EPFL

Fundamentals and processes for photovoltaic devices

Dr. Christian Wolff

Chapter XIV
Thin Film technologies & Emerging PV

Outline:

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PV technologies

Crystalline silicon
Mono and multicrystalline

Status: main marketshare (> 90%)

Thin films
CdTe (CIGS)

Status: trying to maintain market share (<10%)

Market

Concentrator technologies
Mostly III-V based

Status: low market share, many start-ups

Emerging technologies
Nano inorganic, Organic/polymer
Dye sensitized / Perovskites

Status: niche application/many start-ups, lab efficiency up to 27%

Novel PV concepts
Quantum dots, intermediate band,…
Status: attempt of demonstration

Difference thin film / wafers: Advantages & drawbacks

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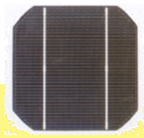
Crystalline silicon



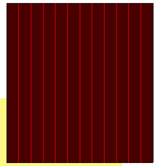
Advantages:

- High efficiency demonstrated (PERC, HIT, IBC…); exceed 20% at module level and reaching >24%
- >97% of the market Mass production effective at reducing costs
- Benefitted from microelectronics background

Drawbacks

- Wafer preparation (numerous steps)
- Cost reduction mostly by up-scaling

Thin films



Advantages:

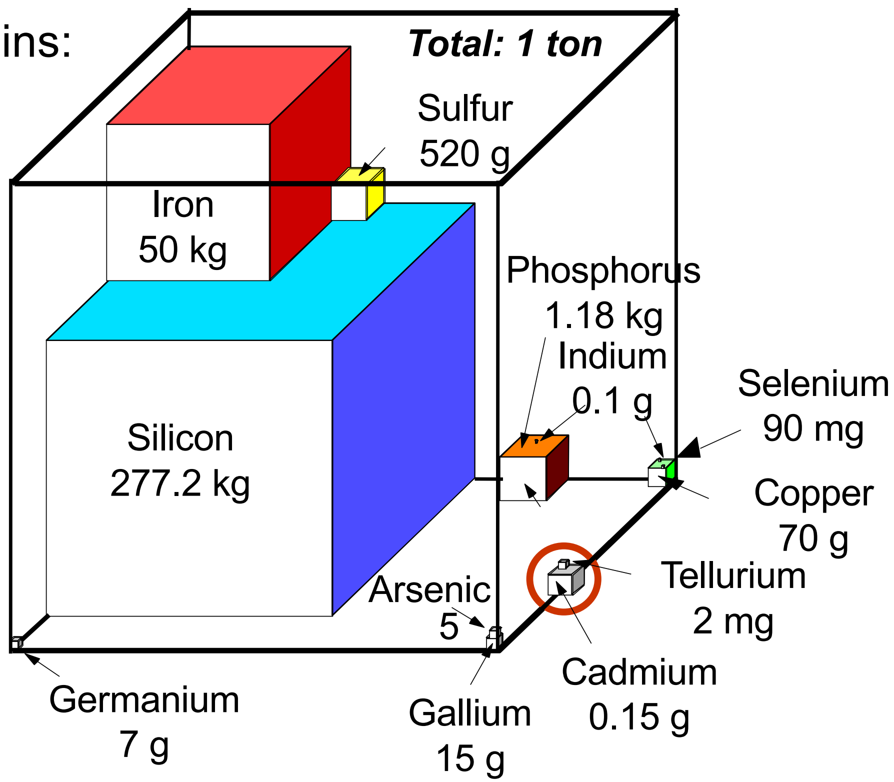
- Reduced material use (a few µm of semiconductor)
- Flexible modules possible
- Lower energy payback time
- Better building integration (colour, versatility)

Drawbacks

- Moderate efficiency: 13-20% **at module level**
- Less field experience (stability,…)

Availability of PV materials

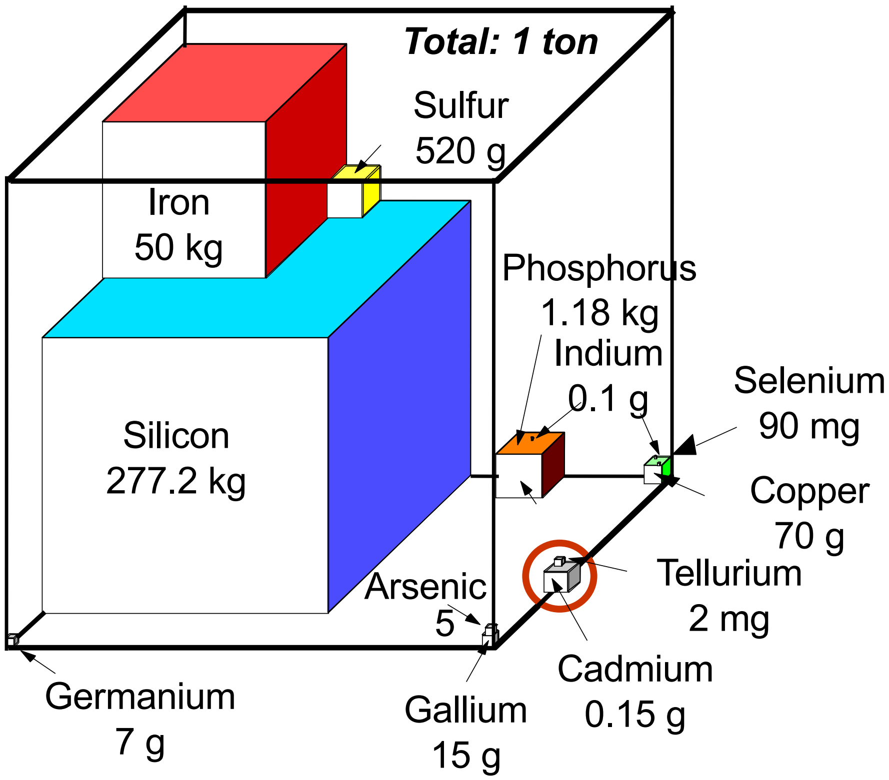
An average ton of earth crust contains:



Advantage of thin film cells **partially** lost due to scarcity

Availability of PV materials

An average ton of earth crust contains:



Too simple picture!

Beyond global availability also political scenarios play a role ⇔ monopolies?

Example from emerging PV:

Cesium is critical material for halide perovskites

ALL current mining activities outside of Europe with primary providers in China & Canada

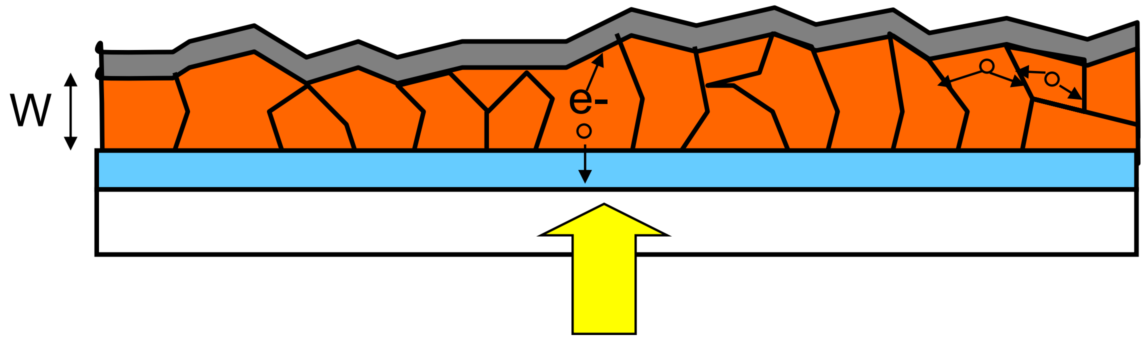
political stability ⇔ resource scarcity ?

Polycrystalline thin films

Most thin films are polycrystalline with typical grain size of 0.1 to a few µm (or amorphous)

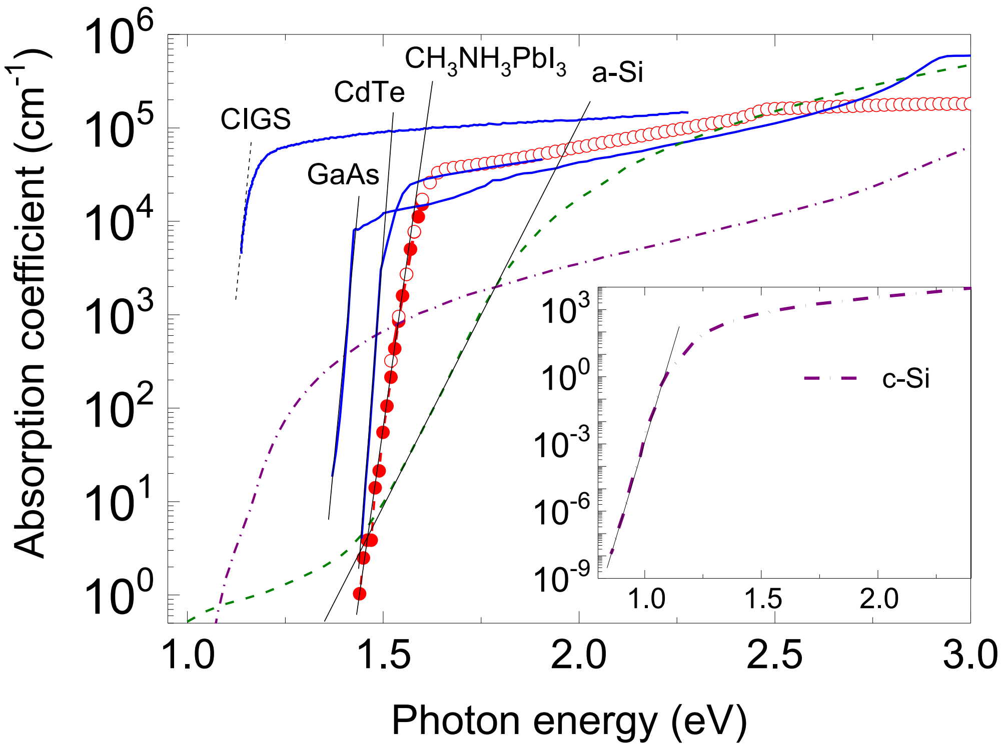
- Impurities and crystalline point defects can be numerous (→ bulk recombination)
- Grain boundaries yield additional recombination paths (except for self-passivation in GIGS)

→ Work with low device thickness ($W > L_D$) to ensure charge collection



Thin film solar cell materials

Optical absorption coefficients of various absorber materials



- Amorphous Si (a-Si) (now niche products, still calculators etc.)
- CdTe
- $Cu(In,Ga)Se_2$
- perovskite $(CH_3NH_3)PbI_3$ (MAPI, methyl-ammonium-lead-iodide)

"Wonder" polycrystalline materials:

- Direct gap => strong absorption, light with energy above the bandgap is absorbed within a few µm thickness
- low absorption below gap important for transmission in tandem cells (and high Voc, not the case for a-Si)

DeWolf, J. Phys. Chem. Lett (2015)

How can emerging PV reduce scarcity and electricity cost ?

$$\frac{\text{cost}}{\text{energy}} = \frac{\text{fabrication} + \text{installation} + \text{maintainance} + \ \ldots}{\text{efficiency} \times \text{lifetime}}$$

How can emerging PV reduce scarcity and electricity cost ?

$$\frac{\text{cost}}{\text{energy}} = \frac{\boxed{\text{fabrication}} + \boxed{\text{installation}} + \boxed{\text{maintainance}} + \ \ldots}{\boxed{\text{efficiency}} \times \boxed{\text{lifetime}}}$$

Examples:

- **Lower energy consumption in fabrication**
- **Decentralize fabrication (shipping), reduce weight**
- **cleaning (drones/smart machines)**
- **Improve encapsulation, materials development**

