Photovoltaics

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yesterday: Devices

- Overview on technology and economics
- Some semiconductor basics
- Solar cells as p-n junctions

today: Efficiencies

- Fundamental limits to efficiency: Shockley-Queisser limit
- Real efficiencies
- How to go beyond

the Shockley-Queisser limit

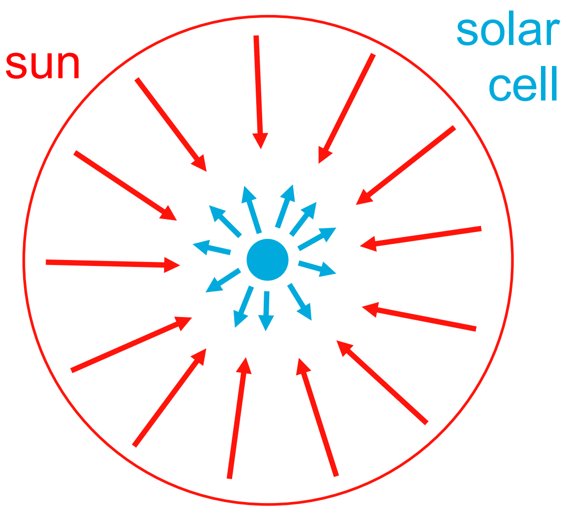
Shockley, Queisser
"Detailed Balance Limit of Efficiency of p-n Junction Solar Cells"
J. Appl. Phys. 32 (1961) 510

Basic approach to efficiency: 2nd law of thermodynamics

Carnot efficiency: $\eta_{\max} = \frac{T_{sun} - T_{cell}}{T_{sun}} = 95\%$ with $T_{sun} = 6000\text{K}$ and $T_{cell} = 300\text{K}$

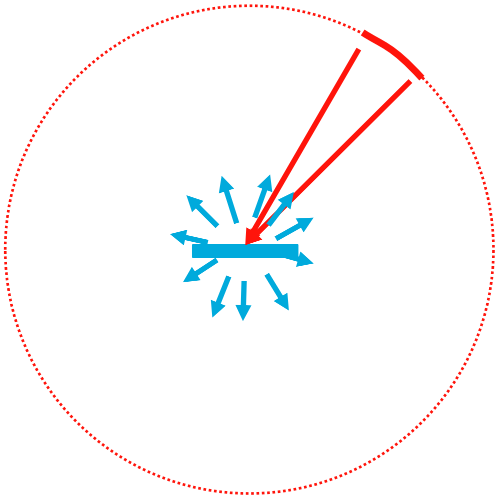
requires the sun as reservoir, i.e. all around the solar cell
and full use of spectrum

the sun as a reservoir:



steady state at Voc:
radiative equilibrium

limited angle of sun: $6.85 \cdot 10^{-5}$ sr



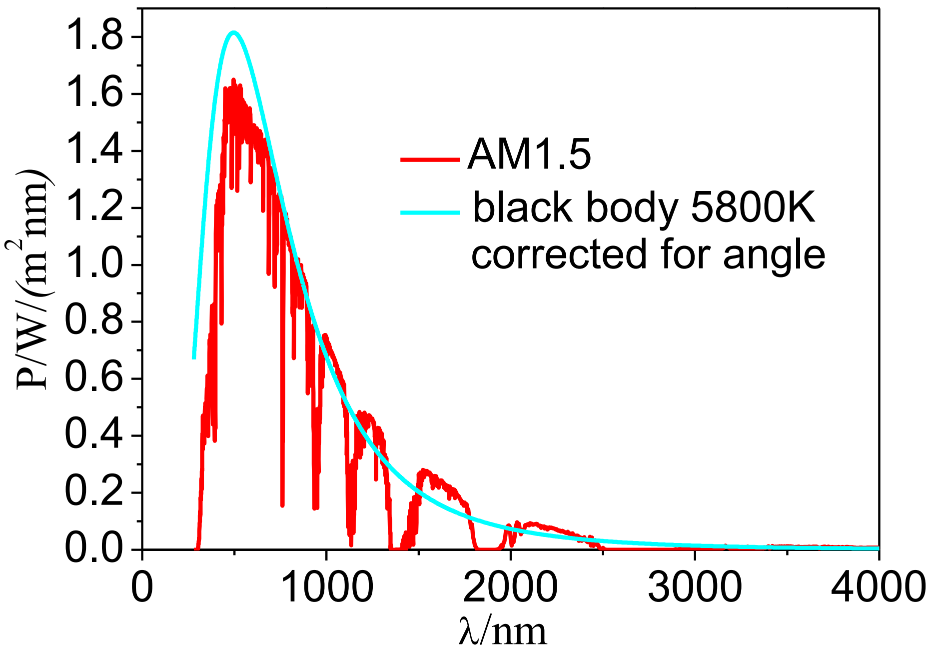
entendue factor

cells radiates into 4π
$\Rightarrow$ increase in entropy
$\Rightarrow$ $\eta < \eta_{\max}$

The solar spectrum and the absorption of a semiconductor

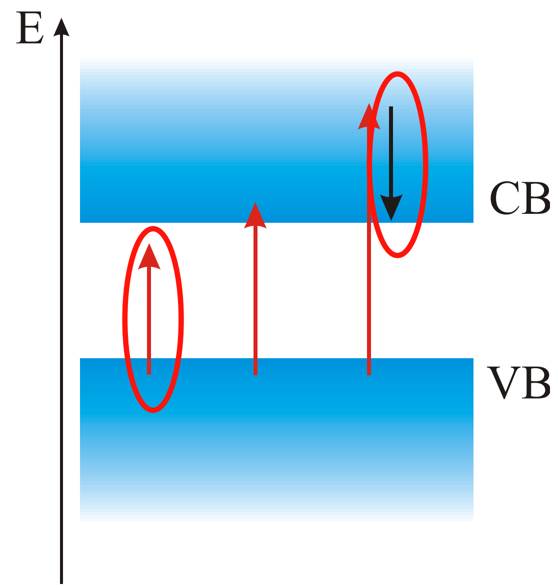
use measured solar spectrum on Earth
⇐ takes entendue factor into account

takes absorption in atmosphere into account



AM1.5: reference spectrum
BB: taking solar angle into account

we can not use all solar photons
and we can not use all their energy:



incomplete absorption

thermalisation

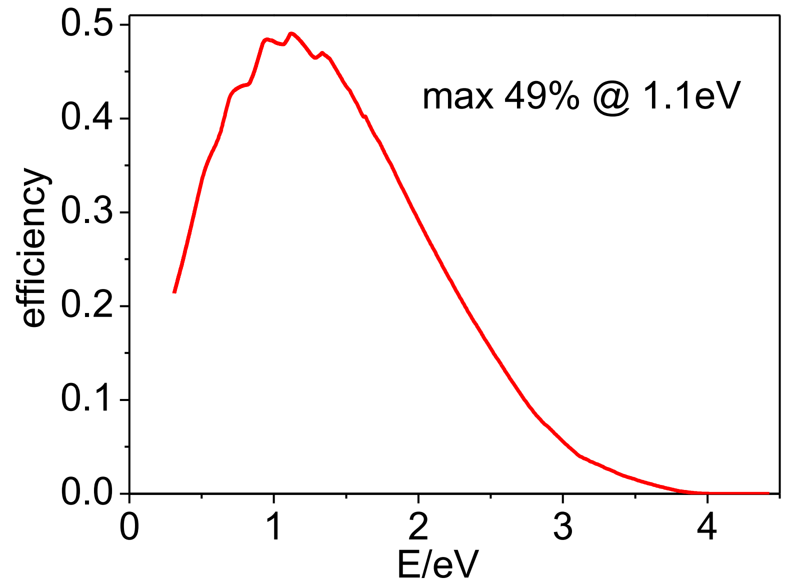
A first estimation of the efficiency

ideal solar cell: no ohmic losses
complete absorption
complete collection

$$QE = \begin{cases} 1, E \geq E_G \\ 0, E < E_G \end{cases}$$

$$\eta_{ult} = \frac{E_G \int_{E_G}^{\infty} \Phi_{sun}(E) dE}{\int_0^{\infty} E \Phi_{sun}(E) dE}$$

