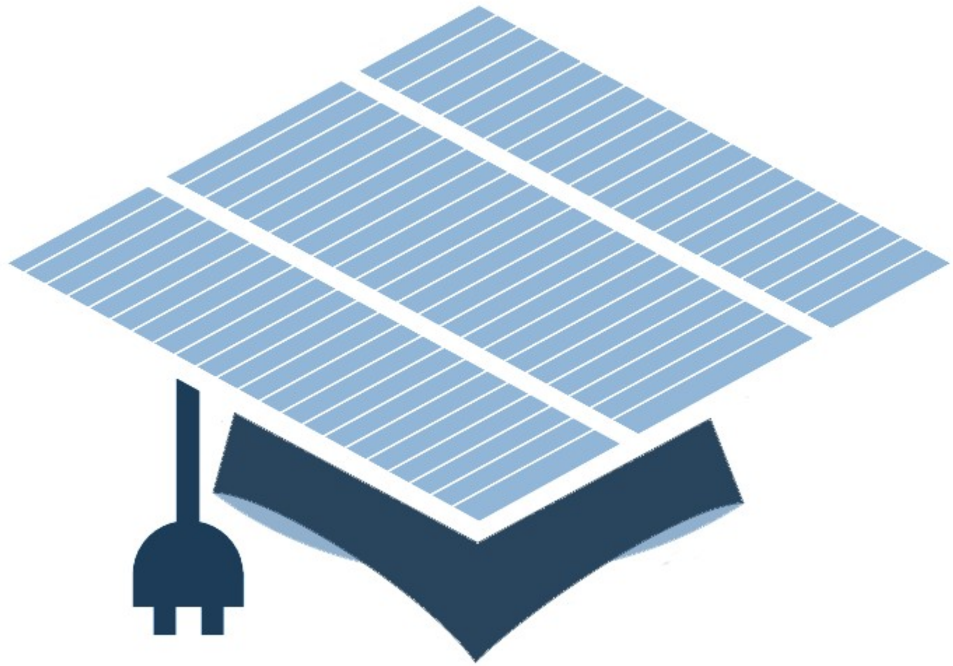


Lecture 3
Fundamental Limitations of Solar Cells

R. Treharne

Nov 5th 2014

UNIVERSITY OF LIVERPOOL

Why can't a solar cell have a 100% efficiency?

(Or even close to 100%?)

Can you answer this?

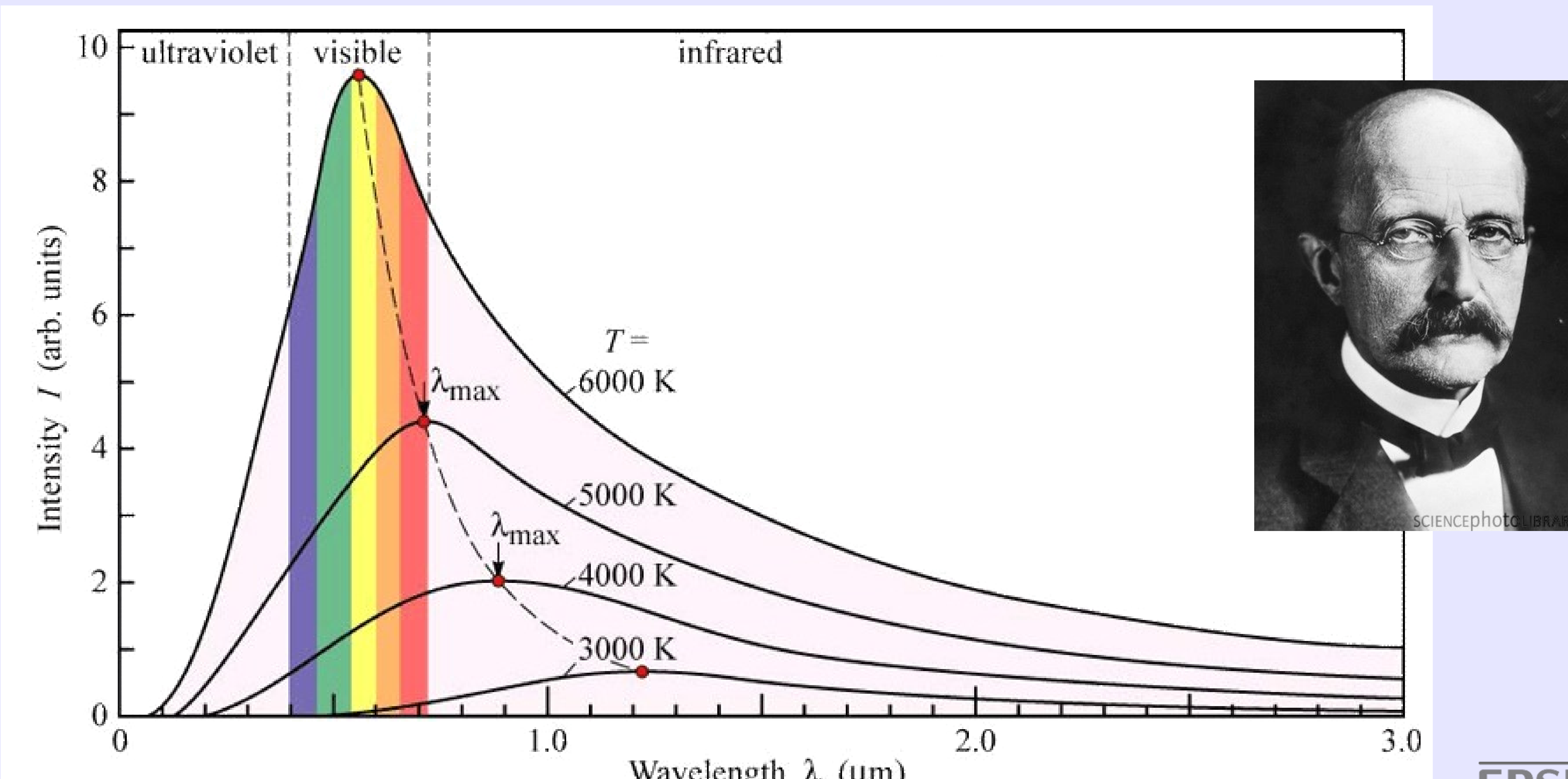
Lecture Outline

- Black Body Radiation
- Detailed Balance
- The Shockley-Queisser Limit
- Requirements for real physical systems
- Exceeding the SQ limit (funky solar)

Black Body Radiation

A **black body** absorbs all radiation regardless of frequency or angle of incidence.

A black body in thermal equilibrium emits radiation according to Planck's Law.



Planck's Law

Photon Flux – Number of photons of energy *E* per unit area per second

$$b(E) = \frac{2F}{h^3 c^2} \left(\frac{E^2}{e^{E/k_B T} - 1} \right)$$

Units – Number of photons of energy *E* per unit area per second

Planck's Law

Photon Flux density from a spherical black body

$$b(E)=\frac{2F}{h^3c^2}\left(\frac{E^2}{e^{E/k_BT}-1}\right)$$

Look familiar?

c.f. Ideal diode

Units – Number of photons of energy *E* per unit area per second

Planck's Law

Photon Flux – Number of photons of energy *E* per unit area per second

$$b(E)=\frac{2F}{h^3c^2}\left(\frac{E^2}{e^{E/k_BT}-1}\right)$$

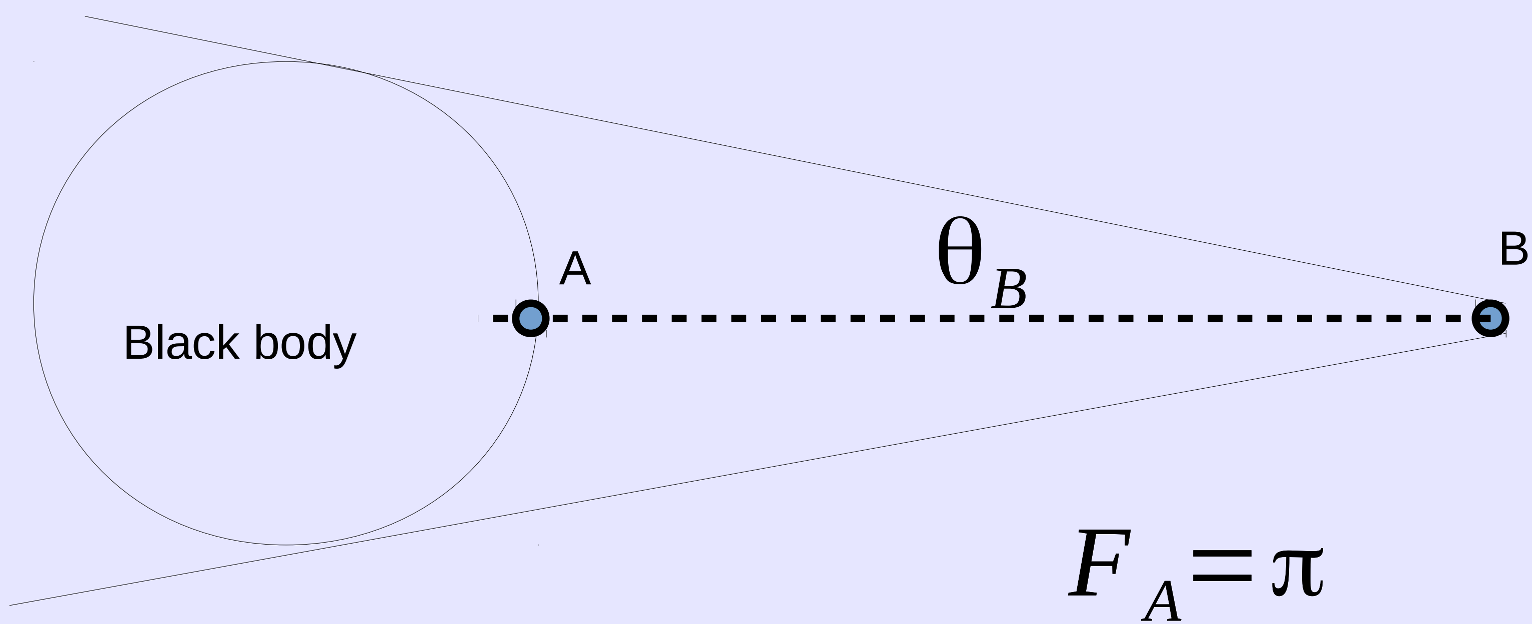
What the heck is this?

Units – Number of photons of energy *E* per unit area per second

Planck's Law

$$F = \pi \sin^2 \theta$$

Geometrical factor



$$F_A = \pi$$

$$F_B = \pi \sin^2(\theta_B)$$

Irradiance

Irradiance - Emitted energy flux density

$$L(E) = Eb(E)$$

This is what solar spectrum data is measured in

Irradiance

Irradiance - Emitted energy flux density

$$L(E) = Eb(E)$$

This is what solar spectrum data is measured in

Power Density given by

$$P = \int_0^\infty L(E)\,dE$$

EPSRC
Engineering and Physical Sciences Research Council

Irradiance

Irradiance - Emitted energy flux density

$$L(E) = Eb(E)$$

This is what solar spectrum data is measured in

Power Density given by

Stefan-Boltzmann Law

$$P = \int_0^\infty L(E)\,dE = \sigma_s T^4$$

$$\sigma_S = \frac{2\pi^5 k_B^4}{15 c^2 h^3}$$

Stefan's constant

EPSRC
Engineering and Physical Sciences
Research Council

The Sun (again)

The sun is a **black body emitter** with a temperature of 5760K

At its surface, the Power density is:

$$P_s = 62 \text{ MW m}^{-2}$$

what is the power density of the Sun's emitted radiation at the Earth's surface, P_E?

$$P_E = \frac{F_E}{F_S} P_S \sim 1353 \text{ m}^{-2}$$

Detailed Balance

What are we doing?

