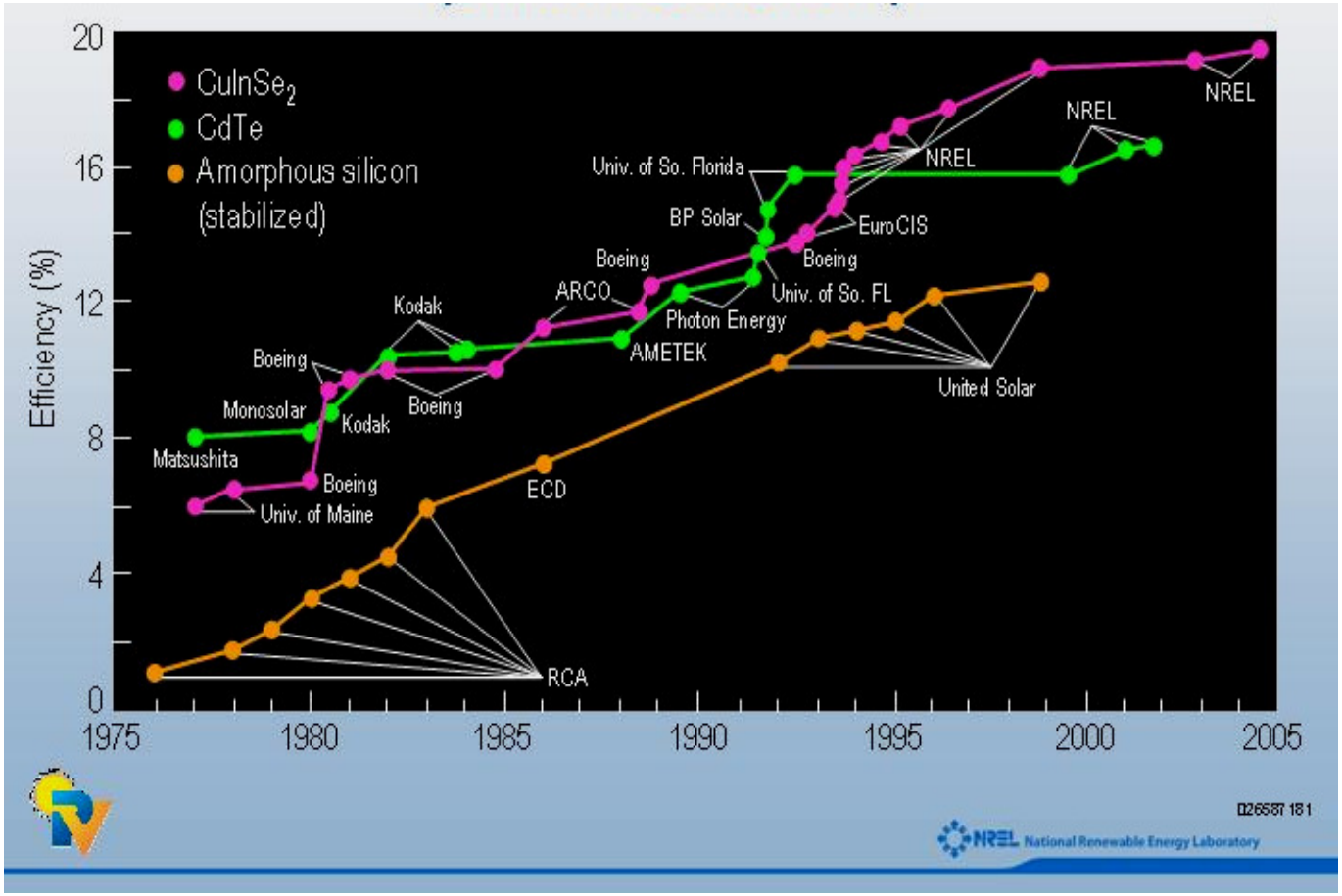
Thin film solar cells

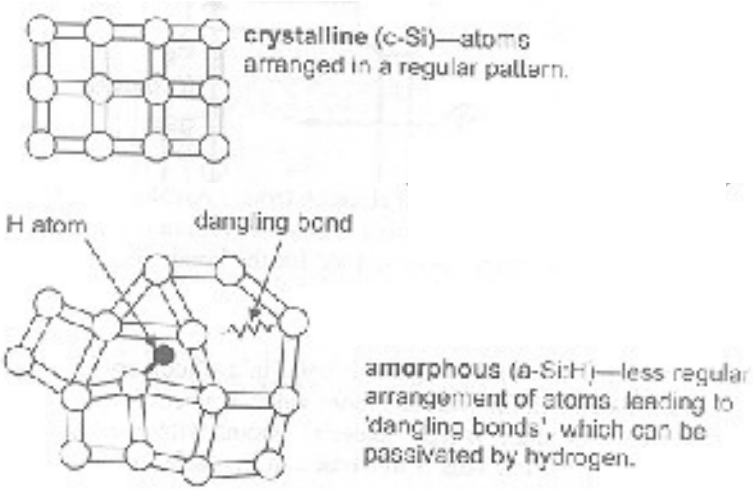
pn junction:
a:Si cells

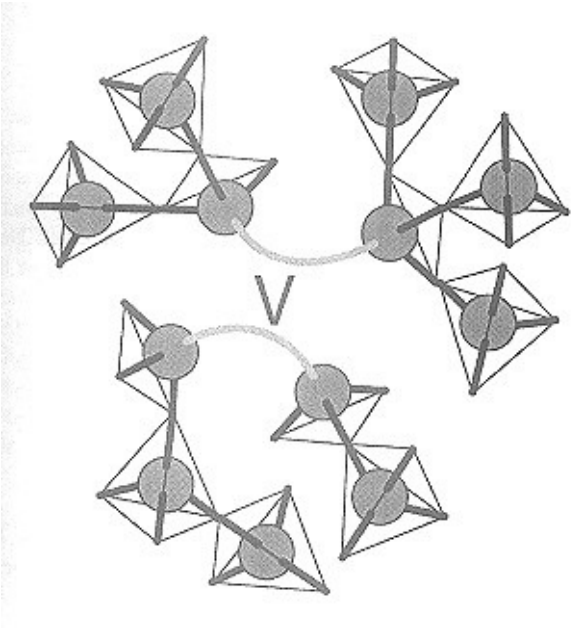
heterojunction cells:

- CIGS-based
- CdTe-based



Amorphous Si



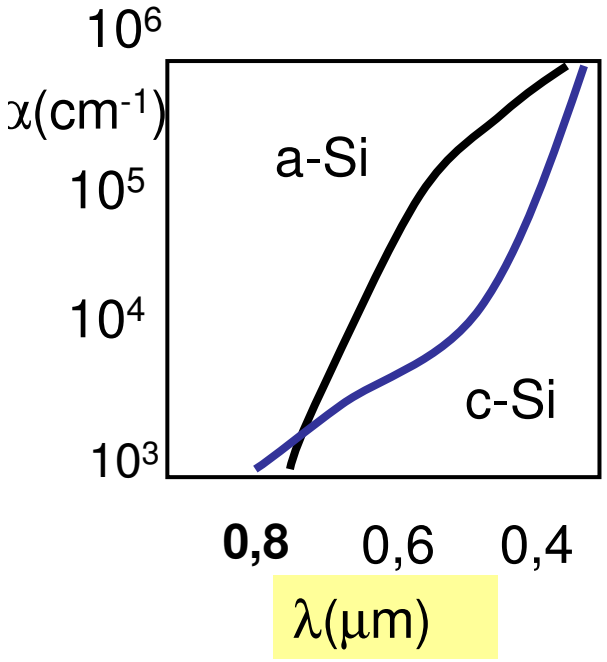


large concentration of defects $N_T > 10^{16}$ cm^{-3} („dangling bonds" D^+, D^-, D^o)

passivation of defects by hydrogen to ~10^{15} cm^{-3}

doping more difficult, e.g. if we increase a number of free electrons by adding P the concentration of D^- defects increases also

a-Si:H



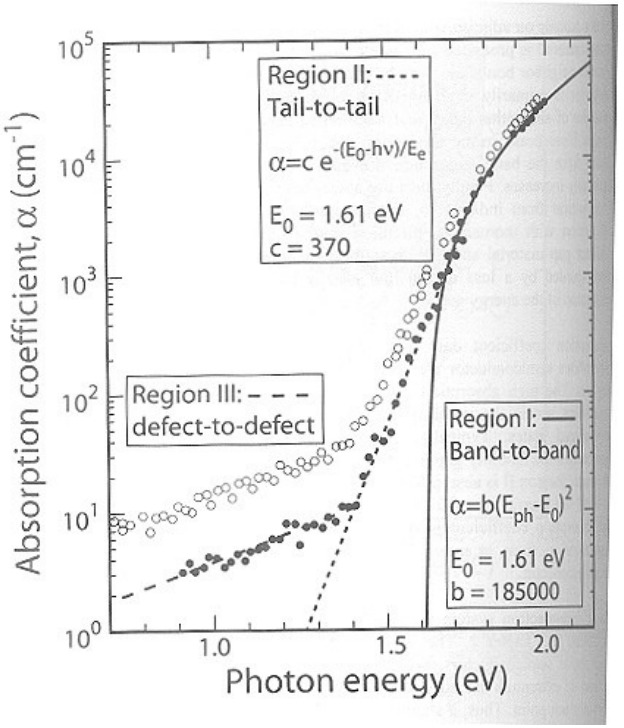
direct bandgap 1.7 eV, E_g>E_g(c-Si)