→



original calculation by Trivich and Flinn (1955)

More fundamental losses

$$\eta_{ult} = \frac{E_G \int_{E_G}^{\infty} \Phi_{sun}(E)dE}{\int_0^{\infty} E\Phi_{sun}(E)dE} = \frac{(E_G / e) \cdot eN_{E_G}}{P_{solar}}$$

$$QE = \begin{cases} 1, E \geq E_G \\ 0, E < E_G \end{cases} \Rightarrow j_{SC} = eN_{E_G}$$

basic assumption of Shockley-Queisser limit

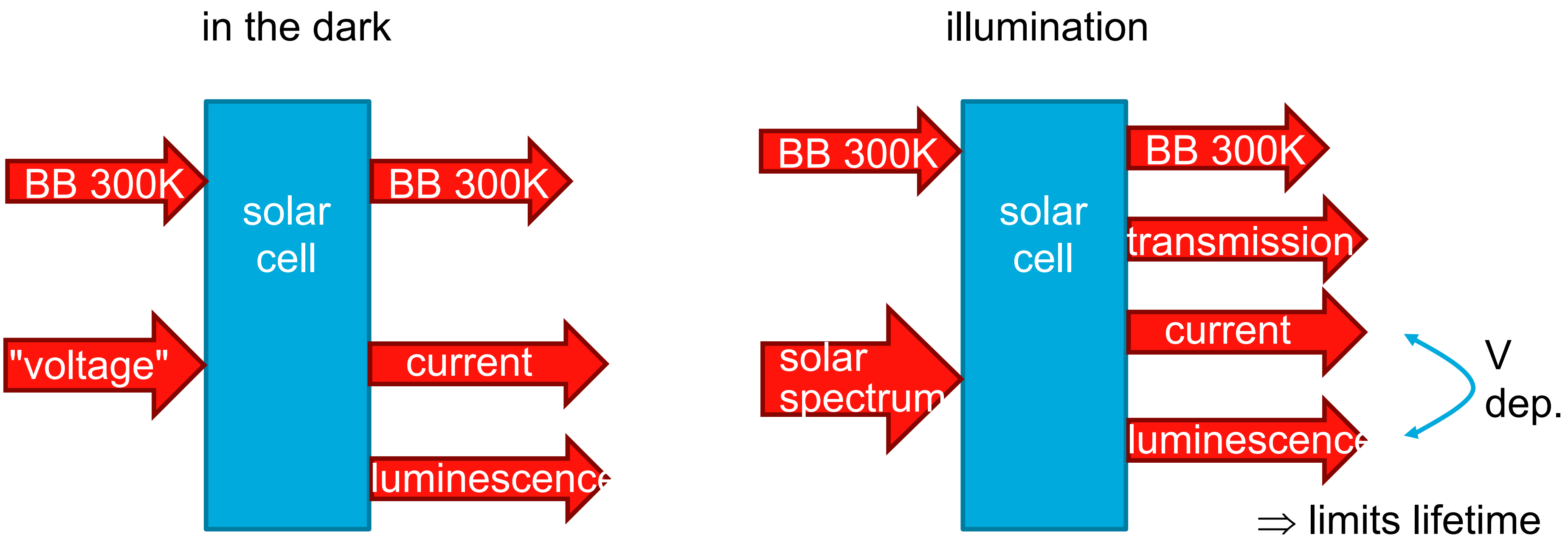
infinite absorption coefficient
and/or infinite mobility

compare: $\eta = \frac{j_{sc} \cdot V_{oc} \cdot FF}{P_{solar}}$

$V_{OC} = E_G / e$ → not achieved because of radiative equilibrium

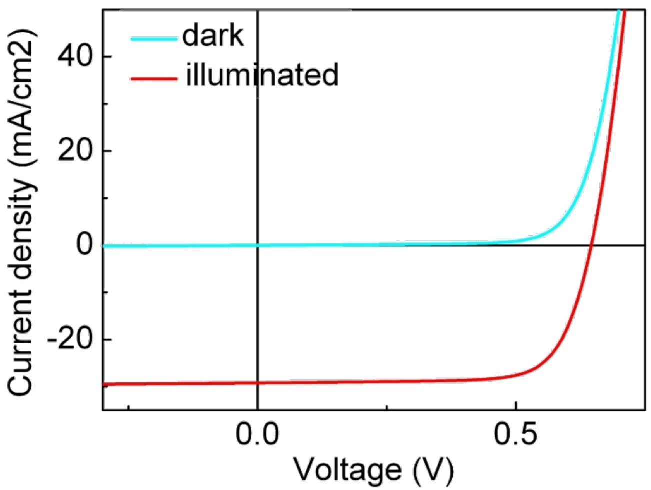
$FF = 1$ → not achieved because of IV characteristic

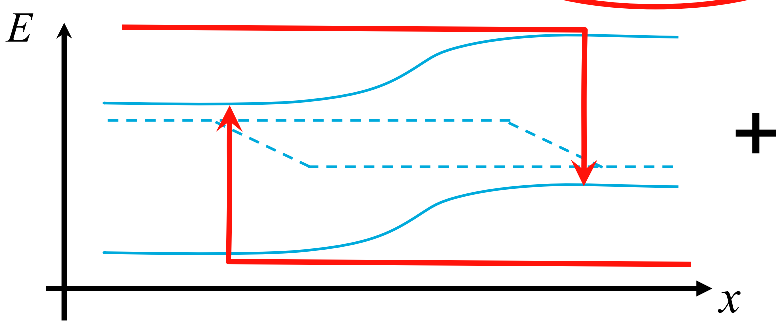
Radiative equilibria - detailed balance



⇒ limits lifetime

⇒ limits V_{OC}





Detailed balance

emission from a semiconductor: $\Phi(E) \sim np \sim e^{\Delta E_F/kT} = e^{eV/kT}$

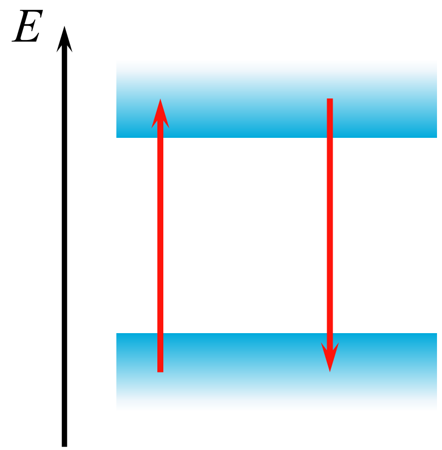
$$\Phi(E) = \Phi_0\, e^{eV/kT}$$

in equilibrium: $\Phi(E) = \Phi_0$ black body emission

$$\int_{E_G}^{\infty} \Phi_{BB}\, dE$$

solar cell at V_{OC}: $\Phi_S = \int_{E_G}^{\infty} \Phi_{sun}\, dE = \Phi_0\, e^{eV_{OC}/kT} \Rightarrow V_{OC} = \frac{kT}{e} \ln \frac{\Phi_S}{\Phi_0}$

j_{SC}



generation

no current!