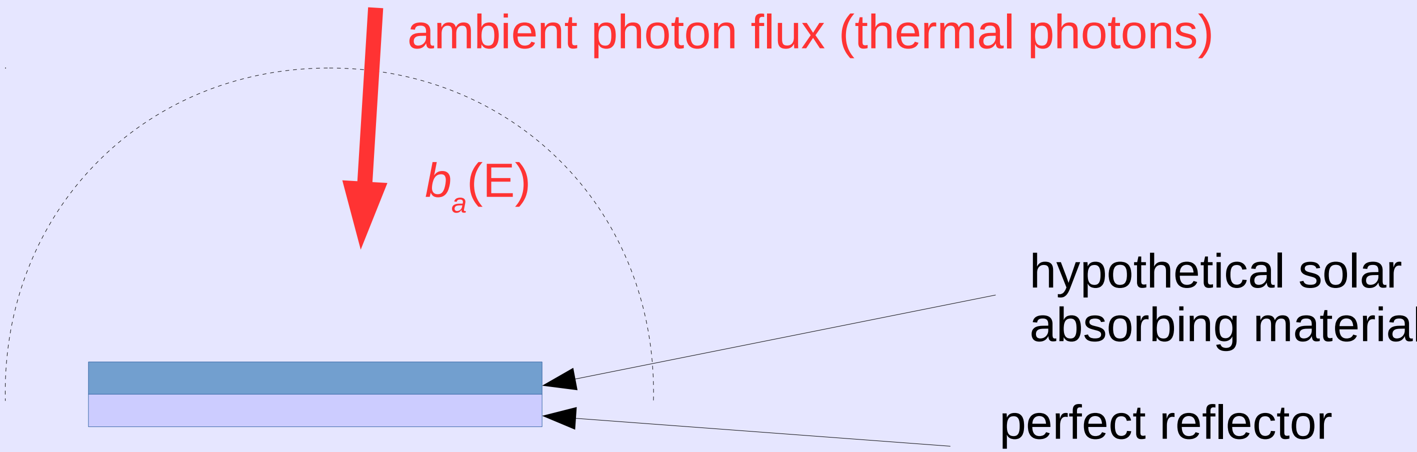
- Counting all photons going in
- Counting all photons going out
- Difference must be converted into electrical (electrochemical potential)

Key Assumptions

- Mobility of carriers is infinite
- All absorbed photons promote electrons
- Only one interface absorbs/emits – other side contacted to a “perfect reflector”

Detailed Balance

In equillibrium (i.e. in the dark)



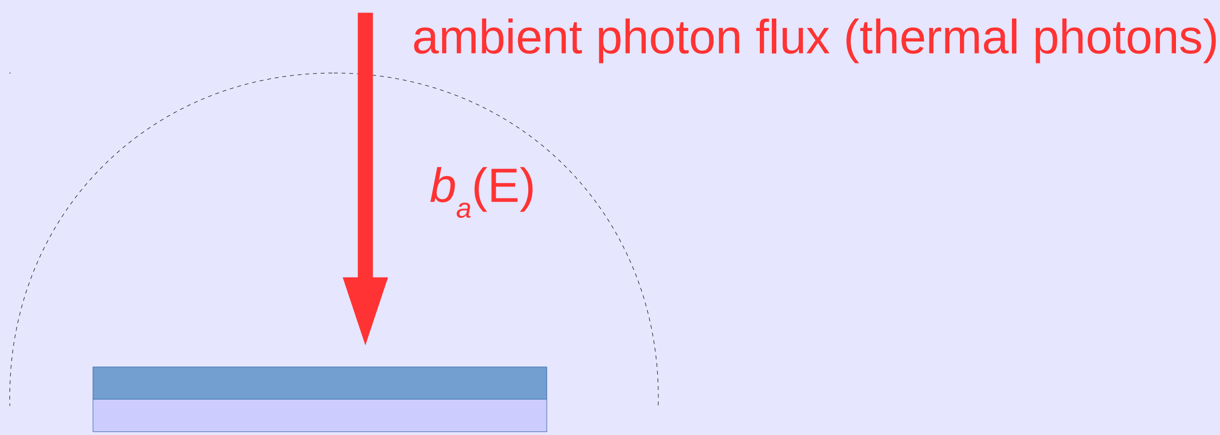
Ambient emits like black-body

$$b_a = \frac{2F_a}{h^3c^2}\left(\frac{E^2}{e^{E/k_B T_a} - 1}\right)$$

$$F_a = \pi$$

Detailed Balance

In equillibrium (i.e. in the dark)



Ambient emits like black-body

$$b_a = \frac{2F_a}{h^3c^2}\left(\frac{E^2}{e^{E/k_BT_a}-1}\right)$$

$$F_a = \pi$$

Reflectance

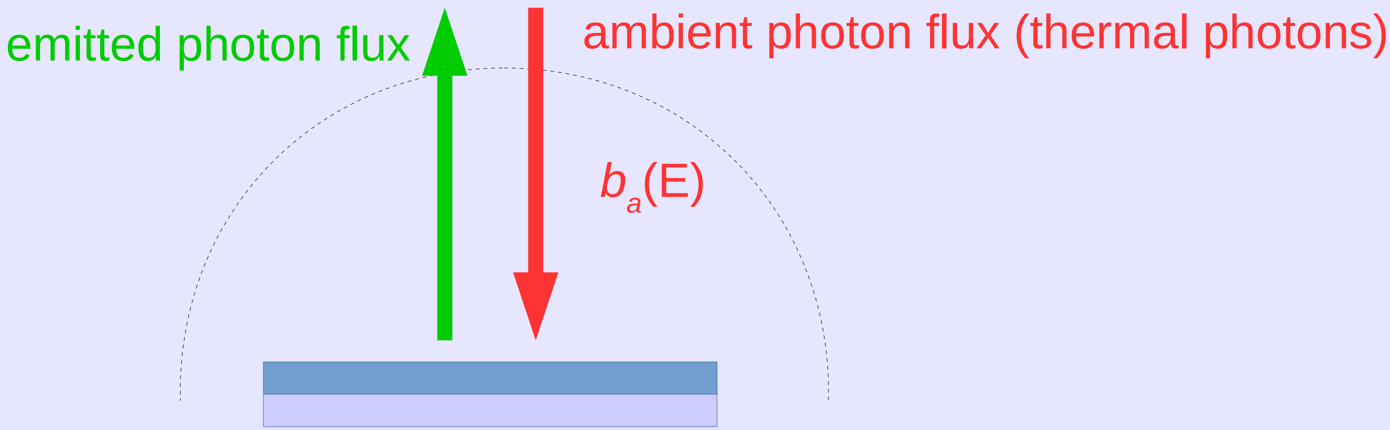
Absorbance

$$j_{abs} = q\left(1-R(E)\right)a(E)\,b_a(E)$$

Absorbed ambient results in an equivalent current density

Detailed Balance

In equillibrium (i.e. in the dark)



Device emits like black-body too!
Can think of as current in opposite direction to j_{abs}

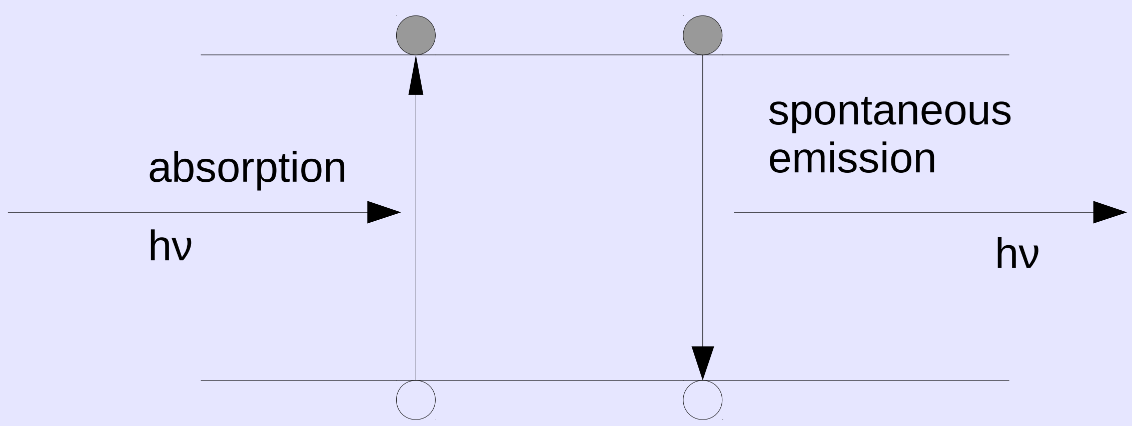
Reflectance
Emissivity

$$j_{rad} = -q\left(1 - R\left(E\right)\right)\varepsilon\left(E\right)b_a\left(E\right)$$

Detailed Balance

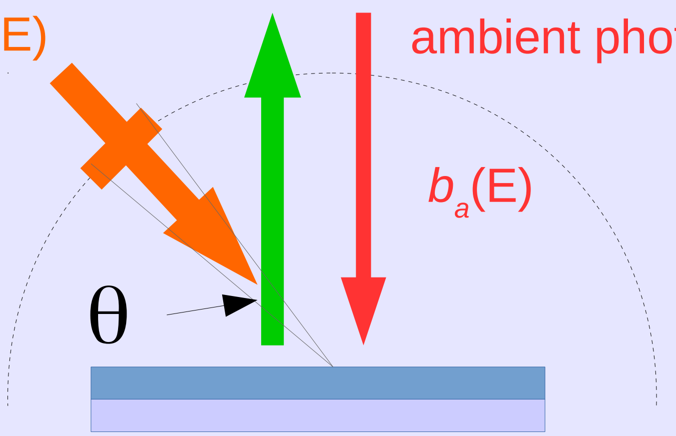
In equillibrium (i.e. in the dark)

$$j_{abs} + j_{rad} = 0 \longrightarrow a(E) = \varepsilon(E)$$



Absorption Rate = Spontaneous Emission Rate

Under Illumination (still steady state)



$$j_{abs} > j_{rad}$$

$$b_s = \frac{2F_s}{h^3c^2}\left(\frac{E^2}{e^{E/k_BT_s}-1}\right) \qquad F_s = \pi \sin^2\theta$$

But does emitted flux change? - YOU BETCHA!

Why? (if emitted flux remained the same as under thermal equilibrium conditions then you could have a solar cell with 100% efficiency)

EPSRC
Engineering and Physical Sciences Research Council

Detailed Balance

Under illumination part of the electron population has raised electrochemical potential energy – i.e. $\Delta\mu > 0$

This means that spontaneous emission is increased!

The emitted flux is increased by:

$$b_{e_s} = \frac{2\pi}{h^3 c^2} \left(\frac{E^2}{e^{(E-\Delta\mu)/k_B T_a} - 1} \right)$$

This is the reason why absorbed solar radiant energy can never be fully utilised in a solar cell.