no well-defined E(k) dependence

no conservation of momentum k

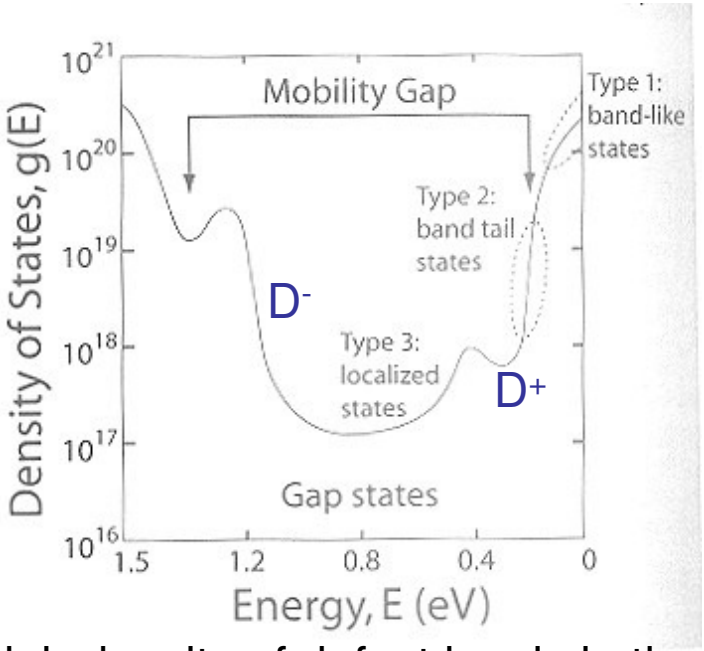
absorption coefficient ~ 10-100 times higher

thin film solar cell cell (~5 μm) possible



Gap states in a-Si

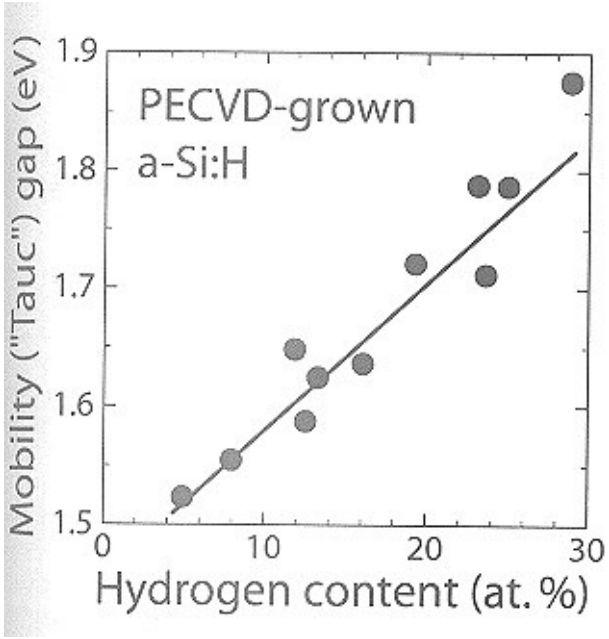
a-Si



very high density of defect levels in the gap

doping not effective

a-Si:H

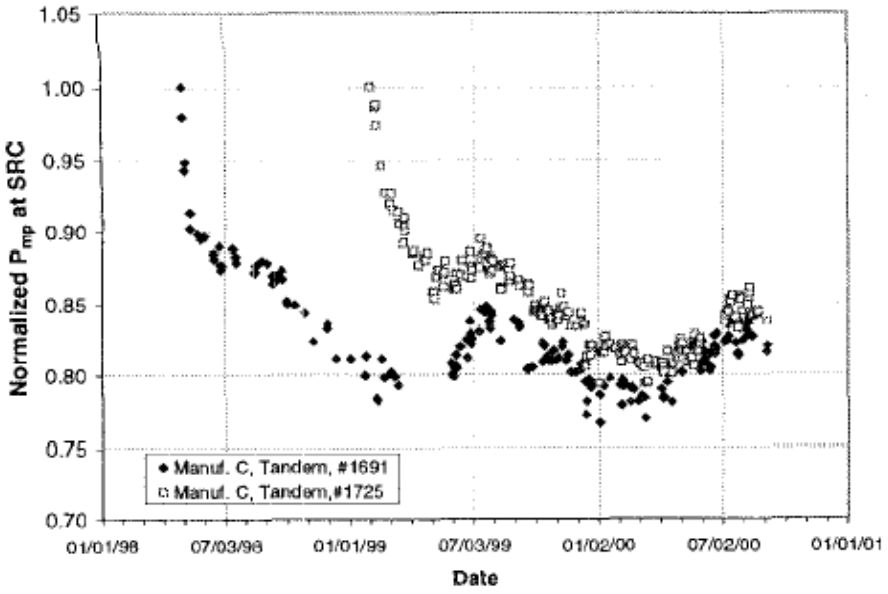


passivation of defects by hydrogen

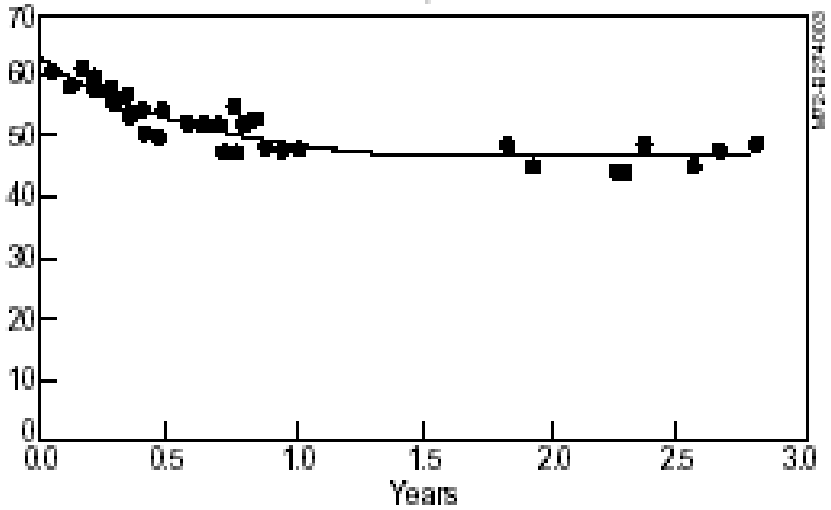
doping possible in Si:H!

Steabler-Wronski effect

device degradation: efficiency loss due to photo-generation of defects



power



Best modules:

η=9,5 % (stabilized)

More degradation when more Si-H_2 bonds present : „hot wire" technique

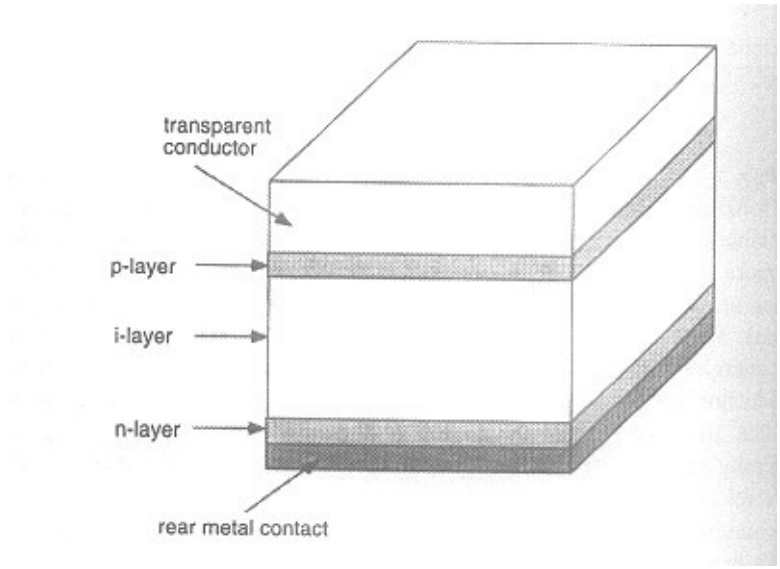
a-Si cell – basic design

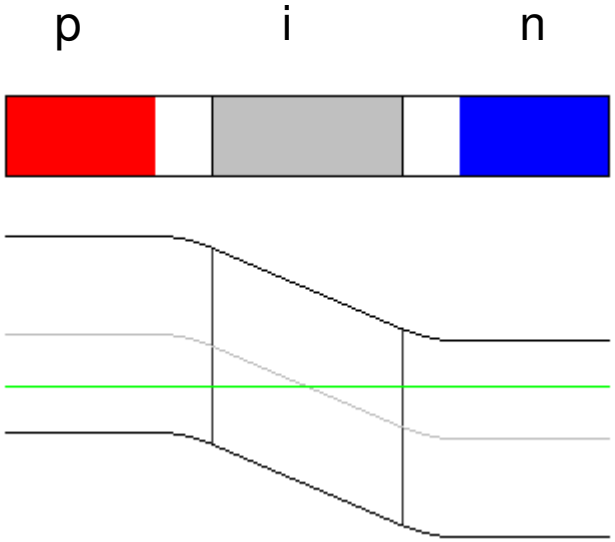
short diffusion length ~100 nm
further decreases with doping

