AMOLF International Nanophotonics Summer School

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Fundamental Limits in “nano” photovoltaics

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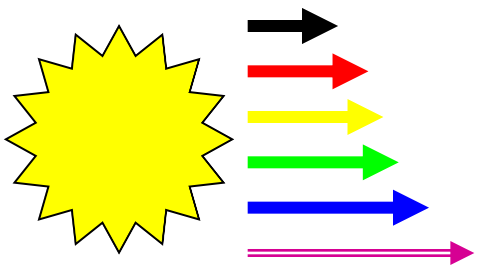
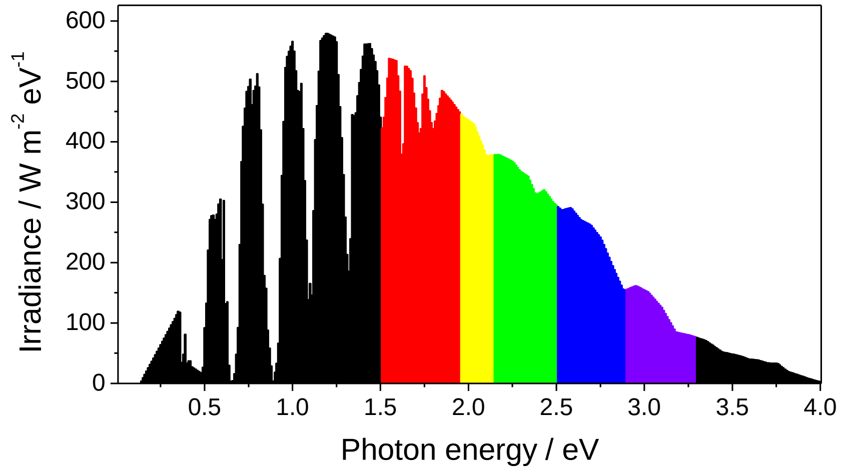
Thanks to: Ned Ekins-Daukes, UNSW
Thomas Kirchartz, FZ Juelich

Imperial College London

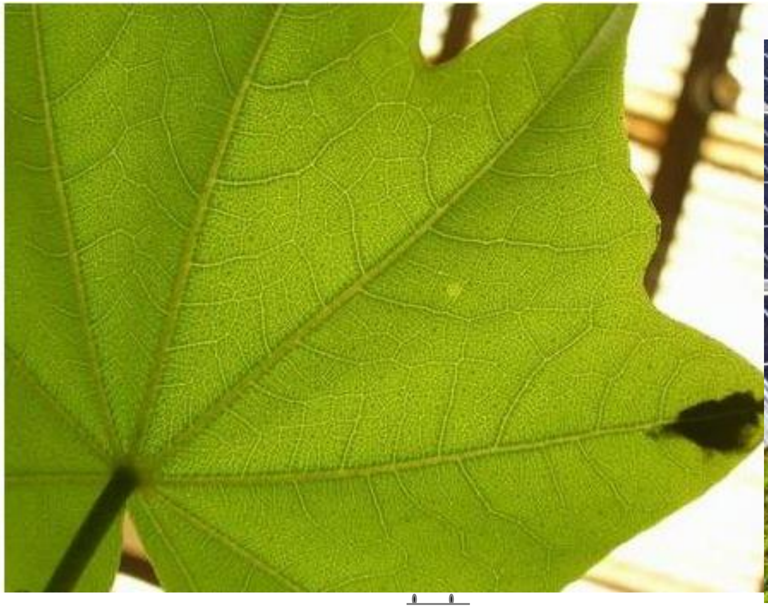
The Centre for Plastic Electronics

Solar energy conversion





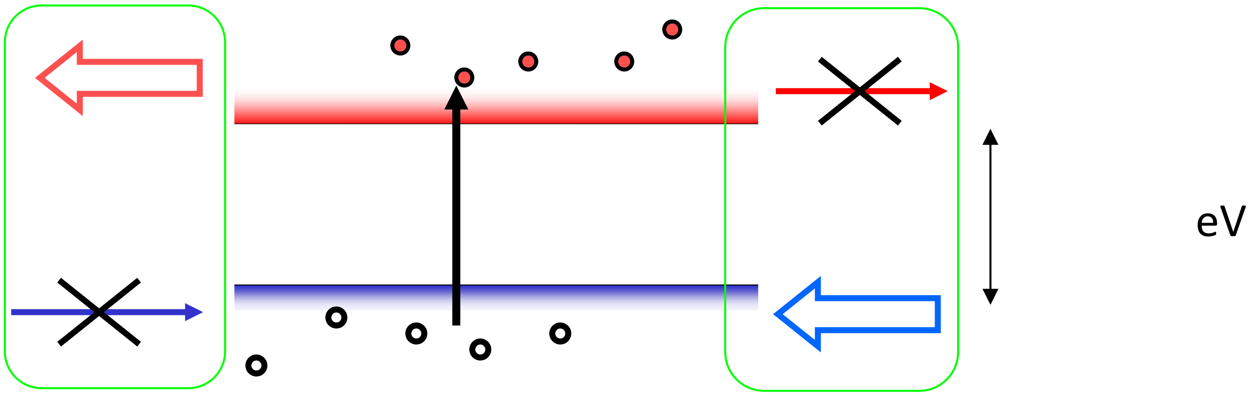
Solar thermal



Solar chemical

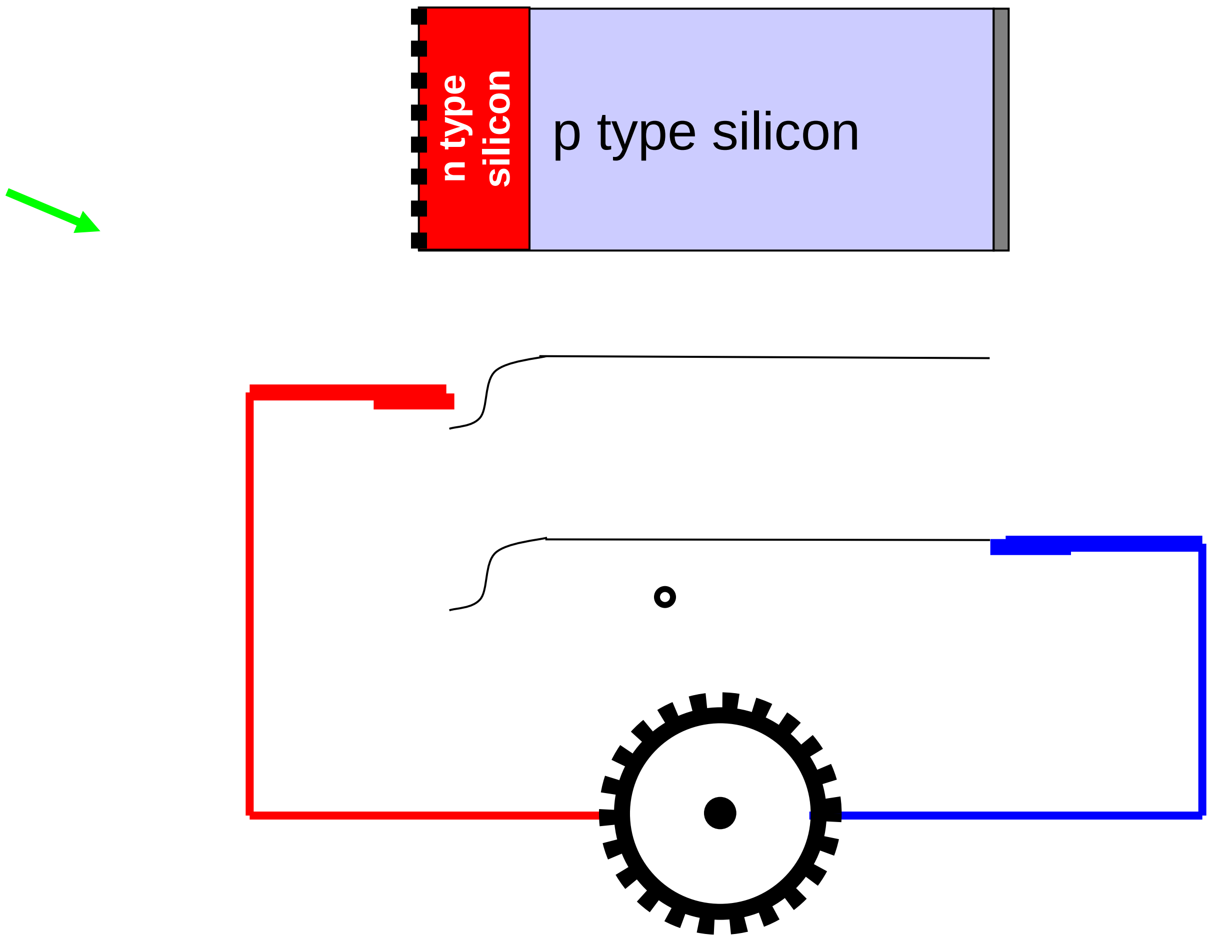
Solar photovoltaic

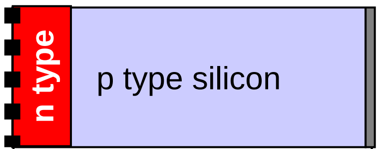
Photons in, electrons out

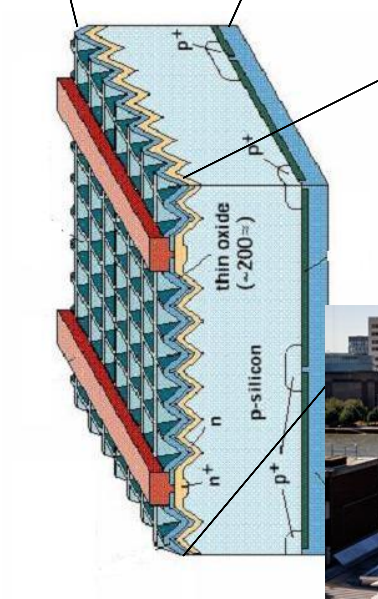


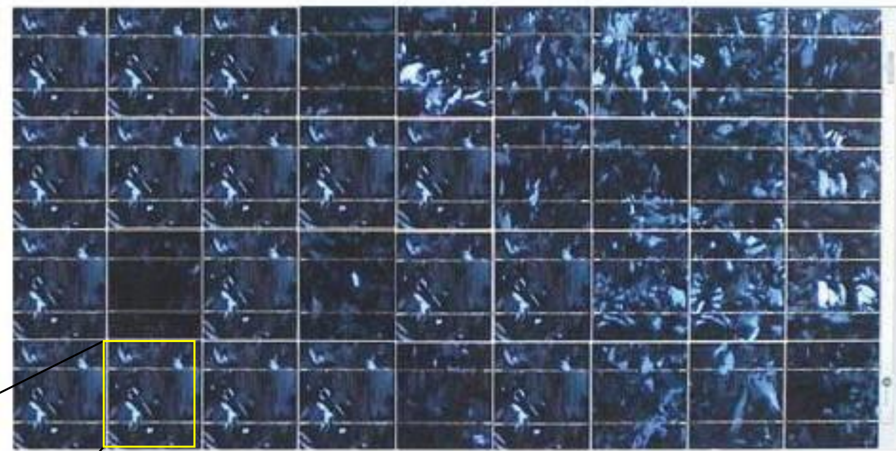
- Photovoltaic energy conversion requires:
  - photon absorption across an energy gap
  - separation of photogenerated charges
  - asymmetric contacts to an external circuit

Photons in, electrons out









efficiency
~ 15-20%

power rating
~ 100-200 W_p

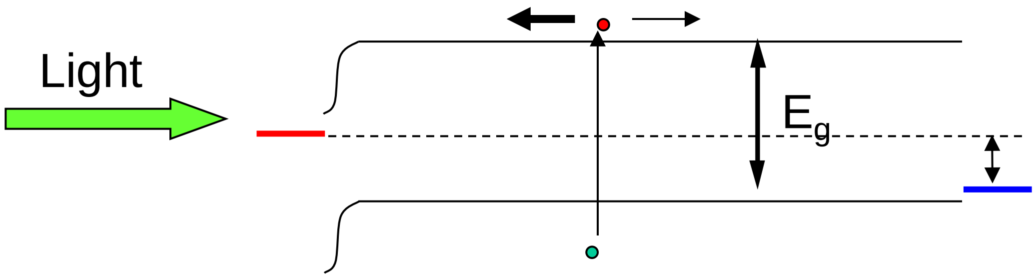
Applications

Blackfriars Bridge
~1.1 MW_p

Solar powered refrigeration
~100 W_p

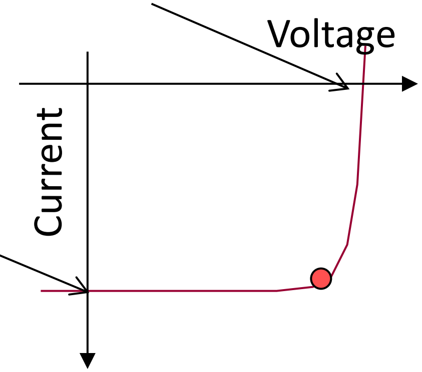
~1 mW_p

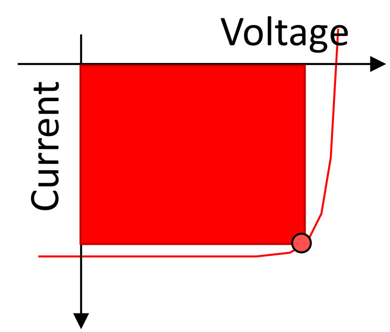
Electrical work and efficiency



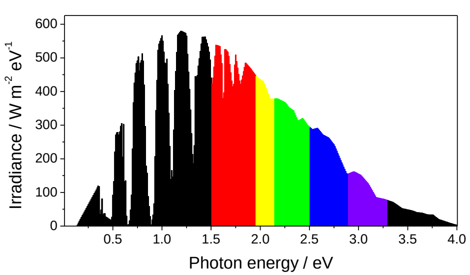
$$\Delta E_F = eV_{oc}$$

$$e\int_{E_g}^{\infty} b_{inc}(E)Abs(E)dE \geq J_{sc}$$





Power Conversion Efficiency = $\dfrac{\textbf{Power converted into electrical work (J x V)}}{\textbf{Radiant Power received from the Sun}}$