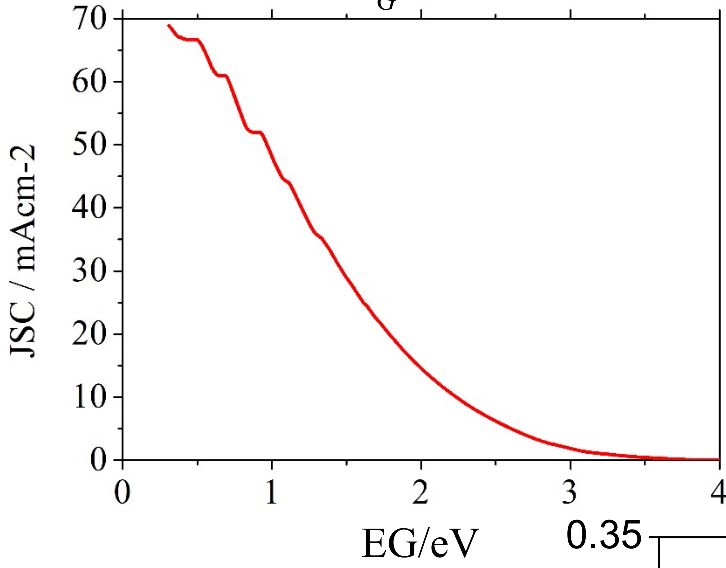
recombination

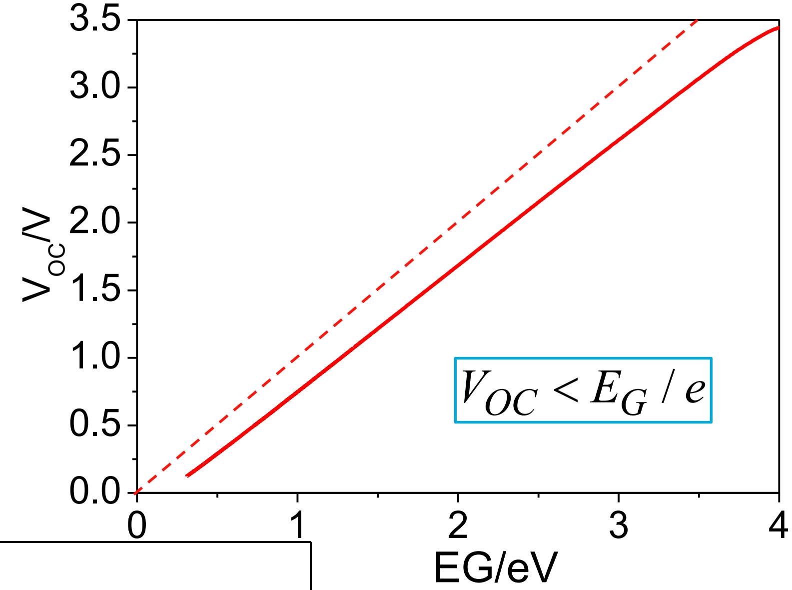
only radiative!