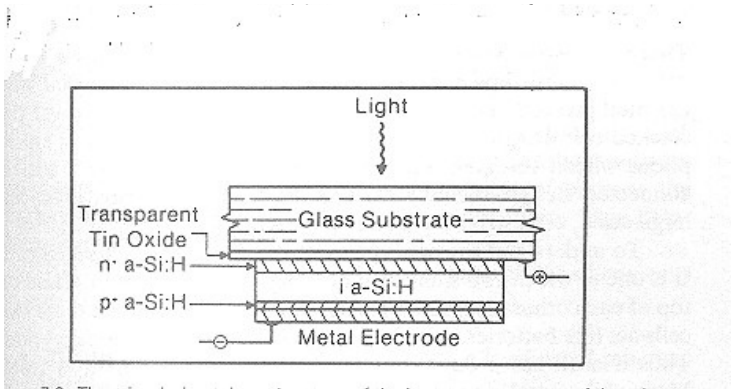
minority carrier lifetime 10 ns

⇩

solution: p-i-n cell





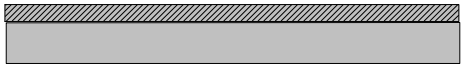


TCO - transparent conducting oxide (ZnO, SnO_2)

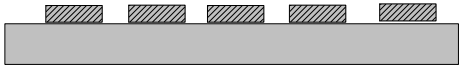
a-Si solar cell

Fabrication steps:

TCO (spray deposition)

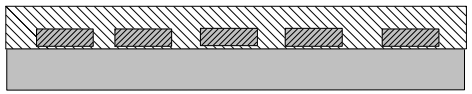


laser scribing

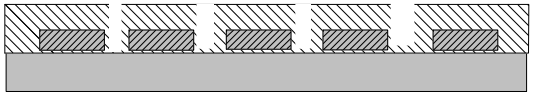


p-aSi (10 nm)
i-a-Si (500 nm)
n-aSi (10 nm)

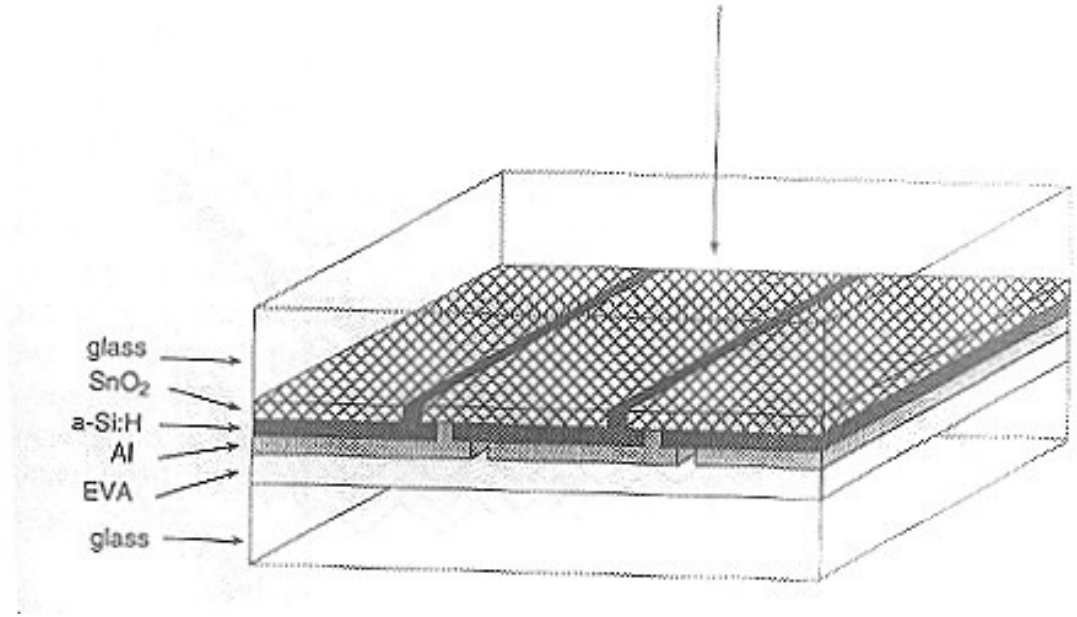
} sputtering SiH4, glow discharge process



laser scribing



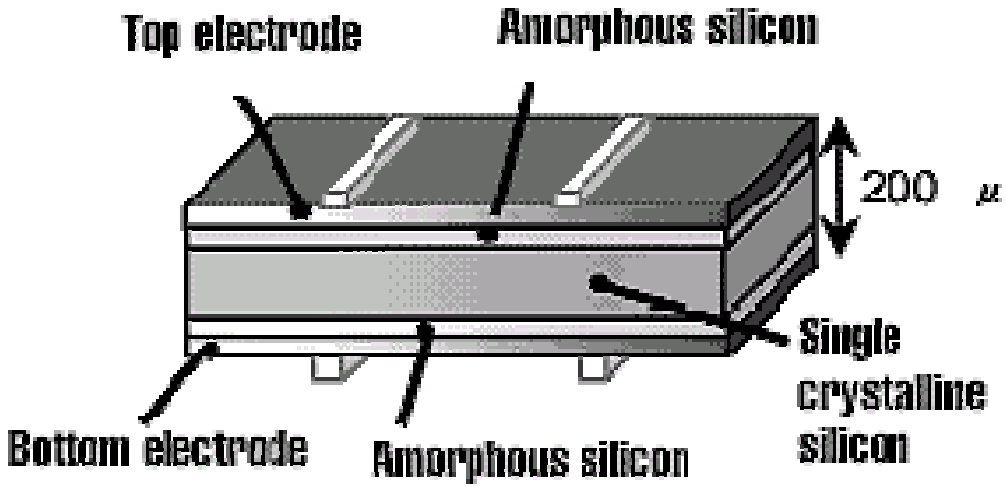
metalization, laser scribing, polymer coating



HIT solar cells *Sanyo*

(Heterojunction with intrinsic thin layer)

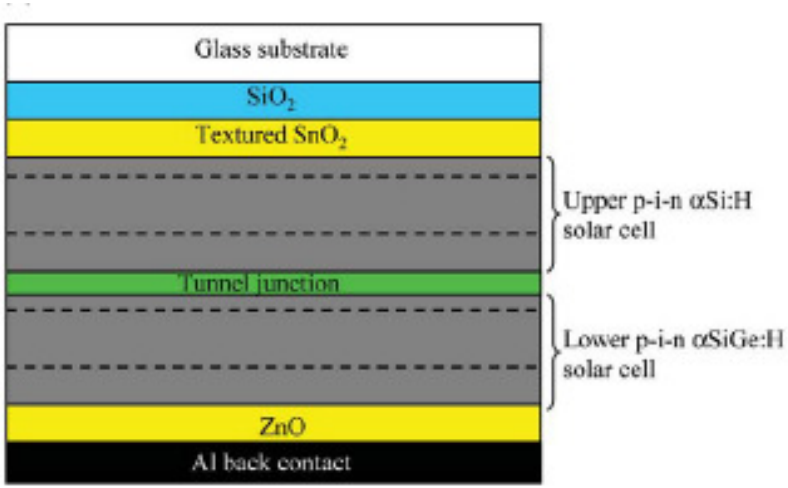
good surface passivation
low temperature processing
(<200 C)