- **New technologies!**

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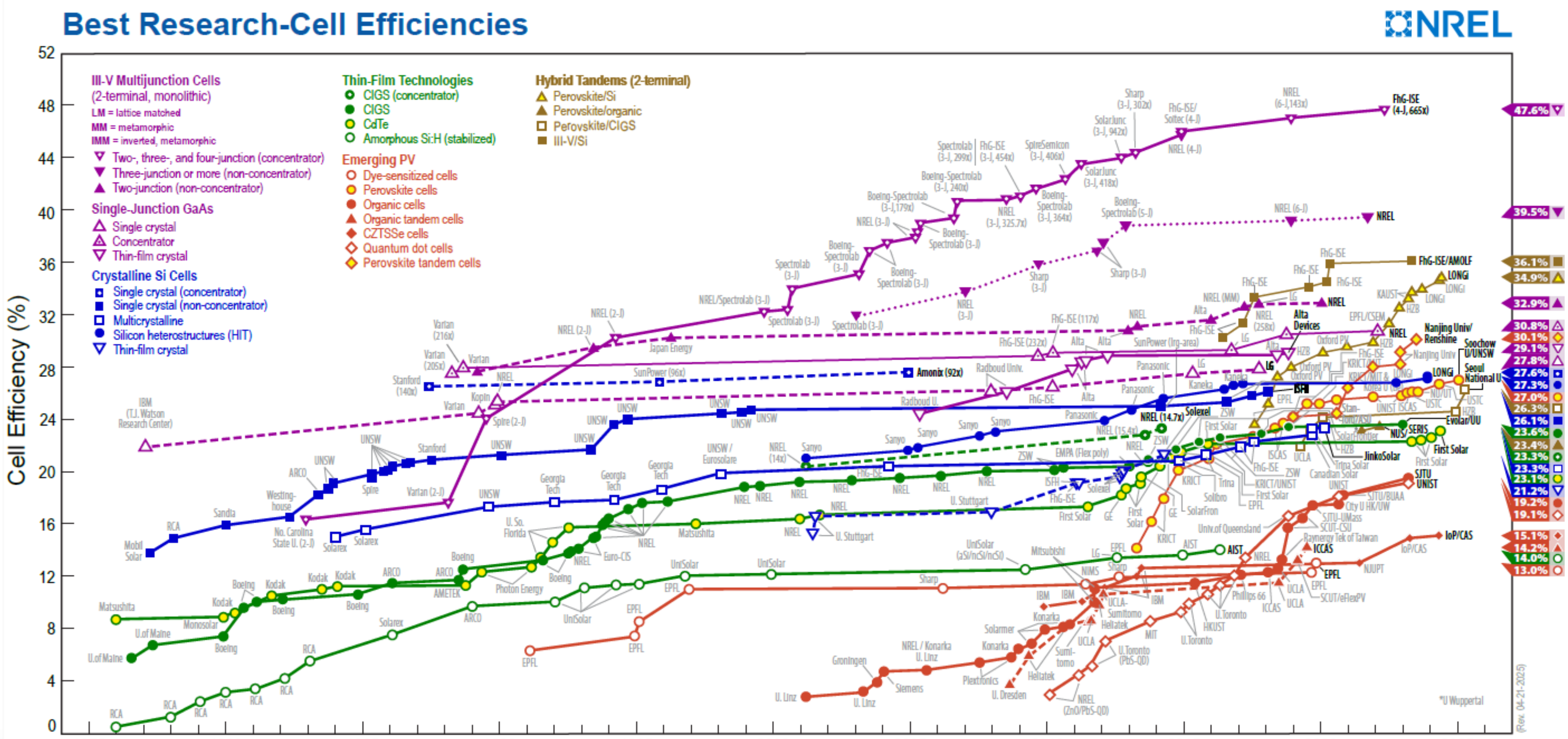
Solar cell efficiencies: NREL chart



Source: www.nrel.gov

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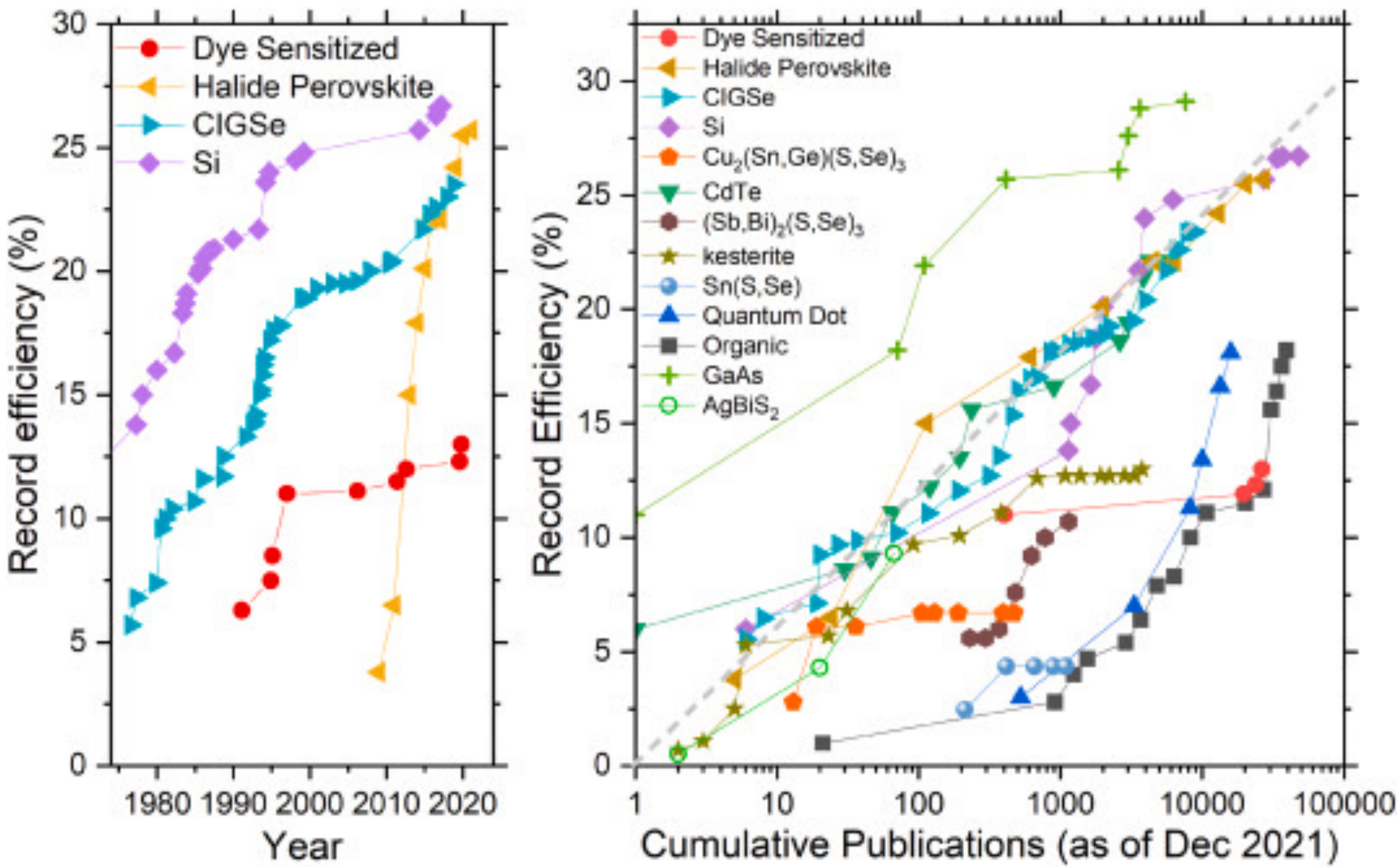
A different view = Efficiencies vs. Effort



- Most technologies lie on single "learning curve", GaAs being the good exception
- Some technologies are more for "believers"
- Other technologies may become available in the future if they are cost-competitive and scaleable

Dale et al. 10.1016/j.solmat.2022.112097

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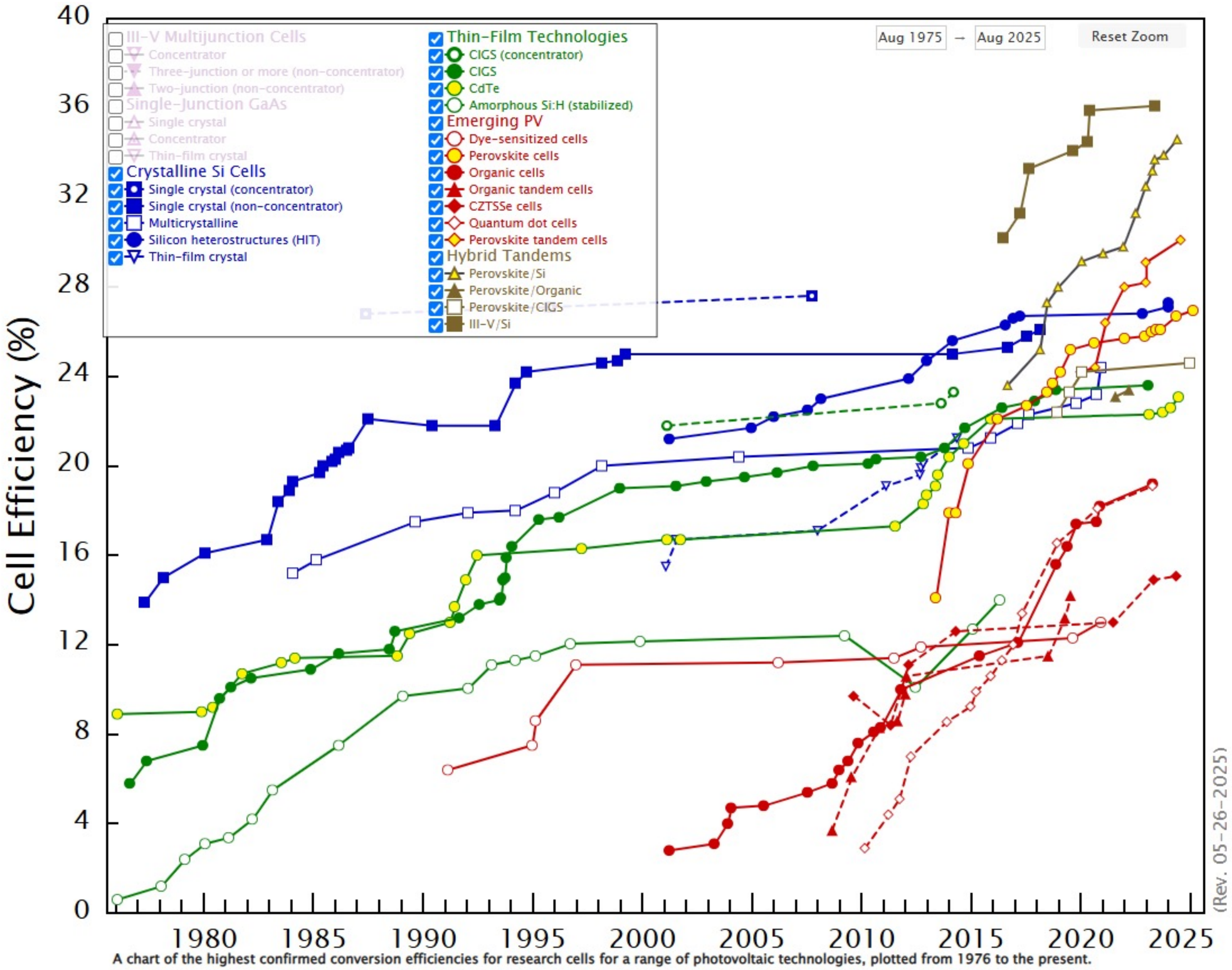
Why are there so few thin-film products?



A chart of the highest confirmed conversion efficiencies for research cells for a range of photovoltaic technologies, plotted from 1976 to the present.

- c-Si is extremely efficient – 27.8%
- Only GaAs and Perovskite can reach a similar level of performance
- GaAs is x100-1000 more expensive
- Perovskite and perovskite-based tandems are not yet mature enough technology

Source: www.nrel.gov

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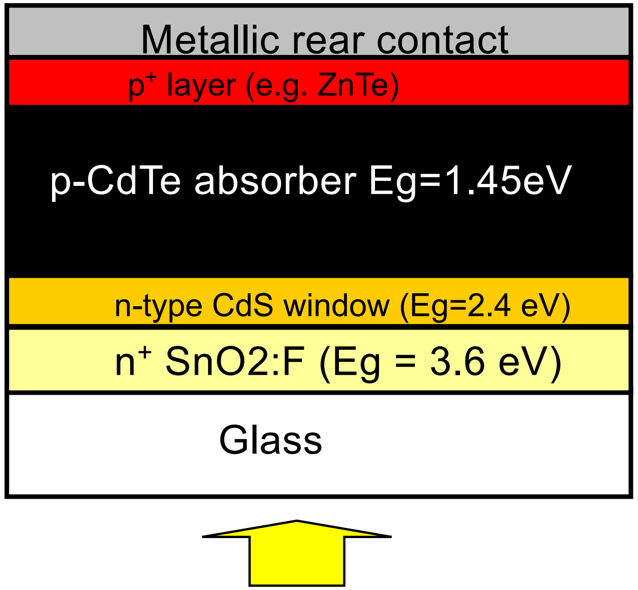
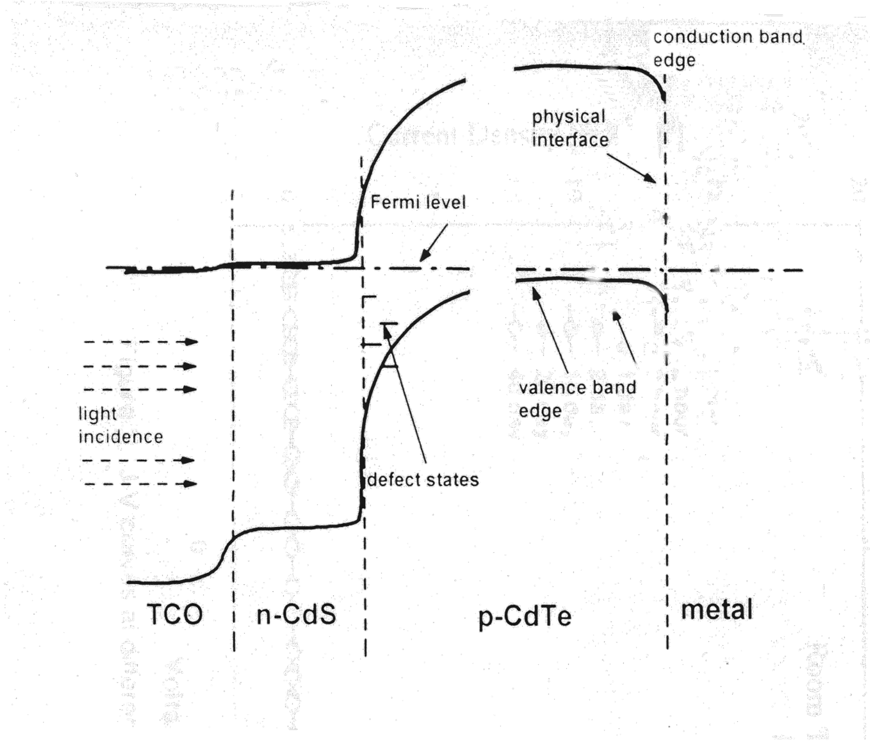
CdTe solar cells: structure





- "Heterojunction" between p-type CdTe and n-type CdS (+TCO)
- Usually deposited on glass coated with a transparent conductive oxide, e.g. SnO_2, light entering through the glass ("superstrate")

CdTe based solar cells: characteristics

- Bandgap of CdTe : ~ 1.5 eV with very high absorption coefficient
  → 2 μm sufficient, but normally 6-10 μm are used for large grains and to avoid shunts
- Best cell efficiency > 21.0%, low thermal coefficient -0.25%/ºC (due to high bandgap)
- Very high radiation hardness (Cd and Te are heavy elements)

- Issues:
  – CdTe inert, elemental Cd in production cycle could be an issue,
    (mostly legal, not necessarily for health!)

