3G rule for attending in person lectures at KIT:

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- ***geimpft* – vaccinated**
- ***genesen* – recovered**
- ***getestet* – tested**

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"Solar Energy" WS 2021/2022

Lecture 16: Losses, Efficiency Limits and Third Generation Concepts

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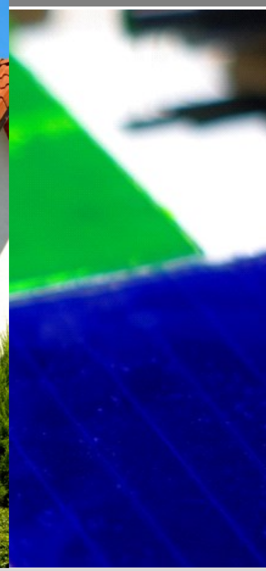
KIT Focus Optics & Photonics



Parts of the material used here have been kindly provided by Prof. T. Kirchartz, and Dr. D. Cheyns.

Fundamental PV Efficiency Limits

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- Going back to thermodynamics: 1st and 2nd laws of thermodynamics as phrased by Clausius in 1865:

  "The total energy of the universe is constant. The total entropy of the universe strives to reach a maximum"

- Useful description of energy is:

  "The capacity ***for*** *doing work. The various forms of energy … include* ***heat****,* ***chemical****,* ***nuclear*** *and* ***radiant energy****. Interconversion between these forms of energy can occur only in the presence of* ***matter****. Energy can only exist in the absence of matter in the form of radiant energy".*

- Remembering that matter itself is: *"A specialised form of* ***energy*** *which has the attributes of* ***mass*** *and extension in* ***space*** *and time" (Lurarov and Chapman 1971)*

Source: Martin Green, "Third Generation Photovoltaics: Advanced Solar Energy Conversion", Springer 2003

Fundamental PV Efficiency Limits

- Entropy:
  - less intuitive concept, but is physically associated with disorder $\Rightarrow$ increased disorder $\Rightarrow$ greater entropy
  - provides a measure of the amount of thermal energy that *cannot* be used to do work.

- Clausius: entropy expressed as heat divided by temperature

  $\Rightarrow$ transfer of a small amount of heat causes a larger change in entropy in a cold body than in a hot body

- Solar: normally have steady-state conditions and equilibrium between energy fluxes, rather than incremental transfers. Associated with an energy transfer as heat at rate $\dot{E}$ to or from a body at temperature $\dot{T}$, is an entropy flux $\dot{E}/\dot{T}$

Source: *Martin Green, "Third Generation Photovoltaics: Advanced Solar Energy Conversion", Springer 2003*

Fundamental PV Efficiency Limits

The most general efficiency limit for any engine and, in turn, also PV is the Carnot limit