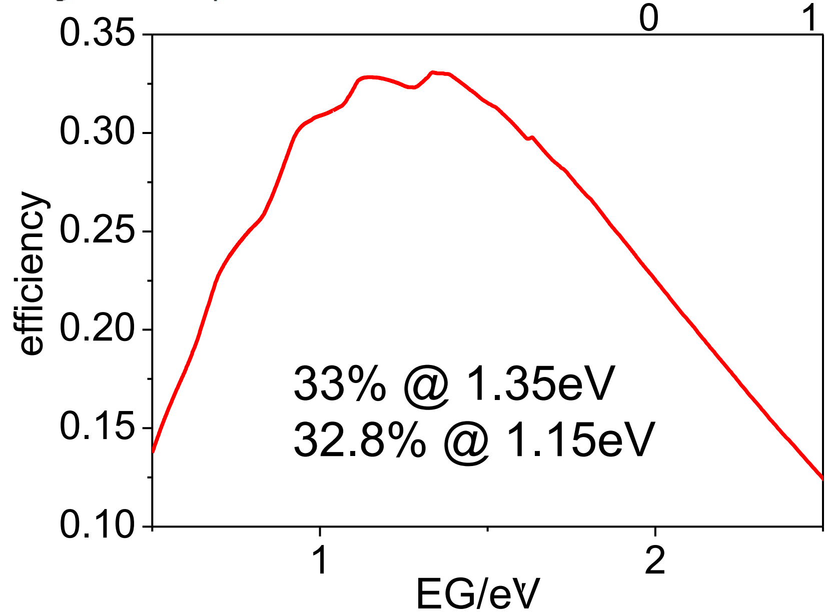
Shockley-Queisser limit

$$j_{ph} = e\Phi_s = e\int_{E_G}^{\infty} \Phi_{sun}(E)dE$$

$$V_{OC} = \frac{kT}{e}\ln\frac{\Phi_S}{\Phi_0}$$





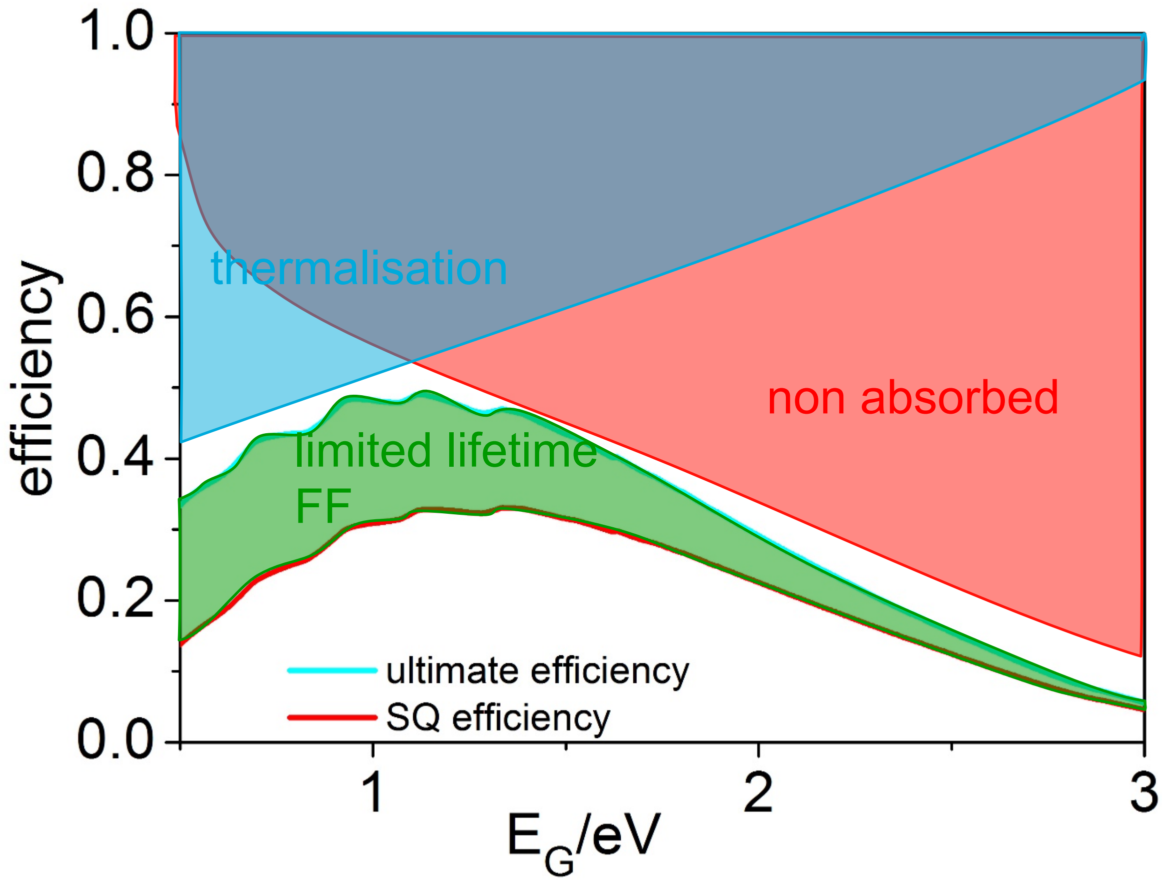


EG/eV

Summary of fundamental limitations

limited solid angle (entendue) plus

just a sketch:



assumptions:

$$QE = \begin{cases} 1, E \geq E_G \\ 0, E < E_G \end{cases}$$

only radiative recombination

no ohmic losses

real solar cells

V_{OC} of real solar cells

ideal solar cell

detailed balance at V_{OC} $$\Phi_{rad} = \Phi_0\, e^{eV_{OC}^{SQ}/kT} = \Phi_S$$

with non-radiative recombination: $$\Phi_{rad} + \Phi_{nr} = \Phi_0\, e^{eV_{OC}/kT} + \Phi_{nr} = \Phi_S$$

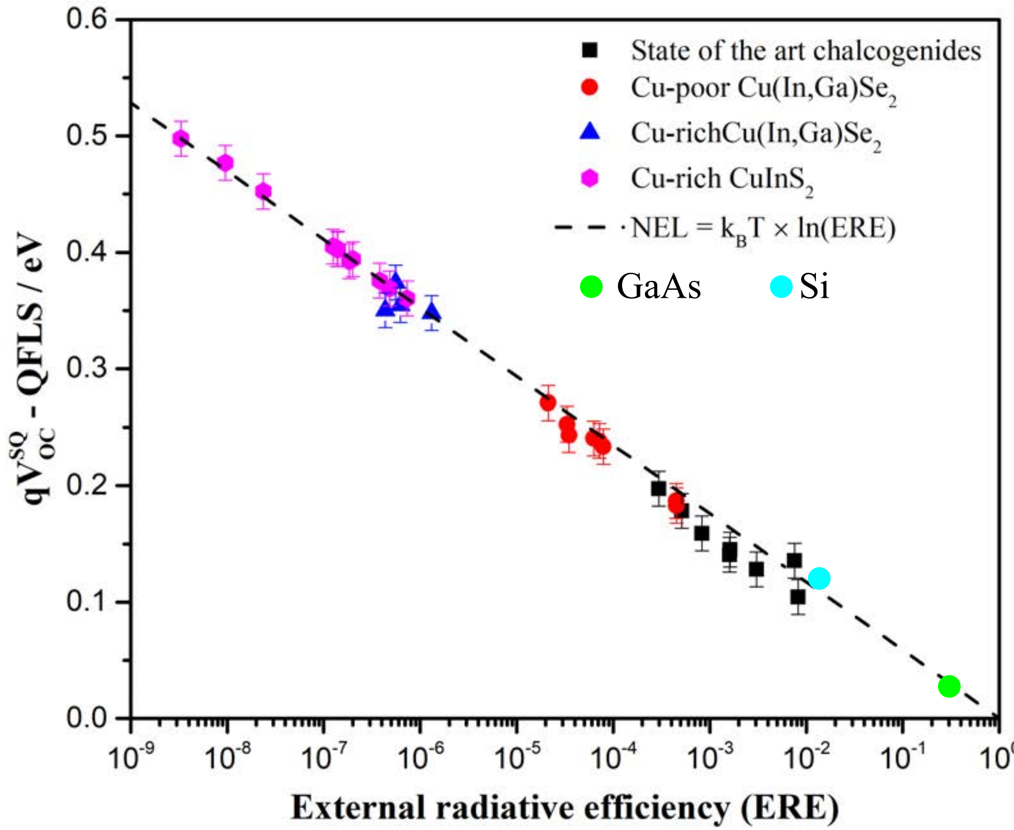
external radiative efficiency:

$$ERE = \frac{\Phi_{rad}}{\Phi_S} = \frac{\Phi_{rad}}{\Phi_{rad} + \Phi_{nr}}$$

$$\Rightarrow \frac{\Phi_0\, e^{eV_{OC}/kT}}{ERE} = \Phi_S = \Phi_0\, e^{eV_{OC}^{SQ}/kT}$$