- Research topics:
  – Back contact (stable, high work function)
  – Thinner cells

CdTe: Market

- Several unsuccessful trials by companies:
  Antec Solar, BP solar, Golden Photon, Matsushita, Abound Solar

First Solar (US)

- 20 years development with "smart copy" of its initial lines
- Continuous efficiency increase
- Hard work on balance of system (BOS) to reduce electricity price

(Only) Leader in thin film production: First Solar (US) with CdTe absorber

Recap lecture 2

Leader in Thin film (and **only** mass producer) : **First Solar** sold 16-17 GW of CdTe modules in 2025 ! Focus on GEN7 modules up to 550 W modules, 20 % efficient, 25 years of development and smart-line copy. Likely direct production costs in the range of 0.16-0.20 cts/W manufacturing costs. Targets 25 GW by 2026. **Sales pipeline of 86 GW …. Unique position in USA = strong benefit from IRA !**

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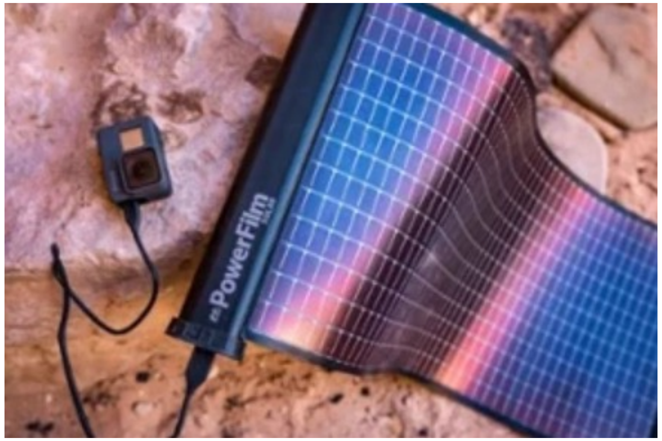
Niche Market with Limited efficiency: Some companies still selling products !



Amorphous silicon (4.1 % modules on website)

CIGS (claims 16.7% efficiency on website)

IOT solutions/products

- Panasonic Amorton (a-Si)
- Perovskia (PK)
- CSEM (a-Si)

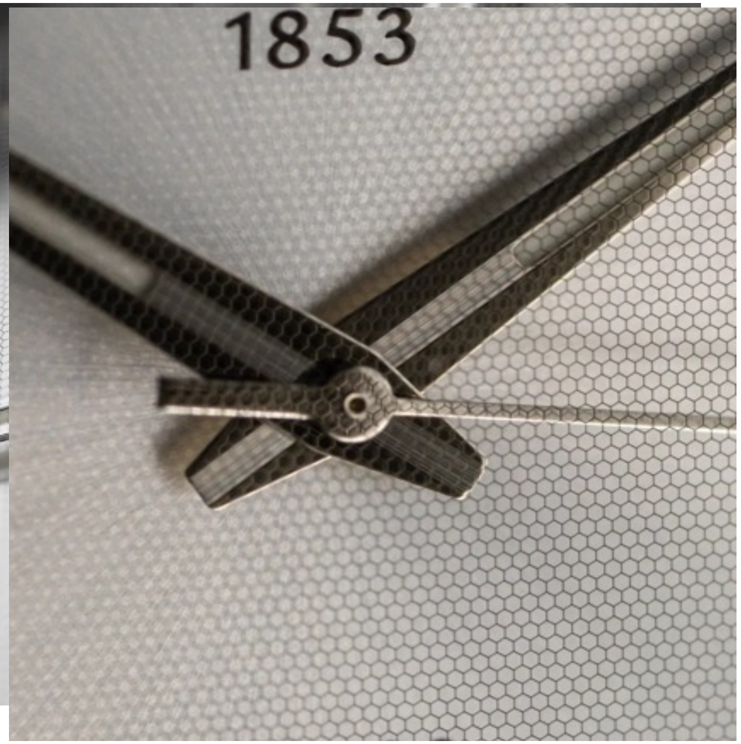
.... THE T-TOUCH SOLAR CONNECT

Solar dials developped by CSEM,
production fully ramped-up by CSEM

csem

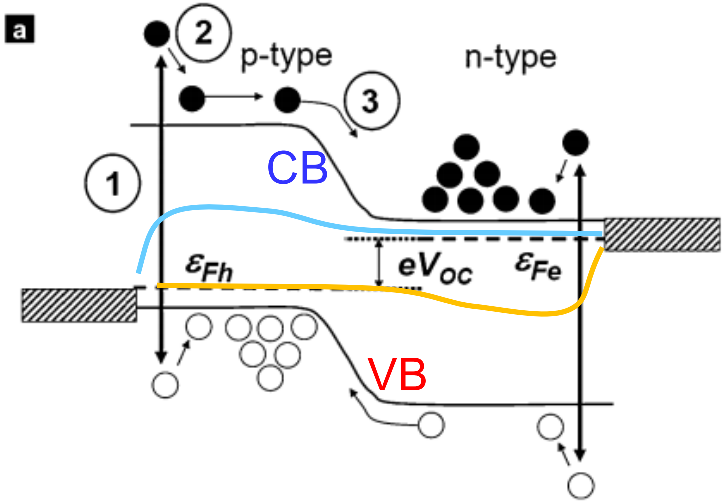
Next Generation from CH!

Honey-comb solar cells

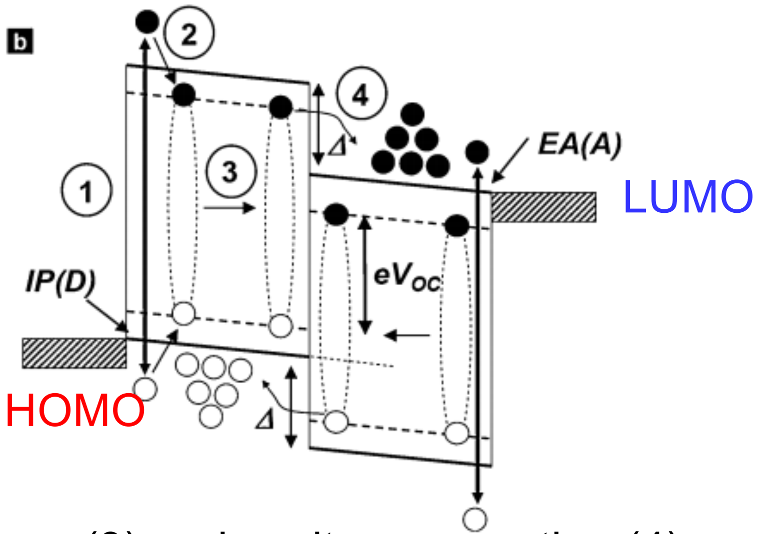


Organic solar cells

Inorganic cell: create free e and h



Organic cell: create exciton (bound e-h pair)

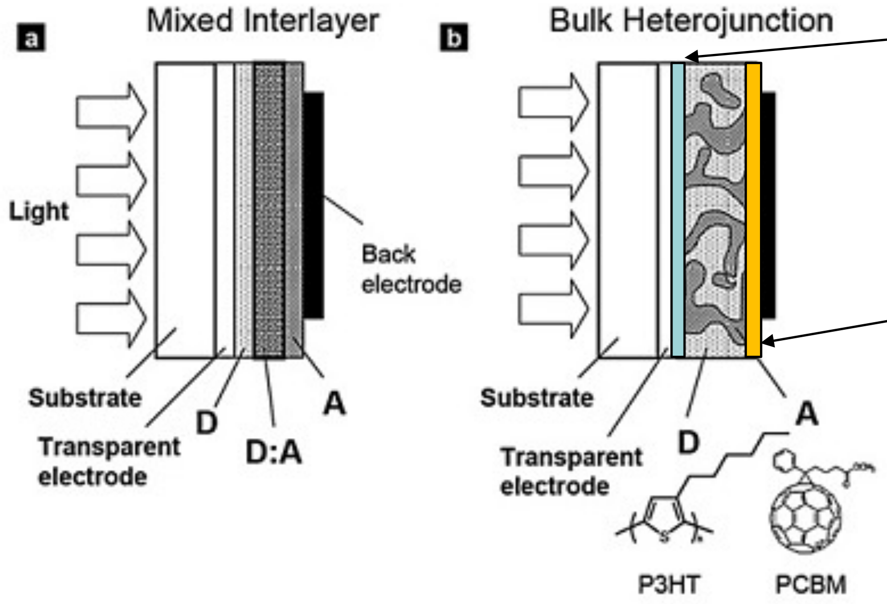


Additional steps: exciton diffusion to interface (3) and exciton separation (4)
Issue: exciton diffusion length

Nomenclature
EA: Electron affinity
IP: Ionization potential (EA + Eg)
HOMO: highest occupied molecular orbital (“VB”)
LUMO: lowest unoccupied molecular orbital (“CB”)

Kippelen, EES (2009)

Organic bulk heterojunction



Insert electron transport layer (ETL), aka hole blocking layer (HBL) e.g. TiO_2

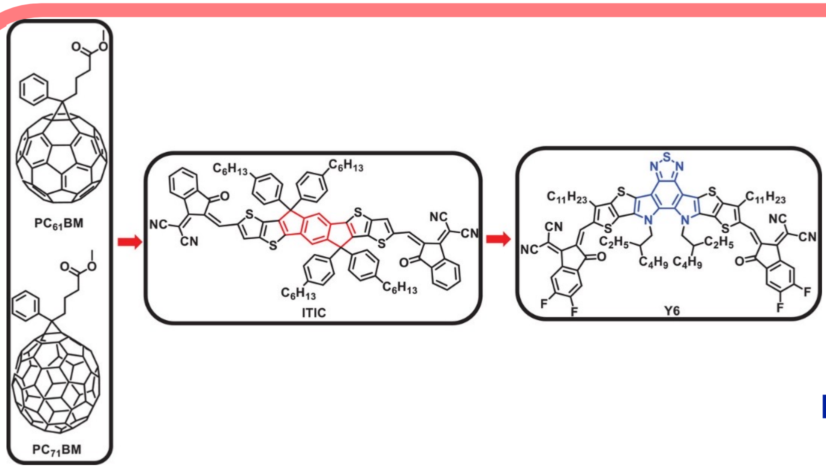
Insert hole transport layer (HTL), aka electron blocking layer (EBL) e.g. MoO_x

P3HT: poly(3-Hexyl-Thiophene)
PCBM: [6,6]-phenyl C_{61}-bytyric methyl ester

Simultaneous deposition of immiscible compounds, immediate demixing:
=> large interface area throughout bulk

Kippelen, EES (2009)

Organic materials typically used in photoactive layer



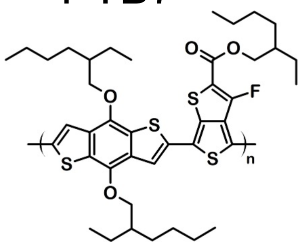
New Development since ~5 years:

Non-Fullerene Acceptors «Y»!