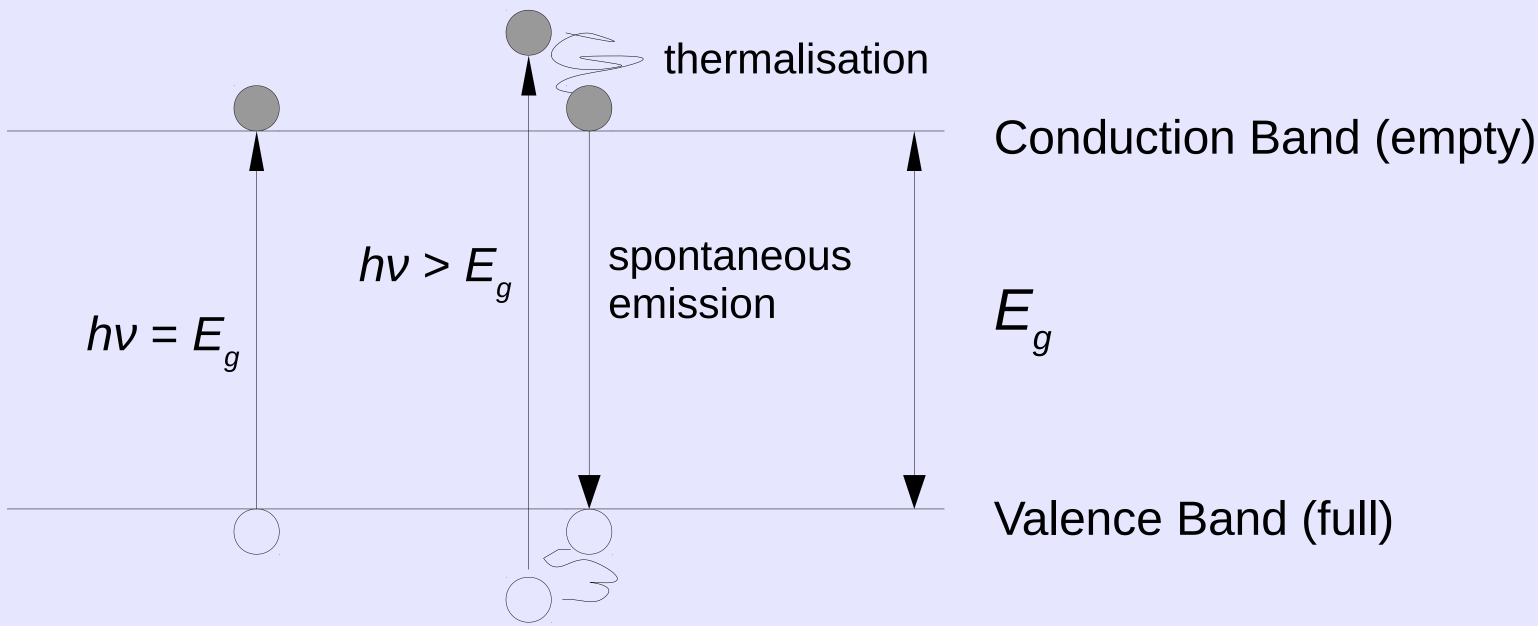
RADIATIVE RECOMBINATION

Max efficiency ~ 86%

This is all a bit abstract – I hope this will become more obvious when we talk about junctions.

EPSRC
Engineering and Physical Sciences Research Council

Two Level System



What sort of materials do we use for solar cells?

Semiconductors

Why?

Because they have a band gap!

No longer a perfect system because of:

THERMALISATION

Key Point

THERMALISATION:

Photons with $E > E_g$ promote carriers that relax to bottom of conduction band through scattering interactions with phonons (transfer of kinetic energy – heat!)

Absorbed photon with $E > E_g$ achieves the same result as $E = E_g$

Thermalisation is the most dominant loss mechanism that limits the efficiency

Photocurrent

Photo-current is due to the **net** absorbed flux due to the sun.
Can calculate by integrating j_{abs} over all photon energies:

$$J_{SC} = q\int_0^\infty C(E)(1-R(E))a(E)b_s(E)\,dE$$

Probability that promoted carriers are collected to "do work"

Photocurrent

Photo-current is due to the **net** absorbed flux due to the sun.
Can calculate by integrating j_{abs} over all photon energies:

$$J_{SC} = q\int_0^{\infty} C(E)(1-R(E))a(E)b_s(E)\,dE$$

Probability that promoted carriers are collected to “do work”

LOOK FAMILIAR?
This is the Quantum Efficiency (external)

Photocurrent

Photo-current is due to the **net** absorbed flux due to the sun.

Can calculate by integrating j_{abs} over all photon energies:

$$J_{SC} = q\int_0^\infty C(E)\left(1-R(E)\right)a(E)\,b_s(E)\,dE$$

Probability that promoted carriers are collected to "do work"

LOOK FAMILIAR?
This is the Quantum Efficiency (external)

Photocurrent

Photo-current is due to the **net** absorbed flux due to the sun.
Can calculate by integrating j_{abs} over all photon energies:

$$J_{SC} = q\int_0^\infty C(E)(1-R(E))a(E)b_s(E)\,dE$$

Probability that promoted carriers are collected to “do work”

LOOK FAMILIAR?
This is the Quantum Efficiency (external)

$$J_{SC} = q\int_0^\infty QE(E)b_s(E)\,dE$$

Now you know how to calculate J_{sc} from an EQE curve (hint hint)

Photocurrent

In a perfect world:

$$C(E)=1$$

and

$$R(E)=0$$

therefore

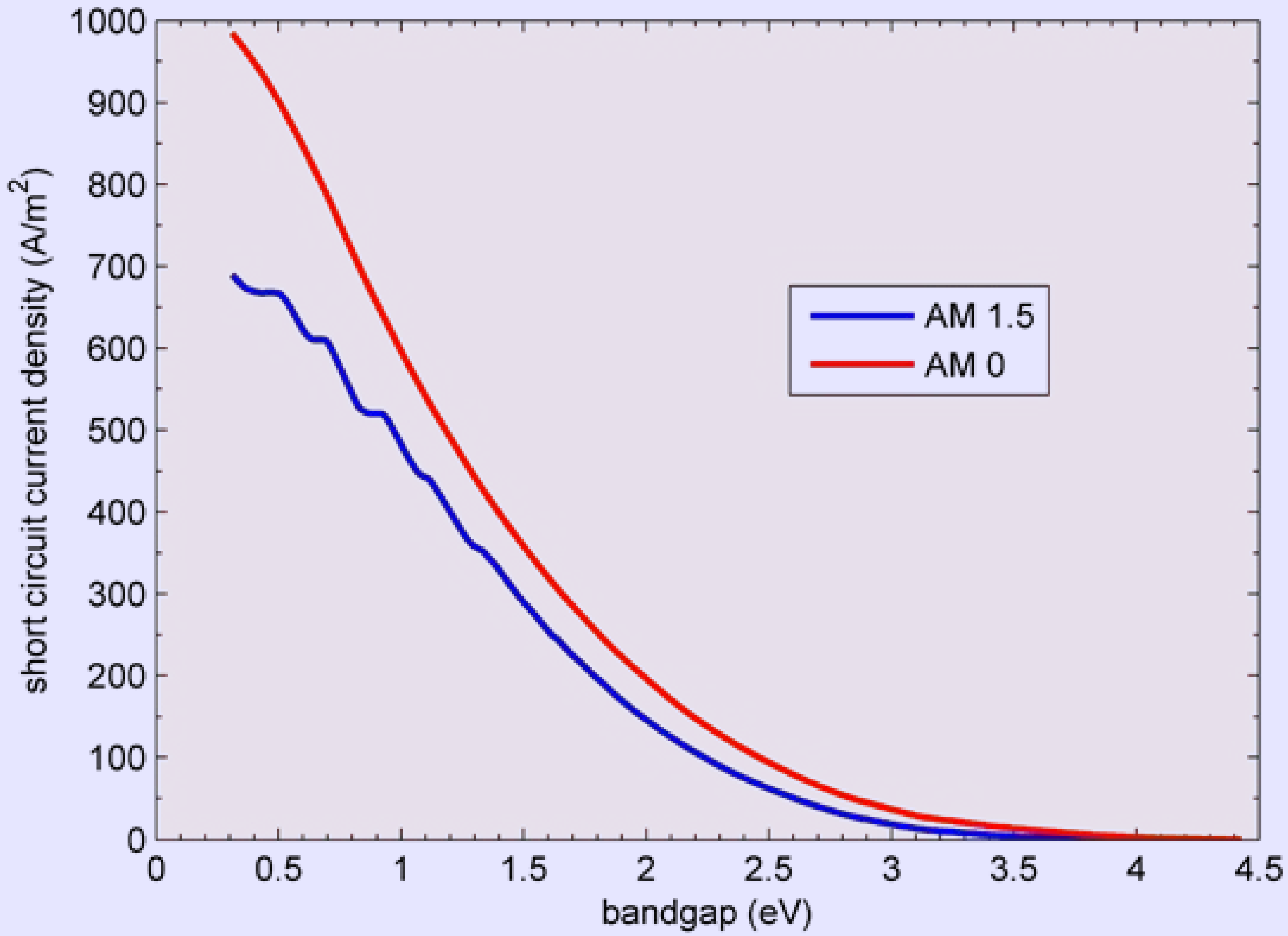
$$QE(E)=a(E)=\begin{cases}1 & E\geqslant E_g\\ 0 & E<E_g\end{cases}$$

so

$$\boxed{J_{SC}=q\int_{E_g}^{\infty} b_s(E)\,dE}$$

In other words $\boldsymbol{J_{sc}}$ is dependent **only** on the **band gap** of the material (for a given spectrum)

Photocurrent



From last lecture

Is the V_{OC} related to the band gap too? - Heck Yes!