Efficiency from the Current density – Voltage (J-V) curve

- J(V) measured under Standard Test Conditions (AM1.5, 1000 Wm^{-2}, 25°C)
- Approximately:

$$J = -J_{sc} + J_0 \left(\exp \frac{qV}{nkT} - 1 \right)$$

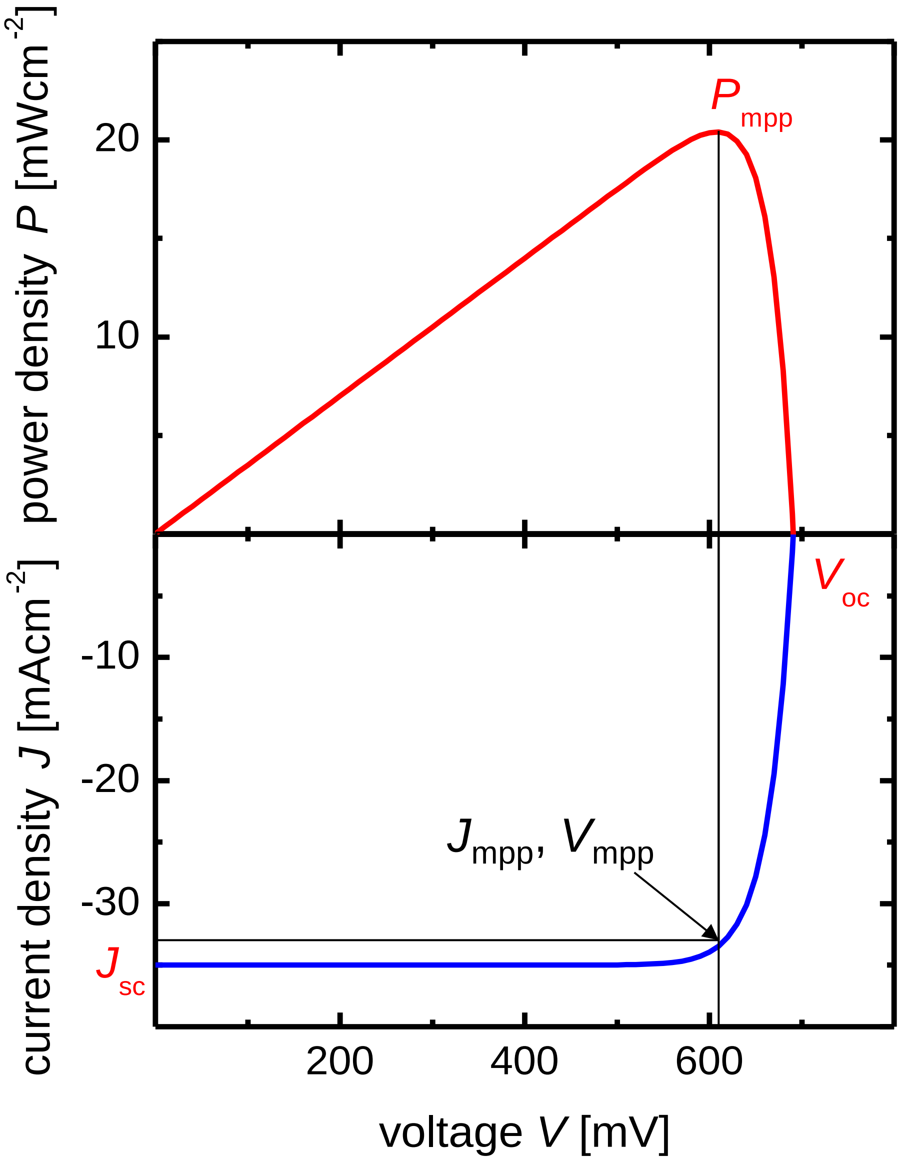
Power conversion efficiency:

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

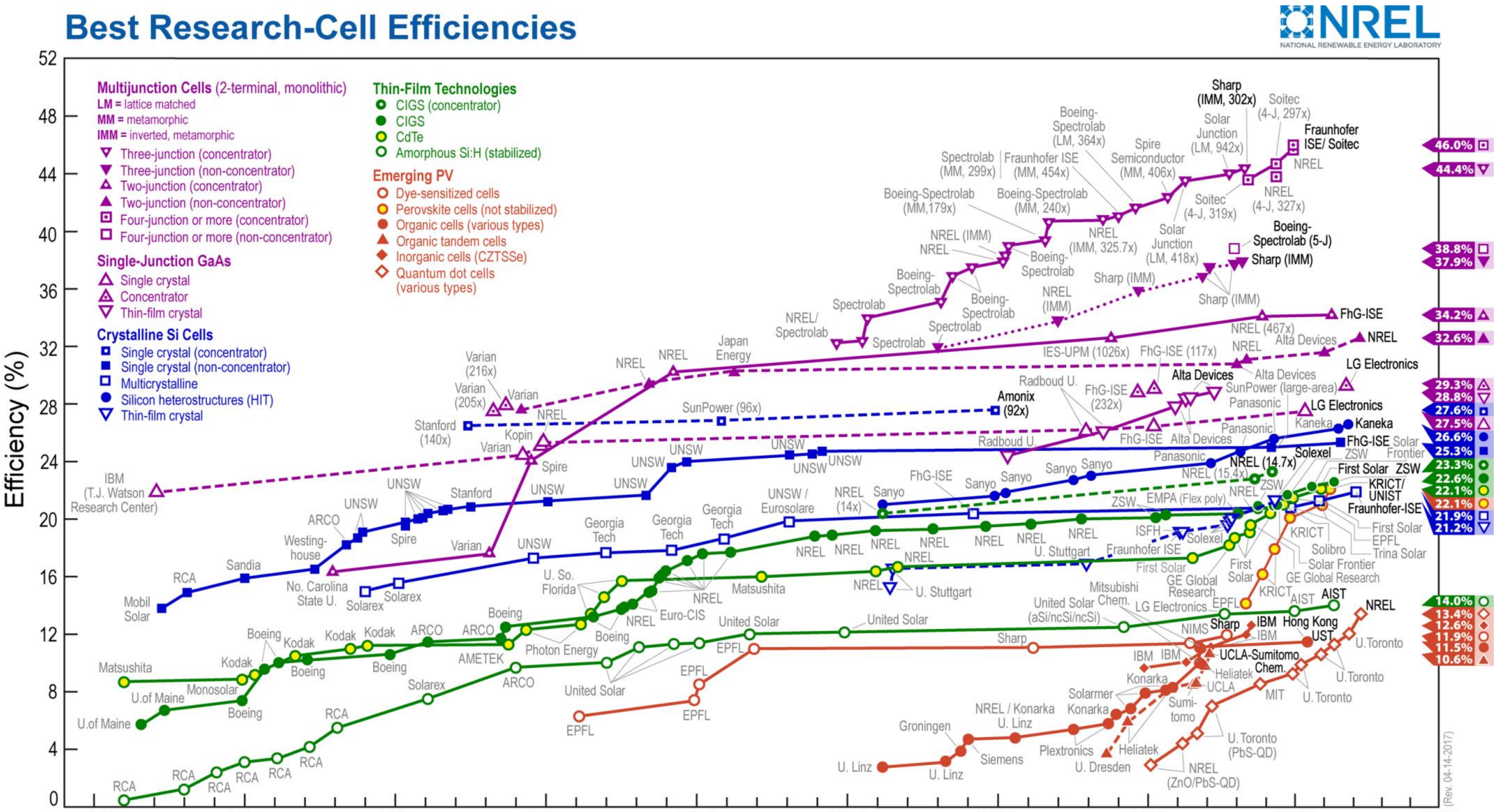
$$FF = \frac{J_{mpp} V_{mpp}}{J_{sc} V_{oc}}$$

$$P_{in} = \int \phi_{sun}(E) E \, \mathrm{d}E$$

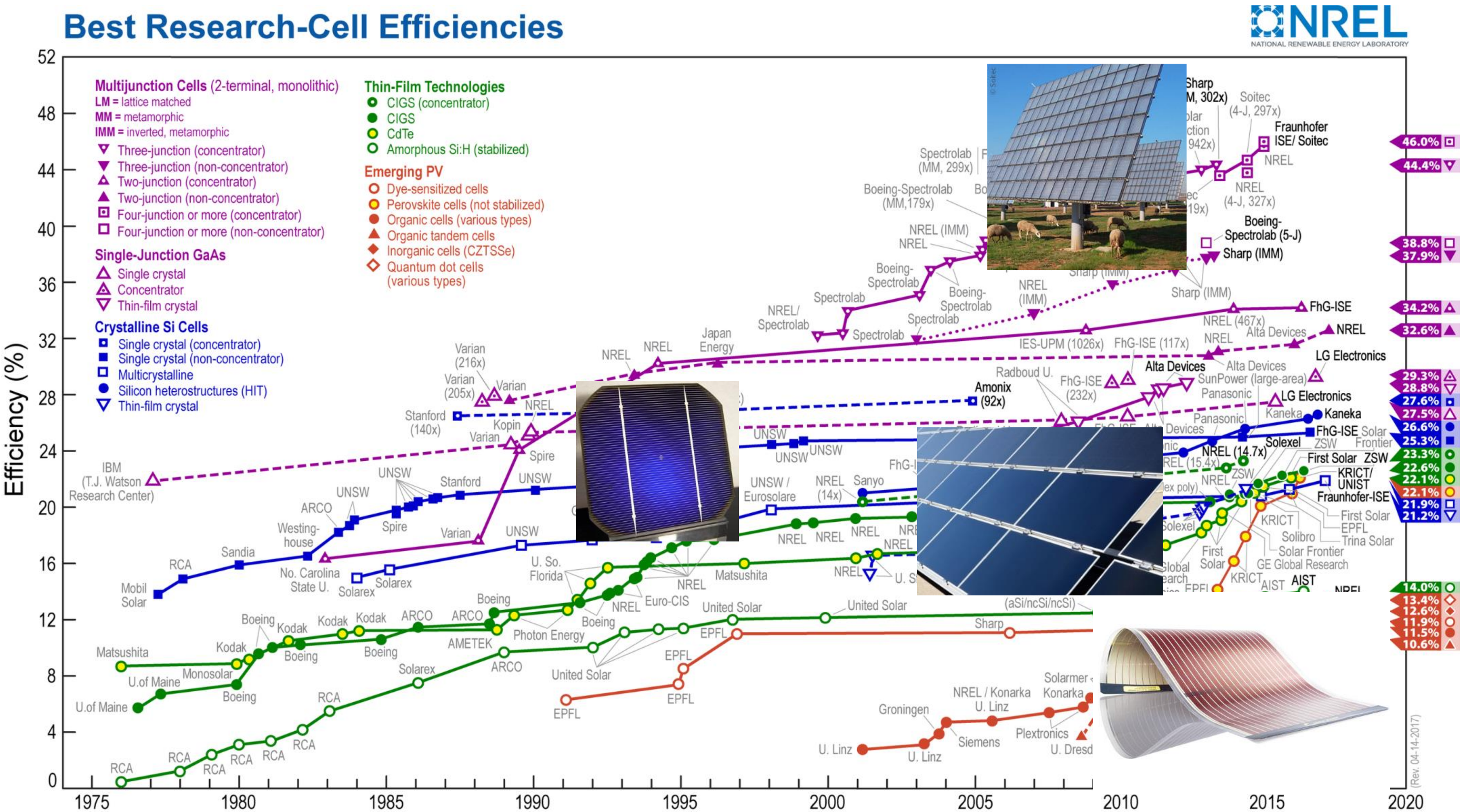
- Short circuit current density J_{sc},
- Open circuit voltage V_{oc}
- Fill factor FF



http://upload.wikimedia.org/wikipedia/commons/3/35/Best_Research-Cell_Efficiencies.png



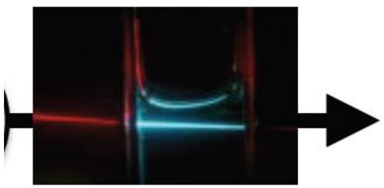
http://upload.wikimedia.org/wikipedia/commons/3/35/Best_Research-Cell_Efficiencies.png

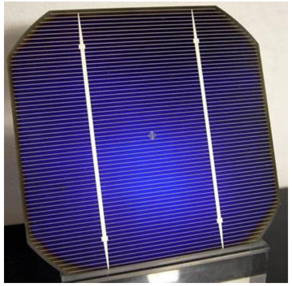


Future directions in solar photovoltaics

"Silicon + X"

Add a layer to silicon to improve performance





Crystalline Silicon

"PV + X"

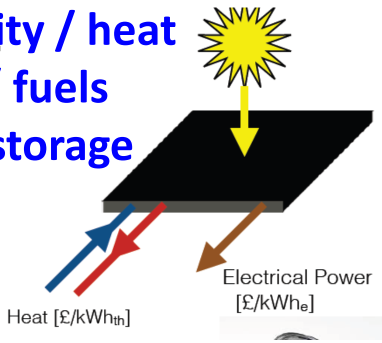
Integrate solar panels with other functions

e.g.

Electricity / heat

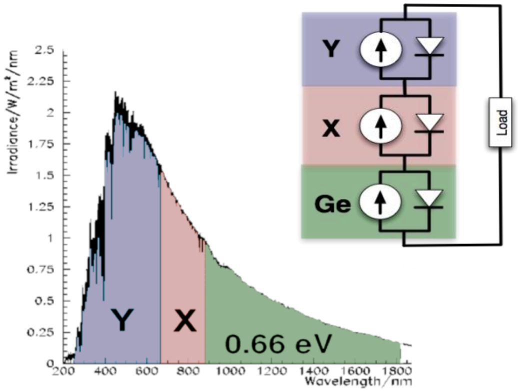
PV / fuels

PV / storage



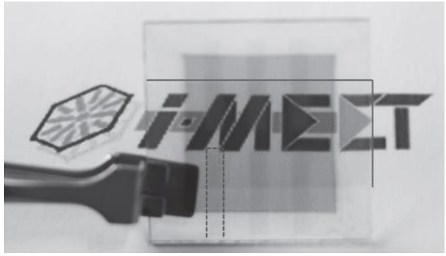
High efficiency designs

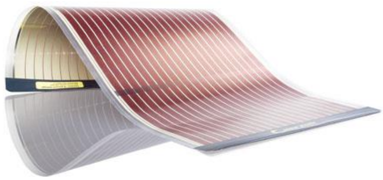
Stack different solar cells together in a multi-junction



Low cost, low energy manufacture

Flexible, solution processible materials

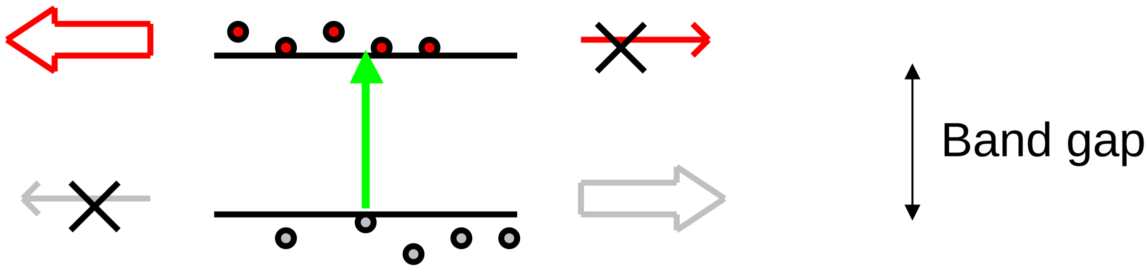




Outline

- **Photovoltaic energy conversion**
- **Limiting efficiency of solar cells**
- **Nanostructures in photovoltaics**
- **Routes to more work per photon**
- **Nanomaterials to approach the efficiency limit**
- **Nanomaterials to reduce costs**

Detailed balance limit



(i) One electron hole pair per photon with $h\nu > E_g$,

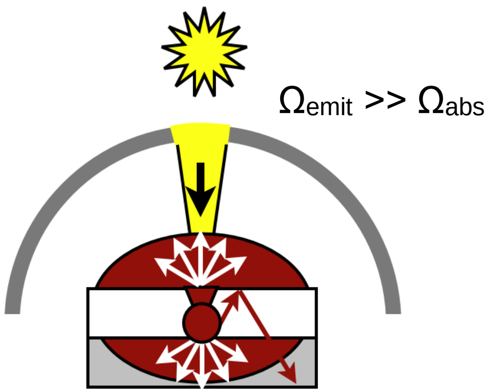
(ii) Carriers relax to form separate Fermi distributions at lattice temperature $T_{ambient}$ with quasi Fermi levels separated by $\Delta\mu$.