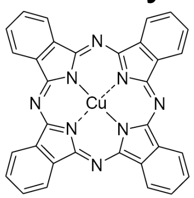
Have allowed
r significant boost in efficiency > 20%

Donors: Wide range of small molecules and polymers

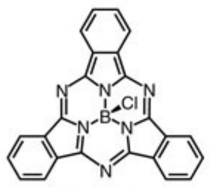
PTB7



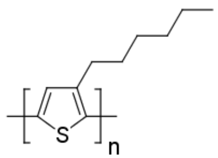
Cu-Phthalocyanine



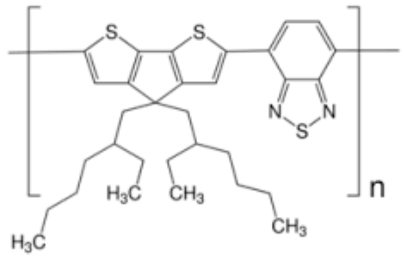
B-Cl Sub-Phthalocyanine



P3HT



PCPDTBT



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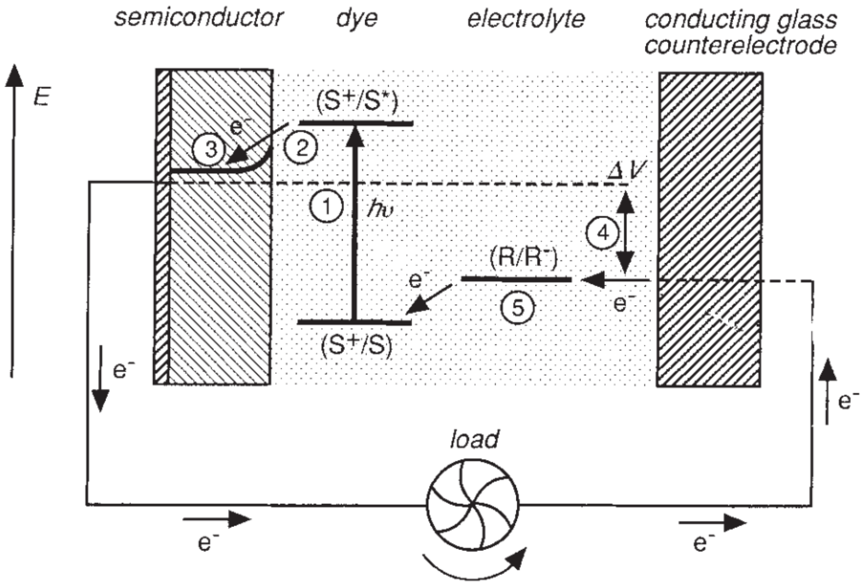
Dye-sensitized solar cells: photochemical excitation

Invented at EPFL (Brian O`Regan & Michael Grätzel)



(1) absorption in dye molecules, (2) rapid electron transfer from LUMO to ETL (usually TiO_2), (5) replenishment of HOMO state from electrolyte (similarity to photosynthesis)

Weak absorption in dye monolayer
=> adsorb on scaffold of (meso-)porous TiO_2

O'Regan, Nature (1991)

Perovskite material

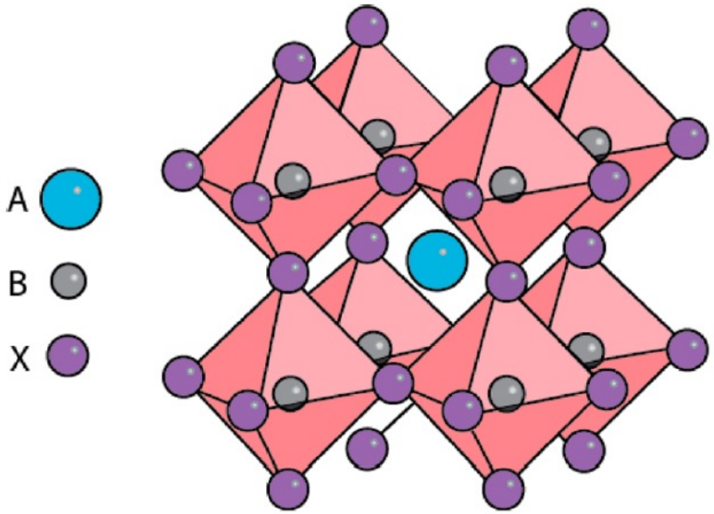
Gustav Rose

German mineralogist discovered $CaTiO_3$ (a perovskite) in 1839 in the Ural mountains (Russia)

Named after Russian mineralogist

Lev Perovski

Perovskite structure



Ideal cubic structure

Green et al., ACS Energy Lett. 2017, 2, 822−830

- Perovskites adopt the structure: A B X_3
  - A = Monovalent cation
    - MA [$CH_3NH_3^+$], FA [$CH(NH_2)_2^+$], Cs^+, Rb^+
  - B = Divalent metal cation
    - Pb^{2+}, Sn^{2+}, Ge^{2+}
  - X = Halide anion
    - I^-, Br^-, Cl^-

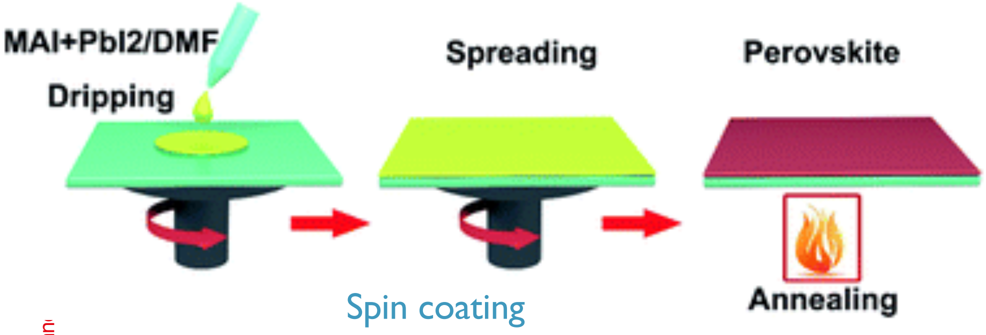
- First Pk cell fabricated in 2009 with an efficiency of 3.8% (Miyasaka's group)!

- Today: 26.95% (~ 0.1 cm^2, Sochoo Uni. (CH))

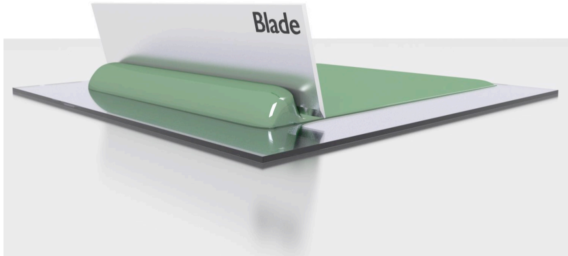
Perovskite fabrication

Solution processing: spin-coating, blade/slot-die coating, ...

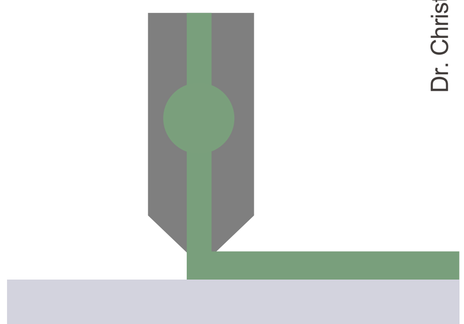
- Low-cost processing



Spin coating
(small size, < 5x5 cm^2)

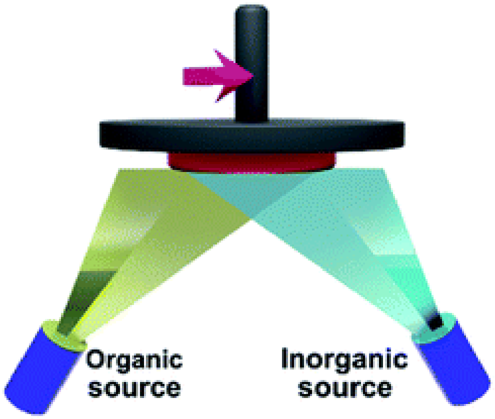


Blade coating
(intermediate size, e.g., up to 20x20 cm^2)



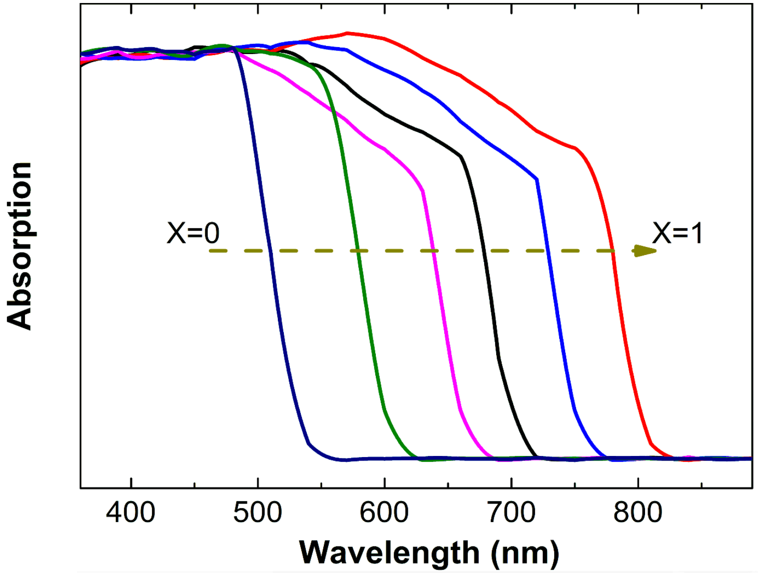
Slot die coating
(large size)

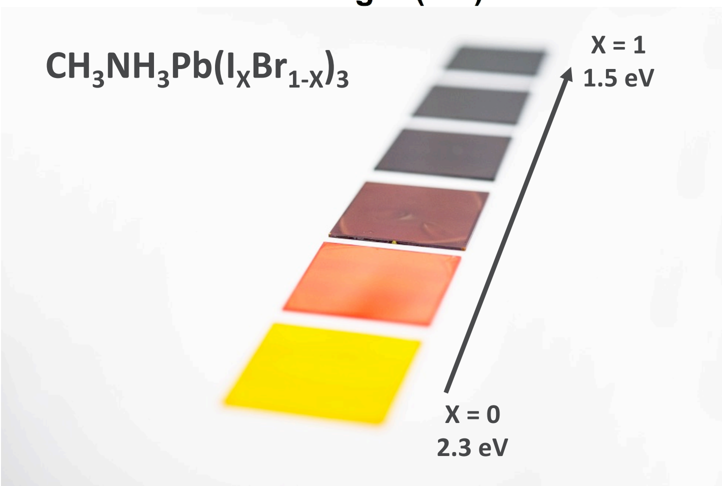
Physical vapor deposition: evaporation, PLD, ...



Chen et al., RSC Adv., 2018,8, 10489-10508

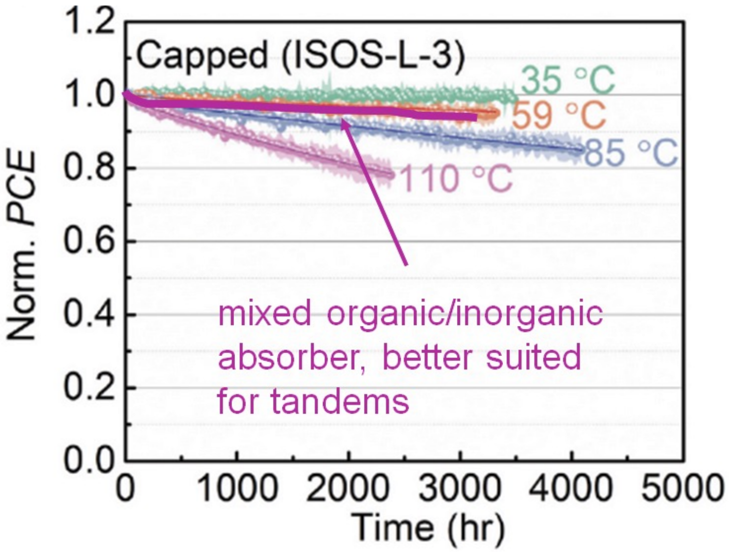
Perovskite properties

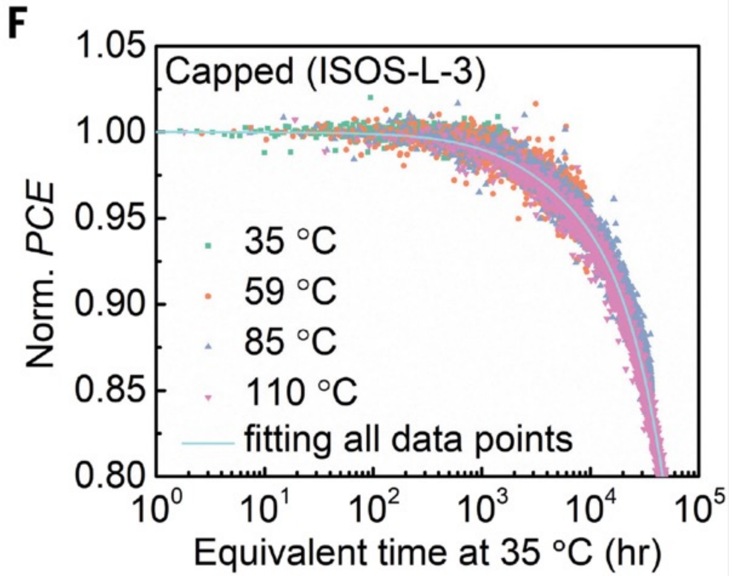




- Low-cost processing
- Direct bandgap semiconductor with high absorption coefficient (>10^5 cm^{-1}) → thin films
- High carrier mobilities and diffusion lengths
- Defect-tolerant material → high efficiency
- Bandgap can be tuned by the composition

Perovskite materials with improved long term stability





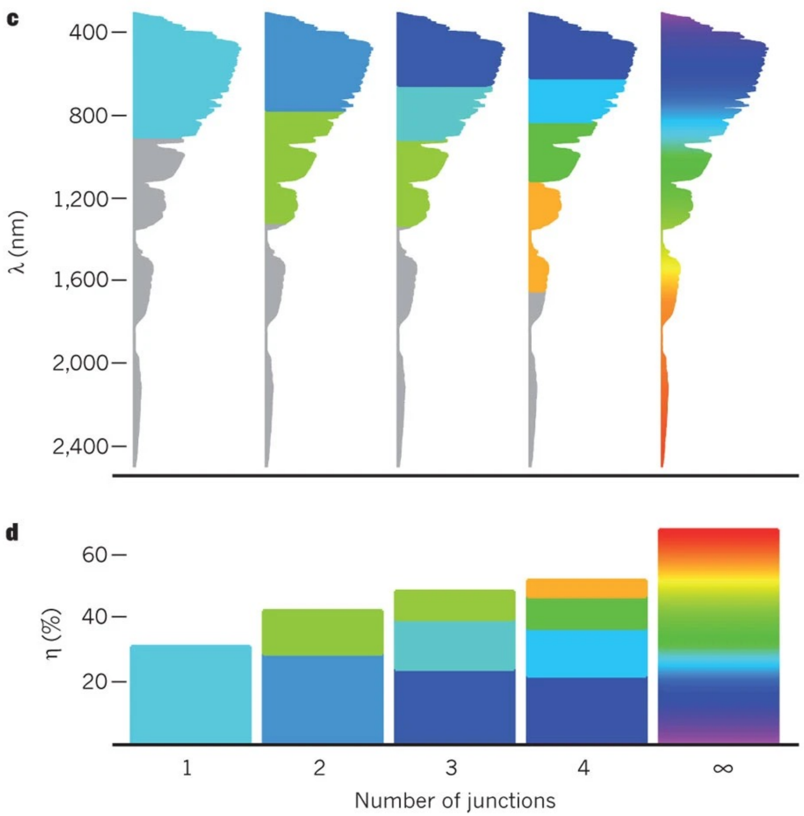
Improved capping layers enable respectable stabilities, e.g., 50.000 h @ 35°C ~30 years until 80% of initial efficiency is reached

(outdoor temperatures exceed 35°C, though)

new perovskite compositions and capping layers

You et al., DOI: 10.1126/science.add8786
Zhao et al., DOI: 10.1126/science.abn5679

The way forward : multi-junction cells



Grätzel et al., 10.1038/nature11476

General idea:

- Reduce thermalization losses (= more voltage) to a greater extent than reduction of current!