$$\Rightarrow V_{OC} = V_{OC}^{SQ} + \frac{kT}{e}\ln ERE < V_{OC}^{SQ}$$

~60meV/decade

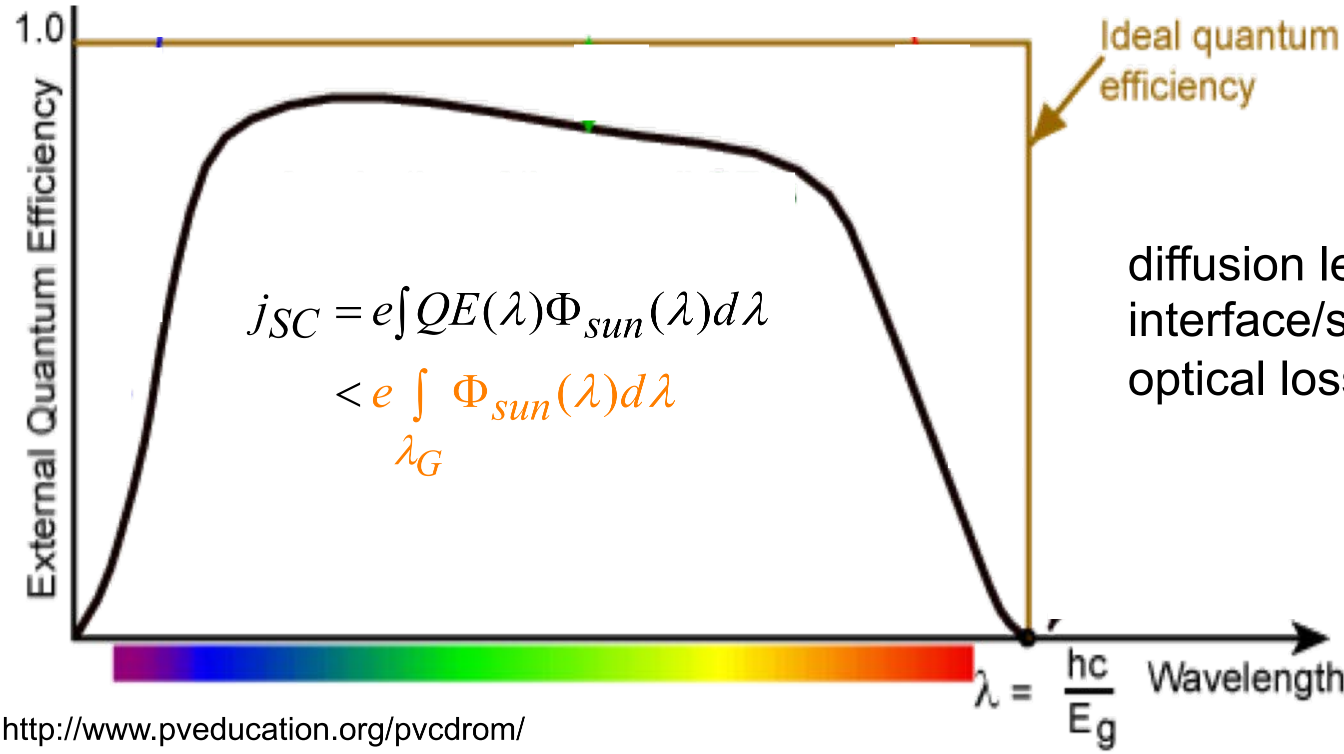


Max Wolter, doctoral thesis, UL

basis: $V_{OC} = \Delta E_F$

√ with reasonably good contacts

jSC and FF of real solar cells



$$j_{SC} = e\int QE(\lambda)\Phi_{sun}(\lambda)d\lambda$$

$$< e \int_{\lambda_G} \Phi_{sun}(\lambda)d\lambda$$

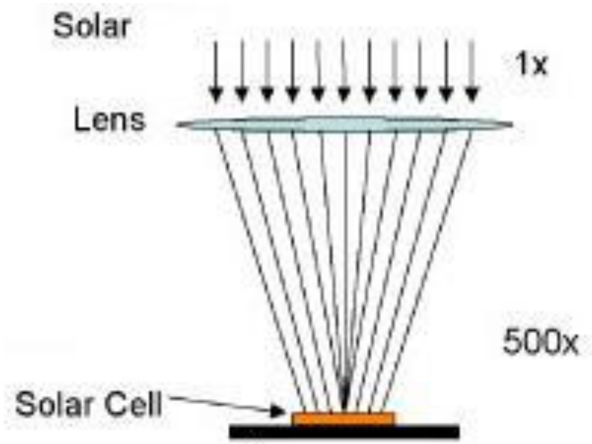
http://www.pveducation.org/pvcdrom/

diffusion length < ∞
interface/surface recombination
optical losses

FF reduced by shunt and series resistances

beyond SQ

Concentrated illumination



mathewb.id.au

why does it improve efficiency?

$$\eta = \frac{j_{sc} \cdot V_{oc} \cdot FF}{P_{in}}$$

j_{sc}: $\times N$

V_{oc}: $\frac{kT}{e}\ln\left(\frac{j_{ph}\times N}{j_0}\right)$

FF: $\Uparrow$

P_{in}: $\times N$

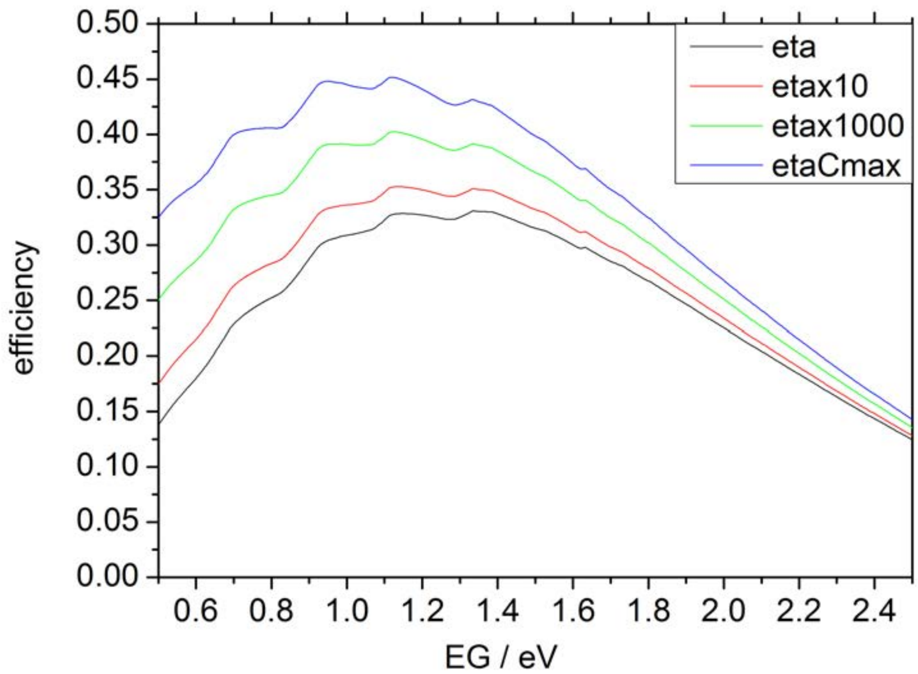
why does it improve the limit?

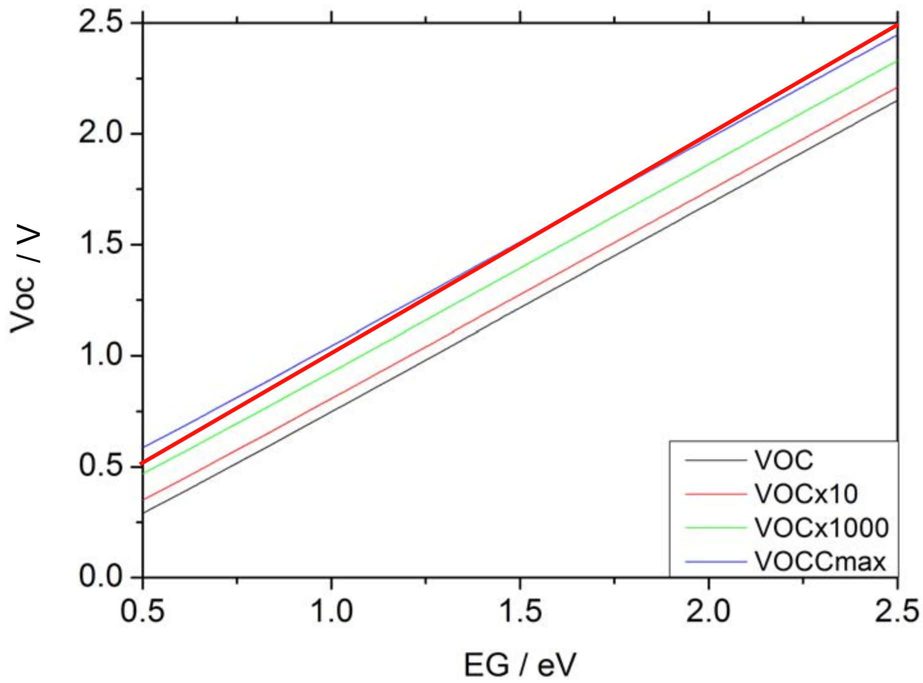
$$\text{SQ:} \quad \Phi_{rad} = \Phi_0 \, e^{eV_{OC}/kT} \le \int_{E_G}^{\infty} \Phi_s(E)dE$$