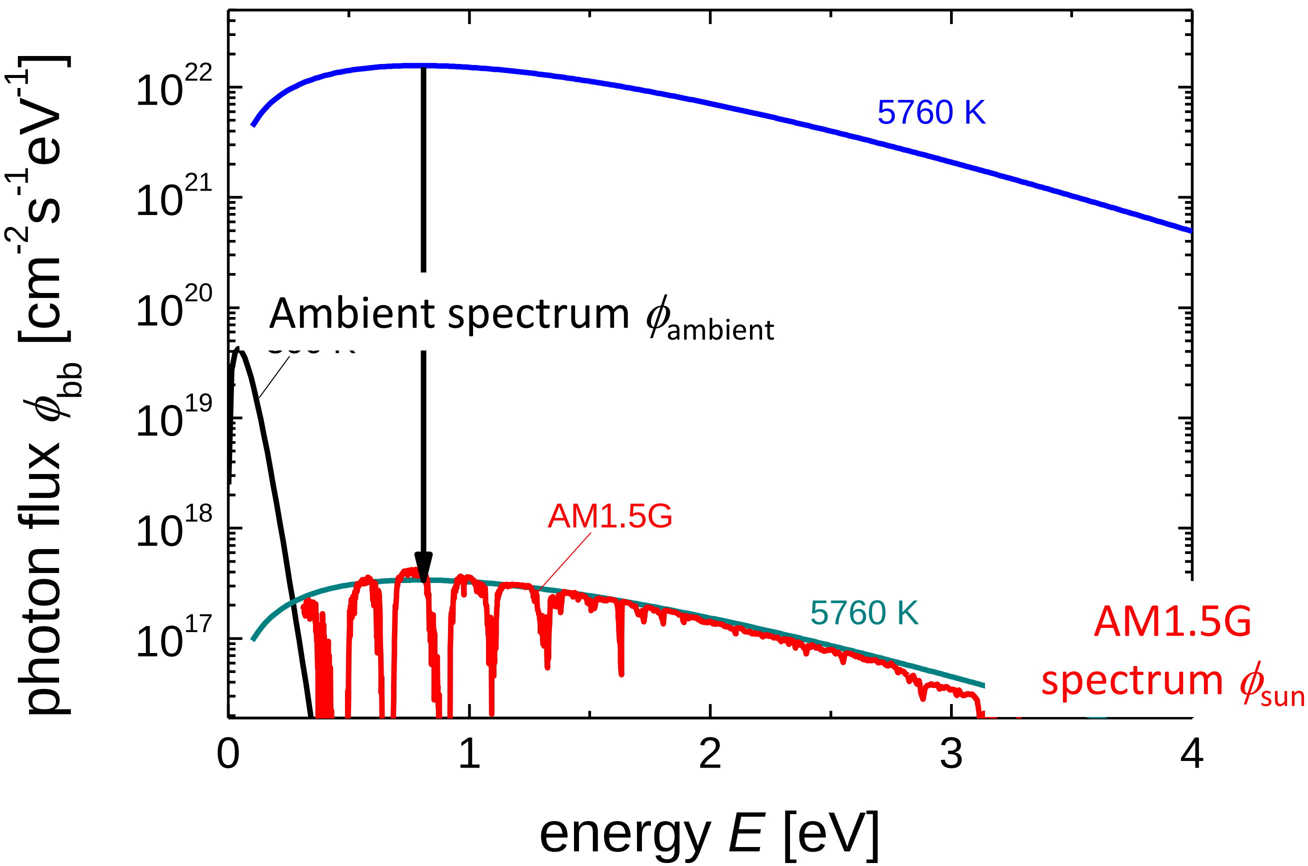
(iii) All electrons extracted with same electrochemical potential $\Delta\mu = eV$

(iv) Only loss process is spontaneous emission

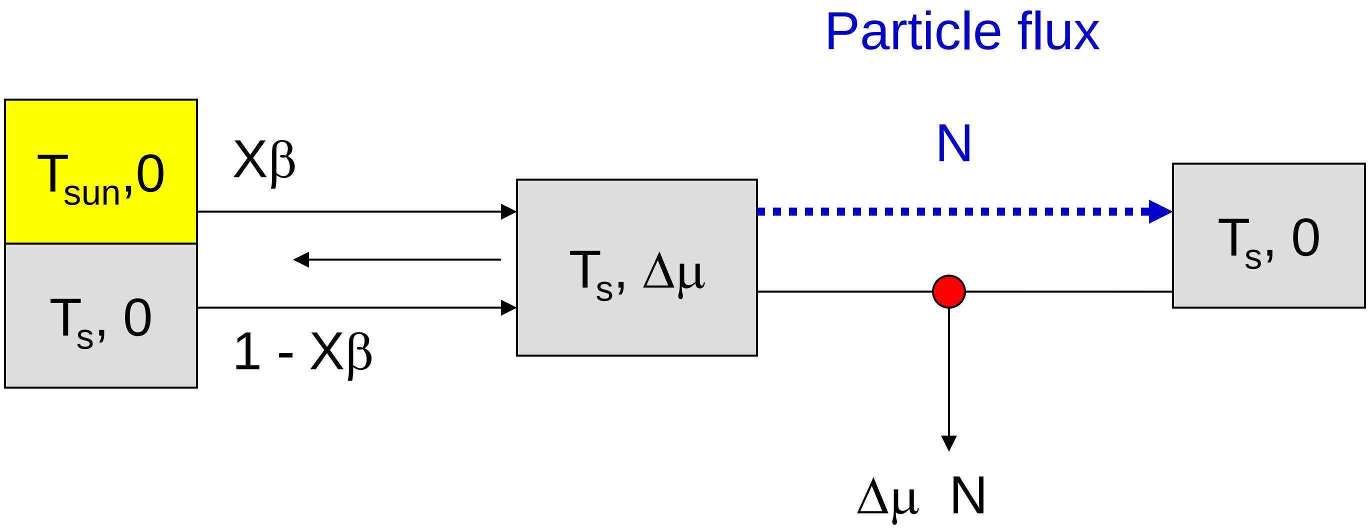
Solar cell absorbs visible light, emits IR light

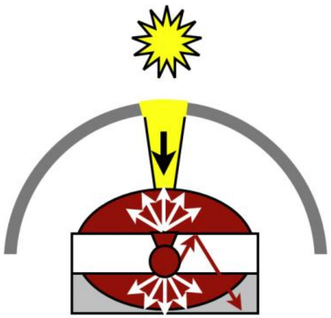
Conventional solar cell





Calculation of limiting efficiency



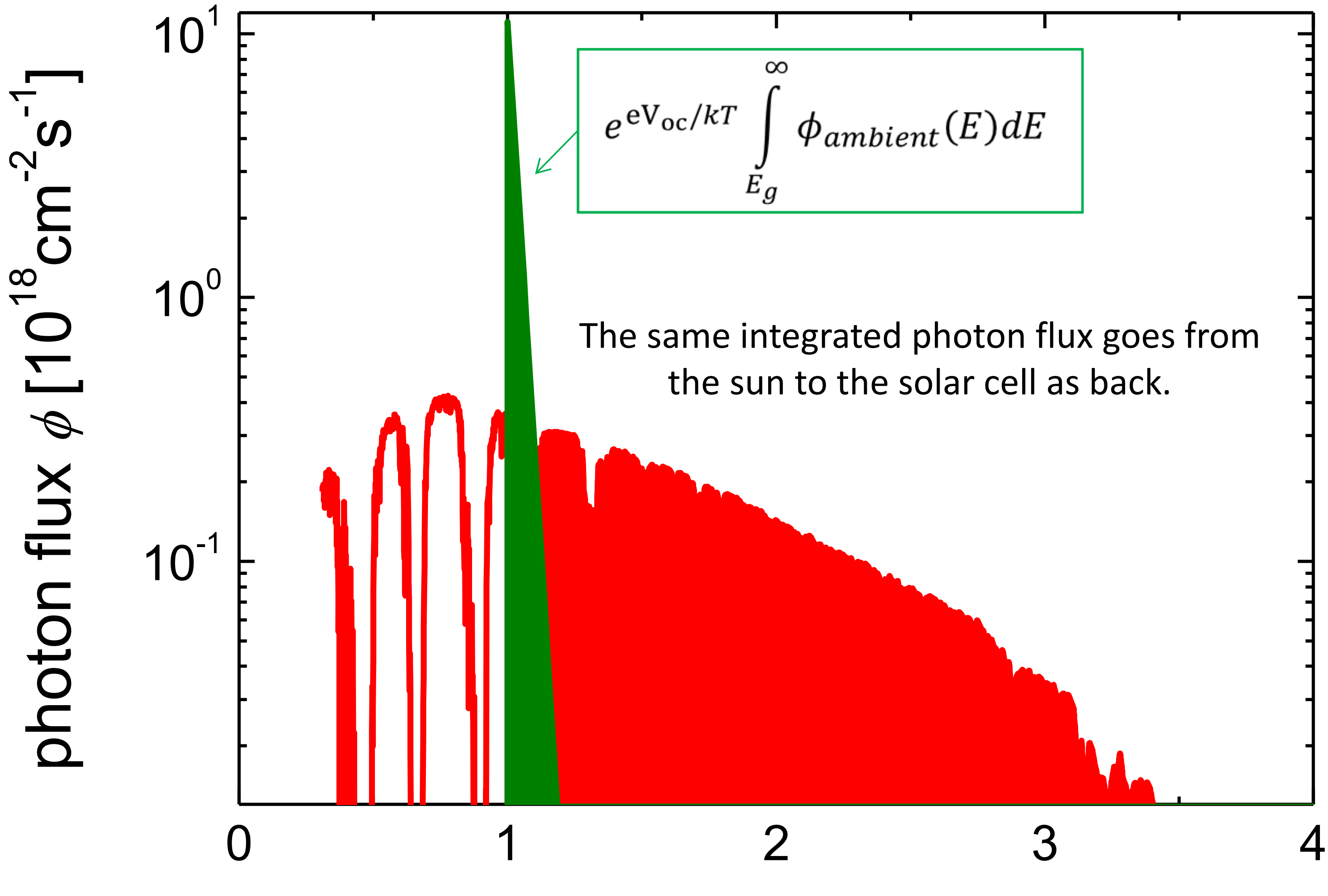


$$\frac{J}{q} = -X\beta \int_{E_g}^{\infty} \phi_{sun}(E)dE - (1 - X\beta) \int_{E_g}^{\infty} \phi_{ambient}(E)dE + e^{\Delta\mu/kT} \int_{E_g}^{\infty} \phi_{ambient}(E)dE$$

$$J = -J_{sc} + J_{0,rad}\left(\exp\frac{qV}{kT} - 1\right)$$

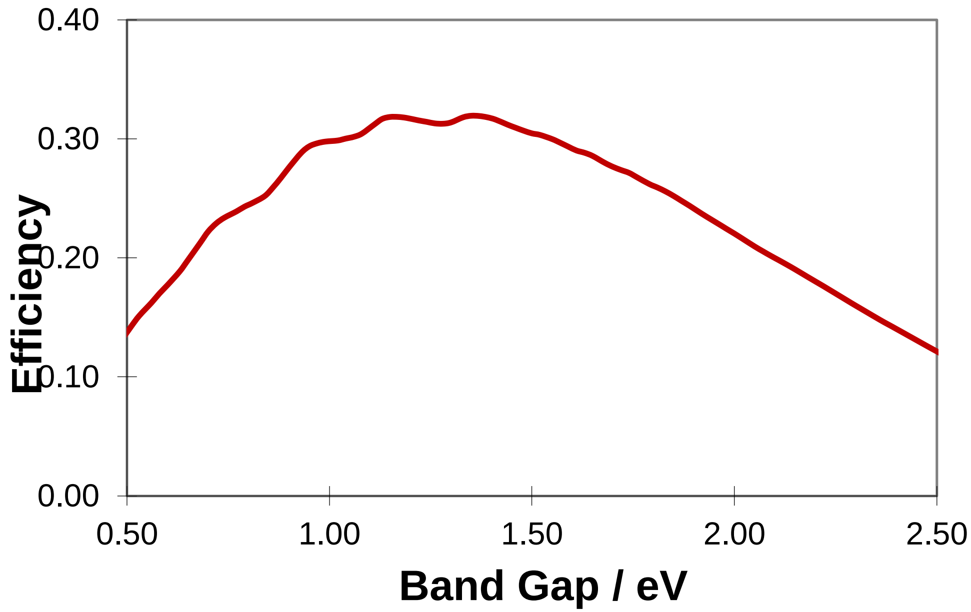
$$P = JV$$

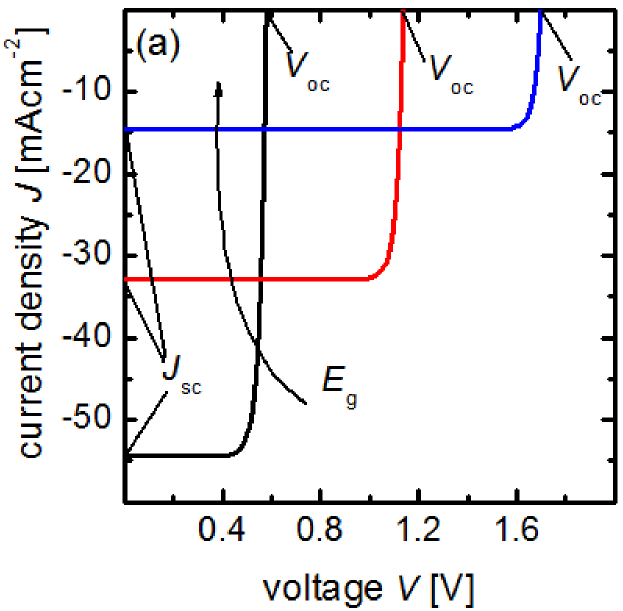
Emission of sun and solar cell at open circuit