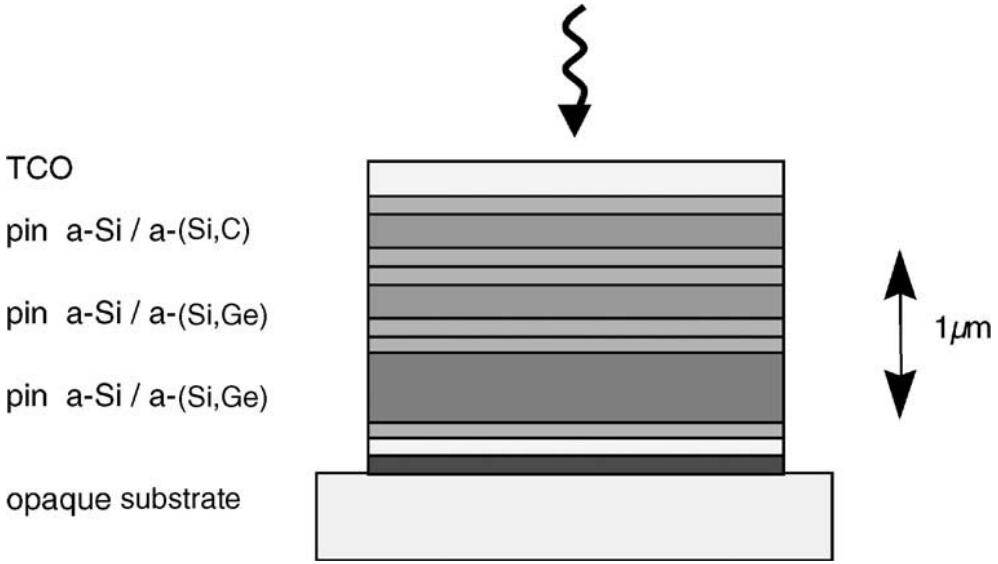
η= 21,5%

modules up to 17%

Multijunction devices



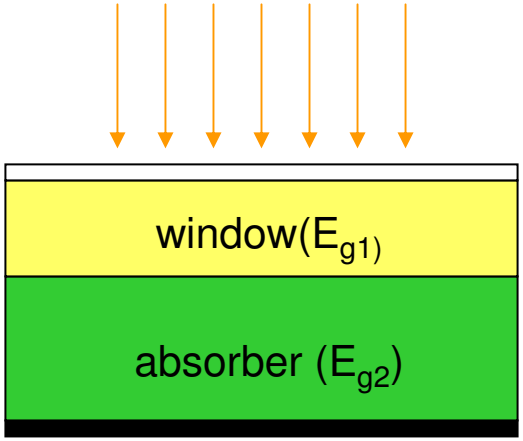
double junction



triple junction

better stability

Thin film heterojunction solar cells

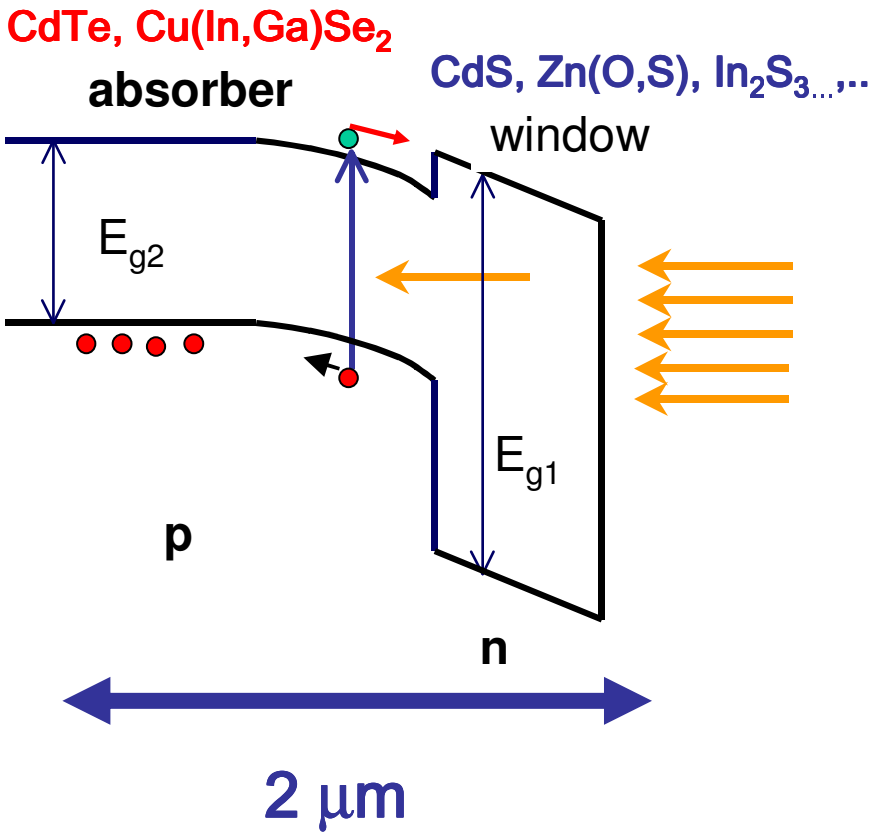


- polycrystalline materials
- good absorption properties – 2-5 μm absorbers
- p-n heterojunctions
- low costs, low energy- and material -consuming technologies

100 x less material than for c-Si

Heterojunction photovoltaic structure

advantages:
maximum generation in the electric field region of absorber:
no problem with front surface recombination
disadvantages:
interface recombination, band edge discontunuities at interface



absorber:

bandgap close to 1.5 eV

p-type doping ~10^{16} cm^{-3}

high absorption coeffient

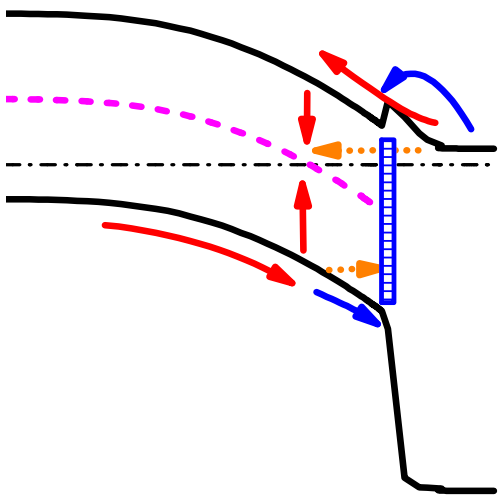
window:

large bandgap (transparent)

good conduction band alignement with absorber

n-type doping 10^{17}-10^{18} cm^{-3}

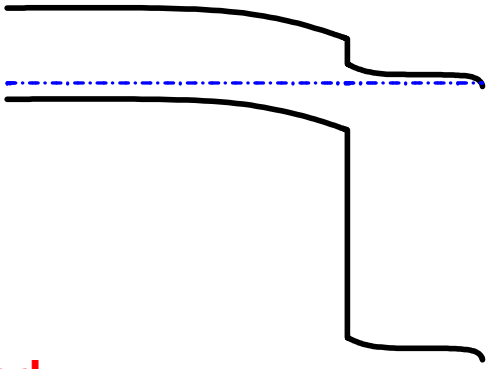
Current transport in the heterojunction



- o **recombination in the bulk of absorber**
- o **recombination via interface states**
- o **tunnelling to interface states**

Conduction band alignement

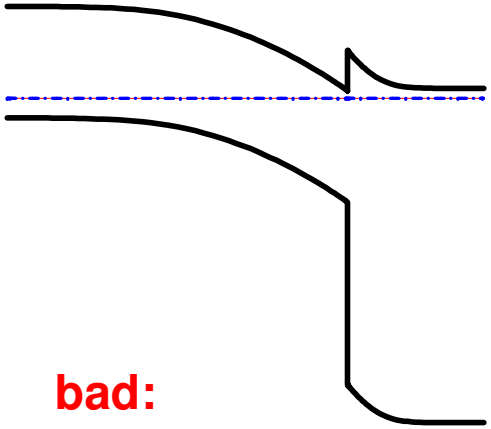
cliff



bad:

loss of the barrier height
increased interface recombination

spike



bad:

barrier for photoelectrons

Material requirements

absorber

- direct bandgap $E_g \approx 1.4$ eV
- p-type electrical conductivity
- high diffusion barrier
- long diffusion length

window

- high energy gap
- high conductivity

- good ohmic electrical contacts
- similar lattice constants
- good band alignement
- stable junction
- availability and low cost of materials and technology
- low toxity of materials

There is not so many materials meeting these requirements!

Semiconducting chalcopyrites from the CIGS family

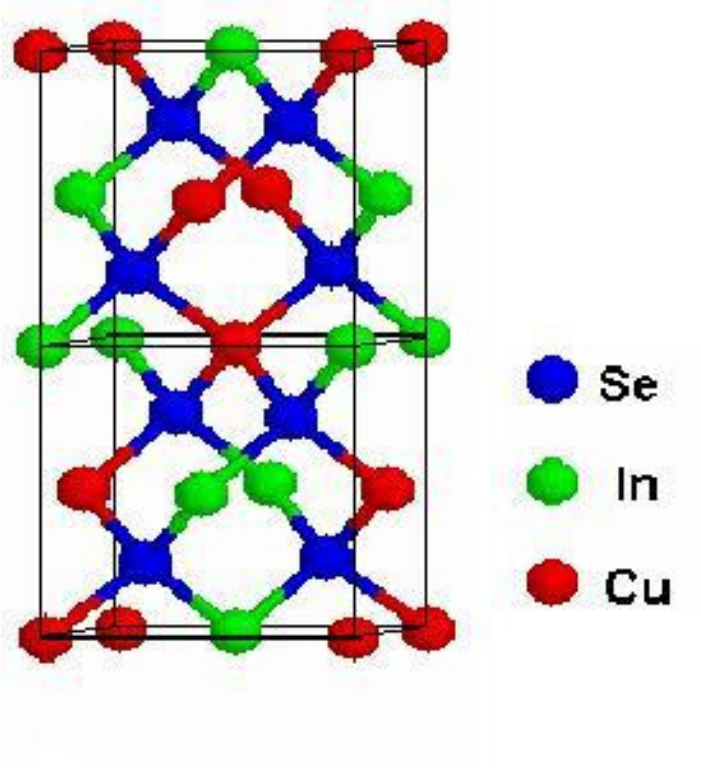
direct bandgap, very high absorption coefficient

$CuInSe_2$	E_g = 1.04 eV
$CuGaSe_2$	E_g = 1.68 eV
$CuInS_2$	E_g = 1.55 eV

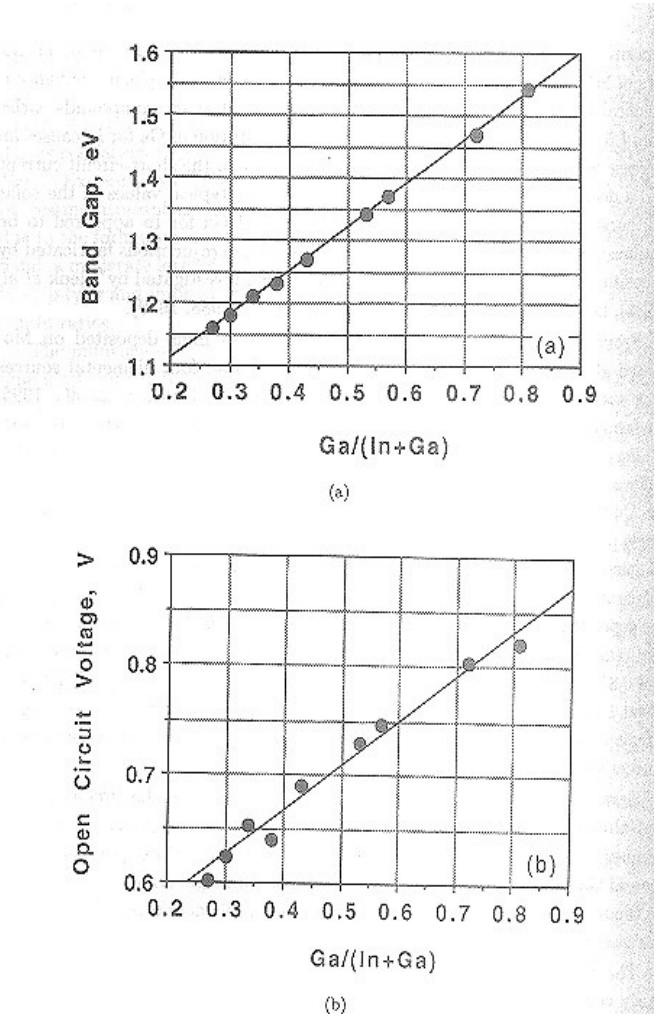
Solid solutions $Cu(In,Ga)Se_2$ i $CuIn(Se,S)_2$