Remember from diode equation

$$V_{OC} = \frac{nk_B T}{q} \ln\left(\frac{J_{SC}}{J_0} + 1\right)$$

This is much more sensitive to E_g than J_{SC} is.

$$J_0 = \frac{q}{k_B} \frac{15\sigma_s}{\pi^4} T^3 \int_u^{\infty} \frac{x^2}{e^x - 1} dx$$

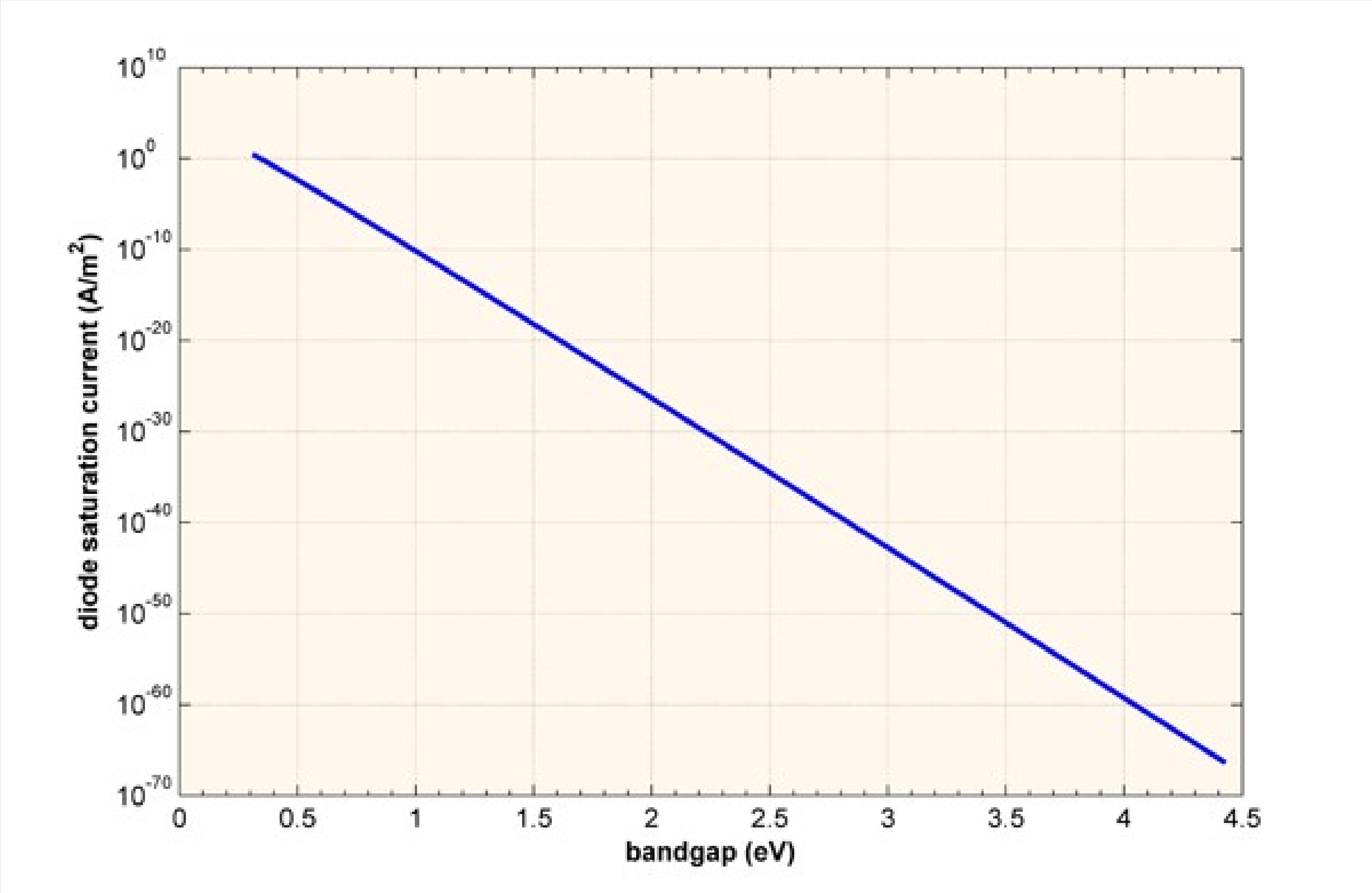
From the detailed balance

where

$$u = \frac{E_G}{k_B T}$$

http://www.sciencedirect.com/science/article/pii/0927024895800042

V_{OC}



J_0 decreases **exponentially** with respect to band gap

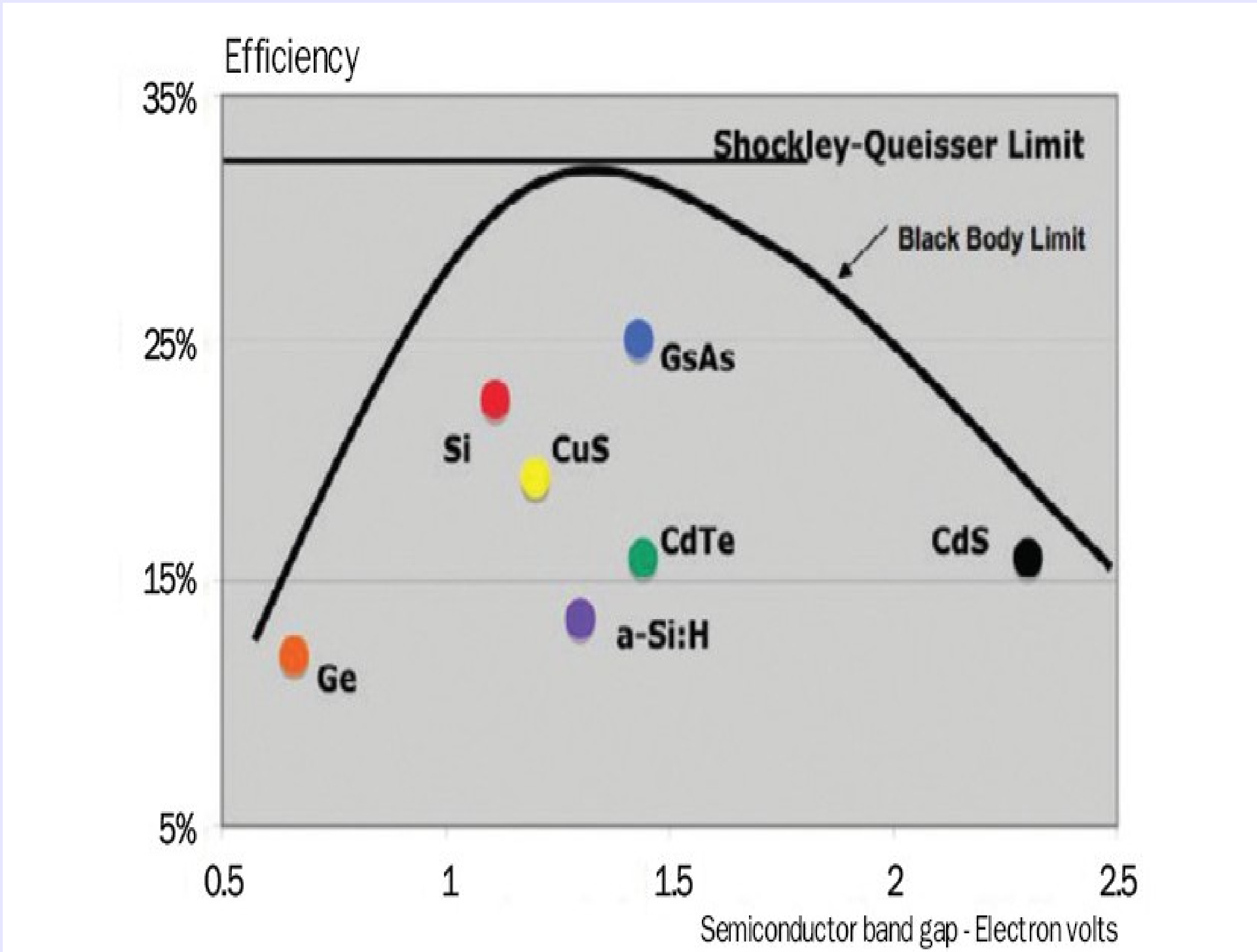
V_{OC}

Therefore:

$$\boxed{V_{OC} \text{ increases with } E_g}$$

Limiting Efficiency

Limiting Efficiency



W. Shockley and H. Queisser, *Detailed Balance Limit of Efficiency of p-n Junction Solar Cells",* JAP, 32(3) 0.510 (1961)

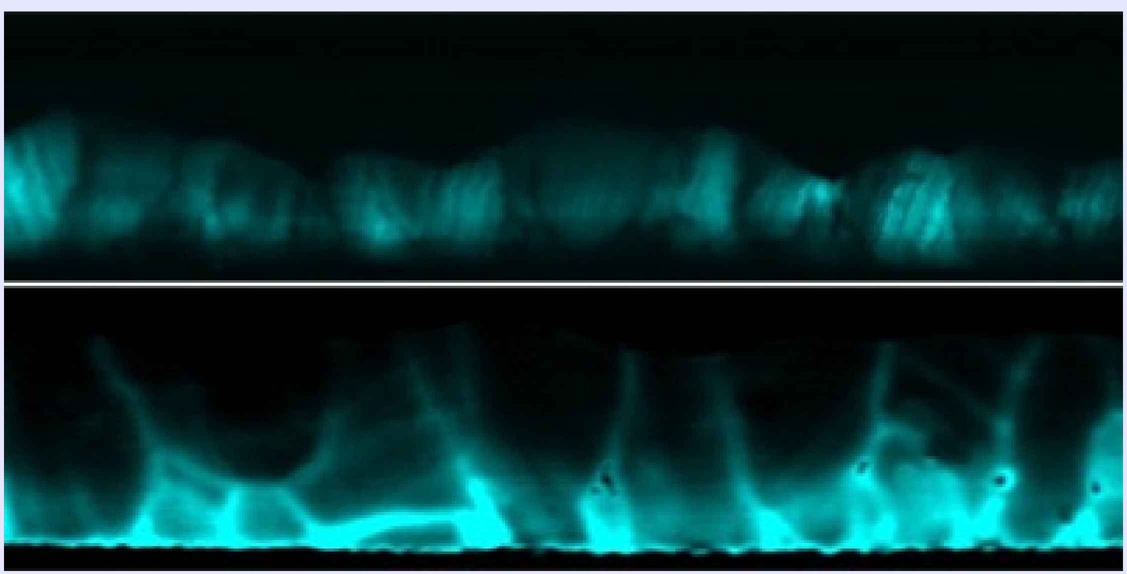
Requirements for ideal PV devices

- PV material has energy gap
- All incident light with $E > E_G$ is absorbed
- 1 photon = 1 electron-hole pair
- Radiative recombination only (i.e. spontaneous emission)
- Generated charges are completely separated
- Charge is transported to external circuit without loss

J. Nelson, *“The Physics of Solar Cells”, pp 35 - 39*

Real World Device Limitations

- Incomplete absorbtion: *C(E) < 1* and *R(E) > 0*
- Non-radiative recombination. (L4)
- Lossless transport? No such thing as perfect conductor.