Graph: courtesy Thomas Kirchartz

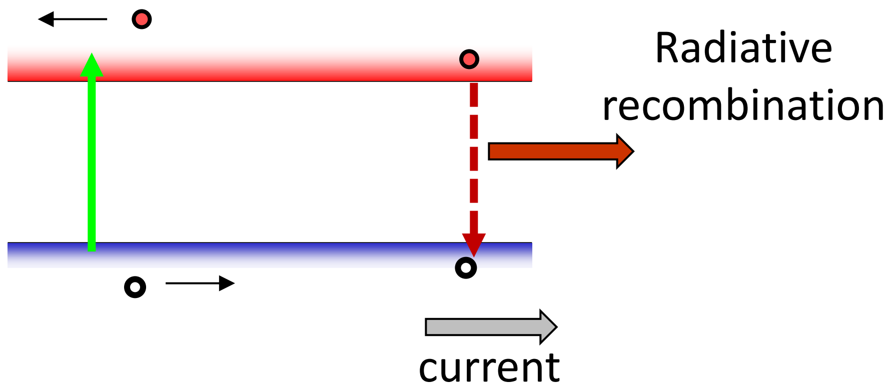
Practical and limiting efficiencies



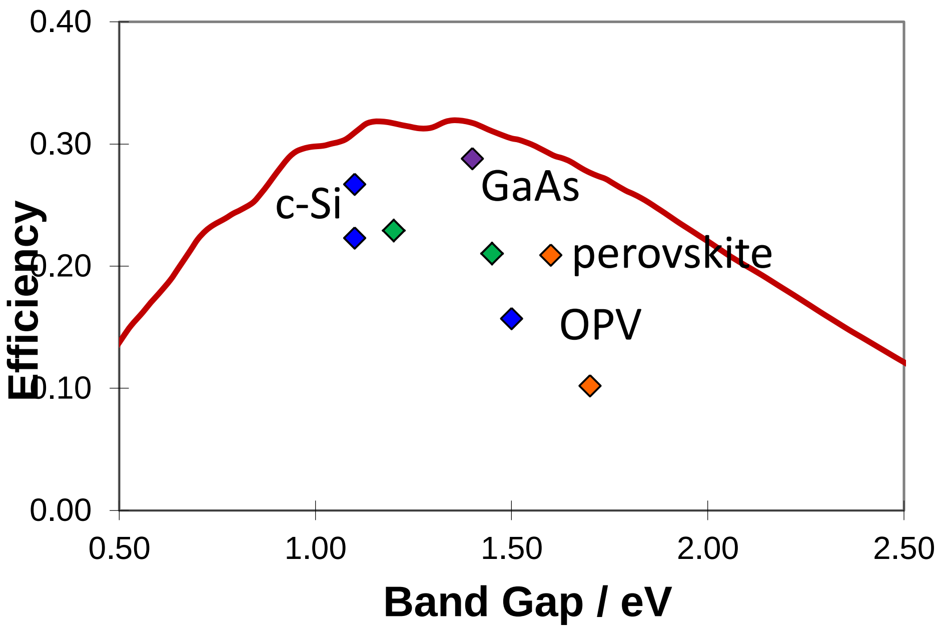


In the ideal (detailed balance) case:
Energy is lost through transmission, relaxation and radiative recombination

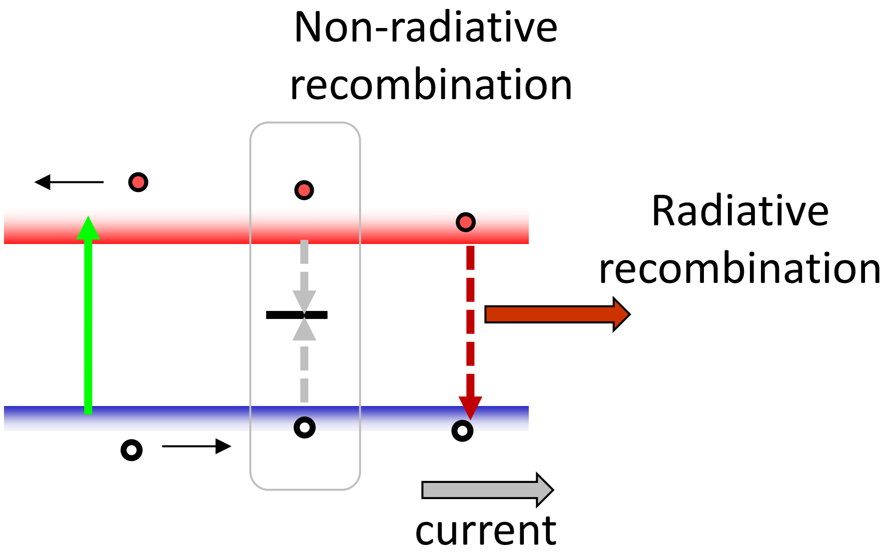
Limiting efficiency depends only on the band gap (and the concentration factor of the light)



Practical and limiting efficiencies

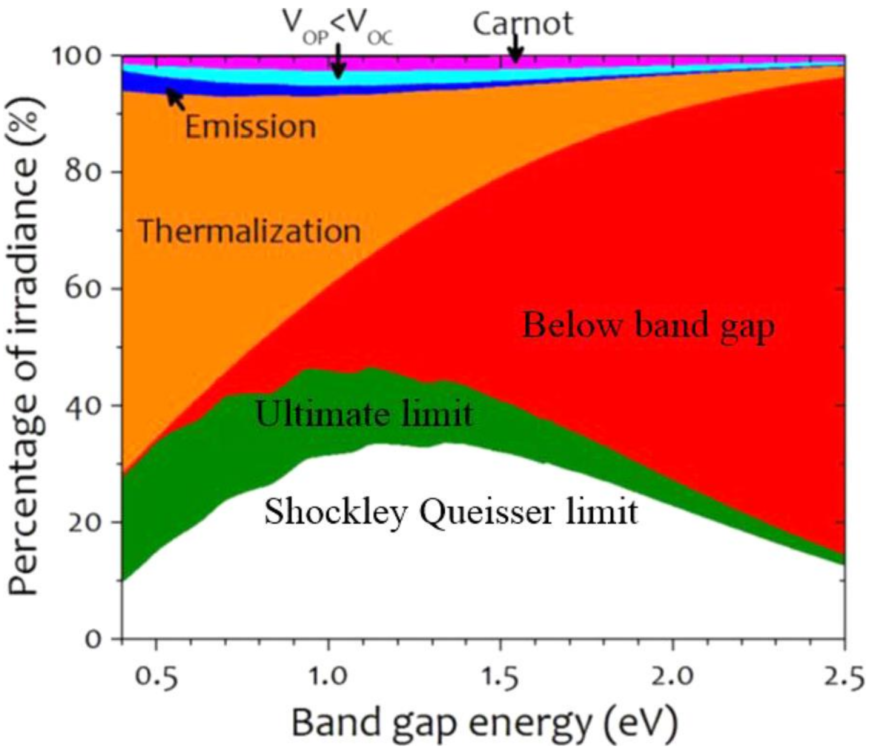


In practice:
Energy is lost through transmission, reflection, relaxation, radiative and non-radiative recombination



Practical and limiting efficiencies

Haverkort et al, Appl. Phys. Rev. (2018)

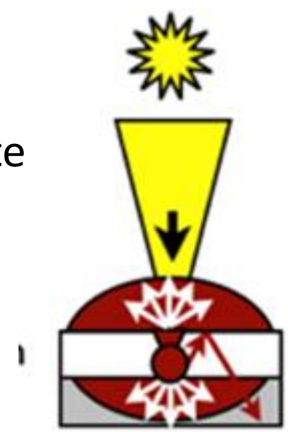


In the ideal (detailed balance) case:
Energy is lost through radiative recombination.

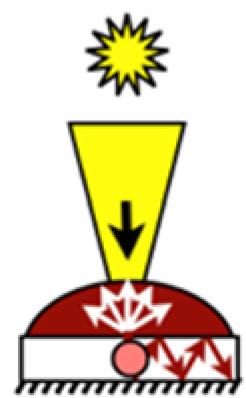
Part of the loss is due to the difference in angular range of absorbed and emitted light. Restricting the angular range of emission brings efficiency closer to the maximal concentration limit

Absorbing substrate

Efficiency: 24.8 %



Spire Corp, IEEE Tr. Electron Dev. 37, 469 (1990)



Optical confinement in a thin-film structure

Efficiency: 28.8 %

Alta Devices, Prog. Photovoltaics 20, 606 (2012)

How bad are the assumptions?

(i) One electron hole pair per photon with $h\nu > E_g$,

Overestimate current by 10-20%

(ii) Carriers relax to form separate Fermi distributions at lattice temperature $T_{ambient}$ with quasi Fermi levels separated by $\Delta\mu$.

~ OK

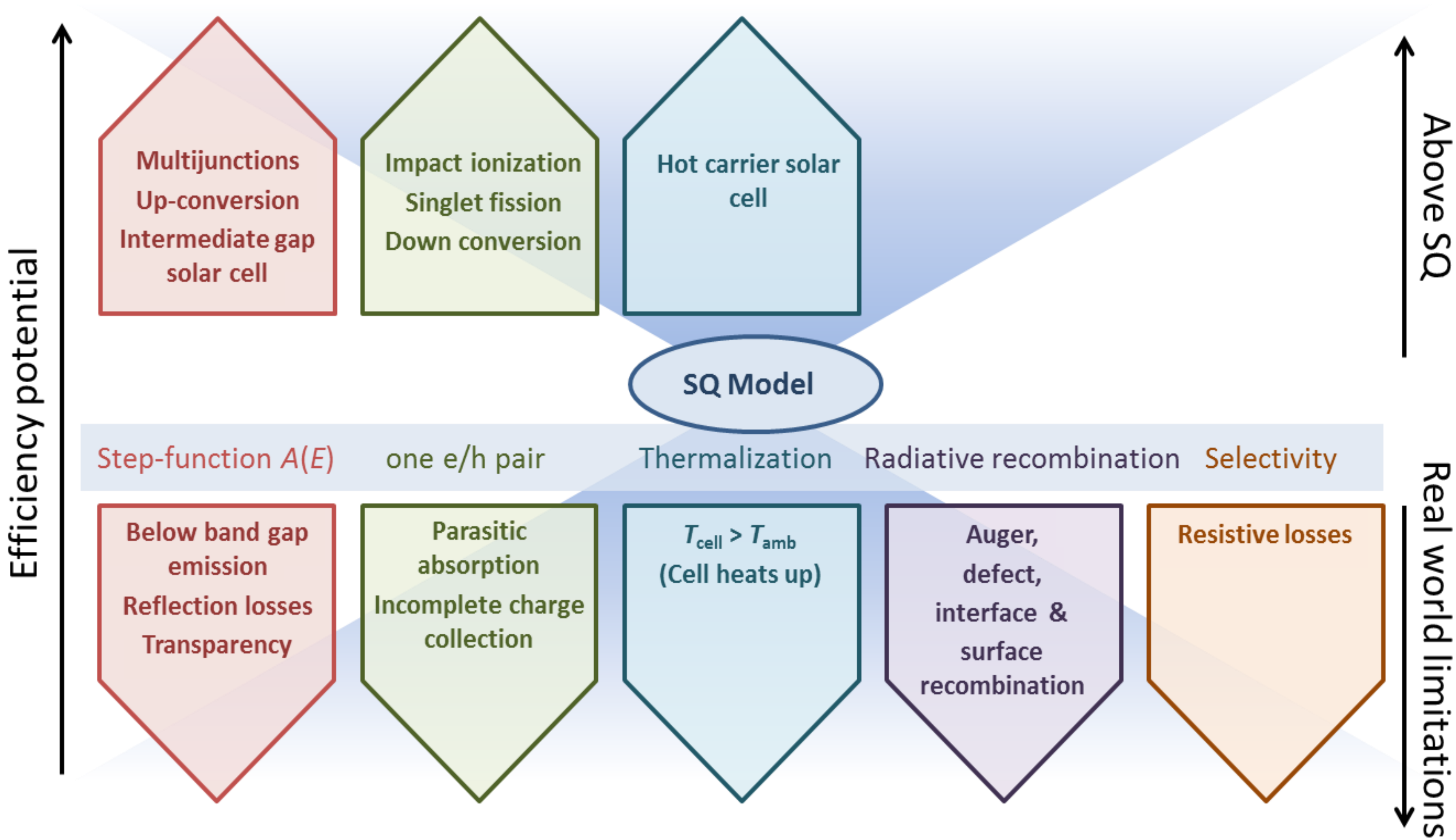
(iii) All electrons extracted with same electrochemical potential $\Delta\mu = qV$

Overestimate eV_{oc} by O(0.1 eV)

(iv) Only loss process is spontaneous emission

Overestimate qV_{oc} by several 0.1 eV
Overestimate fill factor

Assumptions in the Shockley Queisser limit

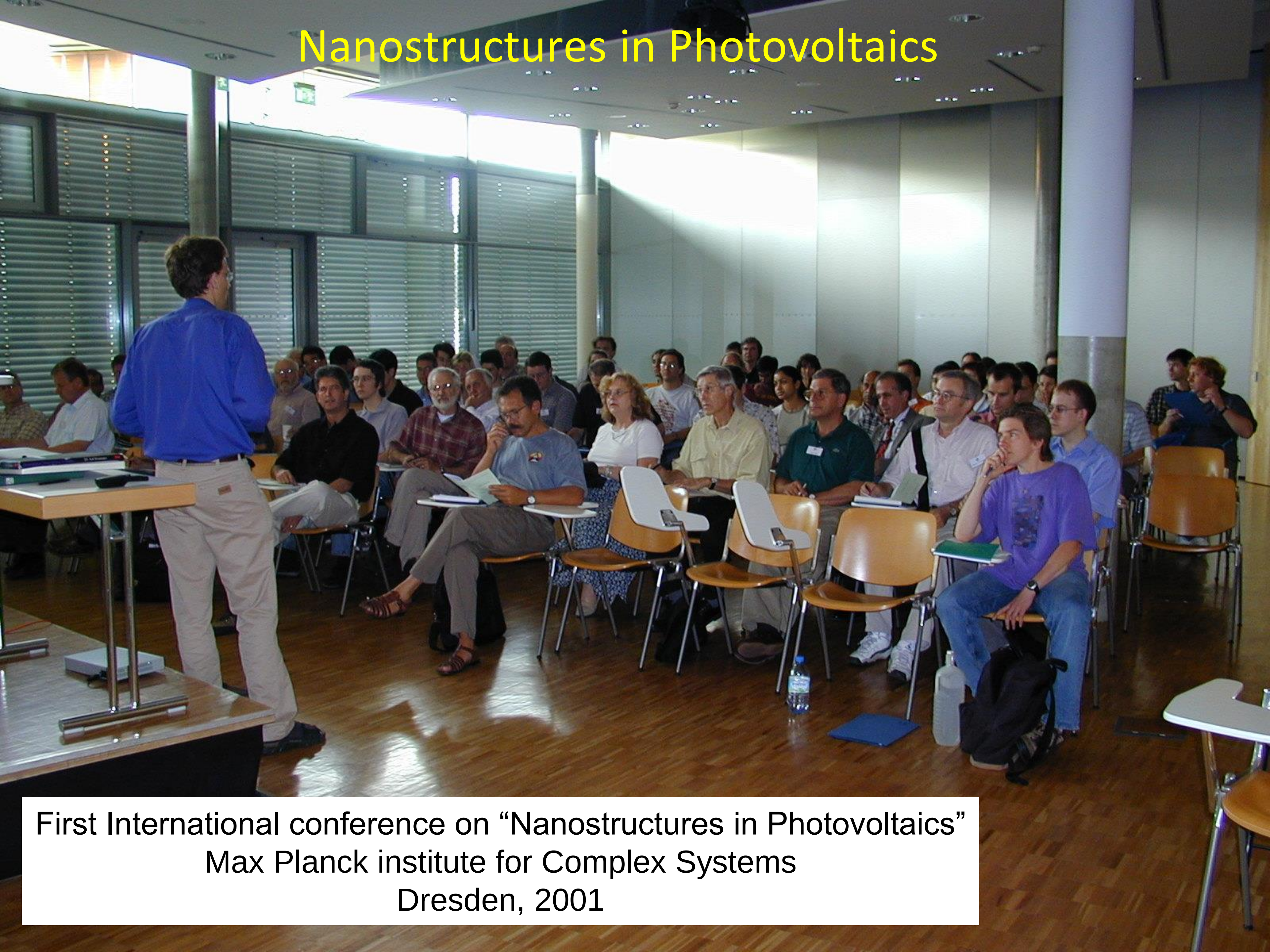


Slide: courtesy Thomas Kirchartz

Outline

- **Photovoltaic energy conversion**
- **Limiting efficiency of solar cells**
- **Nanostructures in photovoltaics**
- **Routes to more work per photon**
- **Nanomaterials to approach the efficiency limit**
- **Nanomaterials to reduce costs**