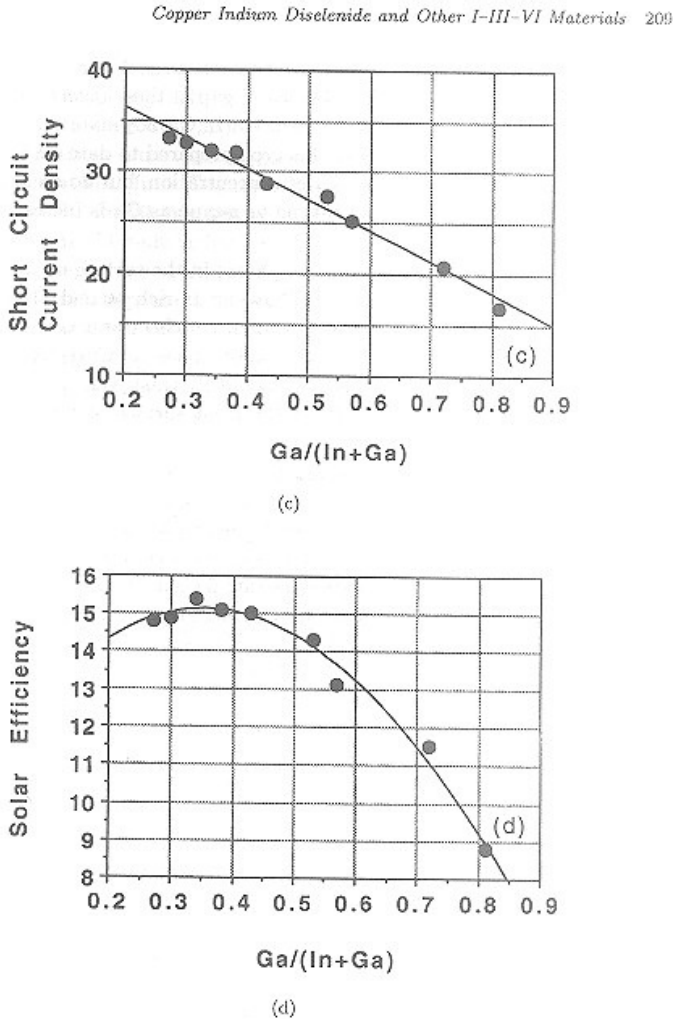
Highest efficiency (record 19.8%)
achieved with **$CuIn_{1-x}Ga_xSe_2$**

x = 0.2 - 0.3 E_g= 1,12 - 1,20 eV



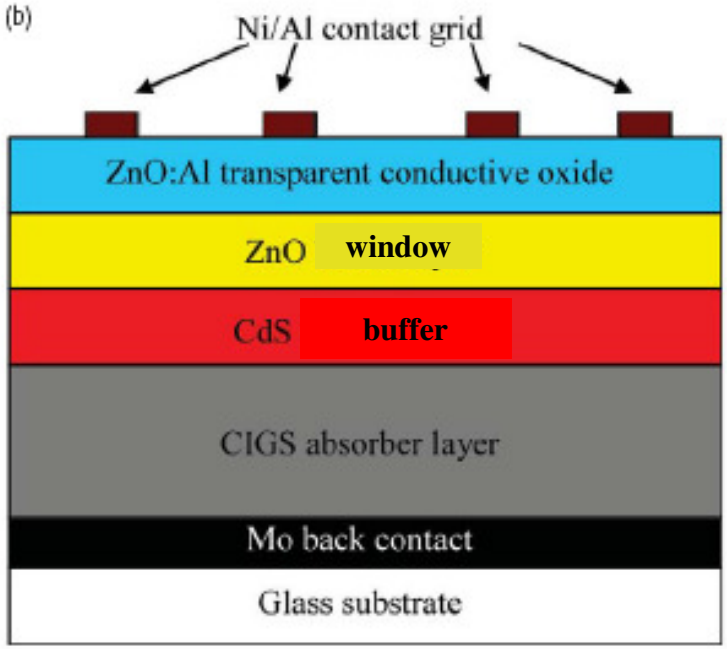
$CuGa_xIn_{1-x}Se_2$ solid solutions as absorbers





Lower efficiency for Ga/(In+Ga)>0.3
Bad conduction band alignement?

Baseline CIGS device



n^+- ZnO:Al (0.3 µm)

i - ZnO (0.1 µm)

n-CdS (50 nm)

p-$CuIn_{1-x}Ga_xSe_2$ (2 µm)