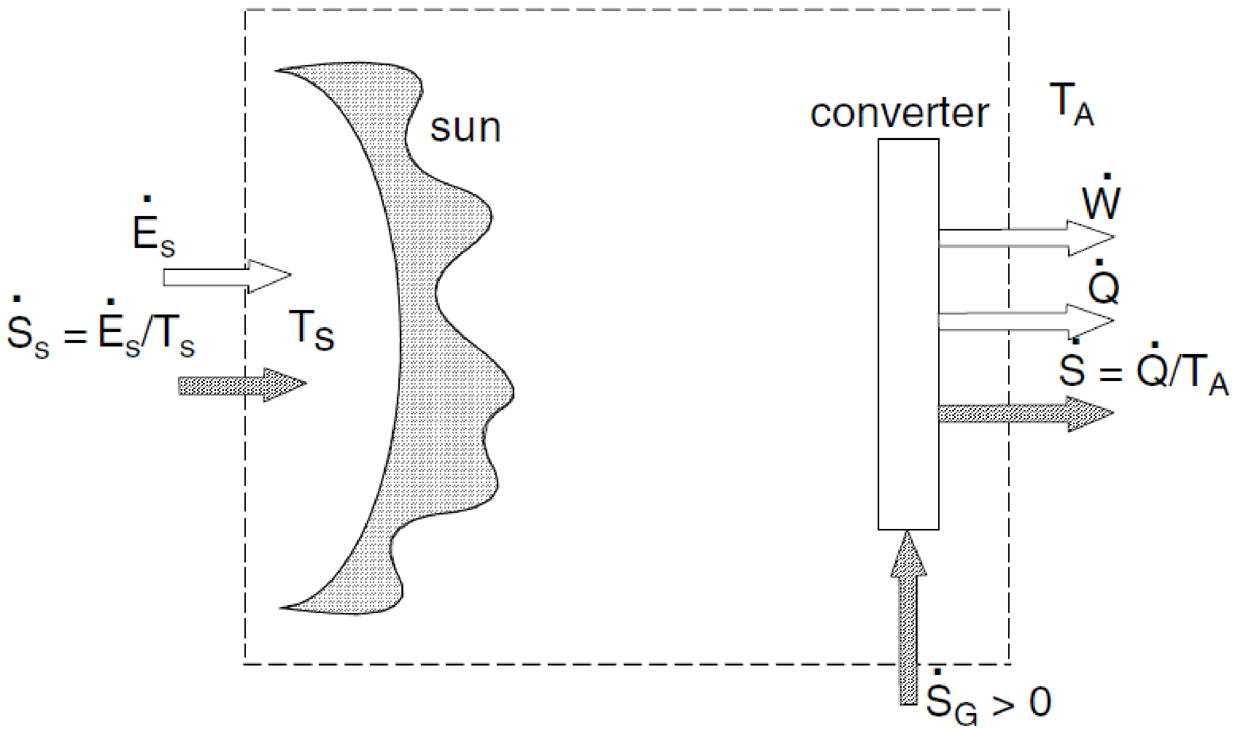

Fig. 3.1: System considered for calculating Carnot efficiency.

Source: Martin Green, "Third Generation Photovoltaics: Advanced Solar Energy Conversion", Springer 2003

Fundamental PV Efficiency Limits

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The most general efficiency limit for PV is the Carnot limit

- Inputs: $\dot{E}_S$ = heat energy flux from sun's interior to fuel its radiative emission

  $\dot{S}_S$ = corresponding entropy flux, given by $\dot{E}_S / T_S$

  where T_S = temperature of sun's photosphere (6000K)

  and $\dot{S}_G$ = entropy generation flux associated with energy conversion (positive for any practical process)

- Outputs: $\dot{W}$ = energy flux in the form of useful work with zero associated entropy flux

  $\dot{Q}$ = heat flux rejected to the ambient, with associated entropy flux $\dot{Q} / T_A$

  where T_A = ambient temperature, 300K

Fundamental PV Efficiency Limits

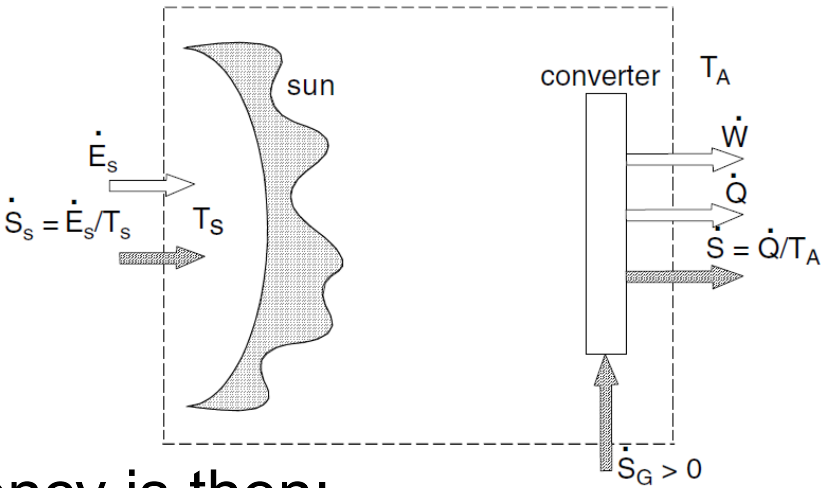
- Can now express 1st and 2nd laws of thermodynamics as energy and entropy flux balance, respectively:

$$\dot{E}_S = \dot{W} + \dot{Q}$$

$$\dot{S}_s + \dot{S}_G = \frac{\dot{Q}}{T_A}$$

and thus

$$\dot{E}_S = \dot{W} + T_A\left(\dot{S}_s + \dot{S}_G\right)$$



and the energy conversion efficiency is then:

$$\eta = \frac{\dot{W}}{\dot{E}_S} = \left(1 - \frac{T_A}{T_S}\right) - \frac{T_A \dot{S}_G}{\dot{E}_S}$$