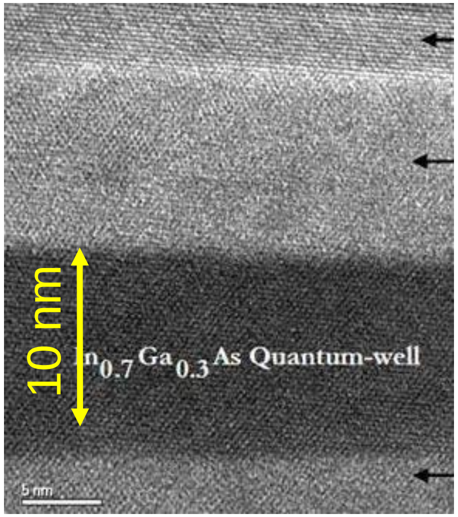
Nanostructures in Photovoltaics



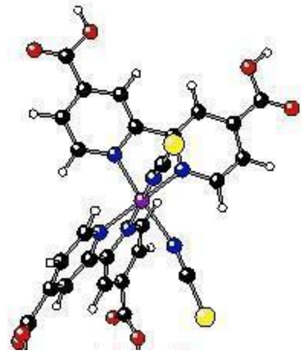
First International conference on “Nanostructures in Photovoltaics”
Max Planck institute for Complex Systems
Dresden, 2001

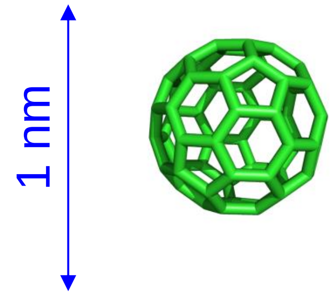
Photovoltaic “nano”-materials

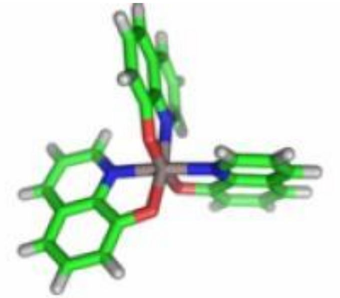
quantum well



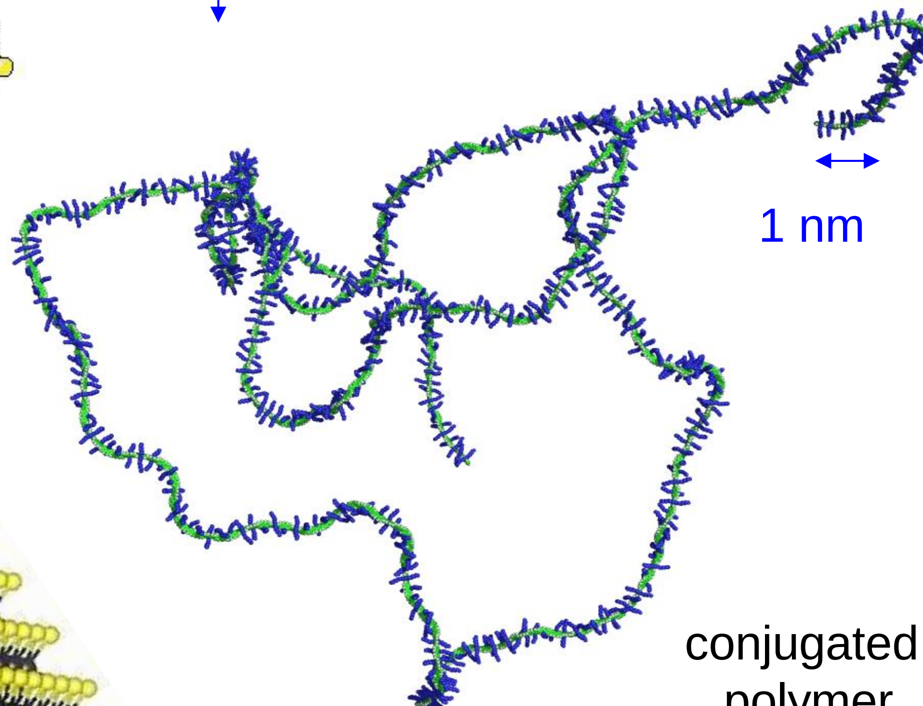
dye



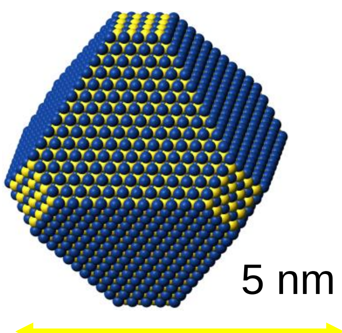




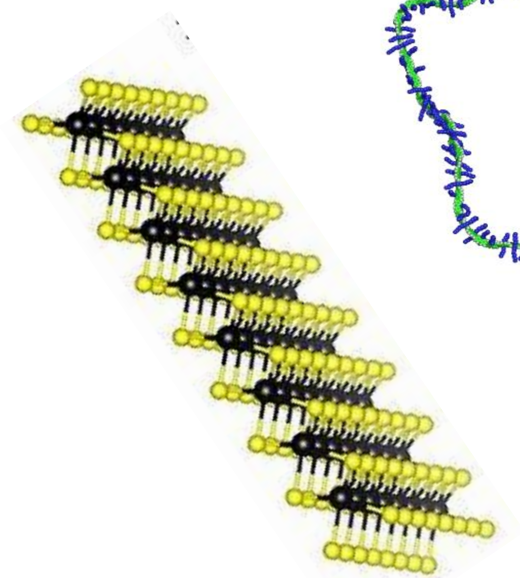
conjugated molecule



conjugated polymer

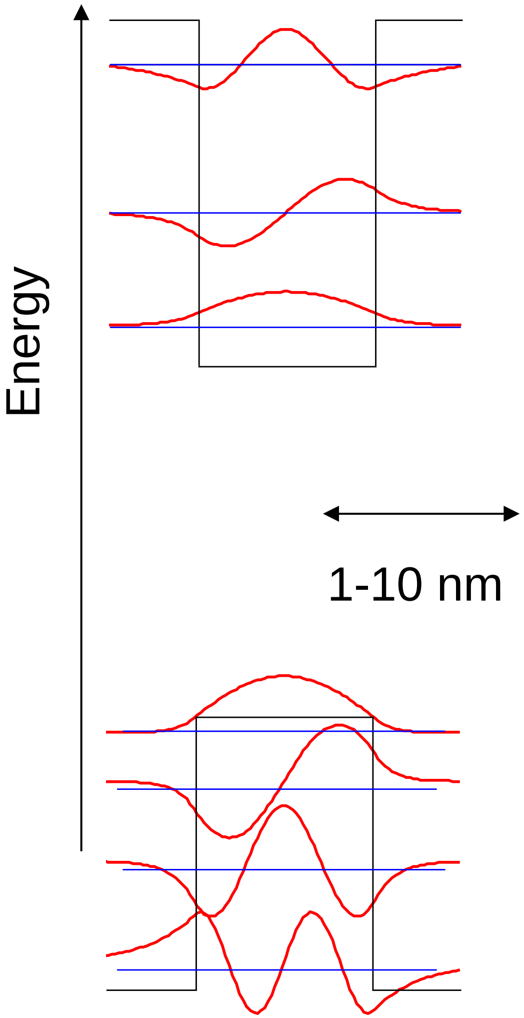


nanocrystal



2D transition metal chalcogenide

Properties of nanomaterials for use in photovoltaics



- Control of the electronic density of states
- Control of the phonon density of states
- Anisotropy in electronic and optical properties
- Access new spectral ranges
- Manipulate the optical response

How can nanomaterials help PV efficiency?

- **Surpass** the SQ efficiency limit (?)
- **Approach** the SQ efficiency limit with imperfect materials
- **Reduce the cost** of reaching a given efficiency

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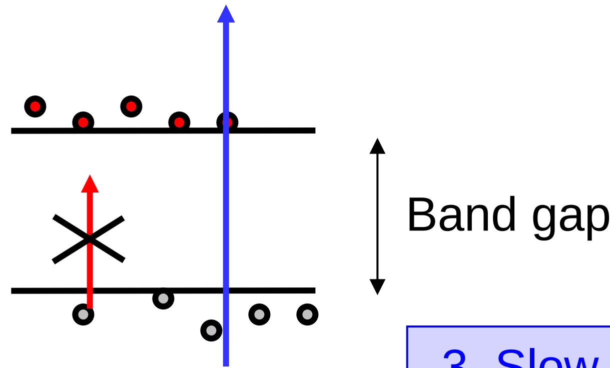
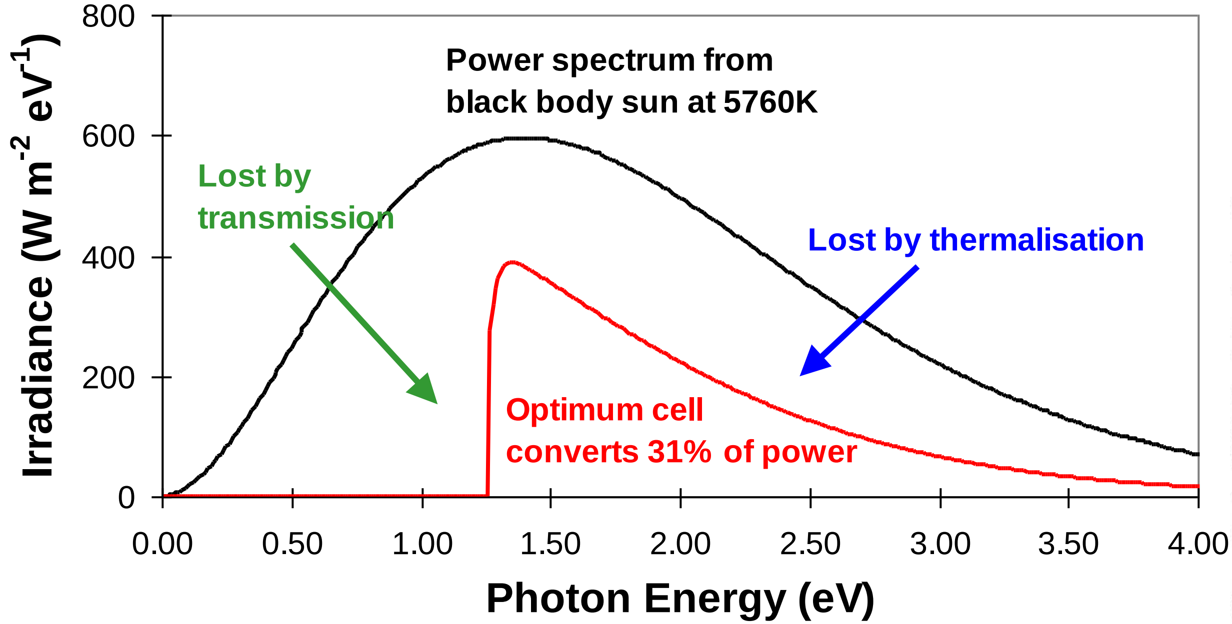
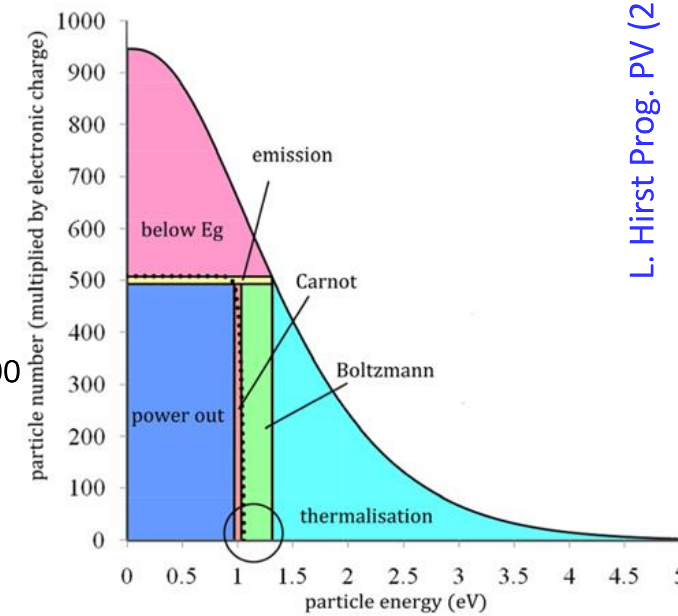
Routes to more work per photon



2. Spectral conversion

3. Slow carrier cooling

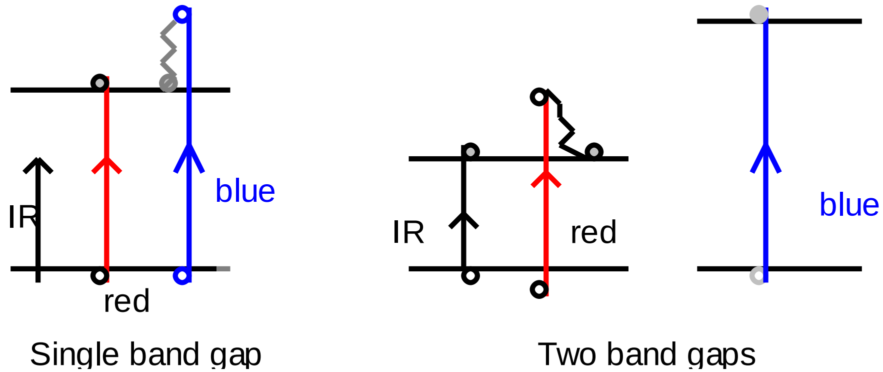


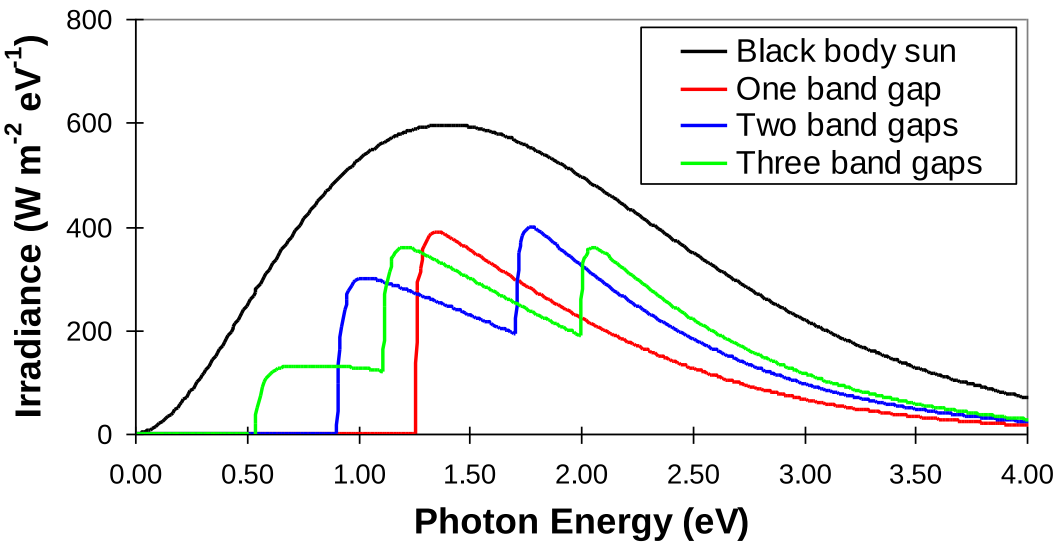


L. Hirst Prog. PV (2011)

1. More band gaps

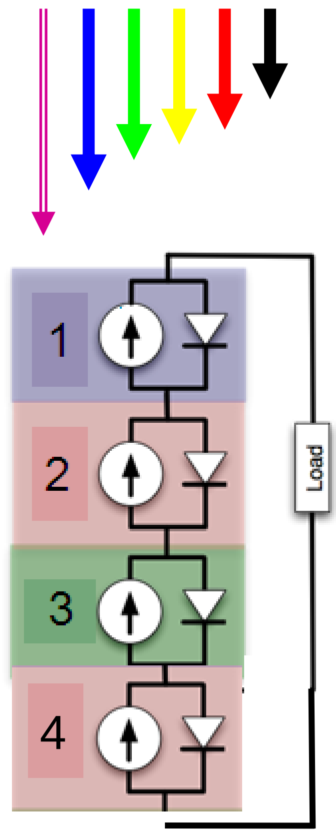
Route 1. Higher efficiency via multiple band gaps