- Example: Perovskite-Silicon Tandem:

- Si: Voc = 0.7V, Jsc = 40mA/cm2, FF = 80%, **PCE ~22%**

- Perovskite: Voc = 1.2V, Jsc = 21 mA/cm2, FF = 80%, **PCE ~20 %**

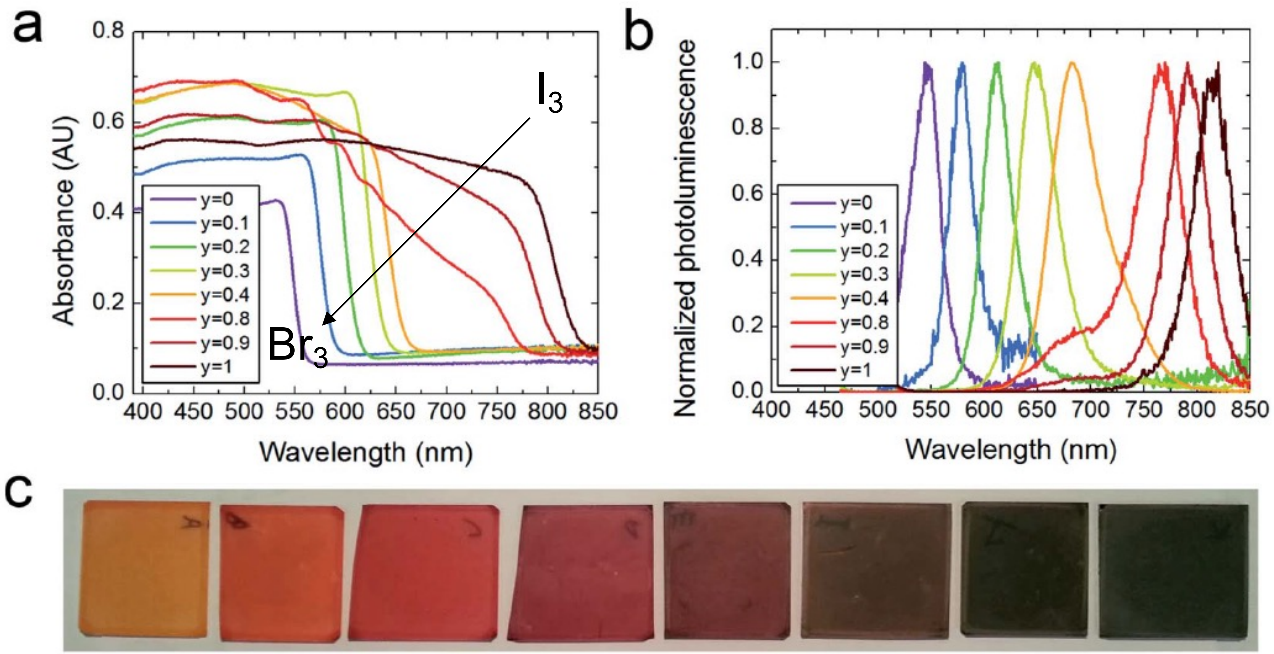
- Tandem: Voc = (0.7+1.2) V, Jsc = 20 mA/cm2, FF = 80% **=> PCE ~ 30% !**

Perovskites with tunable gap - perfect for tandem applications!

Optical band gap tunable from the NIR to the VIS spectra by choice of halogen and «A» cation size

Low sub-bandgap absorptance

A = large cation (CH_3NH_3, $CH_3(NH_3)_2$, Cs)
B = small cation (Pb, Sn)
X = halogen (I, Br, Cl)
e.g.: $CH_3NH_3PbI_3$



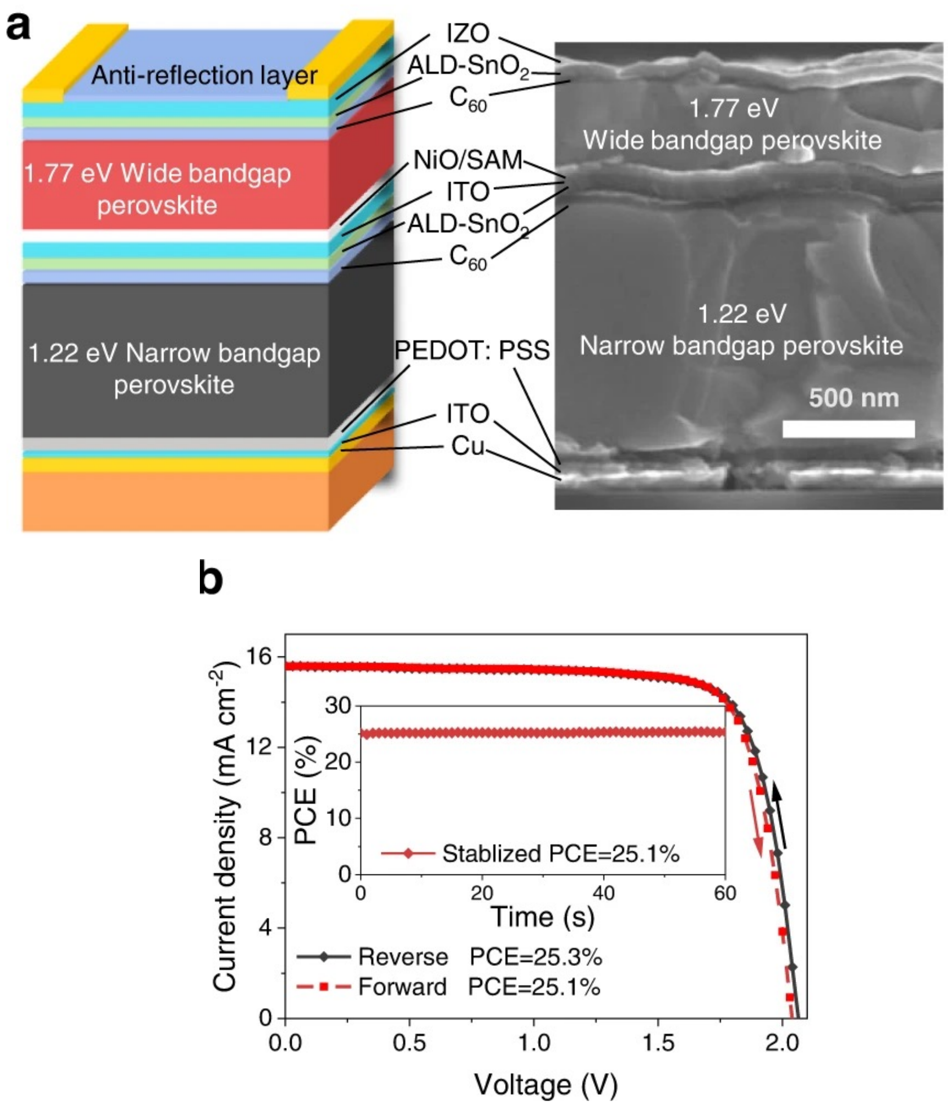
Eperon et al., Energy Environ. Sci. (2014)

Perovskite/Perovskite tandem

- Potential for ultra-low cost *and* high efficiency
- High Voc >2 V

- Still in early research state, but start-ups are emerging, records are now at **>30% (mm²) and 25% (20cm²)!**
- Further research needed on optimization of stability of low bandgap cells (1.2 eV)

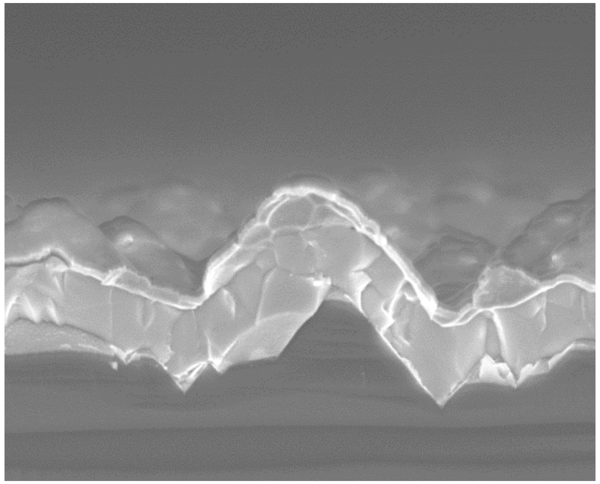
- Potentially good candidate for water-splitting through photocatalysis

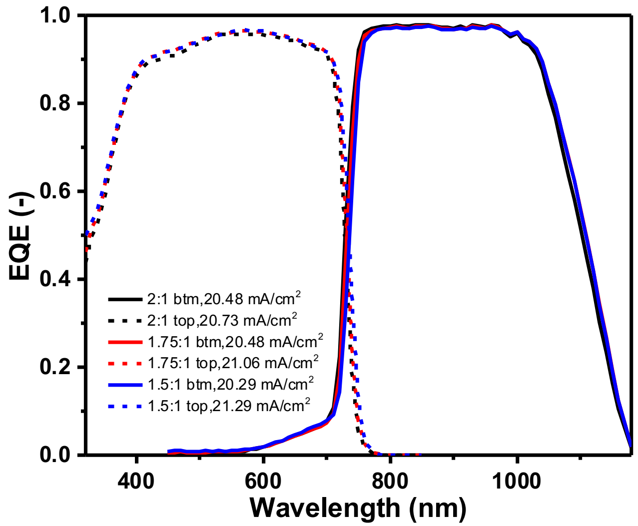


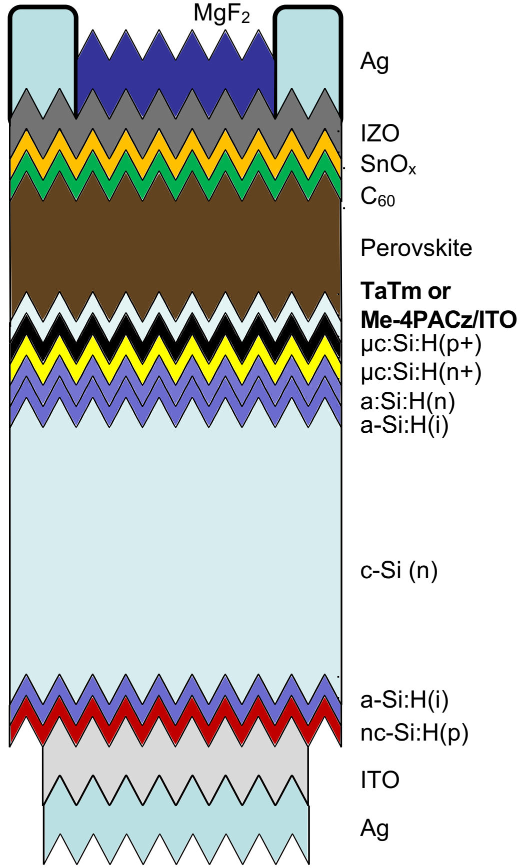
Wang et al., 10.1038/s41467-023-37492-y

Perovskite/c-Si monolithic tandem

- partner to Si (ideally 1.5 eV < E_g < 2 eV)
- high-efficiency, minimal cost increase
- feasible integration
- needs:
  - highly transparent contact between cells ✓
  - flat Si wafer for spin-coating of perovskite ✓
  - OR specialized methods for depositing on textured Si ✓
  - Perovskite stability to match c-Si