$$\times N$$

$V_{OC} \Uparrow$ by 60meV/decade

SQ with concentration





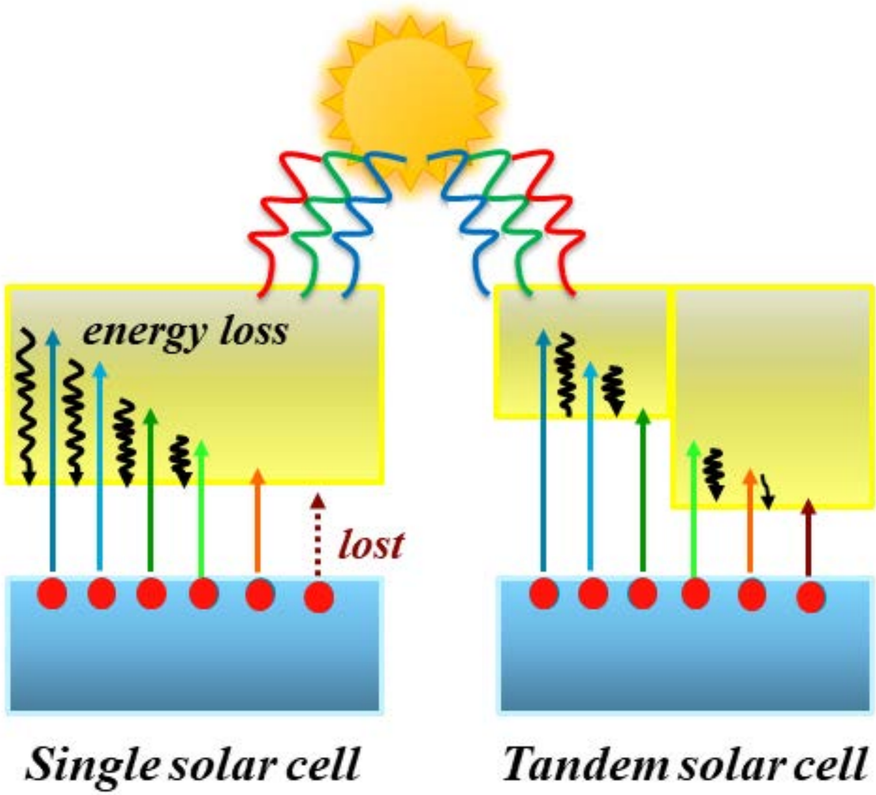
⇒ ultimate efficiency with FF

with real concentrations and reasonable band gaps:

$V_{OC} < E_G$

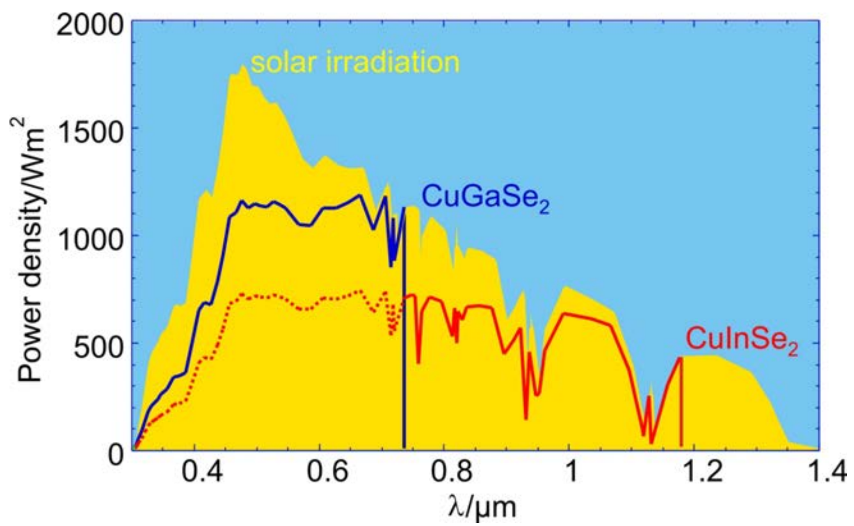
Multijunction cells

the idea:



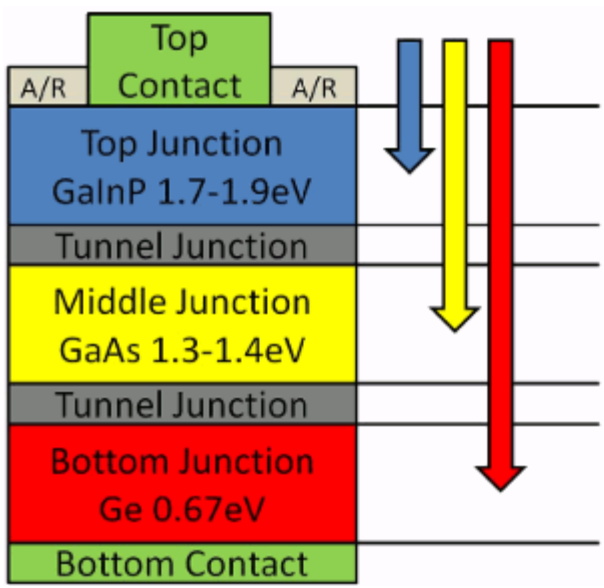
LPV uni.lu

power converted by solar cells:



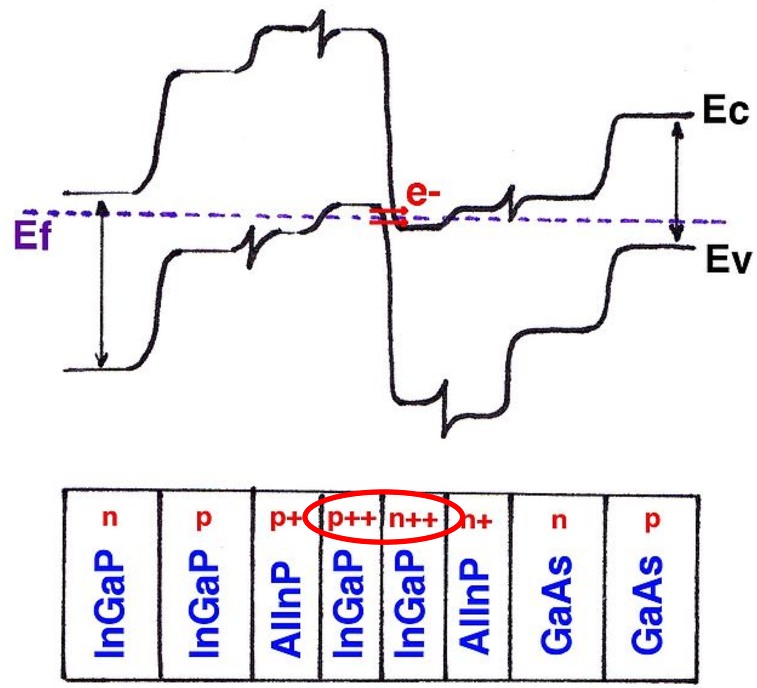
1st challenge: tunnel junction

without tunnel junction: p-n-p-n-....