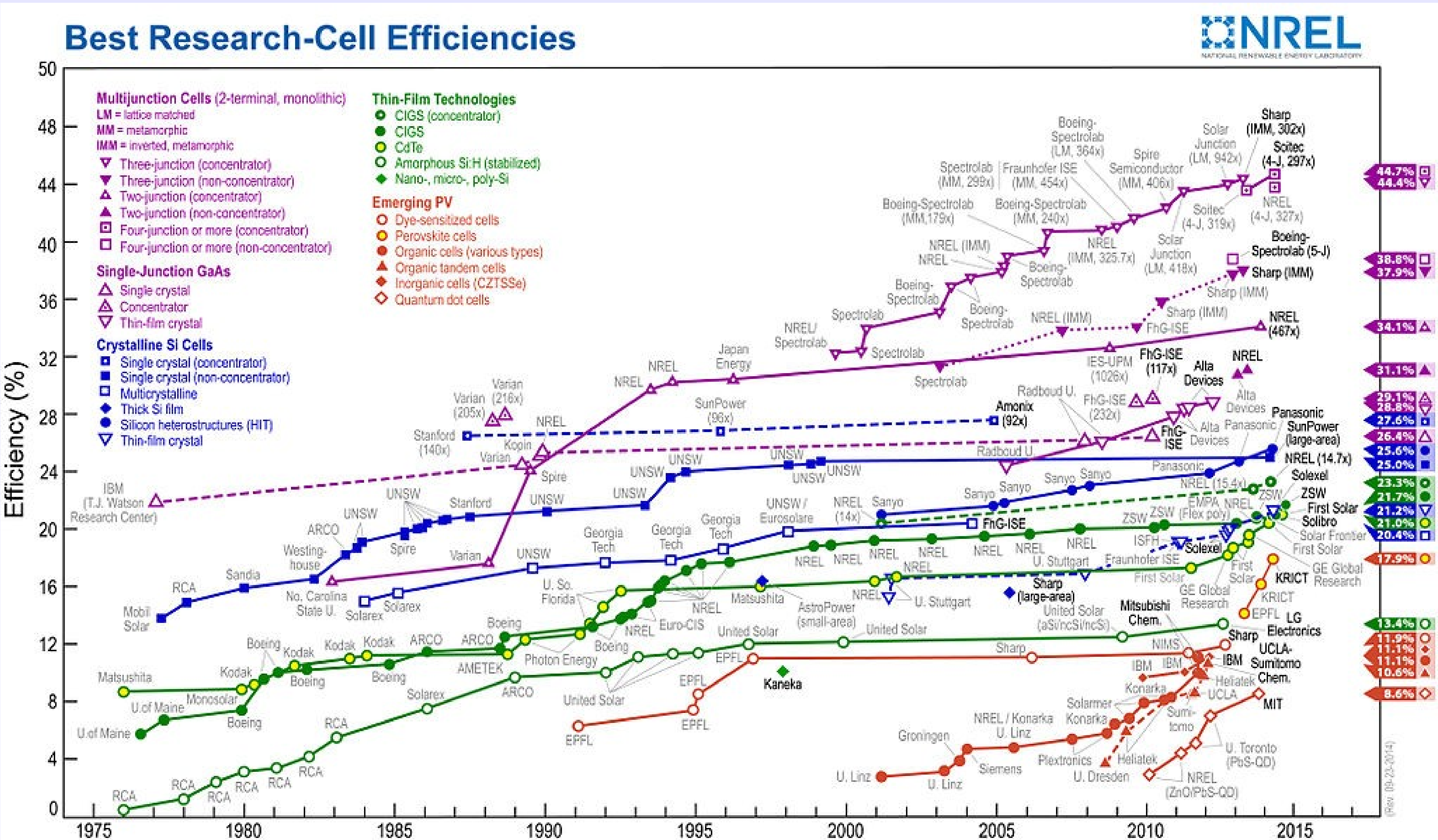
Electron Beam Induced Current (EBIC) imaging of CdTe/CdS solar cell cross section. Grain Boundaries = Recombination!

C. Li *et al., Phys. Rev. Lett.* 112, *156103 (2014)*

Beating the SQ limit

- Tandem Cells
- Multi-junctions
- Concentrator PV
- Hot Carrier solar cells
- Down and up conversion

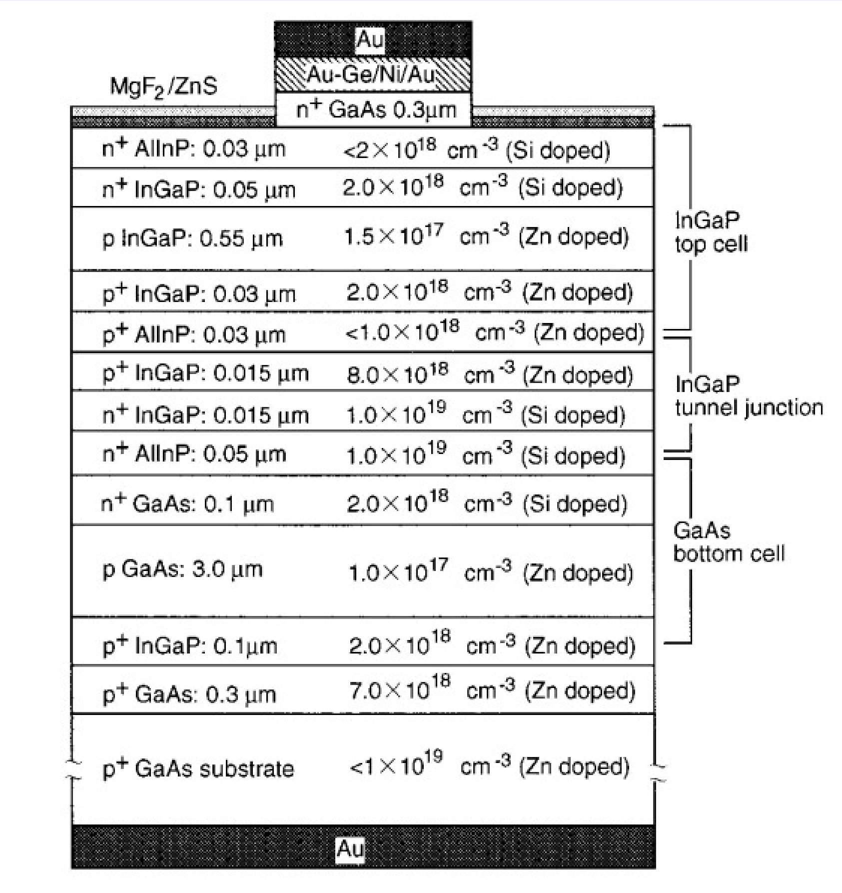
Beating the SQ limit

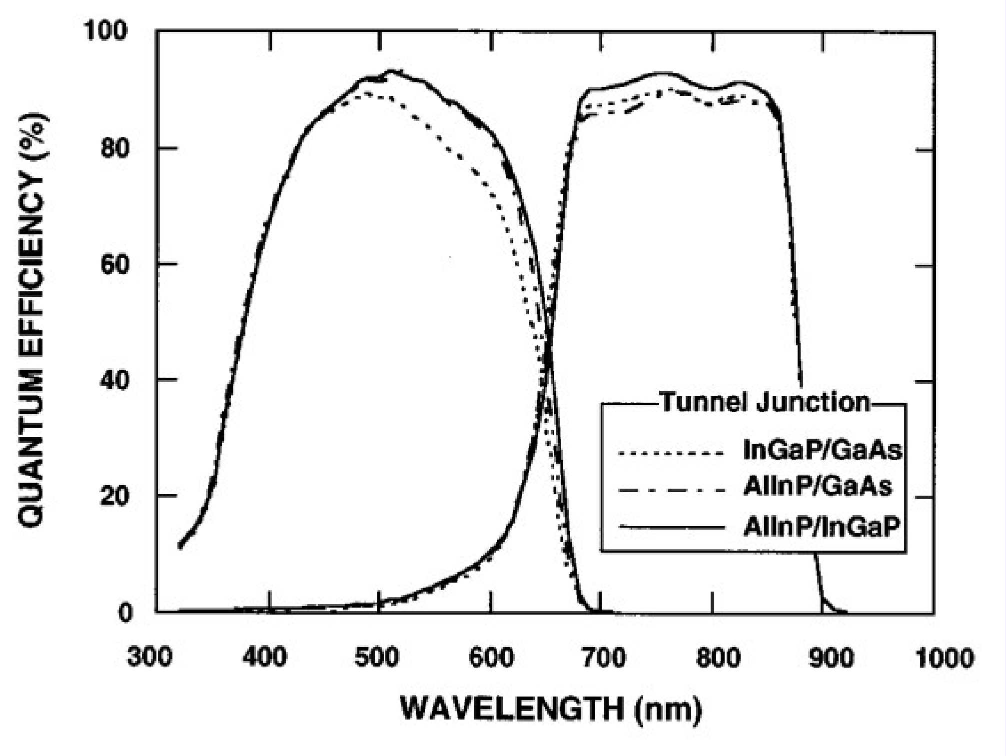


Tandem Cells

Why have one junction when you can have **two?**

GaAs/InGaP

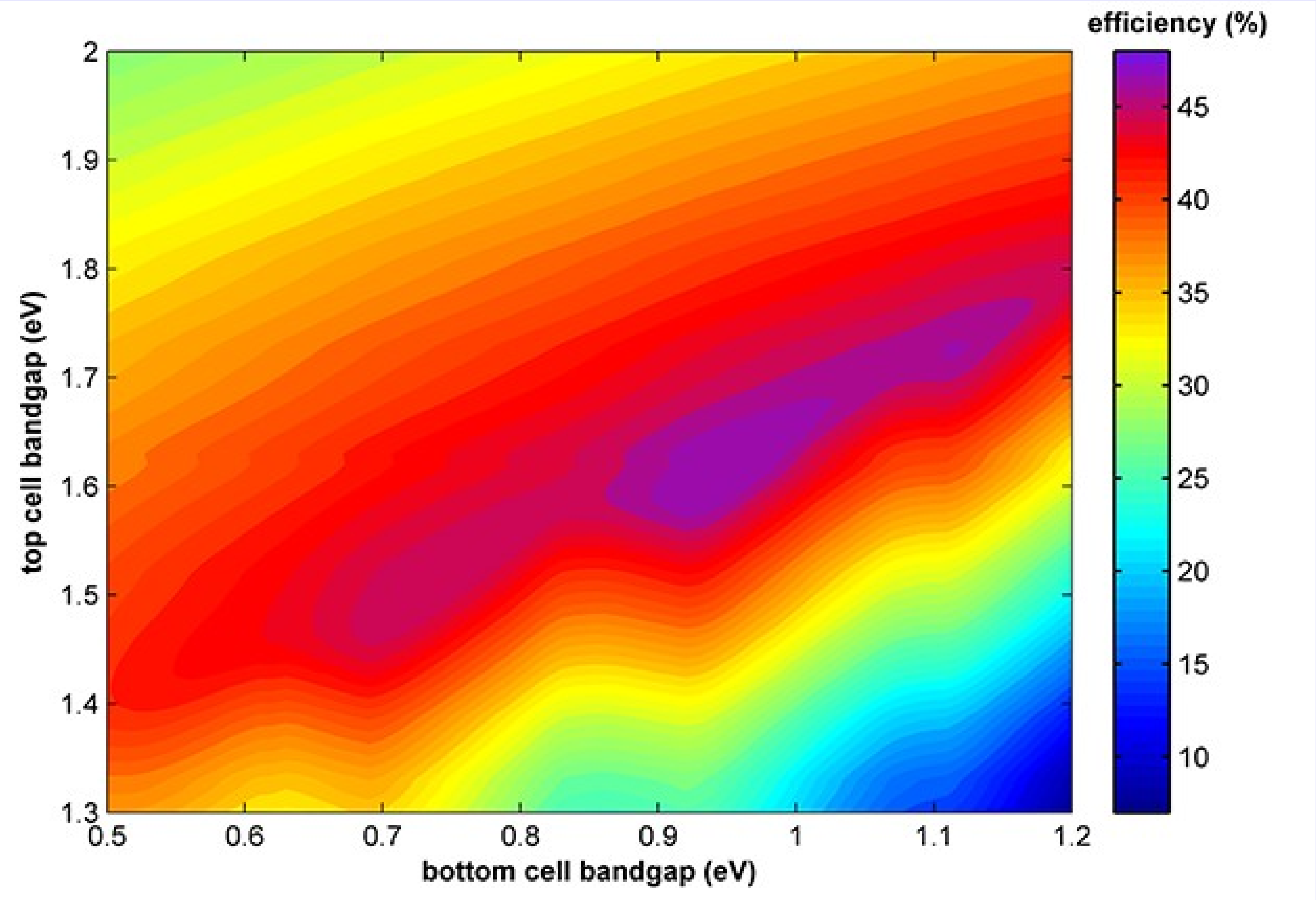




T. Takamoto *et. al.* “Over 30% Efficient InGaP/GaAs tandem solar cells”, APL, 70 381 (1997)

Tandem Cells

Detailed balance calculations for two band gap system:



Maximum theoretical efficiency ~ 46%

Disadvantages of tandems based on III-V's

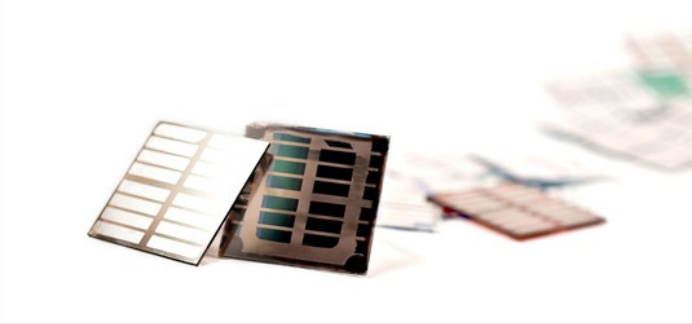
- High precision fabrication required
- Materials balance (tunnel junction)
- High cost (materials + deposition)
- Not practical for concentrator systems

Are there other strategies?