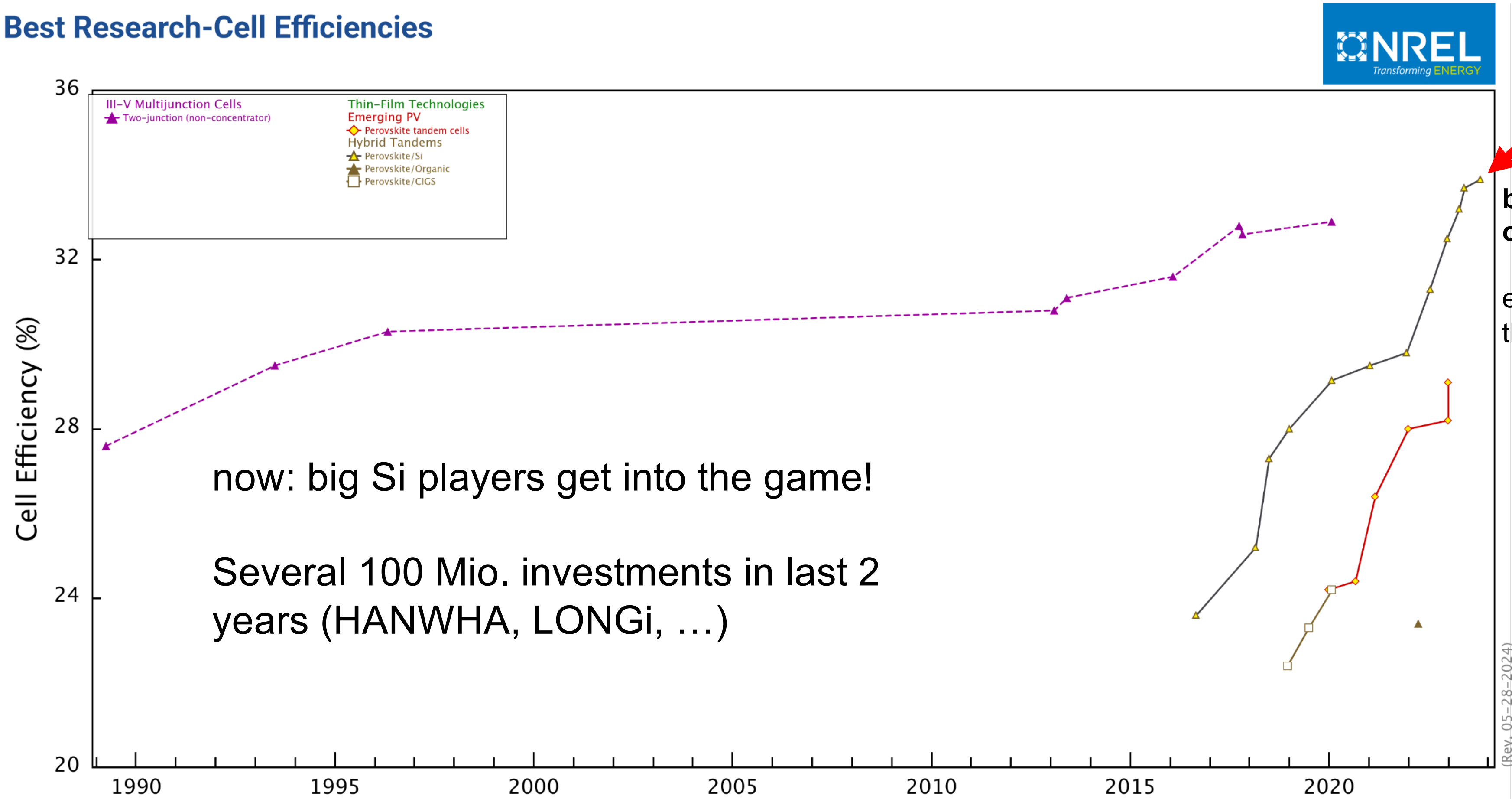






PV-LAB world-record
mid-2022 at 31.3% (Science 2023, Joule 2024)
Record of 34.9% by Longi (2024)

Perovskite tandems are on the run!



now: big Si players get into the game!

Several 100 Mio. investments in last 2 years (HANWHA, LONGi, …)

best tandem of all times!

even better than III-V

Perovskite on the market ?

Perovskite single junction modules

Pescetelli et al., 10.1038/s41560-022-01035-4

Yan *et al.*, 2025 - Science

Some (big) solar players start investing heavily

- GCL
- Microquanta

Labs around the world start prolonged outdoor monitoring and module fabrication

- **No bankable product yet!**

Thin film solar cell and modules efficiencies: summary and status

	CdTe	Chalcopyrites CIGS $Cu(In,Ga)Se_2$ $Cu(In,Ga)S_2$	Organic PV	Perovskites	III-V
Record lab cell efficiency (≥ 1 cm², if not specified)	23.1% (0.5 cm²) 21.0 % (1 cm², since 2014)	23.4% (1 cm² since 2018) 20.4% on plastics, size not given (0.5 cm² ?)	15.8% (cell 1cm²) 14.5% (19 cm² mini module)	27% (0.05 cm²) >24.25% (1 cm² cell) **20.6% (215 cm² mini-module)**	GaAs: 29.1% InP: 24.2% (unconcentrated single junction)
Commercial module efficiency range	17-20%	12-16%	-	-	(normally multijunction)
Main producer(s)	**First Solar**	**Solar Fro... ...rgy, Avan...** ... the co... ...tinue ...n)	**Heliatek**	1) Oxford PV – pero-Si tandems → 28.6% on M4 – 258cm2) and 25% pero-Si module (ISE-Oxford PV) – more efficient than any other c-Si module! 1) Microquanta and GCI - thin film perovskite module in pilot mode (link)	**Emcore** **Spectrolab**
Strength	Fast and "easy process" for absorber deposition	Customer acceptance	Potential low cost	Bandgap tunability, high efficiency	High efficiency
Weakness	Concern on Te availability, reliability of back contact, acceptance linked to Cd	Concern on In availability, sensitive process for absorber deposition	Moderate efficiency	Feasibility, reliability (serious stability concerns)	High cost

bankrupt / out of business

Source: M. Green et al, Solar cell efficiency tables V65 Prog. Photovolt: 2025

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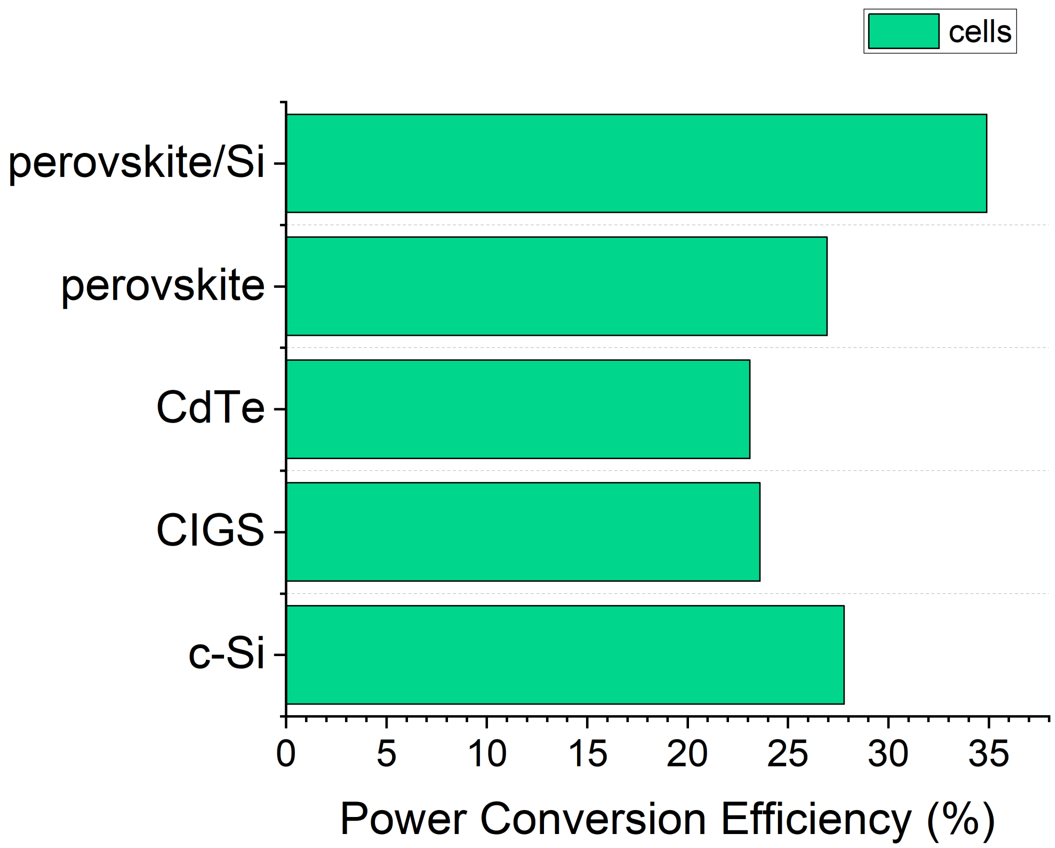
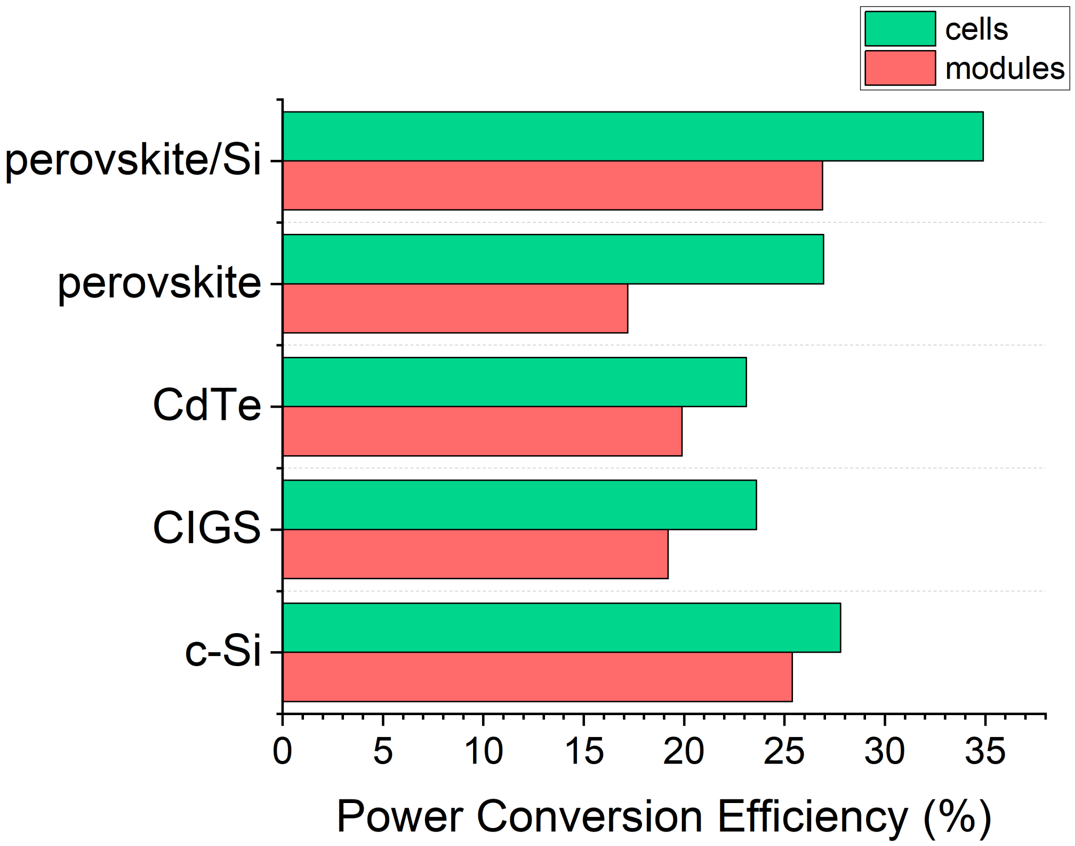
PV module efficiencies: the cell vs module gap:

Dr. Christian Wolff



Source: *M. Green et al, Solar cell efficiency tables V65 Prog. Photovolt: 2025*

PV module efficiencies: the cell vs module gap:



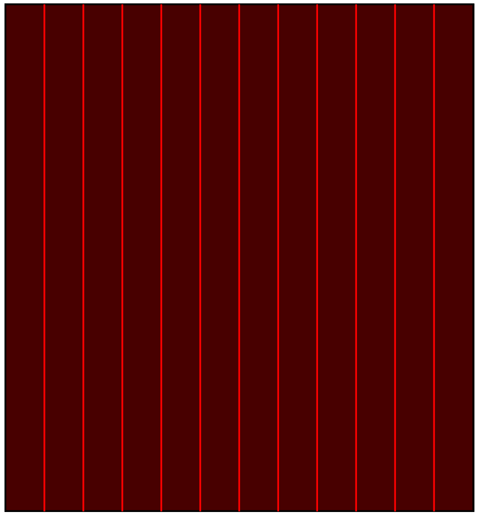
difference btw. champion cell and module: combination of high current (low E_g) and poor current transport in TCO (low σ)

Source: M. Green et al, Solar cell efficiency tables V65 Prog. Photovolt: 2025

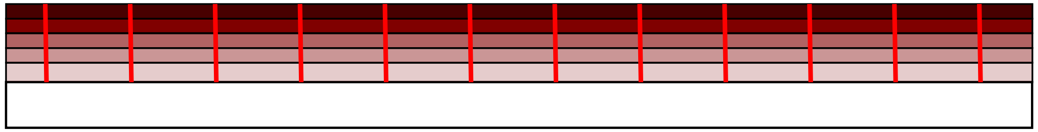
Thin film module: Monolithic integration

Basic process sequence of a thin film module

- Deposit active layers on large area, low cost substrates
- Use "monolithic interconnection" for contact between segments
- Attach metallic ribbons to extract current
- Laminate and add junction box (+ reverse diode that protects the module from reverse polarization)