- η has maximum value of 95% when $\dot{S}_G = 0$,

  $\Rightarrow$ Carnot efficiency for conversion of heat energy supplied from sun's photosphere to terrestrial energy

Fundamental PV Efficiency Limits

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- Interesting point: no information is required about converter itself $\Rightarrow$ so, is there any converter that could, at least in principle, achieve this limiting Carnot efficiency?
- Main requirement is no entropy generation during the transmission, absorption or conversion of the sunlight.
- Planck showed that energy transfer between two black-bodies involves unavoidable entropy production, unless both are at same $T \Rightarrow$ means finite entropy production in an absorber unless absorber emits light of the same intensity as the sun at each wavelength! But then there would be no net energy transfer! So, to achieve Carnot limit, only infinitesimally small amounts of work could be produced, with nearly all of the sun's energy being recycled.

Fundamental PV Efficiency Limits

- <u>Black body η limit</u> considers also the black-body emission of the absorber ⇒ takes into account unavoidable entropy production during absorption and emission of light by the black-body $\dot{S}'_G$

$$\eta = \left(1 - \frac{T_C^4}{T_S^4}\right)\left(1 - \frac{T_A}{T_C}\right) - \frac{T_A \dot{S}'_G}{\dot{E}_S}$$

Nett radiative energy transfer between the sun and the converter (absorber)

Carnot conversion limit for a source of energy at the converter temperature T_C

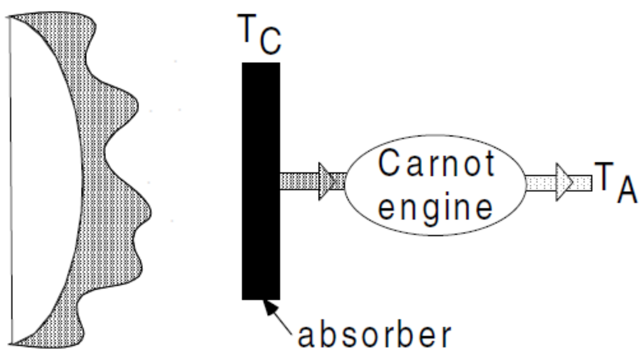
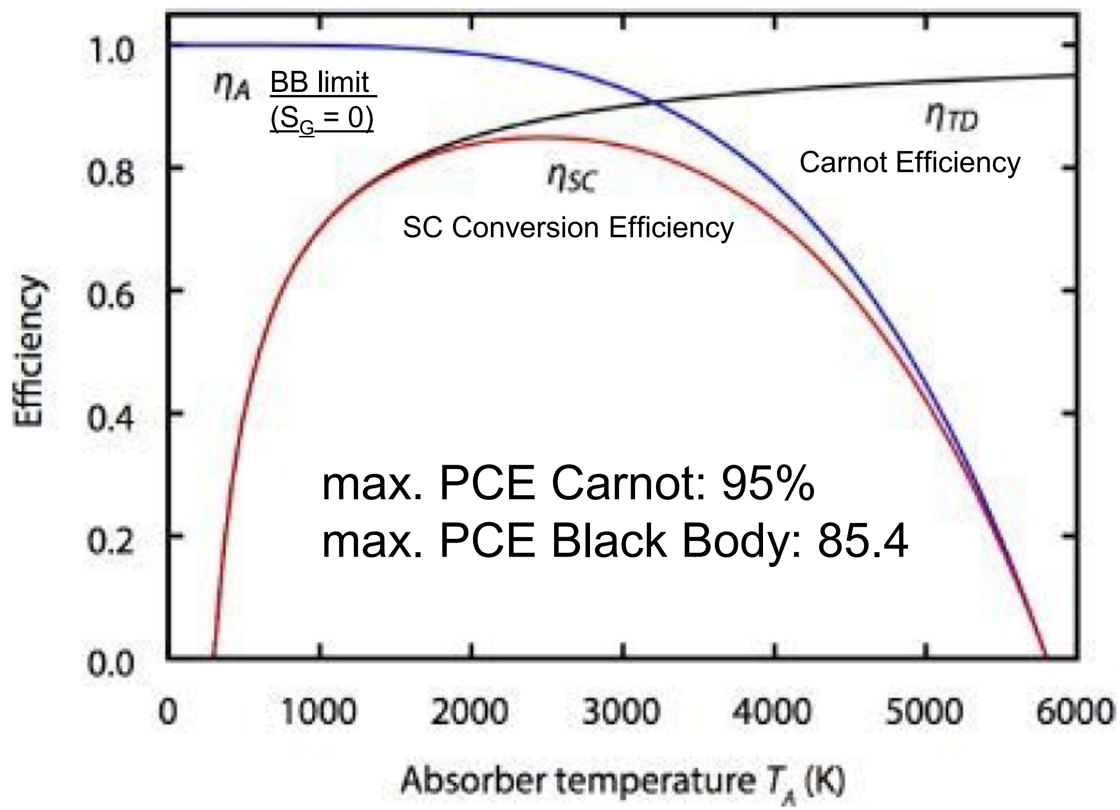