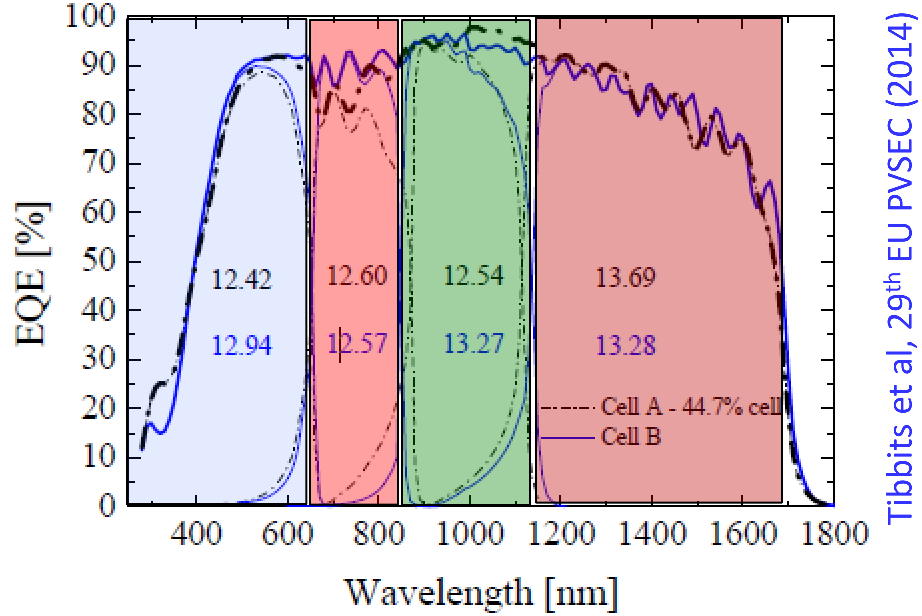


- Multi-junction structures or spectral splitting

III-V Multi-Junction Solar Cells



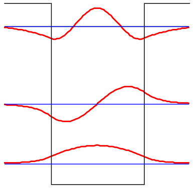
η = 46.5% at 300 Suns

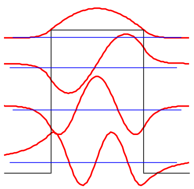


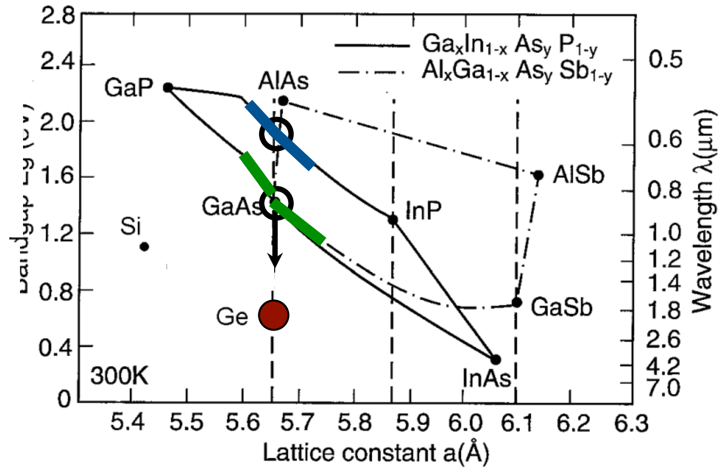
- Limiting efficiency around 46% for a monolithic four-junction cell under concentration

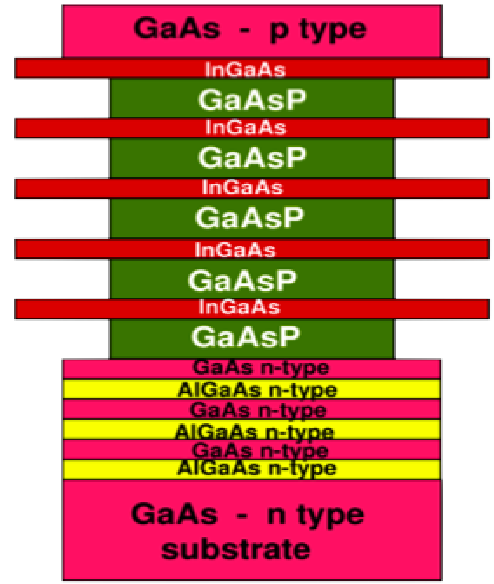
This works, but multijunction III-V structures are expensive to grow

Using nanostructures to achieve multiple band gaps

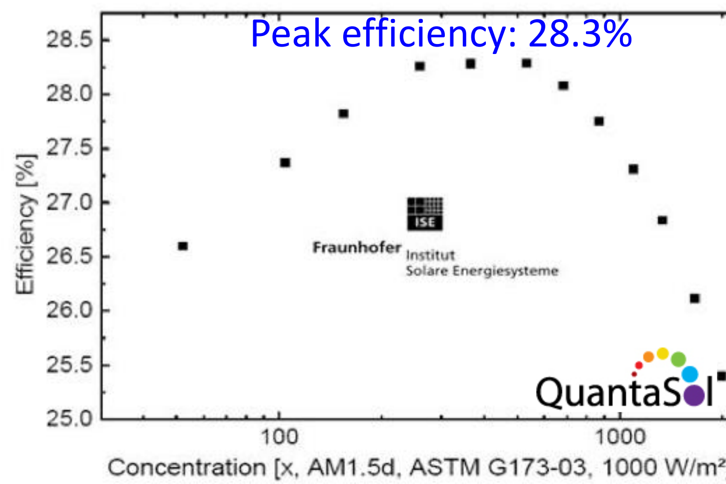








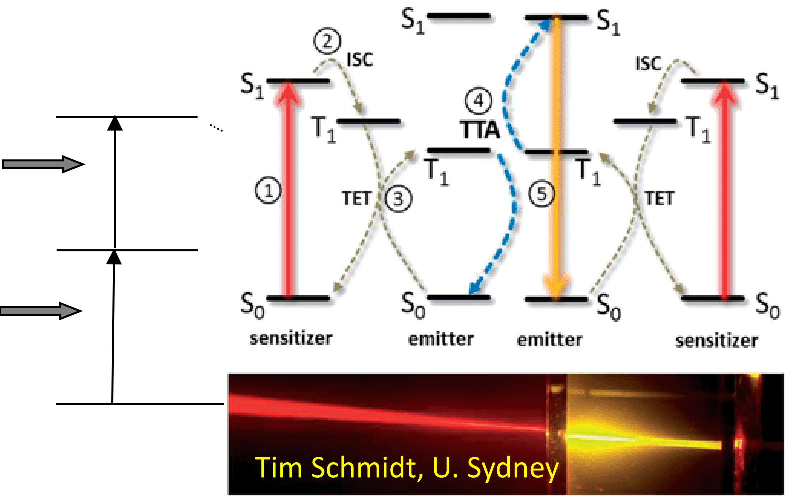
- Quantum well structures could be used to achieve target band gaps for monolithic multi-junctions on selected substrates

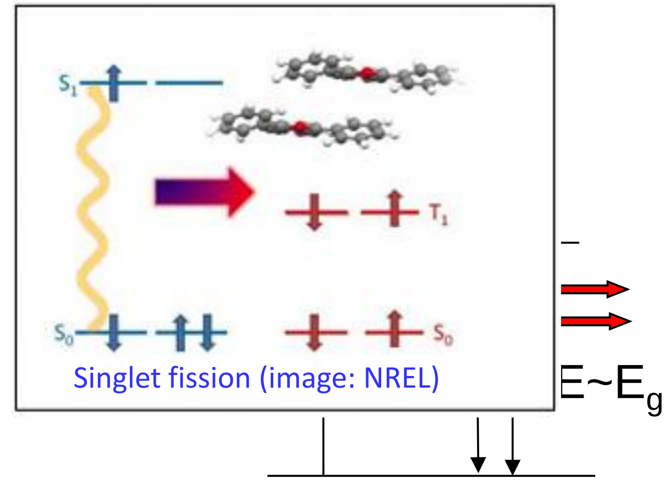


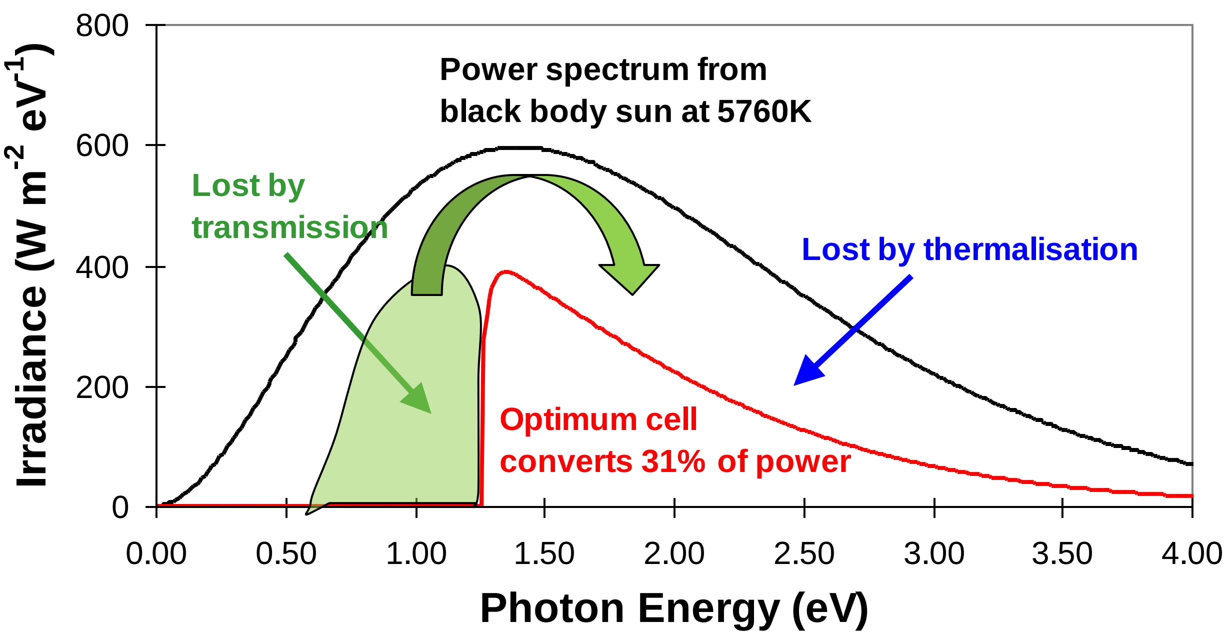
- Strained layer quantum well solar cell: effectively a single junction device

N. J. Ekins-Daukes, et. al., Appl. Phys. Lett., 75, p 4195, (1999)

Route 2. Reshaping the spectrum by up and down-conversion

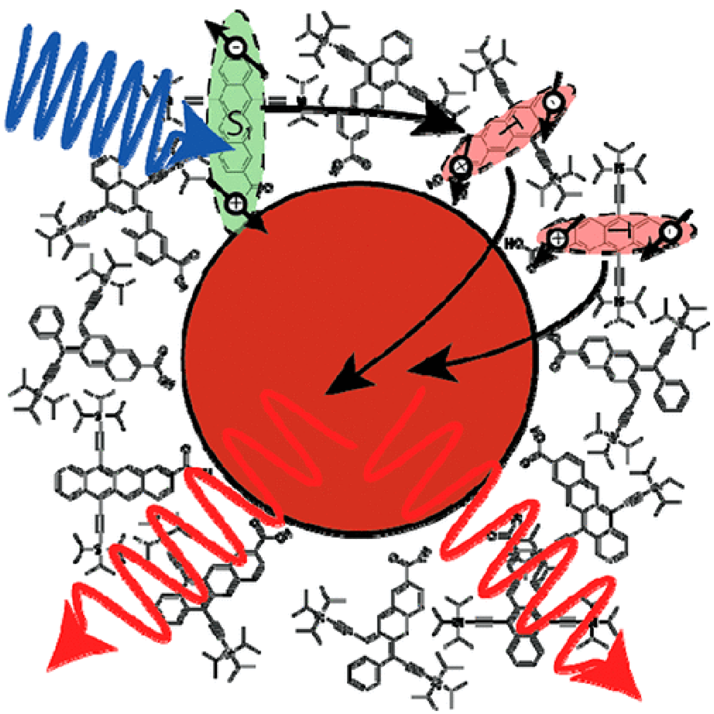


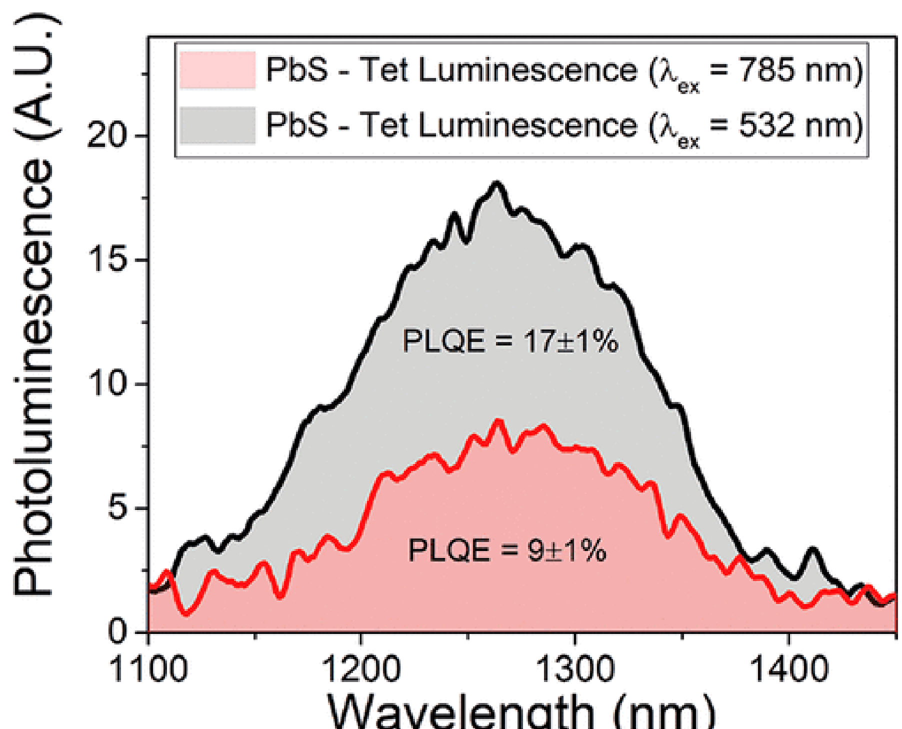




Singlet fission as a downconversion strategy

- Singlet fission: high energy singlet excitons converted efficiently into triplet pairs in some molecular materials
  - Separate triplets into e – h pairs OR
  - Convert into IR luminescence by energy transfer to nanoparticles
- Goal of an optical coating on silicon