Inorganic/Organic Hybrid Tandems

- Cheap
- Easy to make (non-vacuum dep)
- Can apply to existing Si technology

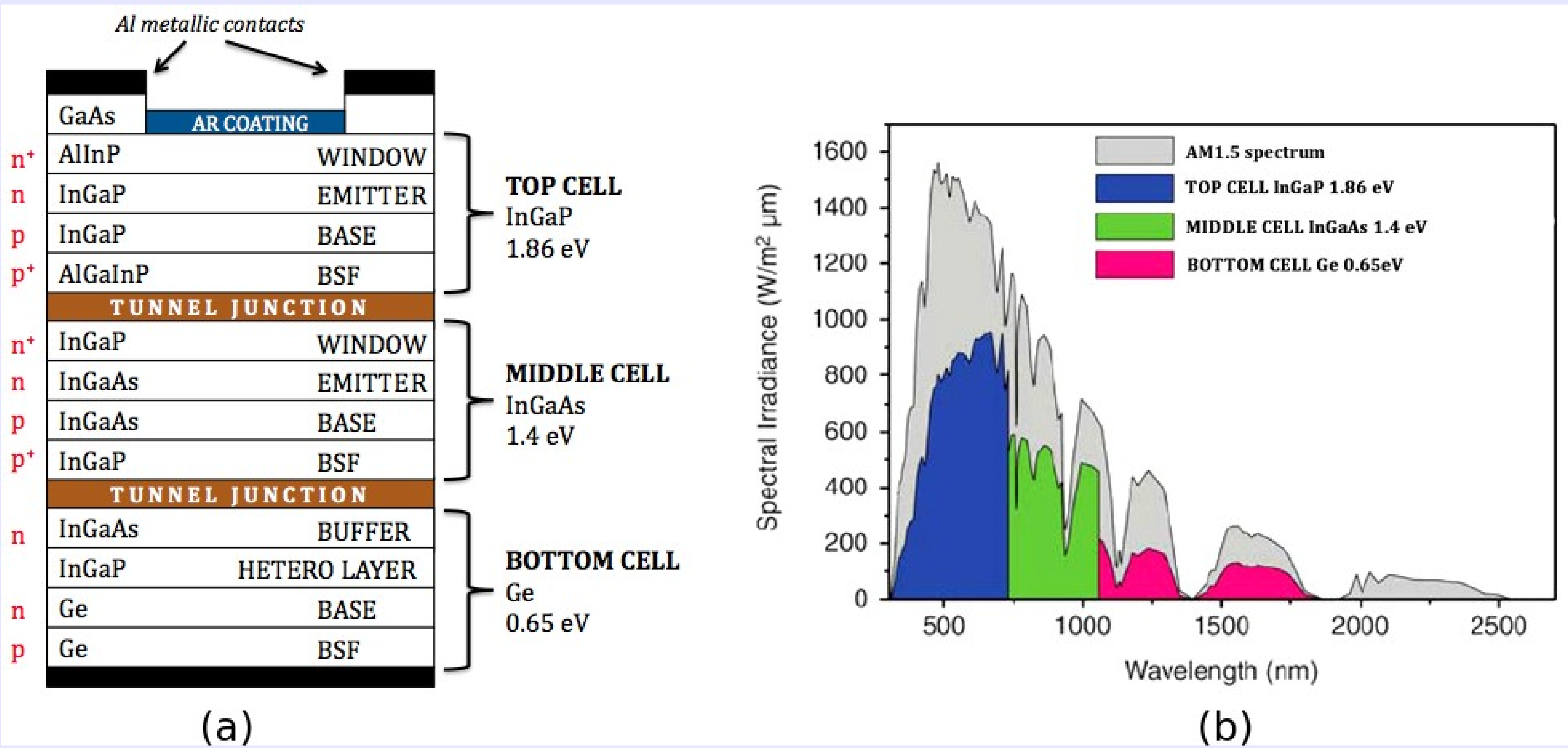
Watch this space



c-Si efficiency boosted by 20% (by using perovskites)

Multi-junctions

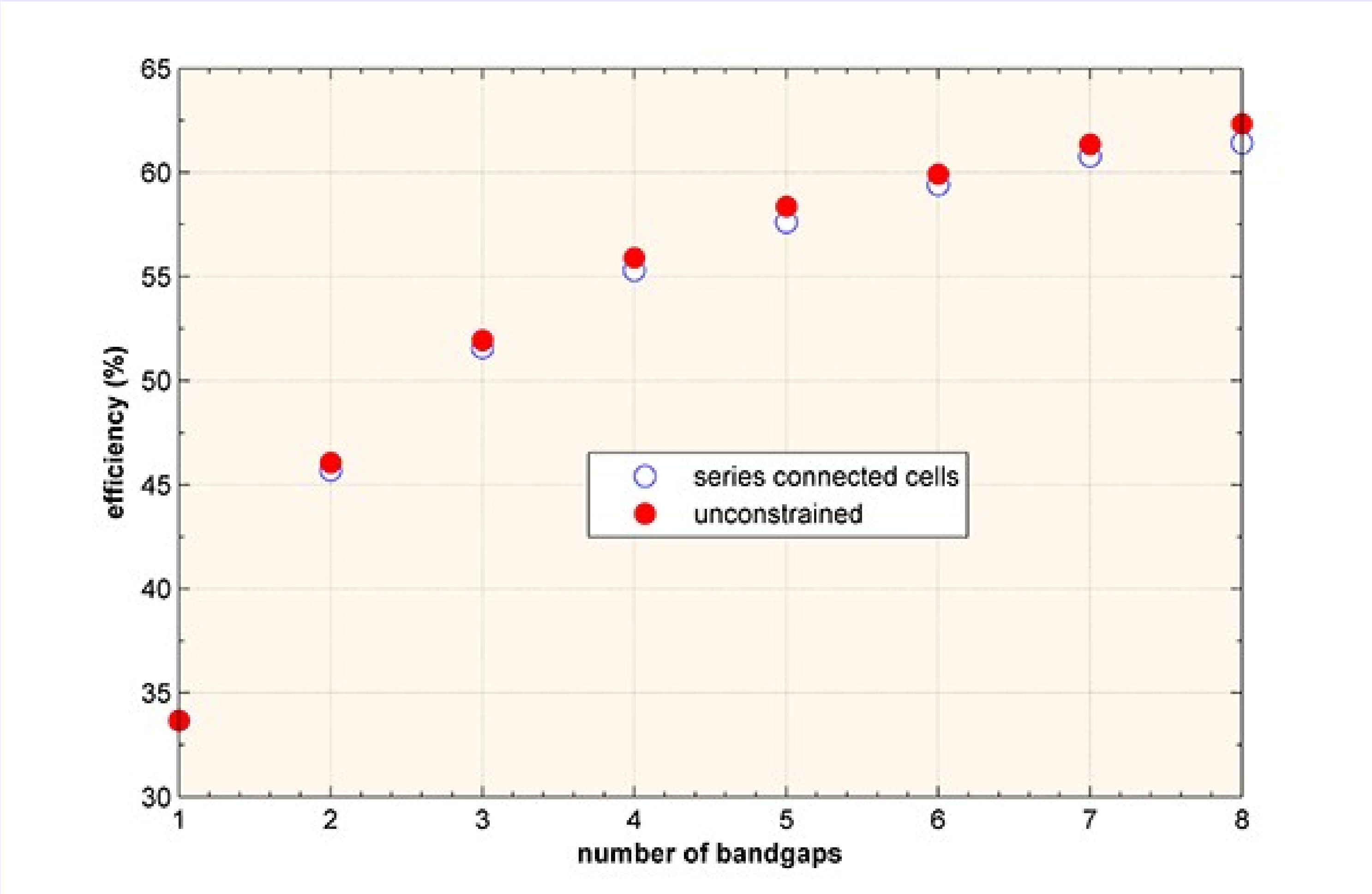
Why have two junctions when you can have three (or more)?



Ge/InGaAs/InGaP – Max η ~ 35%

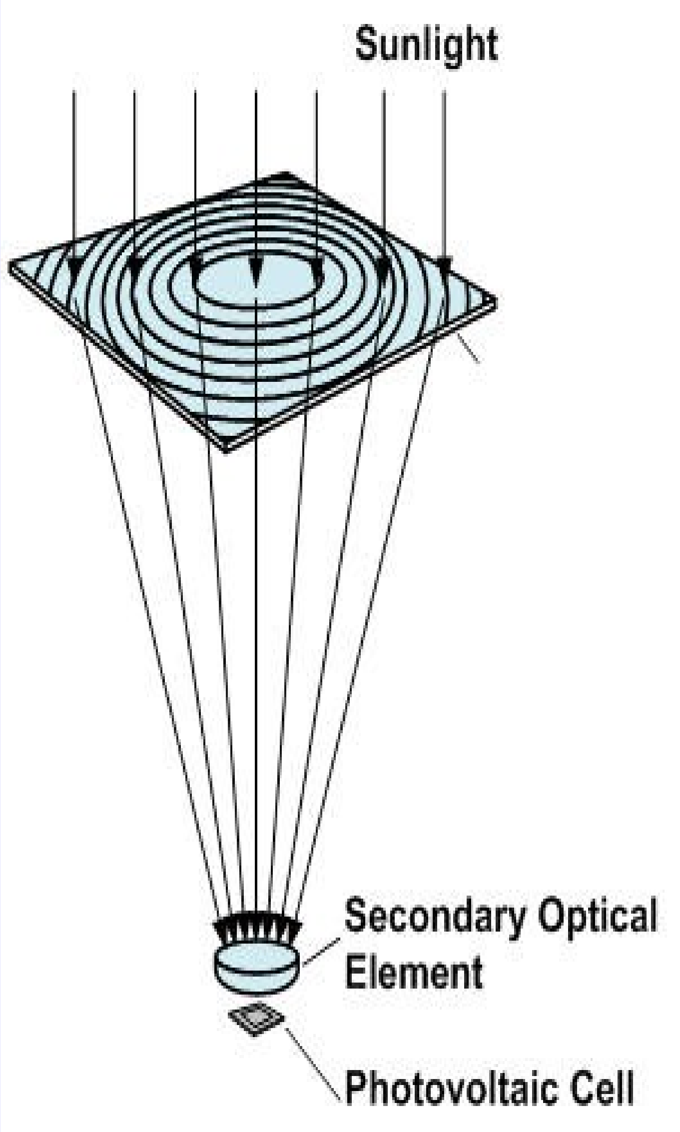
EPSRC
Engineering and Physical Sciences Research Council