Mo

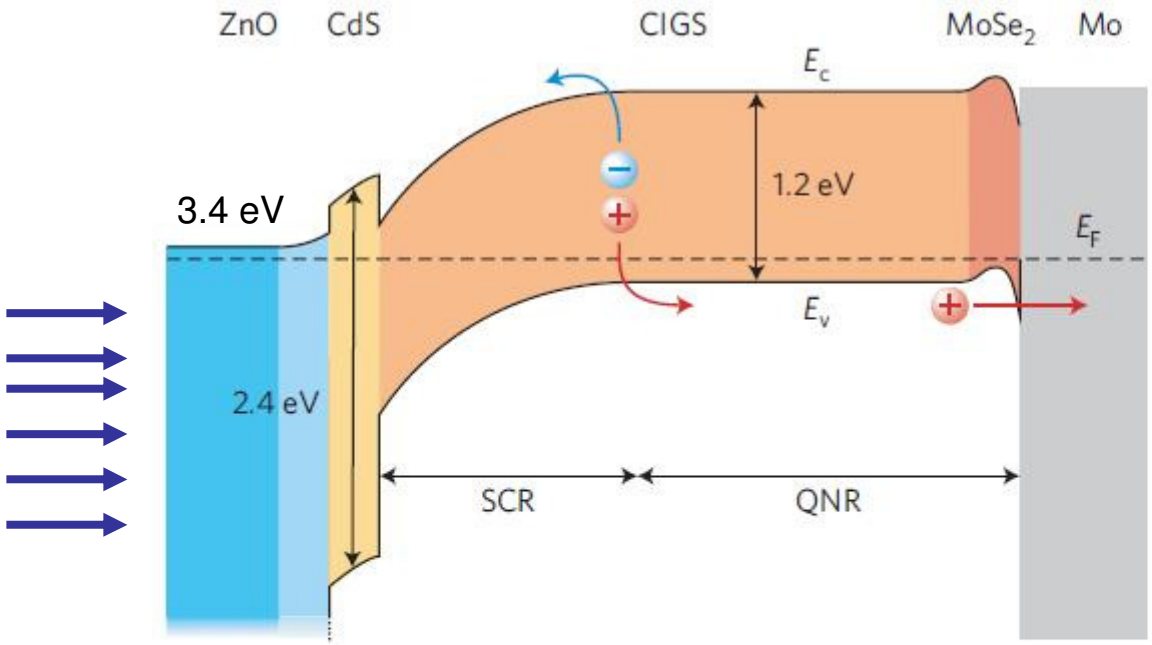
nCdS – buffer

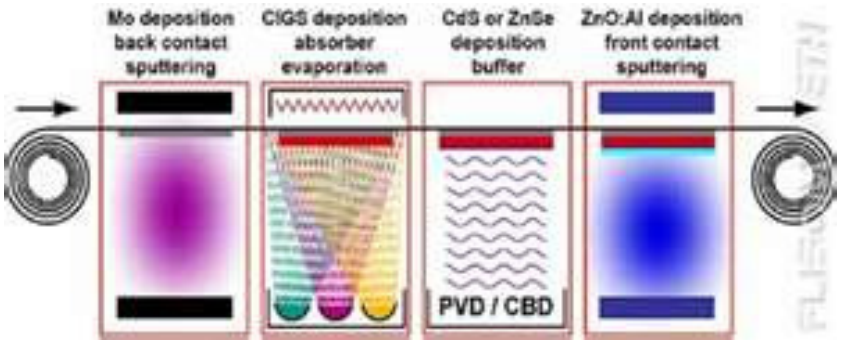
good alignement of conduction bands

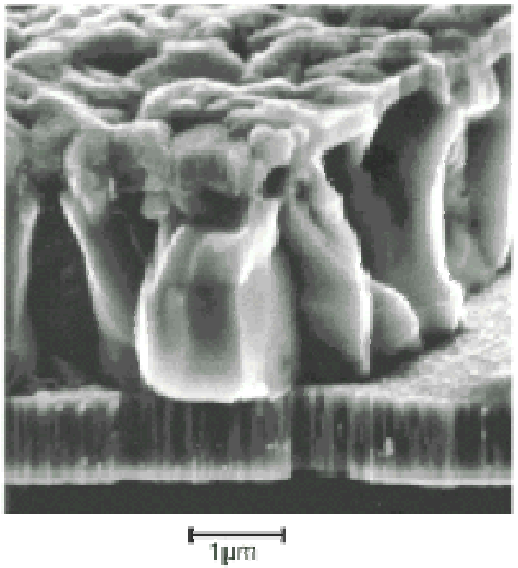
lattice constant matches that of CIGS

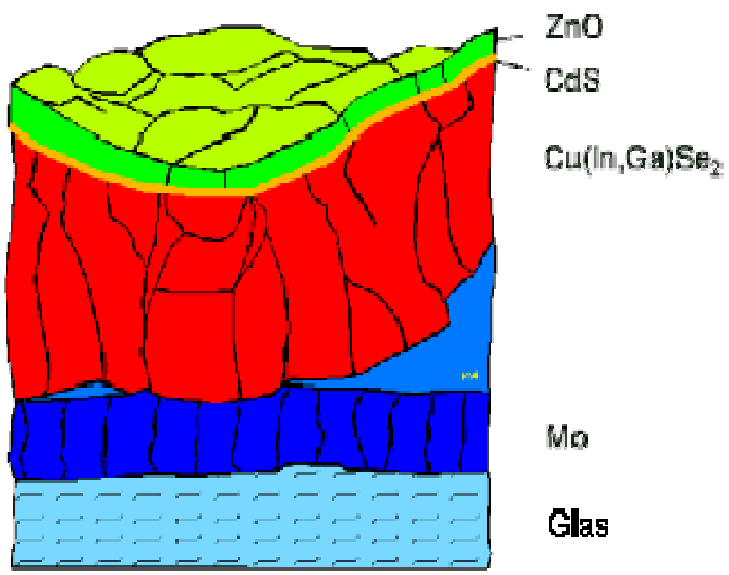
electrochemical treatment of absorber surface

CIGS cell band diagram









ZnO - sputtering

CdS - CBD (chemical bath deposition)

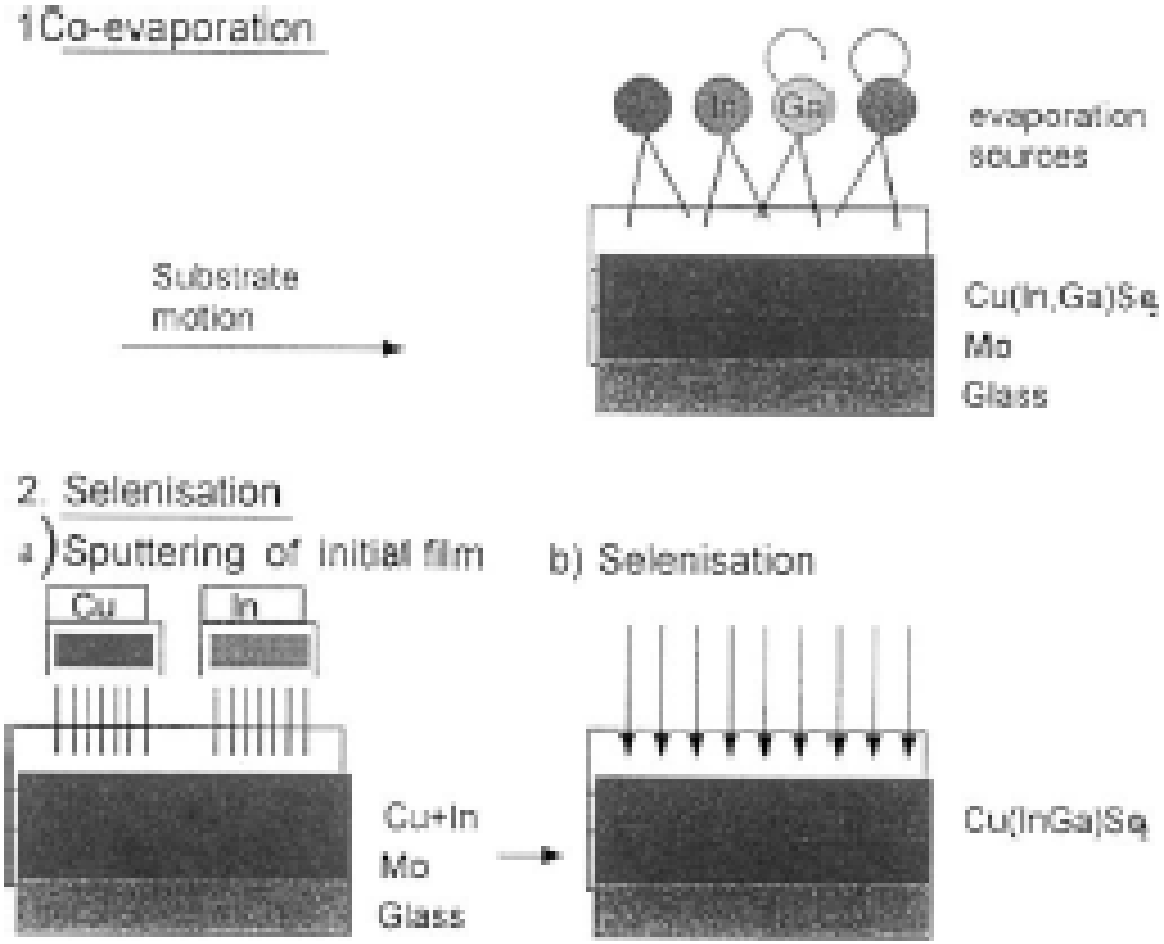
$Cu(In,Ga)Se_2$

- co-evaporation
- selenization of metal layers in Se lub H_2Se vapour
- bilayer process

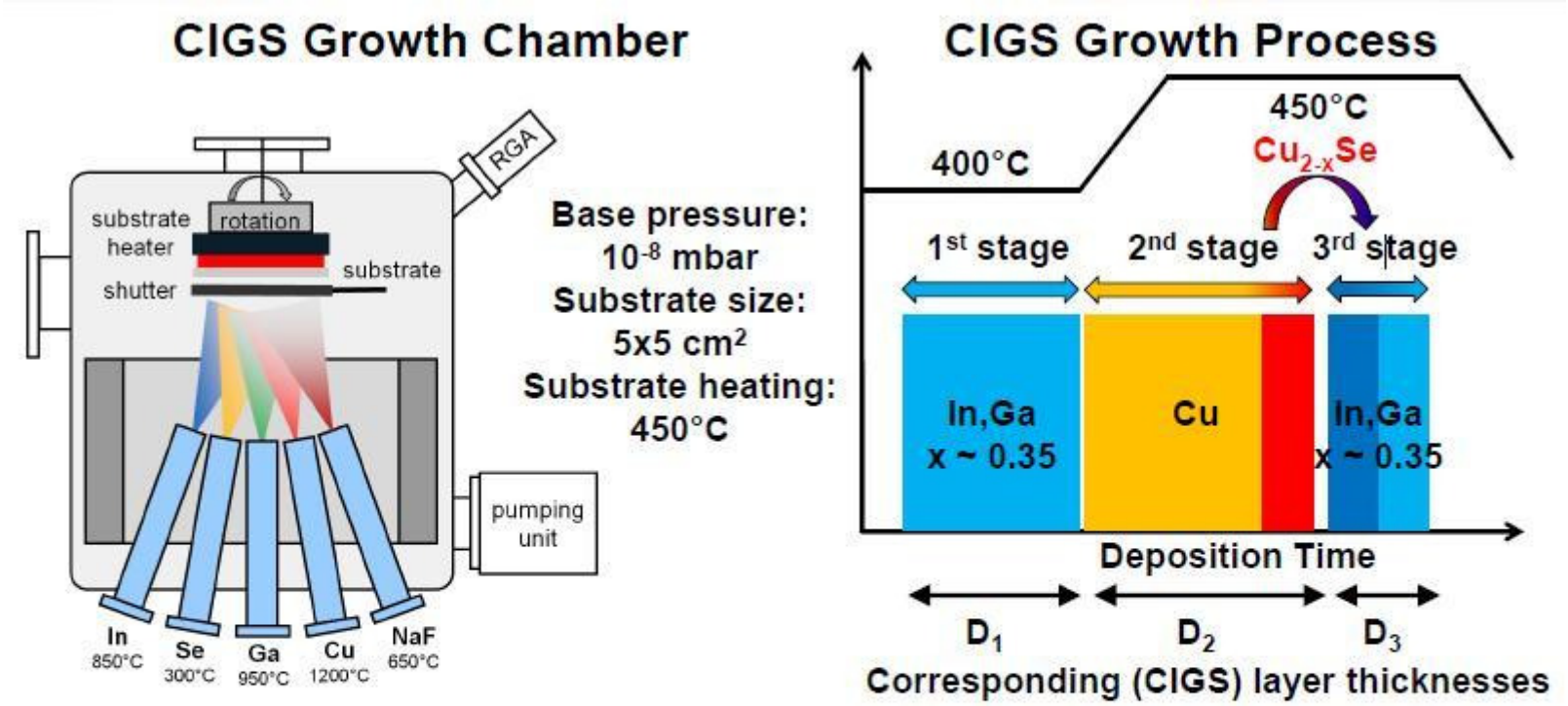
Mo - RF sputtering

soda-lime glass

Preparation of CIGS absorber layer

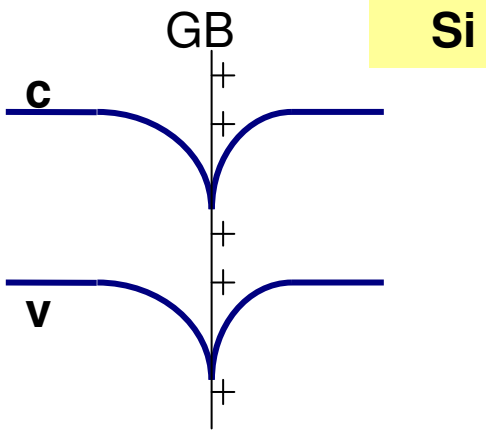


Absorber preparation- „three stage process”