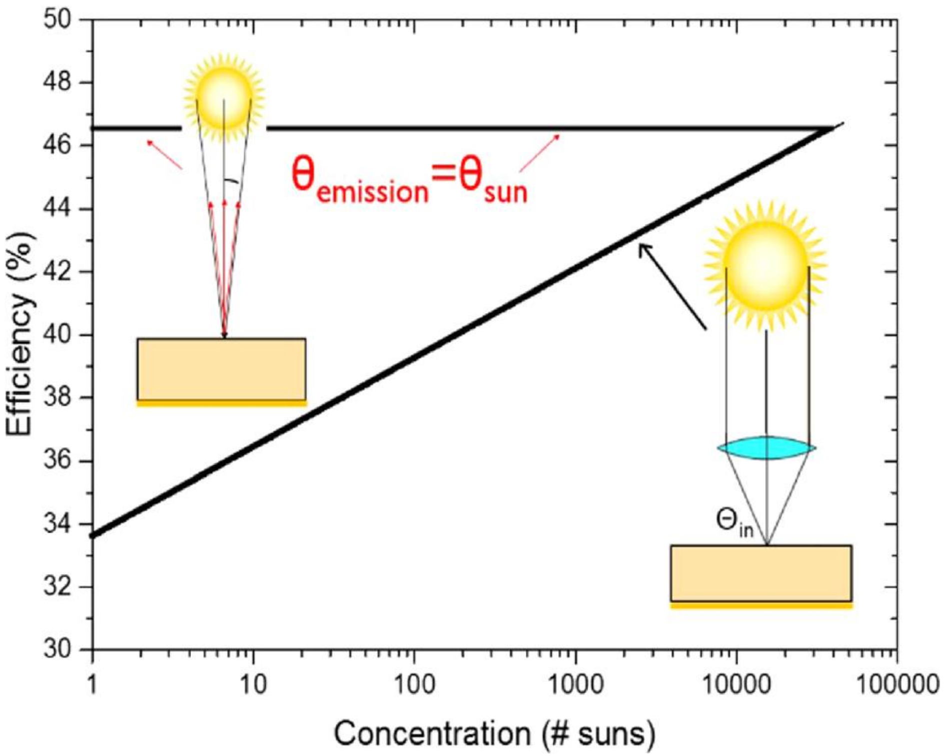


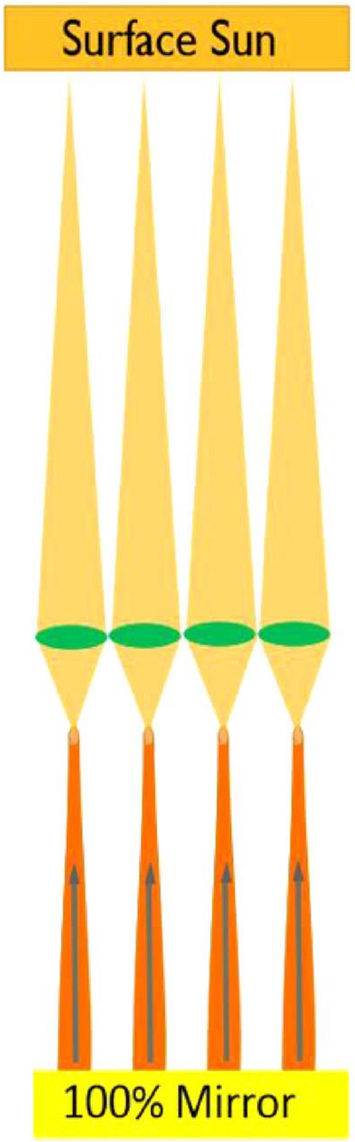


Rao and Friend, Nature Reviews Materials (2017); Davis et al. J. Phys. Chem. Lett. (2018) 961454-1460

Reducing the photon entropy loss

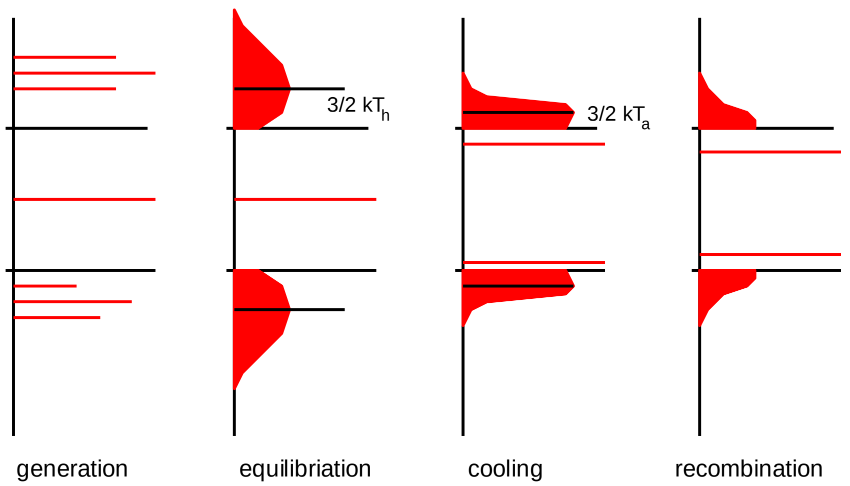
- Approach the 'ultimate' efficiency by restricting the angular range of emission to match the range of absorption.
- May be possible by engineering the optical modes of semiconductor nanowires

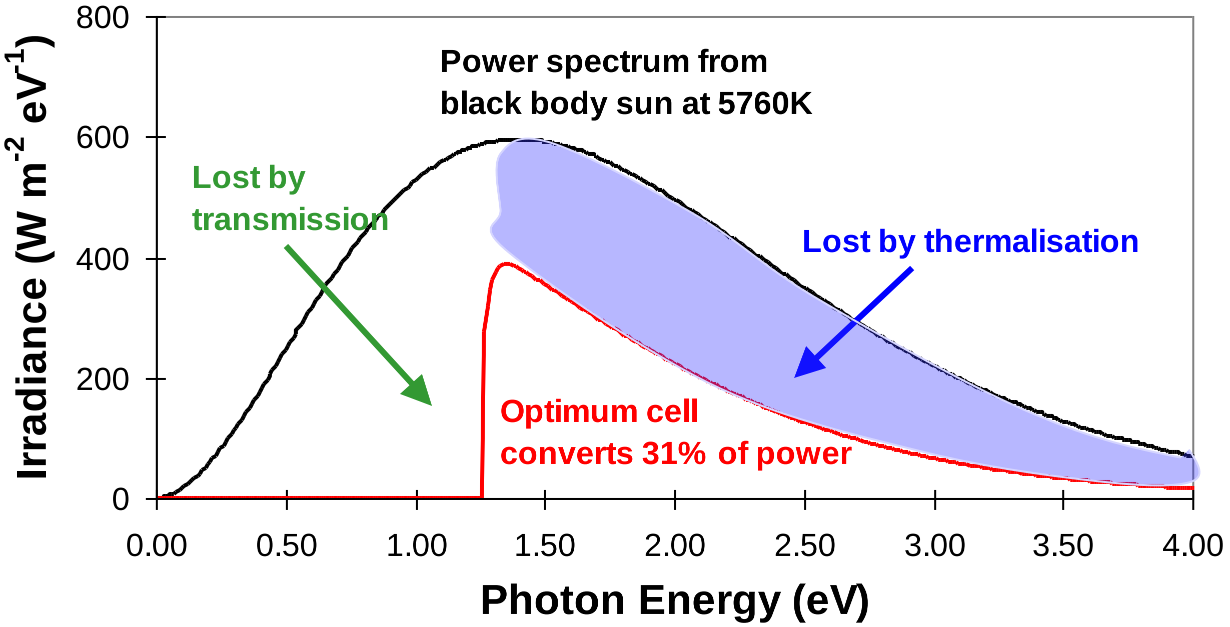




Haverkort et al., Appl. Phys. Rev. 5, 031106 (2018)

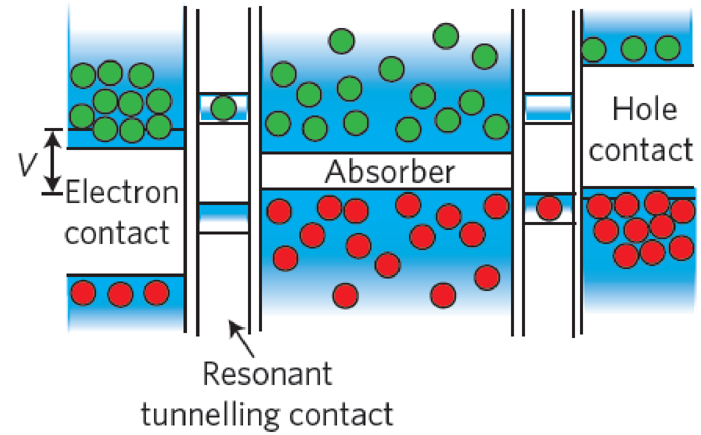
Route 3: More work per photon by slowed cooling





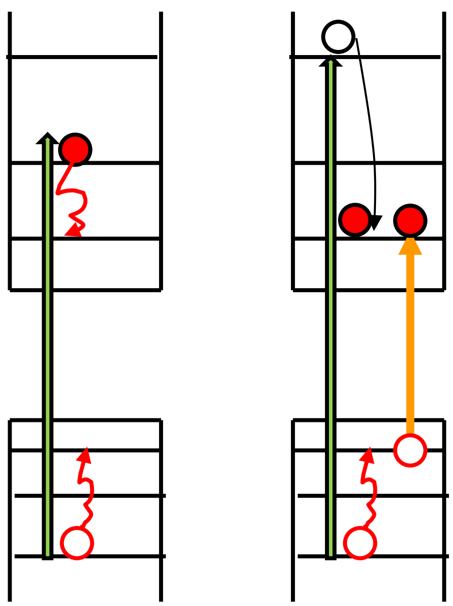
Reduced thermalisation in solar cells

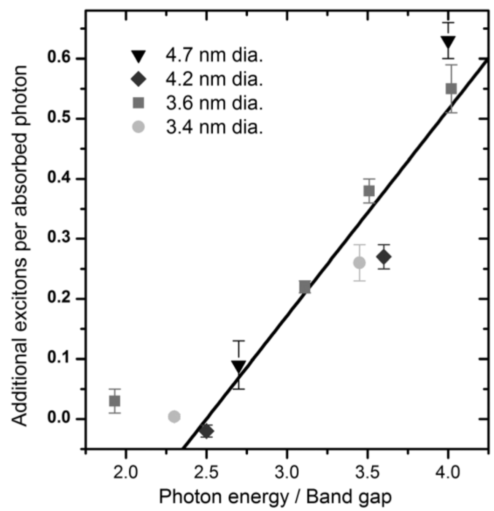
- Eliminating thermalisation of charge carriers with environment could increase efficiency to 85% but not physically achievable



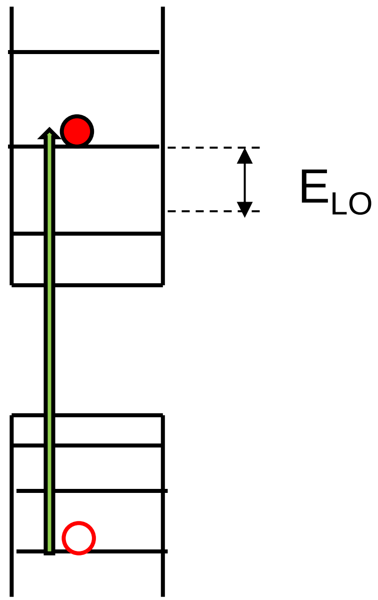
Green and Bremner Nat. Mater 2017

- Approaches that have been studied:
  - Multiple exciton generation
  - Slow cooling via “phonon bottleneck”





Hardman et al., *PCCP* 2011 DOI: 10.1039/c1cp22330e;
Schaller Phys. Rev. Lett 92, pp.186601 (2004)

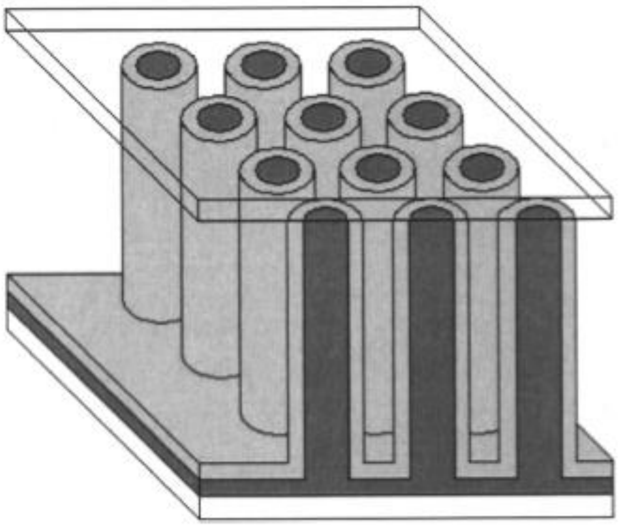


Outline

- Photovoltaic energy conversion
- Limiting efficiency of solar cells
- Nanostructures in photovoltaics
- Routes to more work per photon
- Nanomaterials to approach the efficiency limit
- Nanomaterials to reduce costs

Nanostructures to improve charge collection

- Radial nanowire solar cells can outperform planar junctions only when diffusion length << absorption depth
- Helps to approach limiting efficiency in poor quality semiconductors

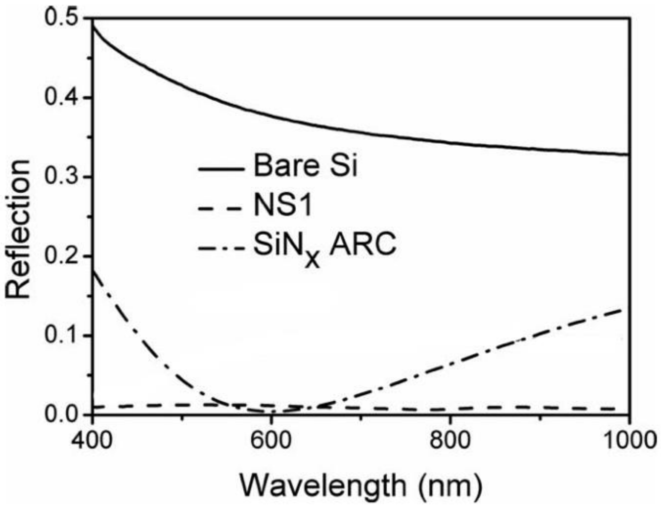


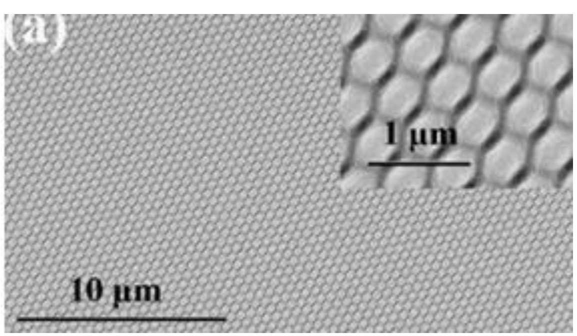
- Comparable to the use of 'bulk heterojunctions' in molecular photovoltaics