Top view



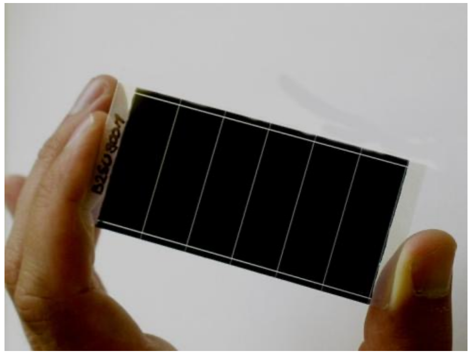
Cross-section

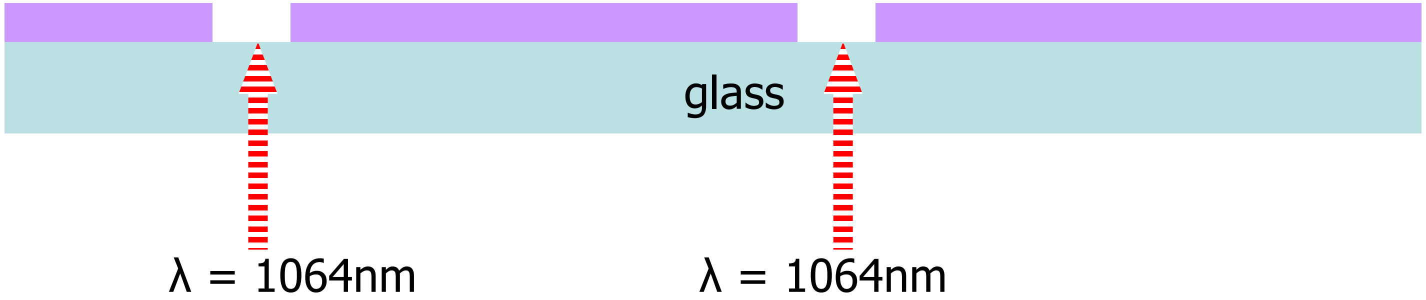
Monolithic serial interconnection

Dr. Christian Wolff

Example: superstrate configuration on glass, e.g. a-Si or CdTe

1. TCO deposition (or metal contact)
2. Laser scribing pattern #1 (λ=1064nm)



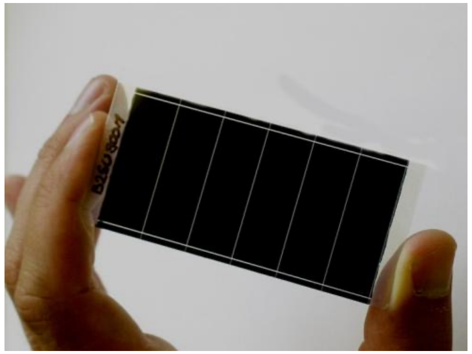


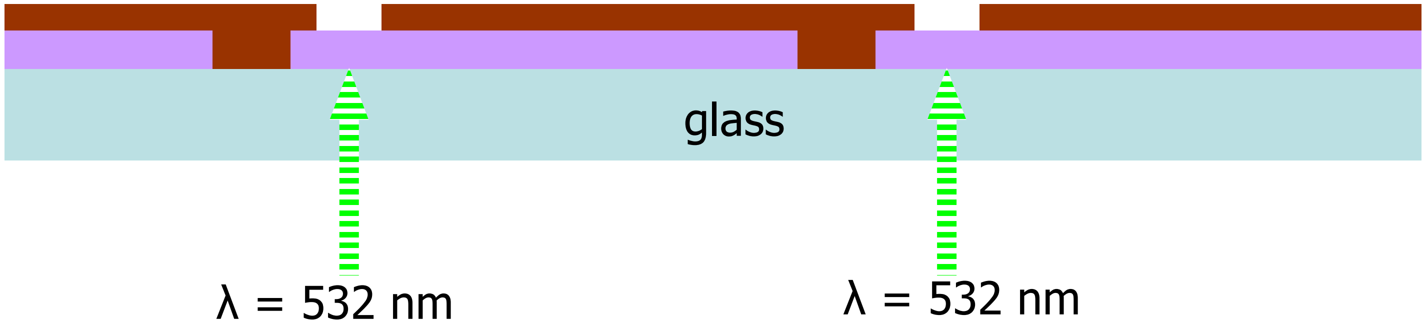
Monolithic serial interconnection

Dr. Christian Wolff

Example: superstrate configuration on glass, e.g. a-Si or CdTe

1. TCO deposition (or metal contact)
2. Laser scribing pattern #1 (λ=1064nm)
3. Deposit n-layer and p-absorber
4. Laser scribing pattern #2 (λ=532nm)





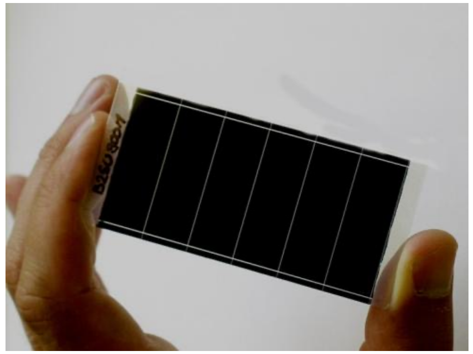
PV-lab IEM NEUCHATEL

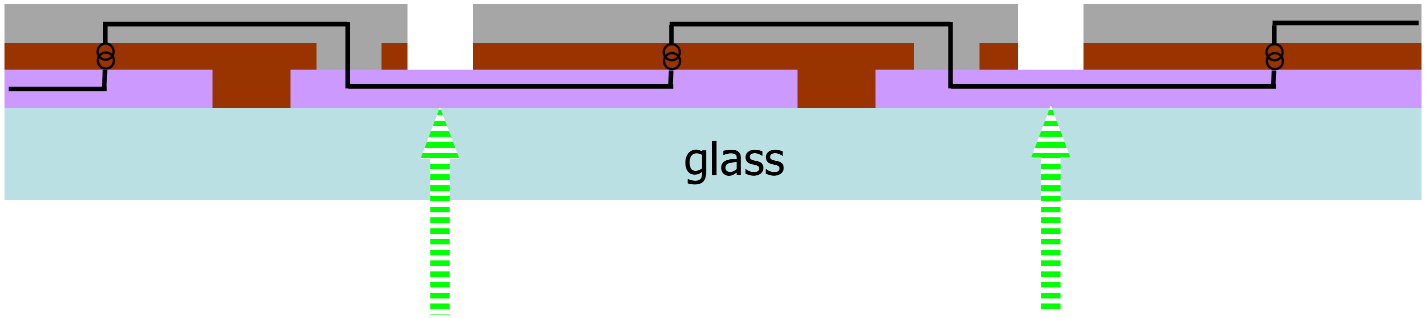
EPFL

Monolithic serial interconnection

Example: superstrate configuration on glass, e.g. a-Si or CdTe

1. TCO deposition (or metal contact)
2. Laser scribing pattern #1 (λ=1064nm)
3. Deposit n-layer and p-absorber
4. Laser scribing pattern #2 (λ=532nm)
5. Deposition of 2nd electrode
6. Laser scribing pattern #3 (λ=532nm)





The ideal scribe width depends on the materials
(e.g. conductivity of the electrode, c.f. assignment)

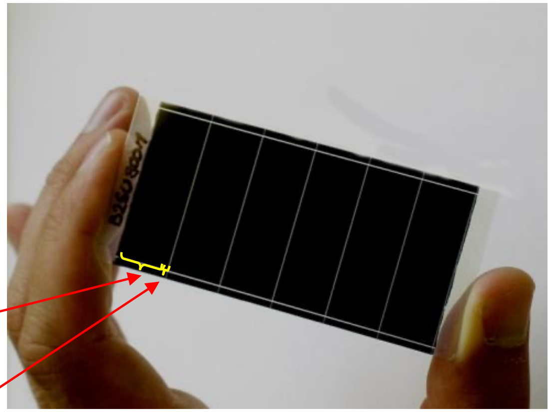
Monolithic serial interconnection

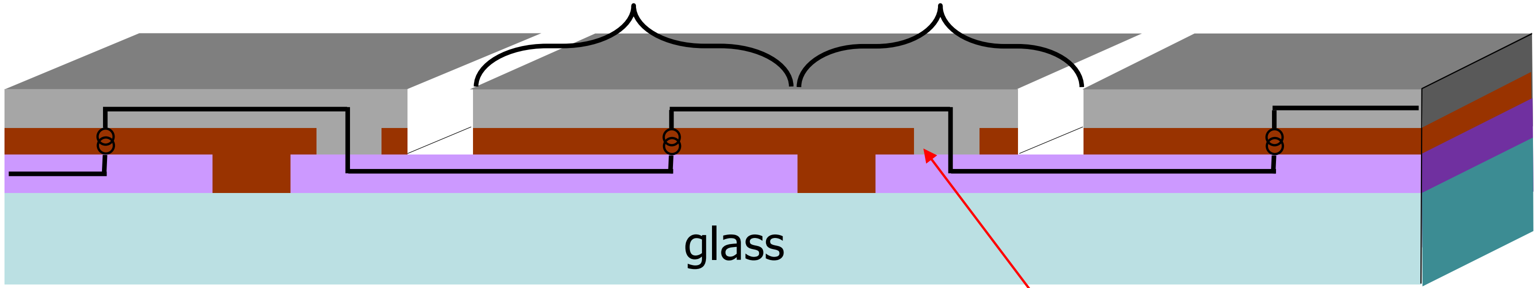
Dr. Christian Wolff

No current generation in the dead area
→ need to minimize its width

Active area:

- Too wide → electric (ohmic) losses inside TCO
- Too narrow → low active to dead area ratio





PV-lab
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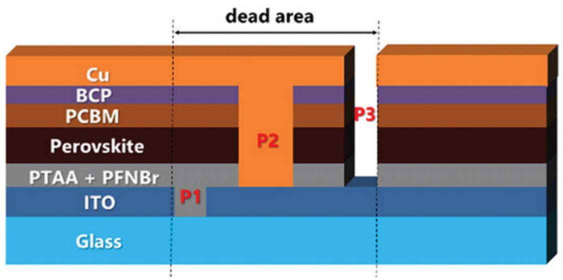
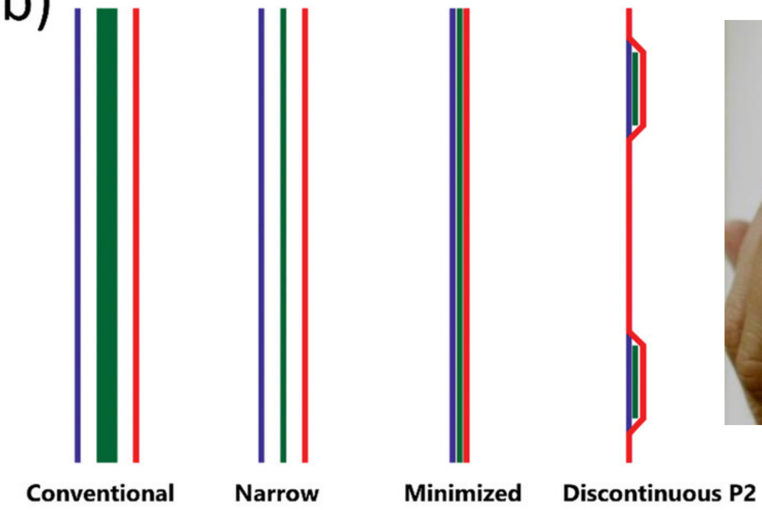
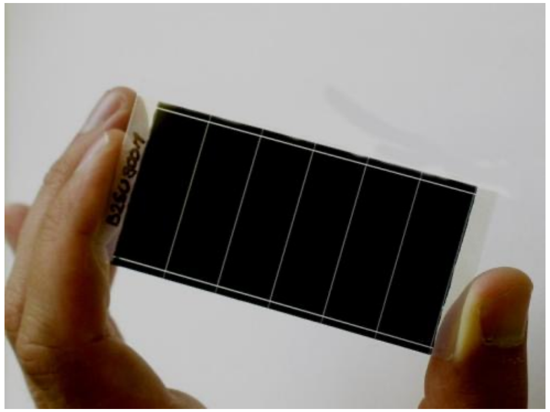
Monolithic serial interconnection

a)

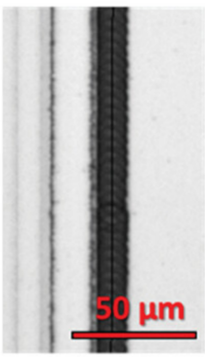


b)

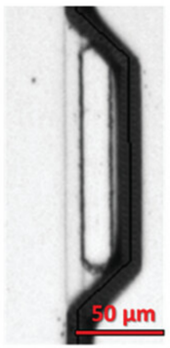




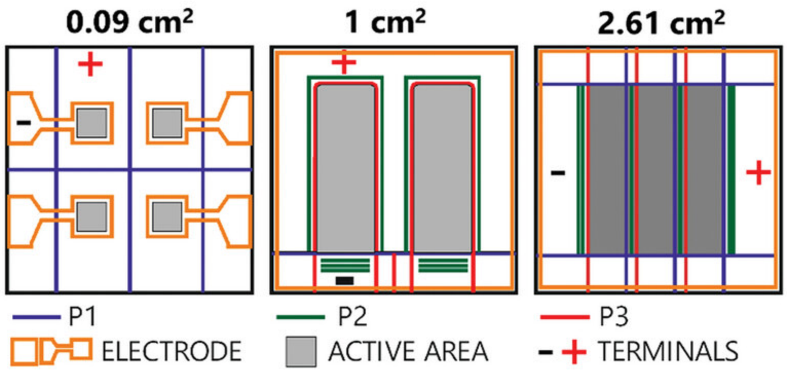
c)



d)



e)