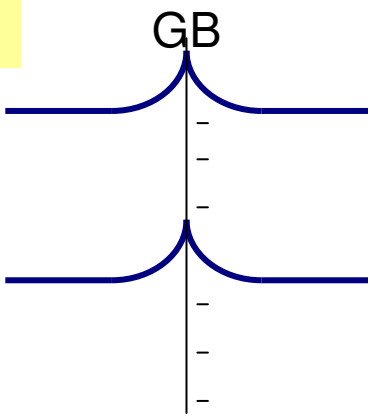


EMPA, 2010

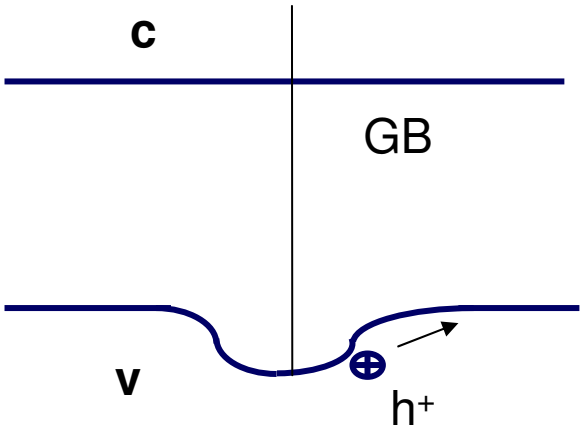
Grain boundaries in CIGS

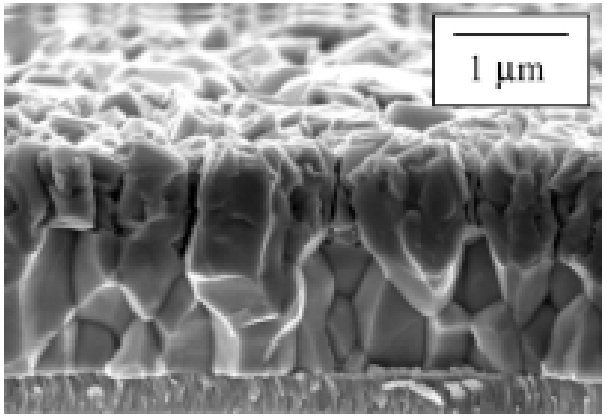


Si i **GaAs**



Grain boundaries in $CuInSe_2$





in CIGS neutral grain boundaries,
lower E_v?

policrystalline material makes better cells than single crystal

segregation of impurities at GB?

Specific problems

Native defects and doping

p-doping by Cu vacancies: Cu-poor composition Cu/(In+Ga+Cu)<1

large concentration of native defects: Se vacancies, In_{Cu} antisites, etc

large deviation from stechiometry tolerated!

metastable changes of photovotaic parameters – light soaking improves the efficiency!

Influence of sodium diffusing from soda-lime glass

Na increases net doping and improves morhology of the layer:

grain boundaries passivated? compensating donors passivated? growth improved by better incorporation of Se (Na_2Se topotaxy)?

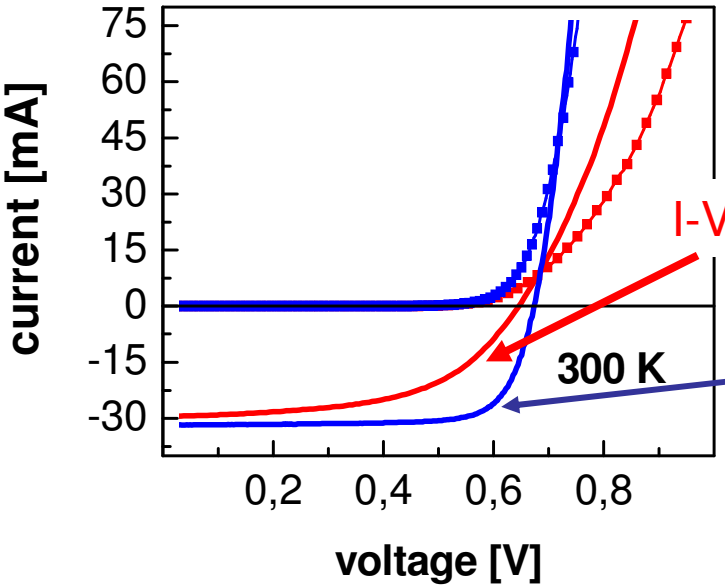
Cd-free buffers:

worse performance (???)

Zn(Mg)O by ALD and Zn(O,S) by CBD *almost* as good as CdS

Metastabilities of junction parameters

„morning sickness"

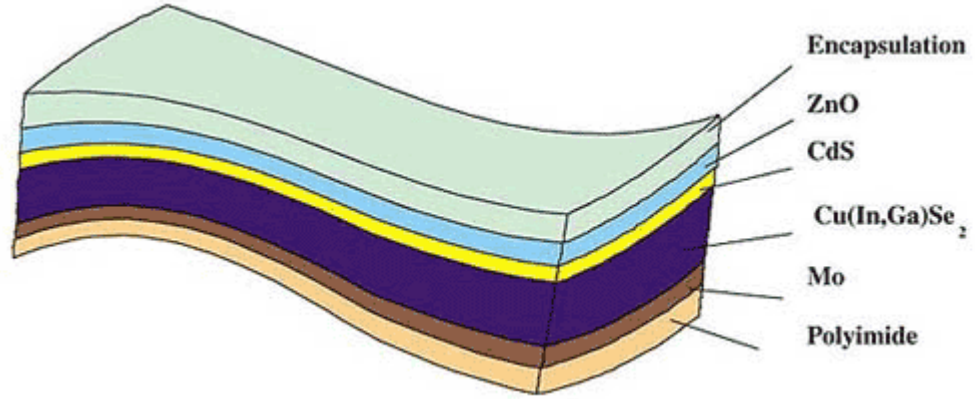


I-V after a long time in darkness -

I-V after white light soaking:
Voc and FF improves

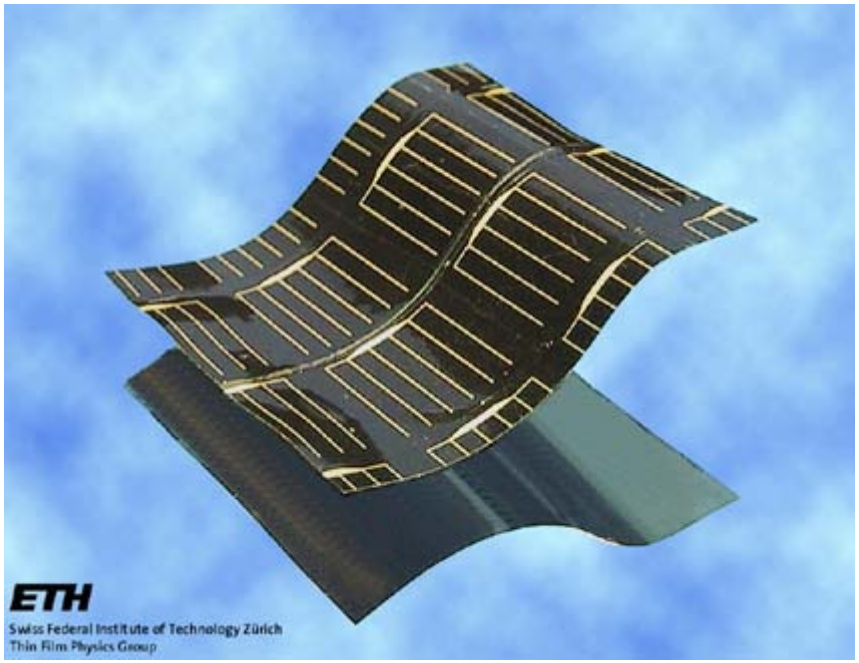
Recent theoretical and experimental findings:
specific properties of V_{Se} and In_{Cu}-related defects

Flexible substrates

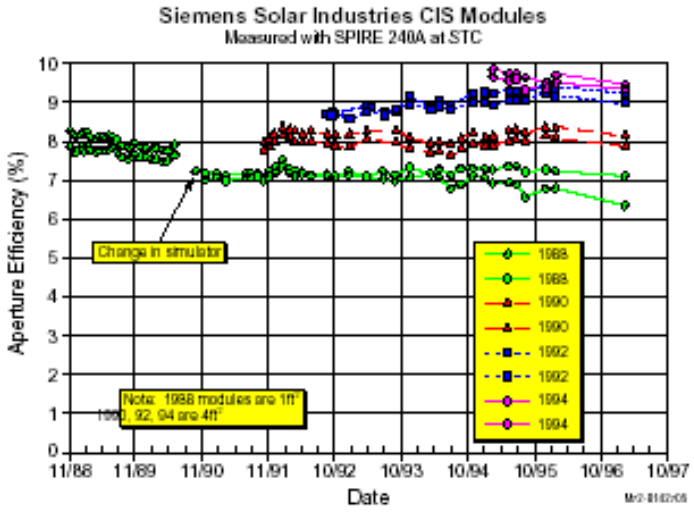


18.7% on polyimide foil (2010)