http://large.stanford.edu/courses/2010/ph240/weisse2/

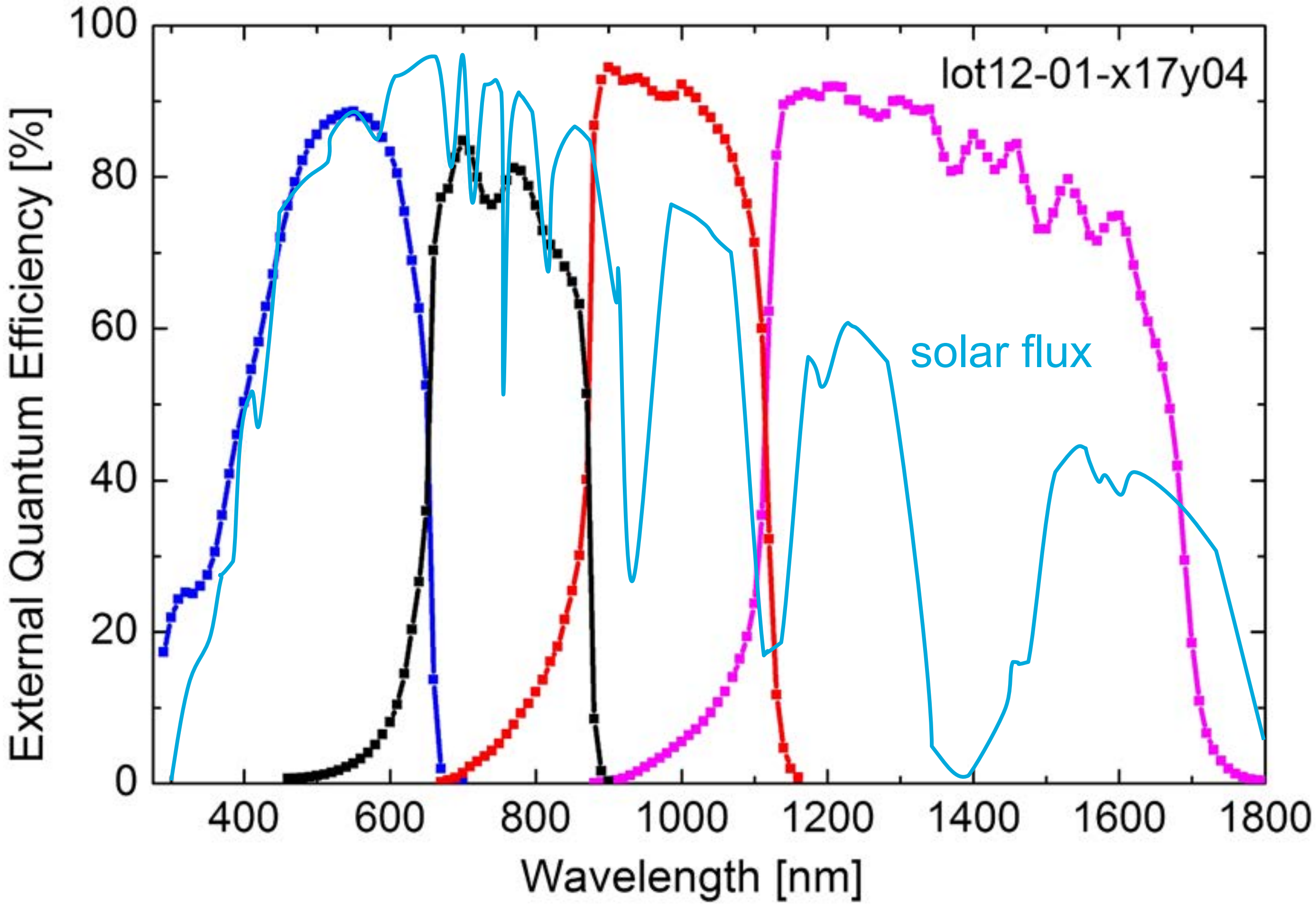
tunnel junction:



https://commons.wikimedia.org/wiki/File:Tunneljunction.jpg

2nd challenge: current matching

QE of 4J cell:

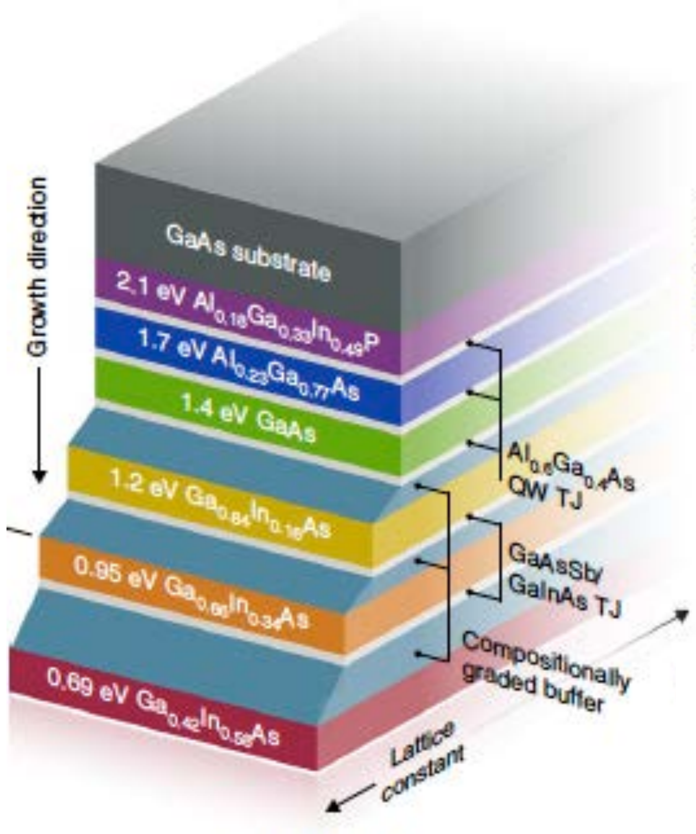


adjust band gaps to same current density

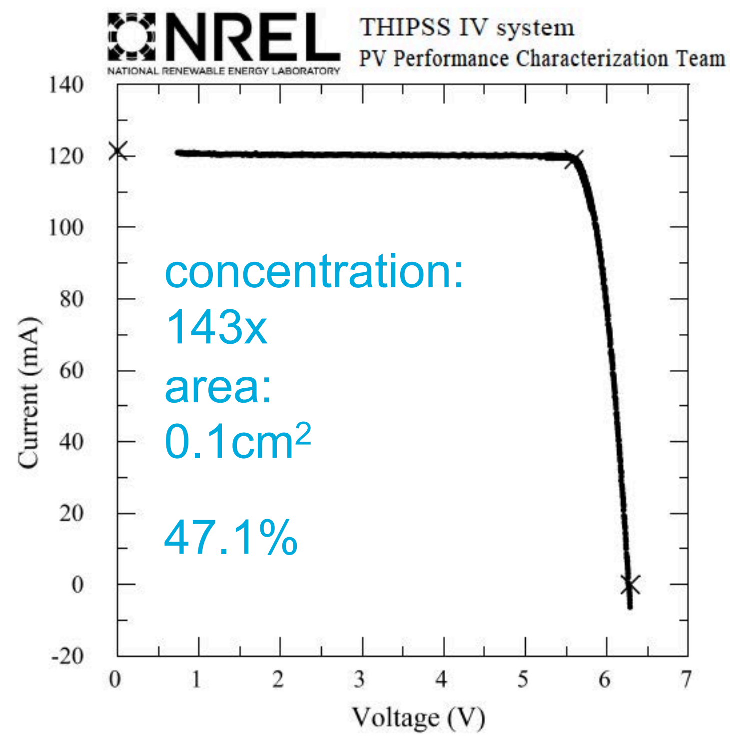
Dimroth, et al., Progr. Photovolt. 22, 277-282 (2014)