B.Kayes et al. Journal of Applied Physics (2005) vol. 97 (11) pp. 114302

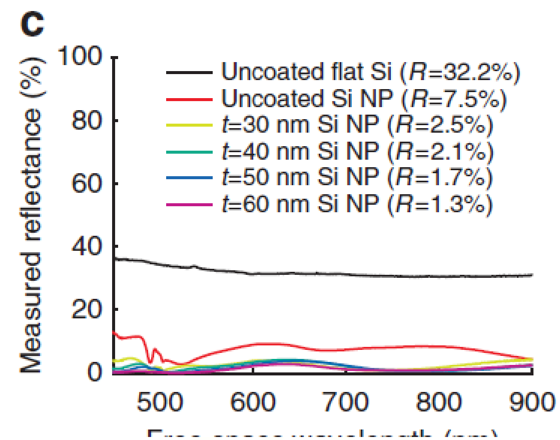
Nanostructures to reduce light reflection

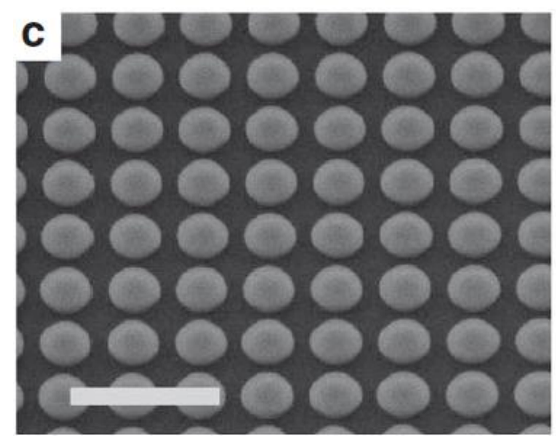
- Array of low geometrical cross section nanowires results in low refractive index and weak refection





- Exploit forward Mie scattering into high index substrate to reduce reflection

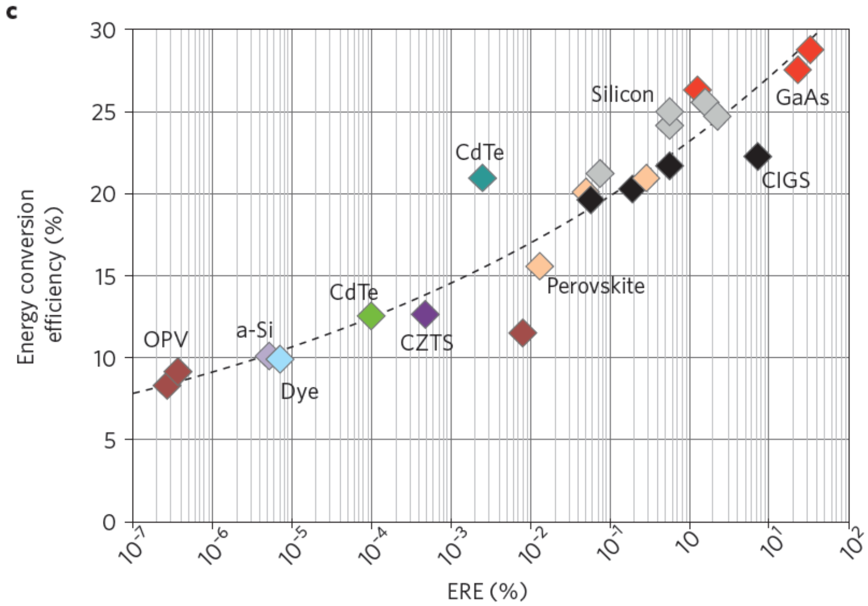




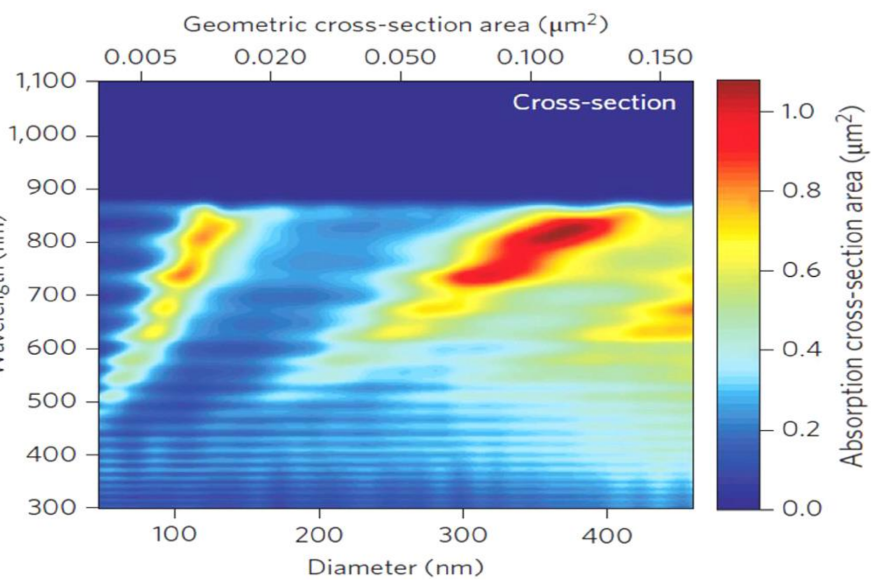
Chen et al. Applied Physics Letters (2009) vol. 94 (26) pp. 263118

Spinelli et al., Nat. Comm. 2012

Nanostructures to improve the radiative efficiency

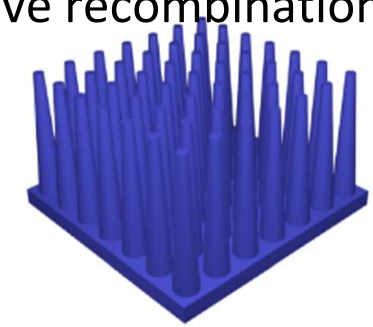


Green and Bremner Nat. Mater 2017

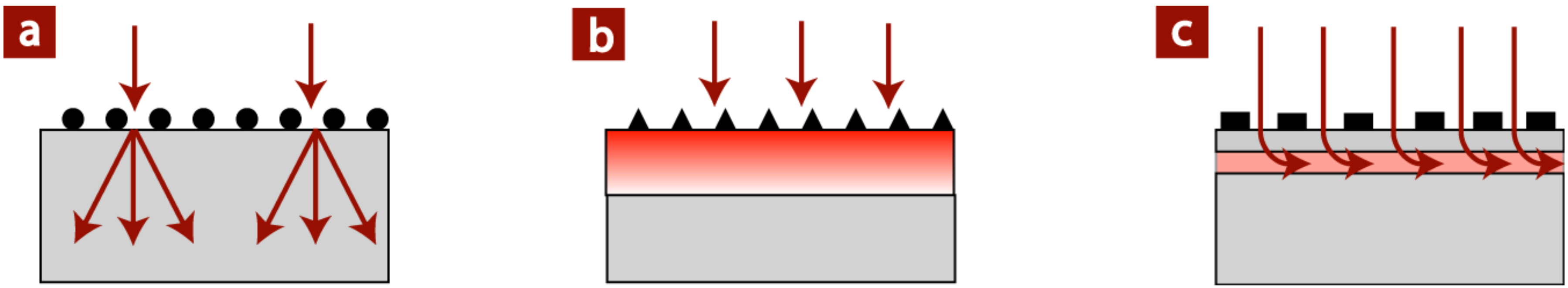


Nat. Photonics, 7, 306–310 (2013)

- Nanowires can show optical cross section > 10x geometrical
- If recombination is proportional to bulk volume can enhance generation relative to non-radiative recombination



Use of Plasmonics in Photovoltaics



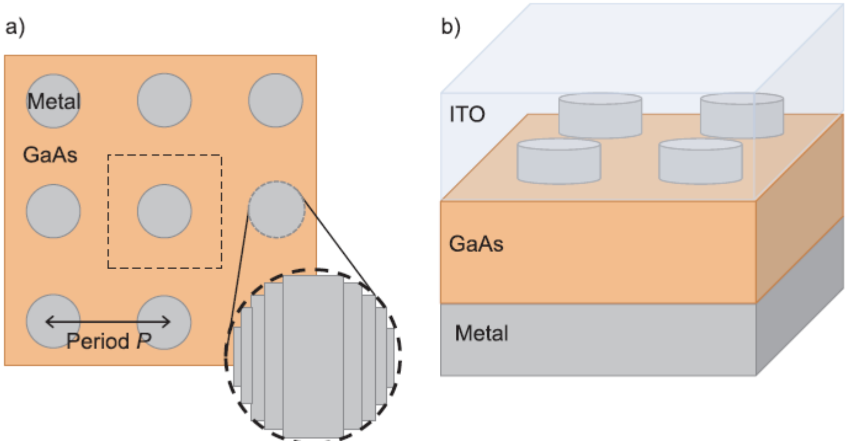
Internal Scattering

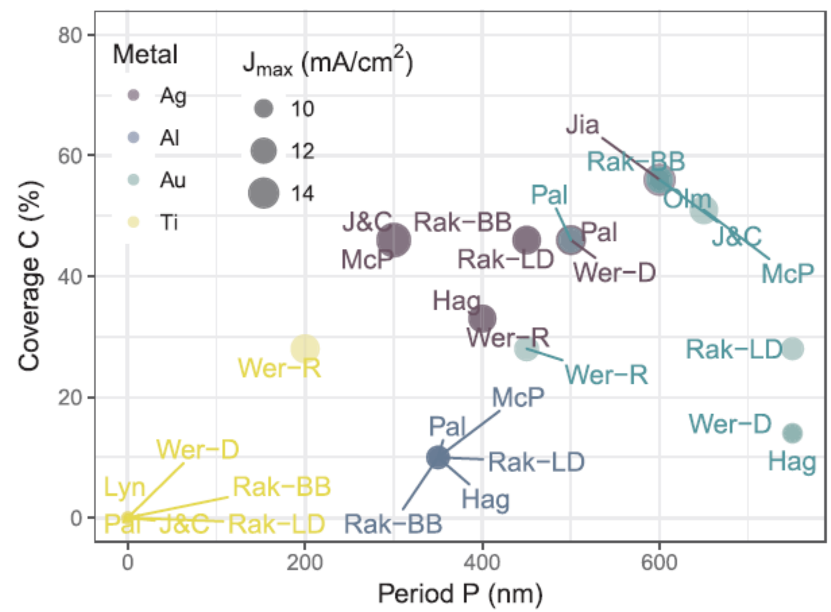
Field Enhancement

Surface Plasmon Polariton Propagation

Use of Plasmonics in Photovoltaics

- Design of nanostructures for plasmonic enhancement depends strongly on accurate knowledge of the dielectric function of the metal used!





See poster by Phoebe Pearce at this meeting

P. Pearce et al., *Solar Energy Materials and Solar Cells* 191 (2019) 133–140

Outline

- **Photovoltaic energy conversion**
- **Limiting efficiency of solar cells**
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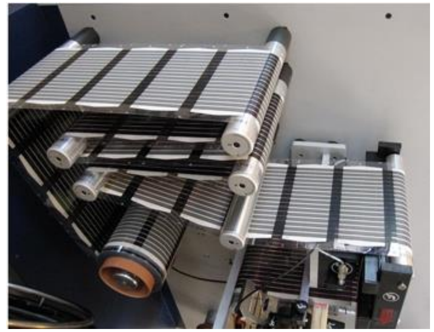
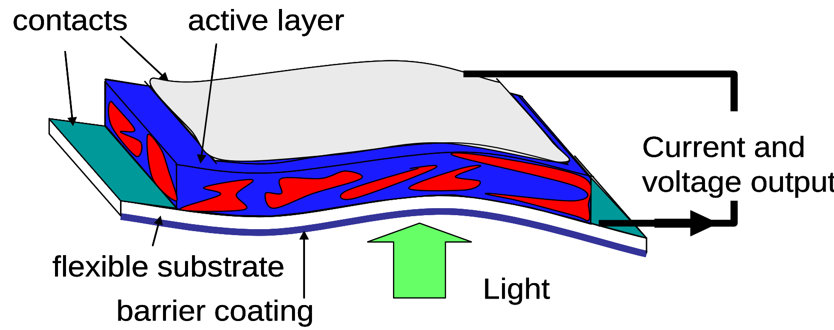
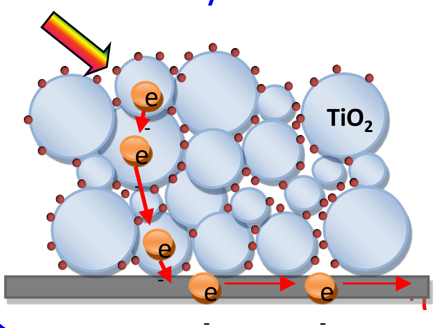
Printable photovoltaics



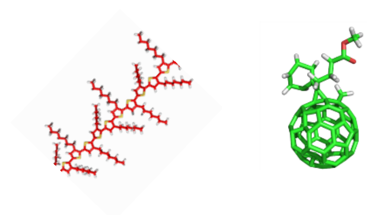


1990- Dye sensitised



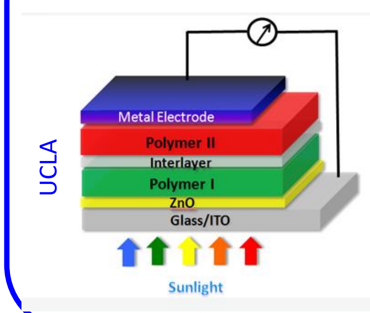
η ~ 13%

2001- Organic (polymer:C60)



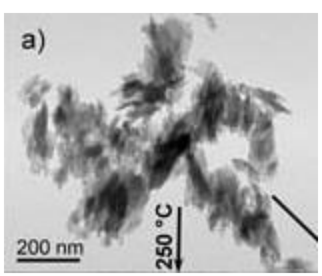
η ~ 16%

2007- Organic tandem



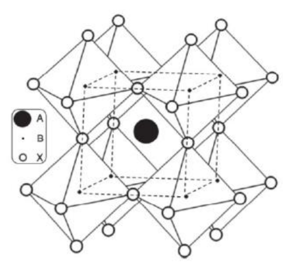
η ~ 17%

2010- Particle slurry CZTS



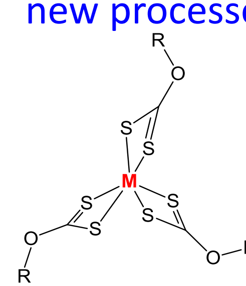
η ~ 13%

2012- Perovskite



η ~ 22%

Other new materials and new processes ...



Summary

- Photovoltaic energy conversion efficiency is limited to 33% in unconcentrated sunlight
- To approach this efficiency need to maximise radiative efficiency; to surpass it we need to reduce losses to light transmission and charge carrier thermalisation
- Nanostructures have capability to modify the electronic and optical density of states
- Several approaches proposed to achieving more work per photon
  - Upconversion, downconversion, multiple gaps, slowed cooling
  - Only multi-junctions are currently practically useful
- Most effective uses of nanostructures to raise efficiency are in manipulating light absorption and emission to approach the theoretical limit

Thank you for your attention!

Questions?