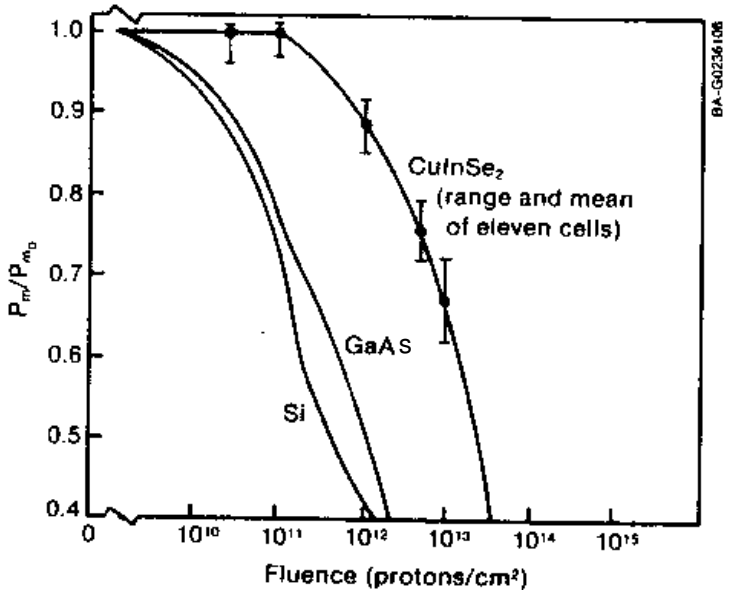
sodium has to be provided for good growth



Stability



irradiation by proton flux



exceptionally good if protected against humidity

radiation hardeness more than 1 order of magnitude better than crystalline absorbers
well suited material for space application!

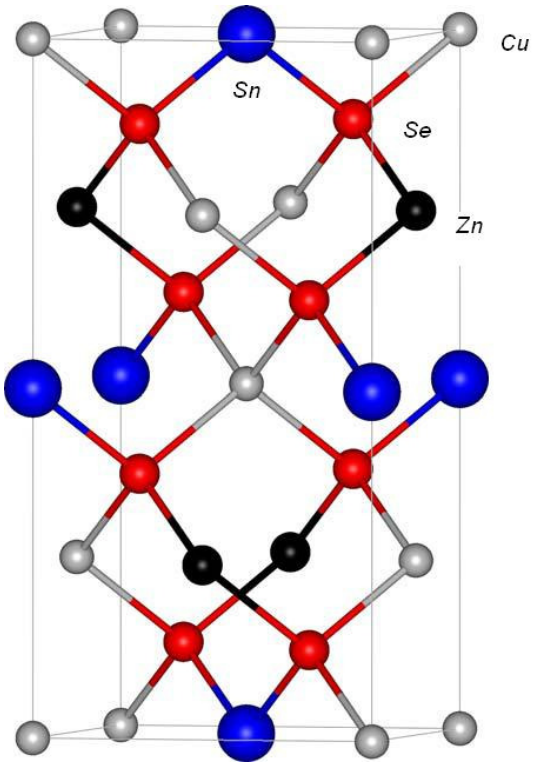
Kesterites – new photovoltaic materials

remedy for shortage of indium

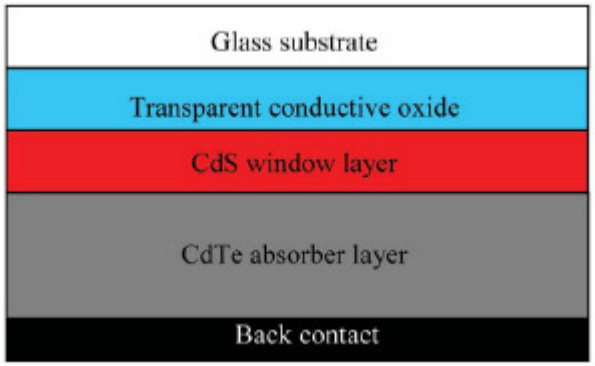
$CuInSe_2 \Longrightarrow Cu_2ZnSnS_4$

Eg=1.5 eV

η=9.6% (IBM 2010)



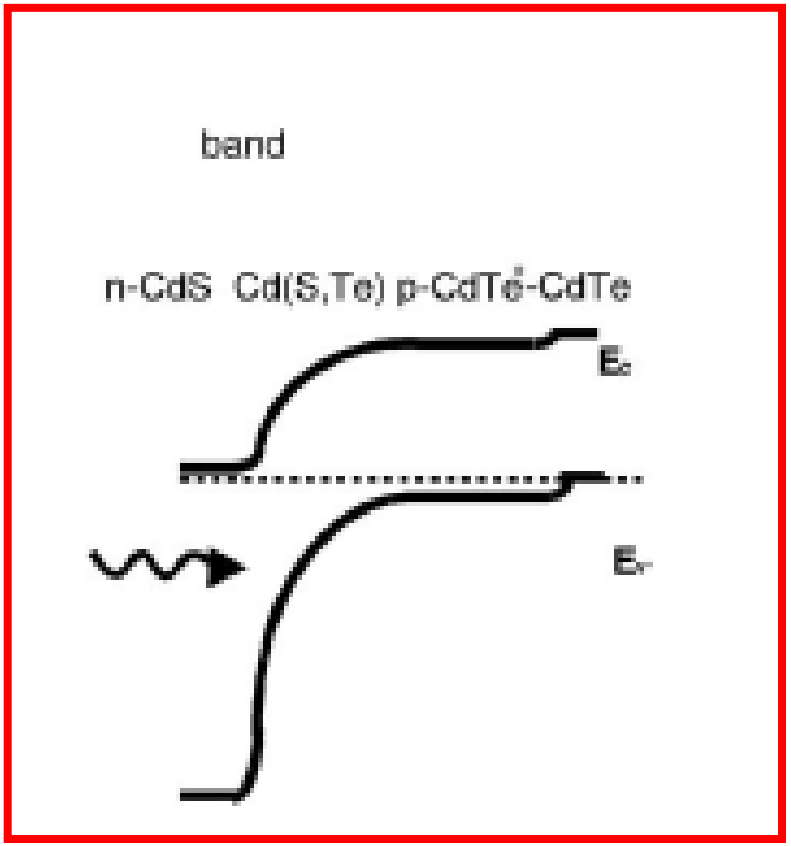
CdS/CdTe heterojunction solar cell



superstrate configuration

absorber:
CdTe 3-5 μm
intrinsic p-type doping ~10^{15} cm^{-3}
direct bandgap Eg =1.5 eV

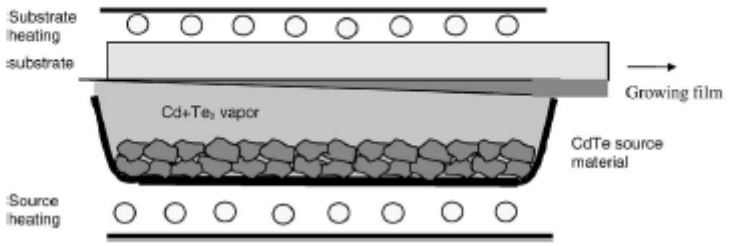
efficiency 16.5% (modules ~10%)



Absorber preparation:
CdTe: PVD, CSS, electrodeposition, spray pyrolysis

$CdCl_2$ treatment at T>400 C:
recrystallisation of CdTe
grains passivation
interface improvement

ohmic back contact: ***difficult***
Cu-Au alloy or ZnTe:Cu, Sb_2Te_3,
.



Close space sublimation process

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process	company	efficiency(%)
CSS	Solar Cell Inc. (USA)	15.8 / 1.05 cm^2 8.4 / 7200 cm^2
electrodeposition	BP Solar	14.2 / 0.02 cm^2 10.1 / 706 cm^2
Screen printing	Matsushita	12.8 / 0.78 cm^2 8.1 / 1200 cm^2
Spray pyrolysis	Golden Photon	12.7 / 0.3 cm^2 8.1 / 832 cm^2
PVD		11.8 / 0.3 cm^2
sputtering		10.4 / 0.1 cm^2

Life cycle assesment of Cd

Cd is a by product of production of metals from zink ores (~80%) and lead ores (~20%) (from wastes)

Table 12
Reference case—atmospheric Cd emissions from the life-cycle of CdTe PV modules *V.M. Fthenakis 2004*

Process	Air emissions (g Cd/ton Cd[a])	Allocation		Air emissions	
		(%)	(g Cd/ton Cd)	(mg Cd/m^2)	(mg Cd/ GWh)
1. Mining of Zn ores	2.7	0	0	0.00000	0.00
2. Zn smelting/refining	40	0	0	0	0.00
3. Cd purification	6	100	6	0.042	7.79
4. CdTe production	6	100	6	0.042	7.79
5. CdTe PV manufacturing	3	100	3	0.021	3.90
6. CdTe PV operation	0	100	0	0	0.00
7. CdTe PV disposal/ recycling	0	100	0	0	0.00
Total emissions			15.00	0.11	19.48

0.02 g of Cd per GWh during life time of CdTe module

power plants based on coal emit minimum of 2 g of Cd/GWh!