Multi-junctions



S. P. Bremner *et. al.* Prog. PV. 16:225-233 (2008)

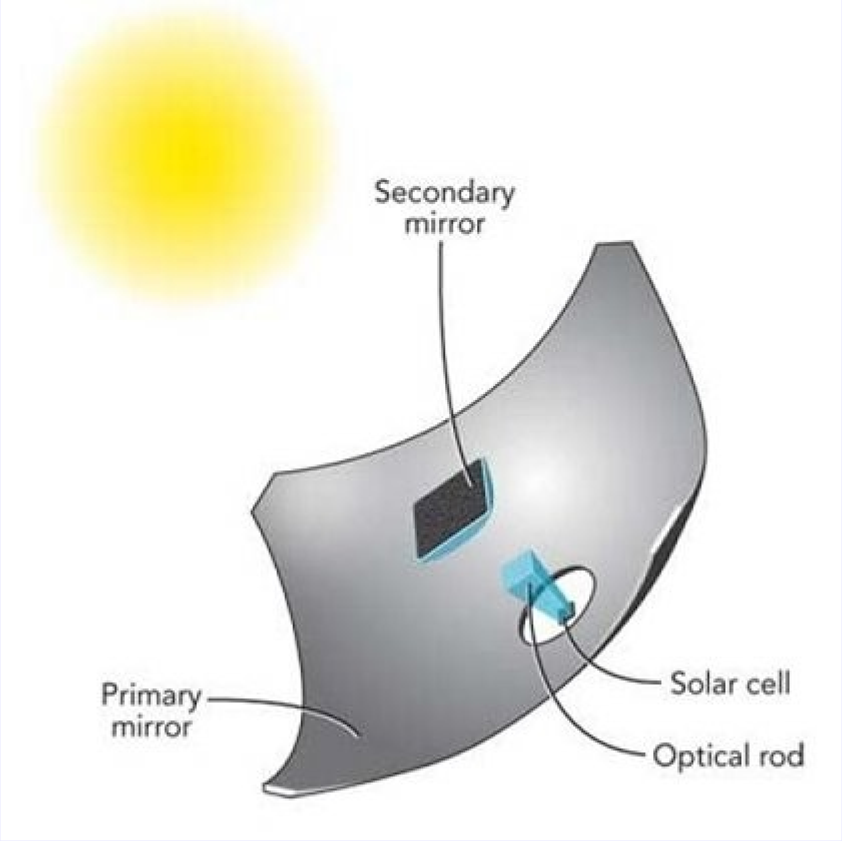
Concentrators



Fresnel Lenses

200 – 300 suns
1 axis tracking

Concentrators

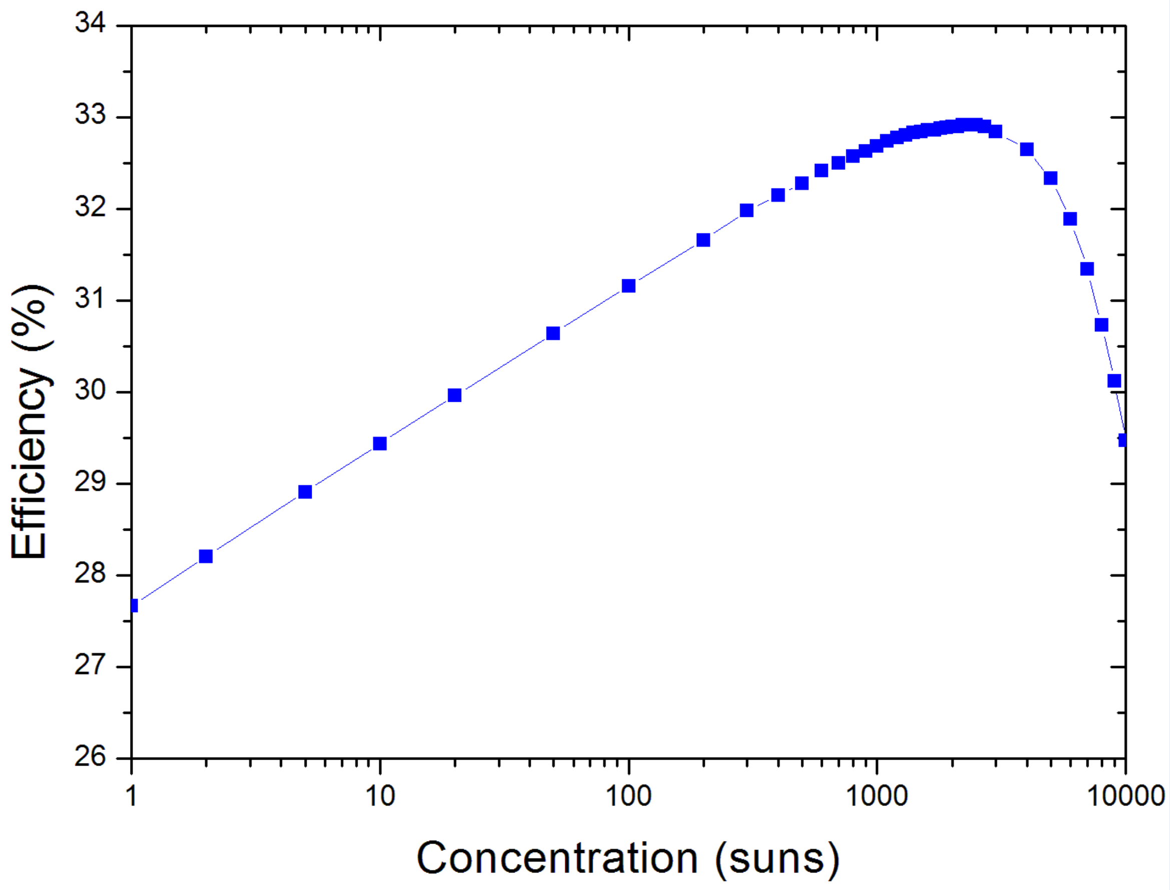


Parabolic Mirror Array

~ 500 suns
25kW output
2 axis tracking

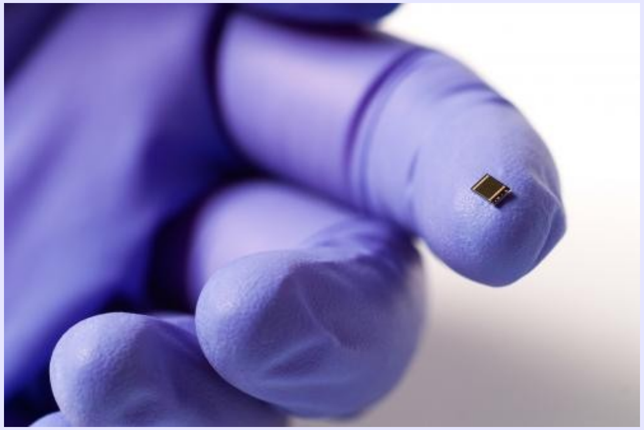
Concentrators

Increase photon flux → increase efficiency



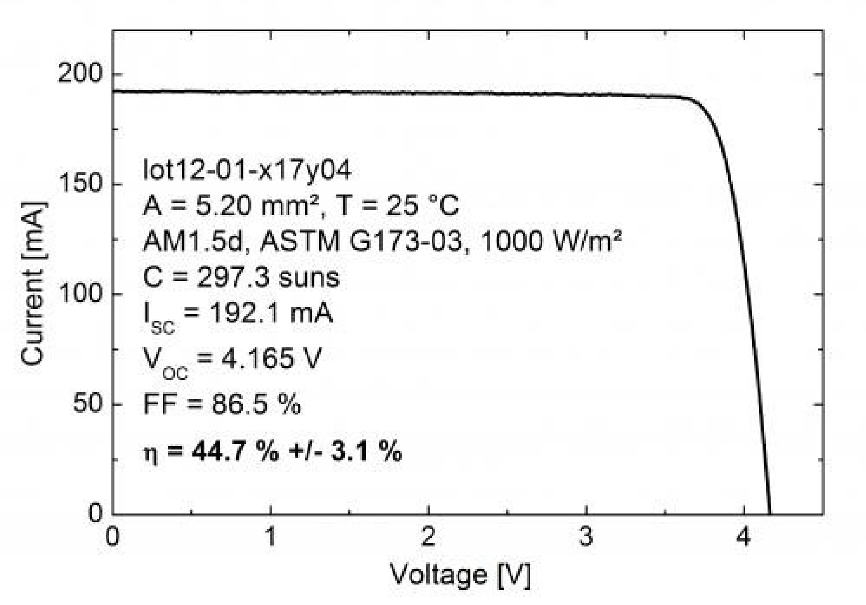
Theoretical prediction for two junction system @ T = 320K

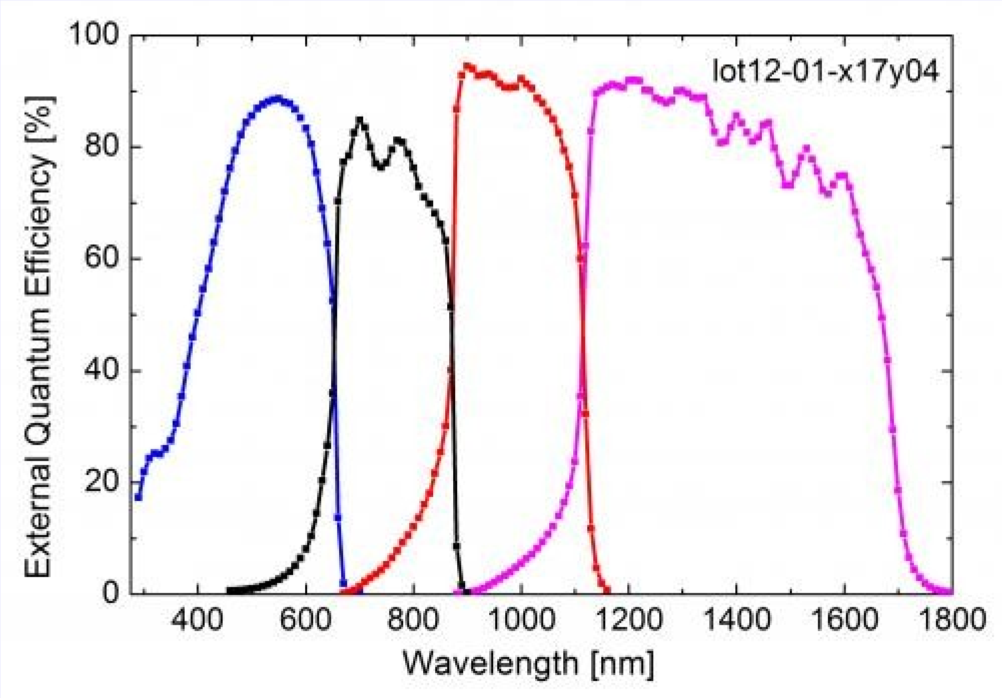
Concentrators



44.7%!