47% efficiency

a stack of 6 junctions
more than 100 layers
“the most complex optoelectronic device in the world”

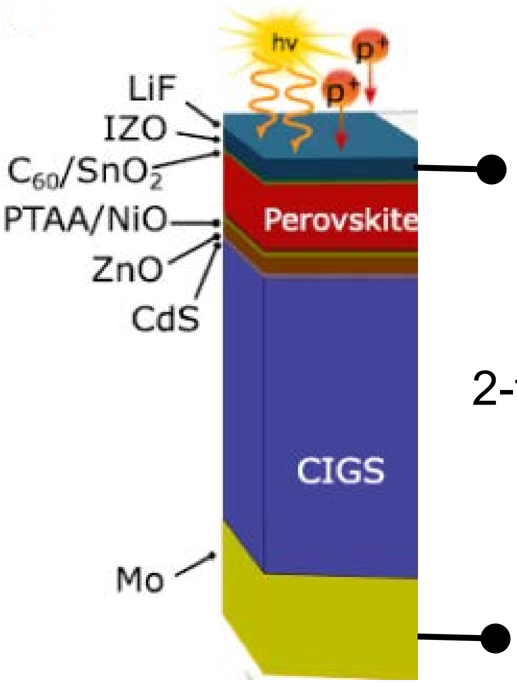


6J IMM structure

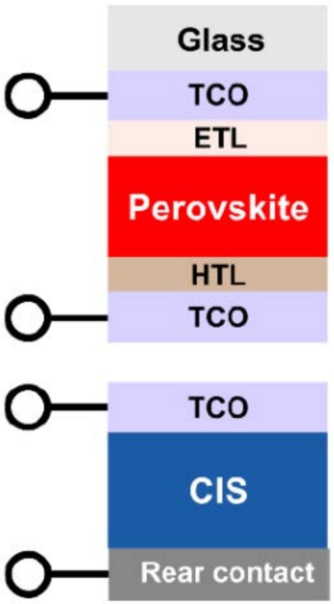


Geisz, France, Schulte, Steiner, Norman, Guthrey, Young, Song, Moriarty,
Nature Energy 5, 326 (2020)

Thin film tandem cells



2-terminal vs. 4-terminal



24.2%

27.4%

very good radiation hardness

- current matching less critical
- more TCO layers

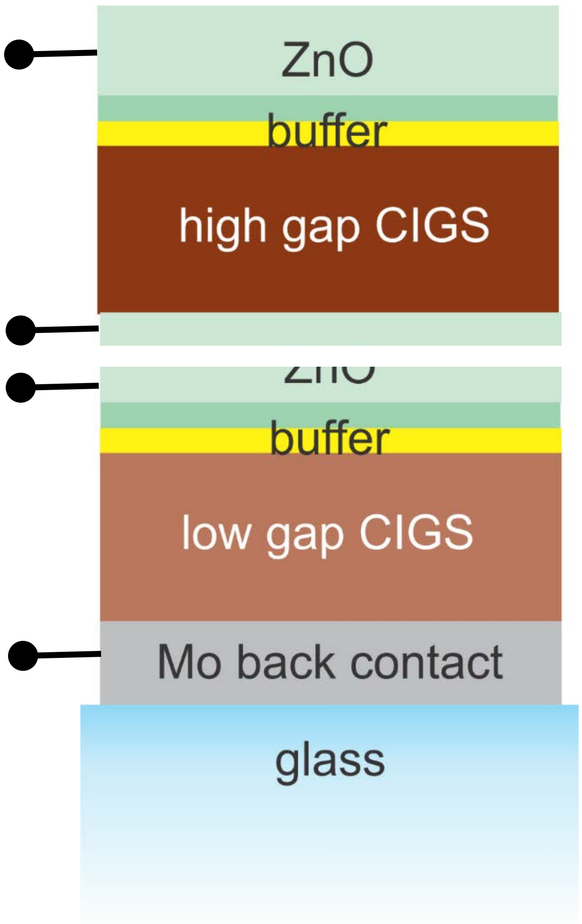
issue: perovskite stability

F. Lang *et al.*, Joule 4, 1054 (2020)

https://www.helmholtz-berlin.de/pubbin/news_seite?nid=21263;sprache=en;seitenid=74699,

https://percistand.eu/sites/percistand/files/downloads/Percistand%20workshop-%209%20June%202021.pdf

Tandem cells in my lab



chalcopyrites CIGS: $Cu(In,Ga)(S,Se)_2$

- high efficiency single junction: 23.4%

Nakamura et al. IEEE J. Photovolt. 9, 1863 (2019)

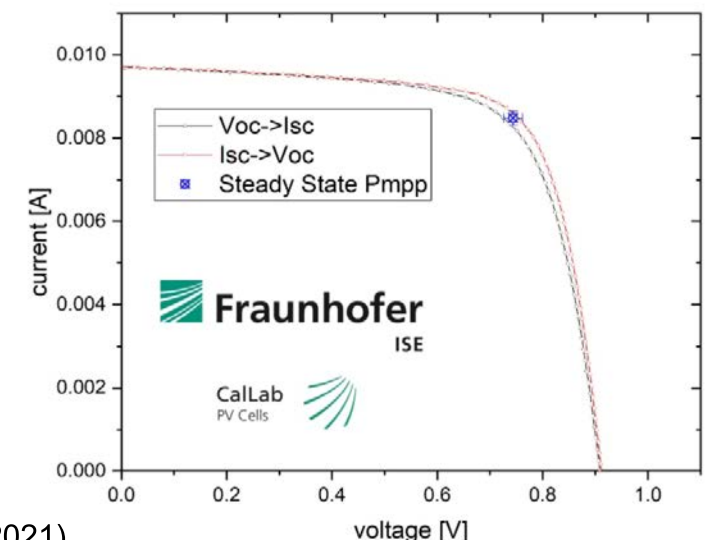
- wide range of bandgaps

$CuInSe_2$: 1.0 eV
$CuGaSe_2$: 1.6 eV
$CuInS_2$: 1.5 eV
$CuGaS_2$: 2.5 eV

- no miscibility gap

$Cu(In,Ga)S_2$

14% with $E_G = 1.59$eV
on Mo back contact



- increase band gap
- increase efficiency
- transparent back contact

Shukla, Sood et al. Joule doi: 10.1016/j.joule.2021.05.004 (2021)

What to remember...

- Shockley-Queisser limit is based on
  - entropic loss due to entendue
  - non-absorption
  - thermalisation
  - limited lifetime due to detailed balance
  - fill factor losses
- real solar cells:
  - $V_{OC}\downarrow$ because of non-radiative recombination
  - $j_{SC}\downarrow$ because of optical and transport losses
- beyond Shockley-Queisser: concentration and multi junction cells

… and one last thought

- efficiency is limited
- there is no unlimited energy

- there will be 10 billion people

- technical solutions for renewable energy indispensable
  but not enough!

- life style changes are indispensable

Societal transformation scenario: https://www.boell.de/en/2020/12/08/societal-transformation-scenario-limiting-global-warming-15degc-low-risk-and-socially