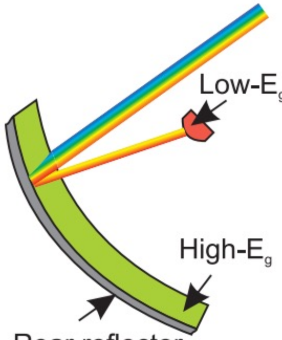
Dead area can be minimized:

<< 1% with smart way

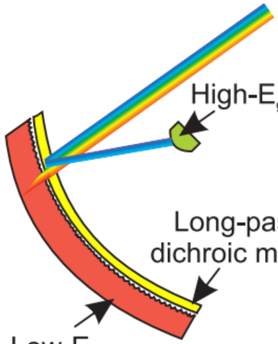
Advanced Energy Materials, First published: 11 May 2024, DOI: (10.1002/aenm.202400115)

Exploratory multijunction cells: employ dichroic mirrors

Tandem concepts with partial concentration



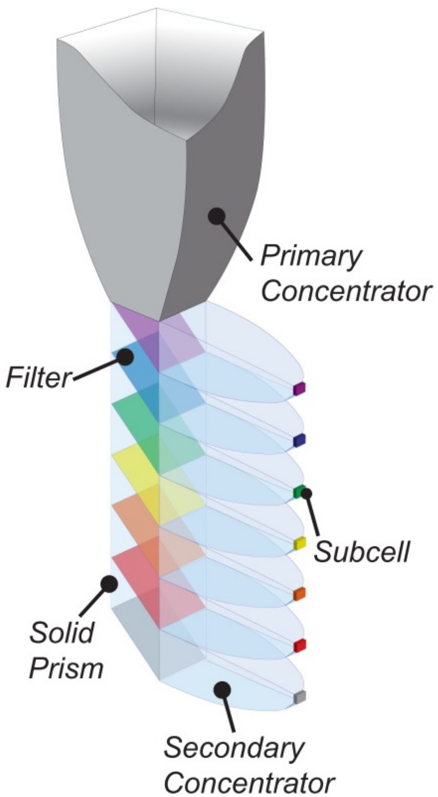
would need high-gap cell with low-cost & large area

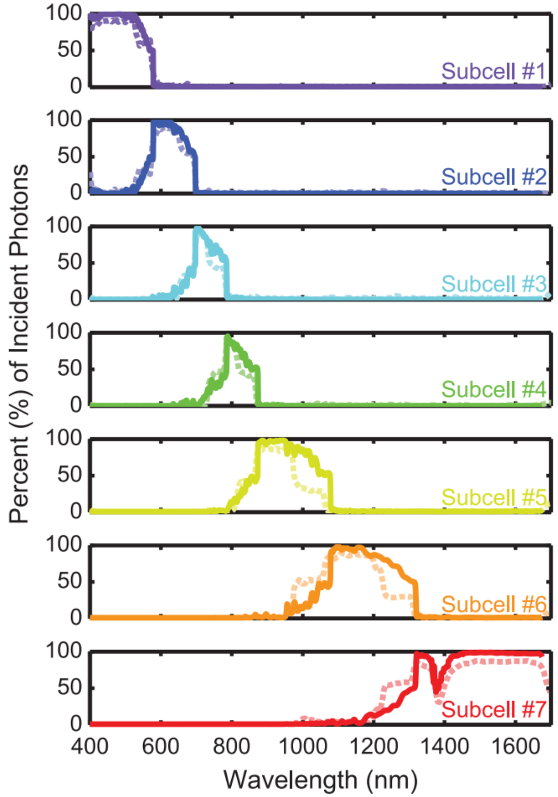


=> use low-gap low cost cell (e.g. Si), add dichroic mirror to concentrate on high-gap high efficiency cell (e.g. GaP)

Zhengshan, JPV (2015)

7-cell concept with 2-stage concentration



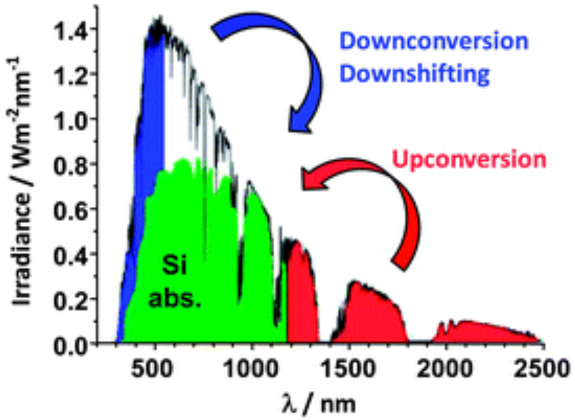


Eisler, JPV (2019)

Novel concepts: what else is possible (and investigated)?

- Up- and down conversion
  - convert two IR photons to one visible
  - convert one UV photon to two visible

  Bottleneck: luminescent efficiency & scarcity of Er

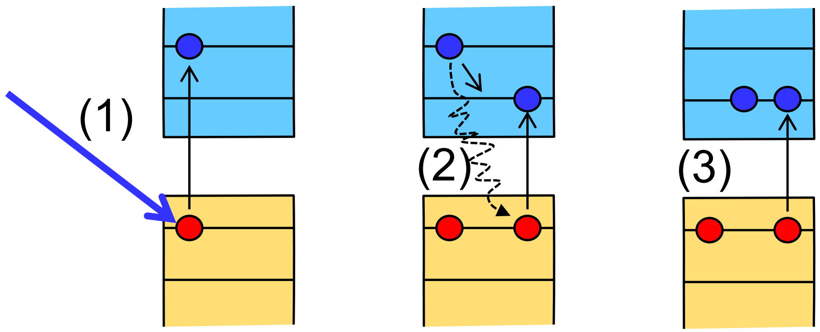


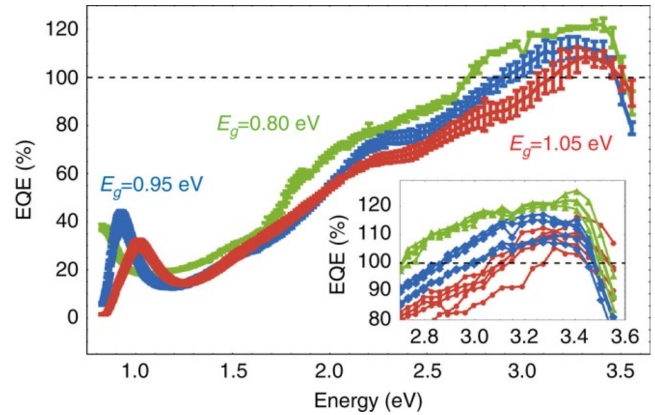
Bünzli, Chem. Sci. 2013

- Multi-exciton excitation
  - essentially an inverse Auger process

  Bottleneck: efficient only for E > $3E_g$

  => might have high current, but will have low Voc

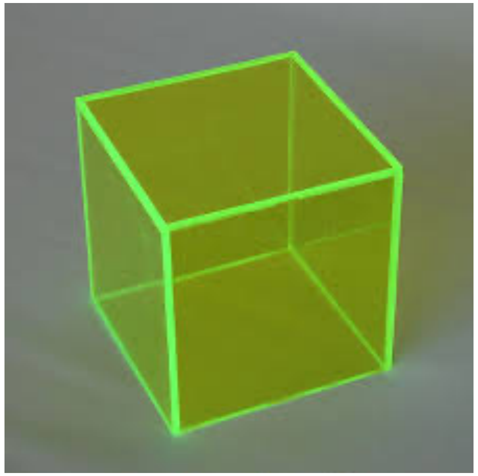




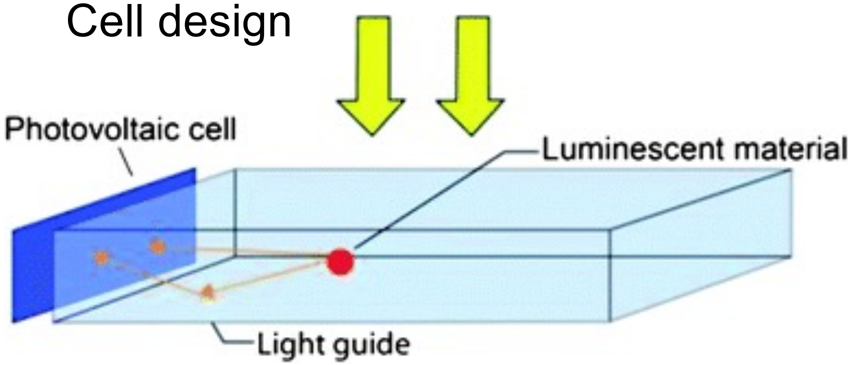
Davies, Nat. Comm. 2015

Luminescent concentrator cells

Exploit edge luminescence
(due to total internal reflection)

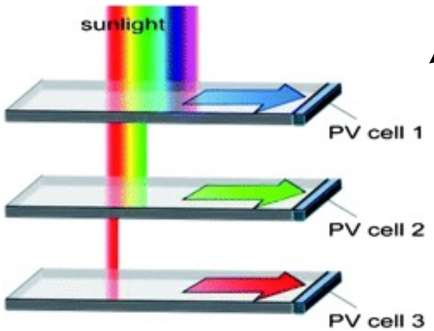


Cell design

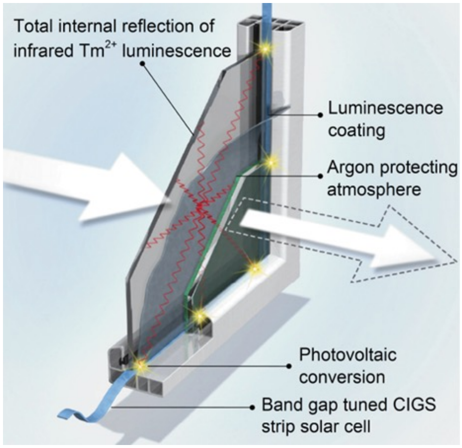


Luminescent spectrum splitting

Smart window



Hernandez-Loyola, EES (2012)



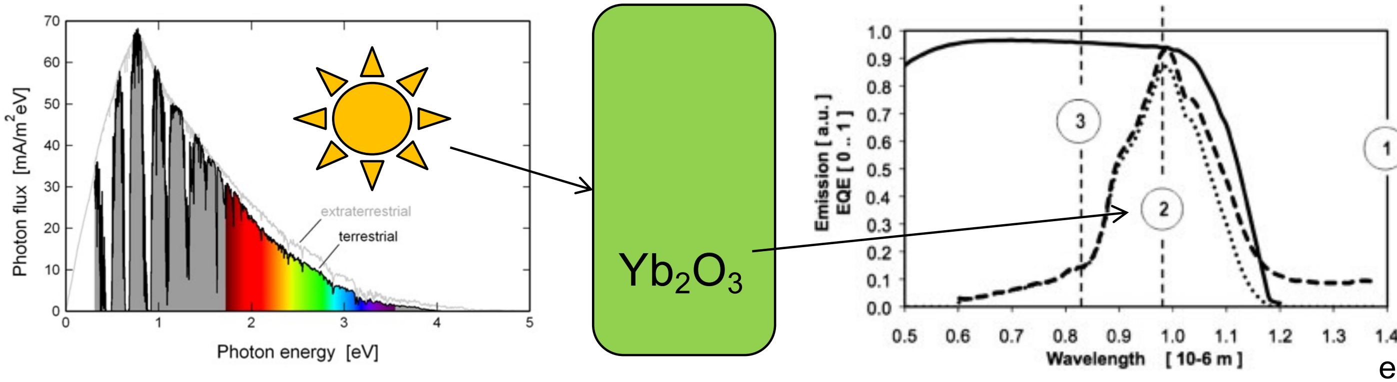
TU Delft

Bottleneck:

moderate luminescent efficiency

Solar thermal PV

Use concentrated sunlight to heat thermal emitter



e.g. B. Bitnar, Appl. Energy (2013)

example Odeillo Solar Furnace (F)

- Requires concentration if used with solar radiation (historical business model of SunPower, soon abandoned)
- Demonstrated for energy scavenging (residential heaters, camping stoves, etc.)

Bottleneck: requires rare earths (Er, Yb, etc)

=> solar thermal steam turbines more cost effective
(and possibility to bridge evening with gas burner)

Conclusions

- Thin films: more delicate, because require mastering on large area. Significant investments are required if not using "Turnkey-Equipment"
- Less material usage, better energy payback time (environmental aspects), lowest possible cost in €/W_p,

⇒ **for mass market:** difficult to compete with c-Si, only CdTe thanks to **IRA in US**
⇒ **Some companies with niche products (truly flexible, IOT)**.

Take home:
- Understand structure of typical thin film devices (CdTe, perovskites) and know their strengths and weaknesses
- CdTe is around 3-4 **%** of the market, silicon the rest!
- Perovskite are promises but no sufficient stability yet for bankable products.
- Promising efficiency increase when combined with c-Si (or tandem Pk-Pk)
- Understand working principles and difficulties of novel concepts