- **Four junction cell based on III-V**
- **Fraunhofer Institute**





Disadvantages of concentrator PV

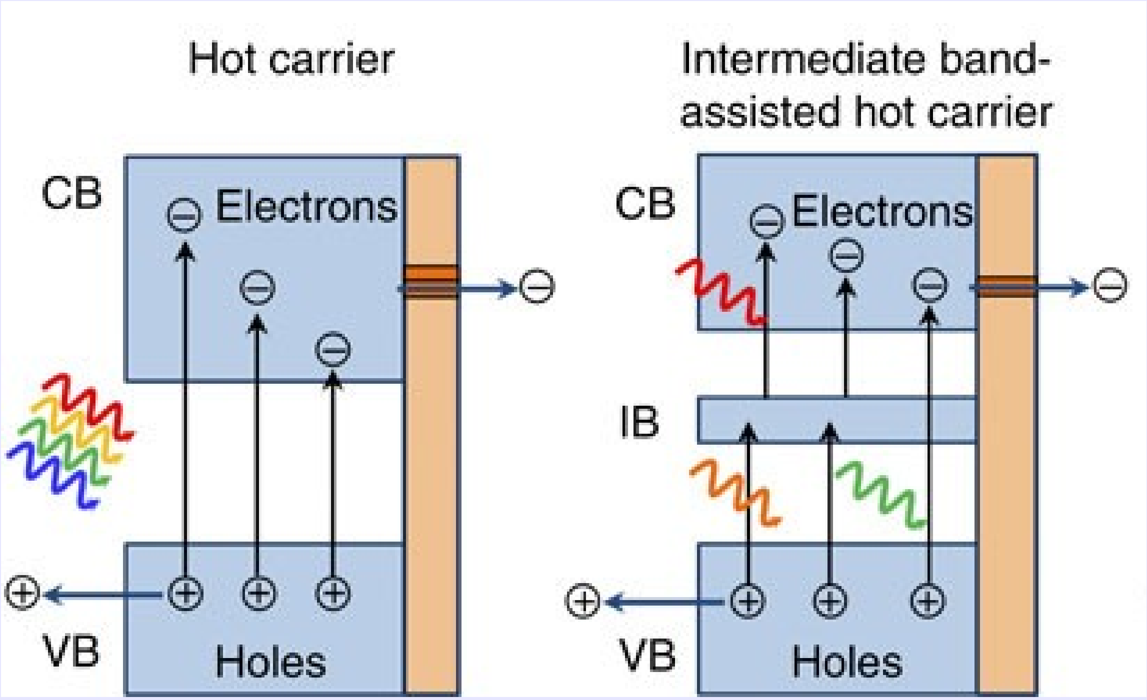
- Need to deal with high Temperatures

  i.e. cooling required

- High installation cost
- Need direct sunlight
- Don't put one on your roof in UK.

Hot Carrier Solar Cells

Can we get the promoted carriers out before they thermalise?



Use “selective” contacts that allow “hot” carriers to be collected before they thermalise (picoseconds!) to bottom of C.B. through scattering with phonon modes

Advantages of Hot Carrier Solar Cells

- Max efficiency ~63%

Disadvantages

- They don't exist!
- Completely Theoretical to date
- Lots of computational DFT studies
- **Expect real devices soon!**

Hot Carrier Solar Cells

WOW! Real hot carrier device demonstrated this 2014

AIP | Applied Physics Letters

Experimental demonstration of hot-carrier photo-current in an InGaAs quantum well solar cell

CrossMark

L. C. Hirst[1], R. J. Walters[1], M. F. Führer[2] and N. J. Ekins-Daukes[2]

+ VIEW AFFILIATIONS

Appl. Phys. Lett. **104**, 231115 (2014); http://dx.doi.org/10.1063/1.4883648

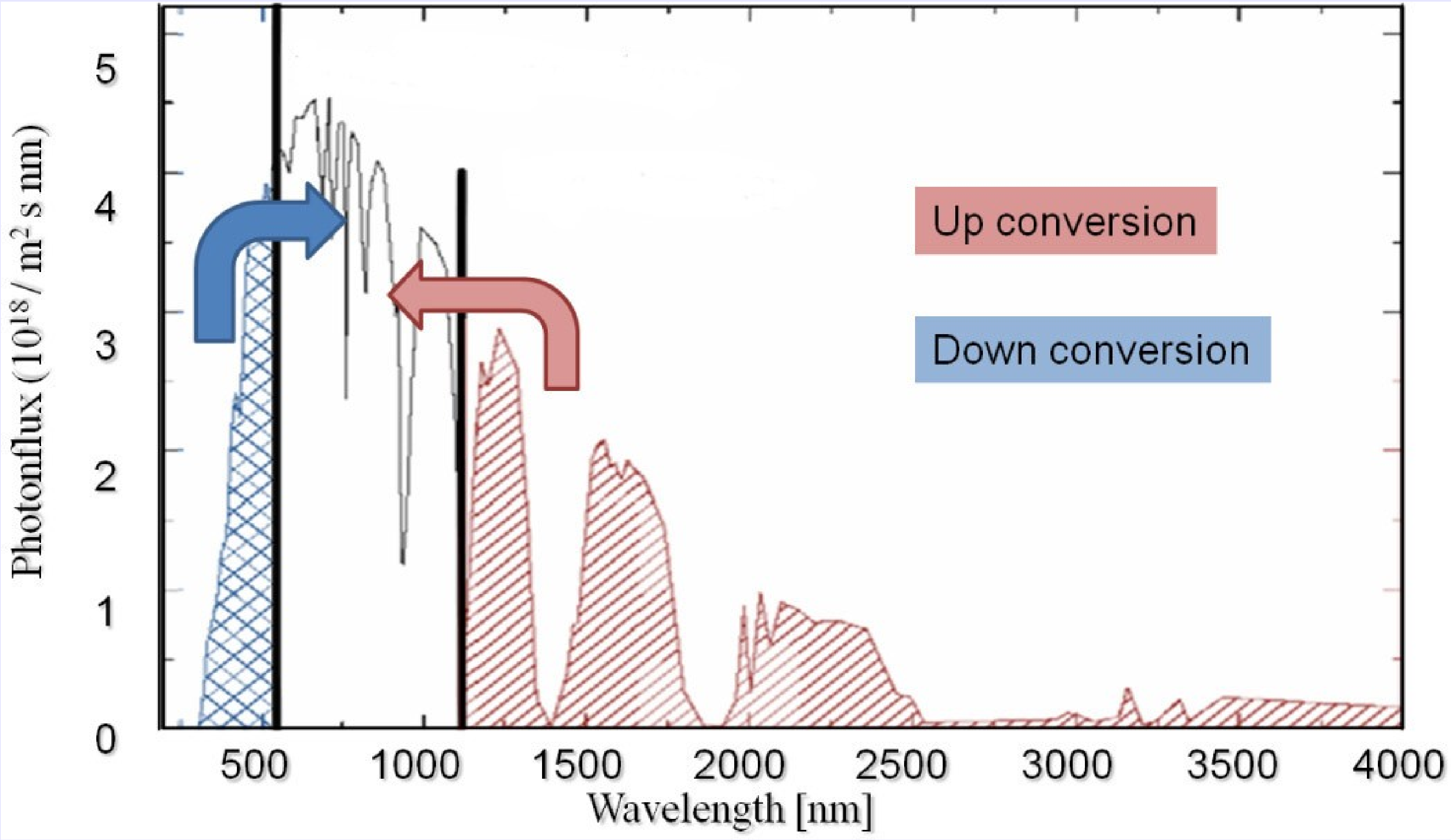
An unambiguous observation of hot-carrier photocurrent from an InGaAs single quantum well solar cell is reported. Simultaneous photo-current and photoluminescence measurements were performed for incident power density 0.04–3 kW cm^{-2}, lattice temperature 10 K, and forward bias 1.2 V. An order of magnitude photocurrent increase was observed for non-equilibrium hot-carrier temperatures >35 K. This photocurrent activation temperature is consistent with that of equilibrium carriers in a lattice at elevated temperature. The observed hot-carrier photo-current is extracted from the well over an energy selective GaAs barrier, thus integrating two essential components of

Key Topics

- Quantum wells
- Photoluminescence
- Carrier generation

http://scitation.aip.org/content/aip/journal/apl/104/23/10.1063/1.4883648

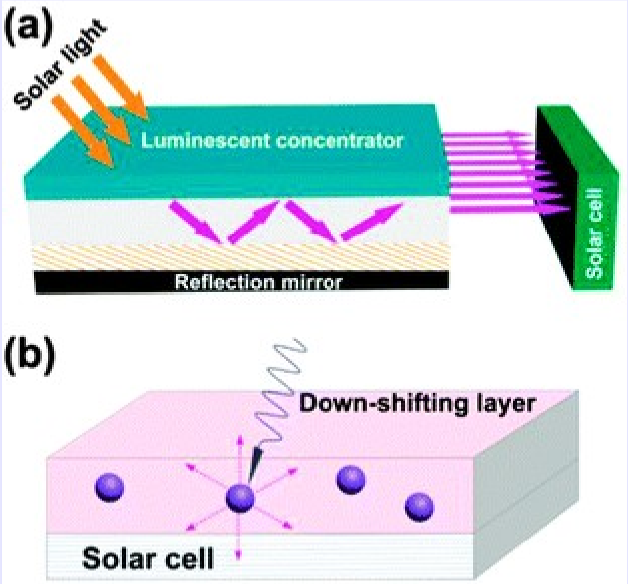
Up and down conversion



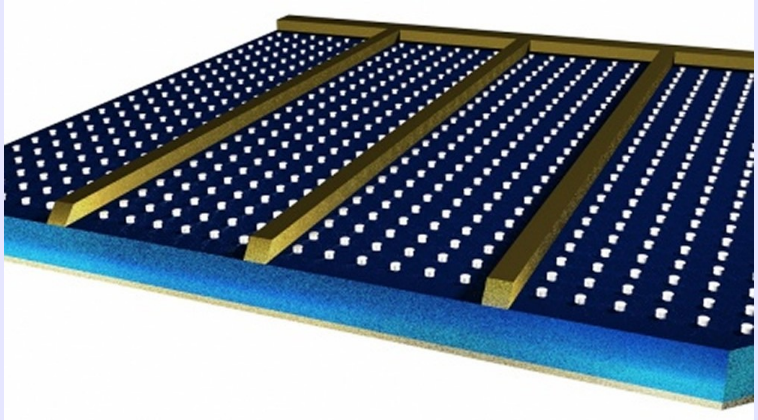
Take Parts of the spectrum that are not used by the device and covert to wavelengths/energies that are. **How?**

Lecture Summary

Luminescent Dyes



Quantum Dots/nanowires



Aluminium dots on GaAs solar cell
“Lego Brick” Structure.
Plasmonic Enhancement

http://www.nature.com/srep/2013/131007/srep02874/full/srep02874.html

Lecture Summary

- Black Body Radiation
- Detailed Balance
- The Shockley-Queisser Limit
- Requirements for real physical systems
- Exceeding the SQ limit (funky solar)

Why can't a solar cell have a 100% efficiency?

(Or even close to 100%?)

Can you answer this?