Fig. 3.3: Ideal solar thermal converter with sunlight absorbed by an absorber at temperature T_C, with heat extracted from this absorber converted to electricity by a Carnot converter.

Source: Martin Green, "Third Generation Photovoltaics: Advanced Solar Energy Conversion", Springer 2003

Fundamental PV Efficiency Limits

- For T_A / T_S = 0.05 (300 K / 6000 K), the solution gives T_C / T_S equal to 0.424 or T_C = 2544 K, corresponding to a maximum efficiency of 85.4%



Source: textbook

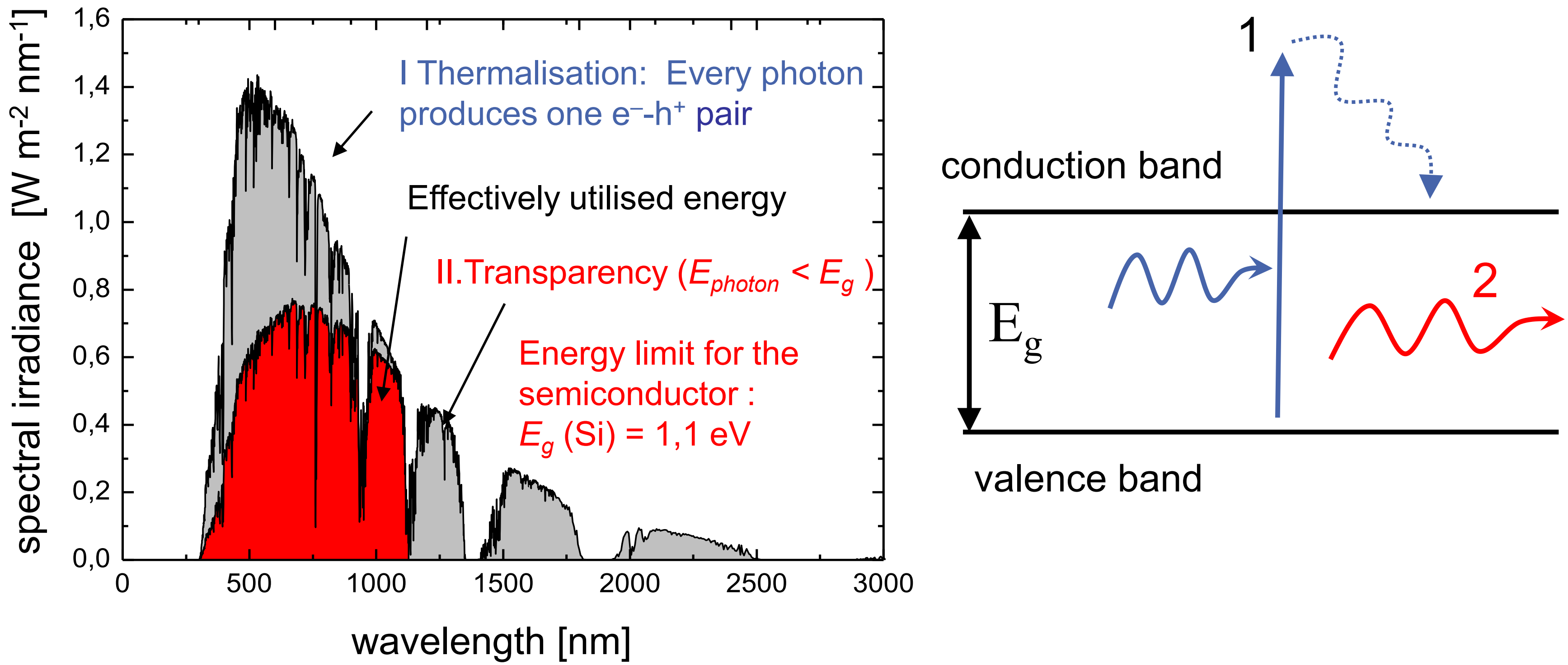
Shockley-Queisser (SQ) efficiency limit

Key Considerations: Consider the single junction solar cell as a black body that obeys fundamental characteristics of a semiconductor:

1. The perfect solar cell will have **no parasitic optical losses** (reflection losses, absorption in TCOs, HTLs, contact layers etc.)
2. The perfect solar cell shall have no absorption (e.g. by defect states) within the bandgap => **Perfect transmission (T=0, A=1) for E < Eg.**
3. The perfect solar cell needs to be a perfect absorber of solar photons and, hence, have properties related to a black-body, at least for E > Eg. => **Perfect absorption (A = 1) for E > Eg.**
4. The perfect solar cell will have perfect charge carrier collection efficiency **=> EQE = 1 for for E > Eg**.
5. The perfect solar cell has no non-radiative losses. It only exhibits radiative recombination.
   => **Plancktian black-body radiation at the absorber temperature**.
6. **Every photon absorbed generates exactly one e – h pair**.

Shockley-Queisser (SQ) efficiency limit

Step 1: Spectral mismatch: The considerations 1-4 define the spectral match of the solar cell, i.e. the maximum current generation.



Shockley-Queisser (SQ) efficiency limit

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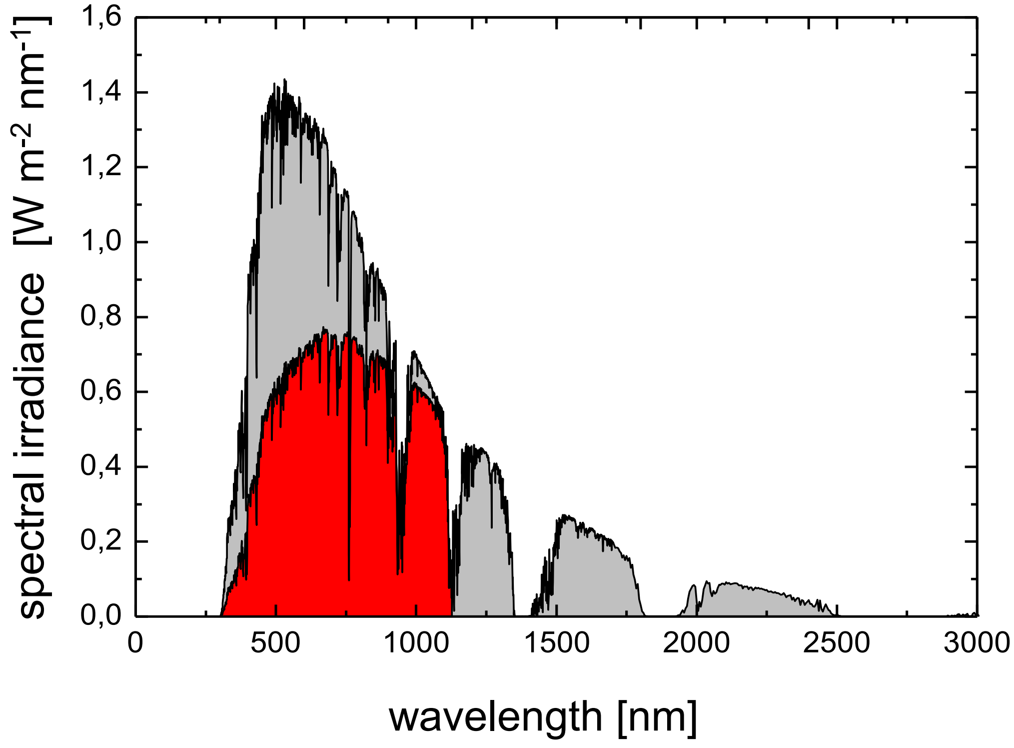
Step 1: Spectral mismatch: The considerations 1-4 define the spectral match of the solar cell, i.e. the maximum current generation.



which leads us to the maximum short-circuit current density:

$$J_{SC} = q \int_0^\infty A(\lambda)\, \Phi_{ph,\lambda} \mathrm{d}\lambda$$

$$= q \int_0^{E_g} \Phi_{ph,\lambda} \mathrm{d}\lambda$$

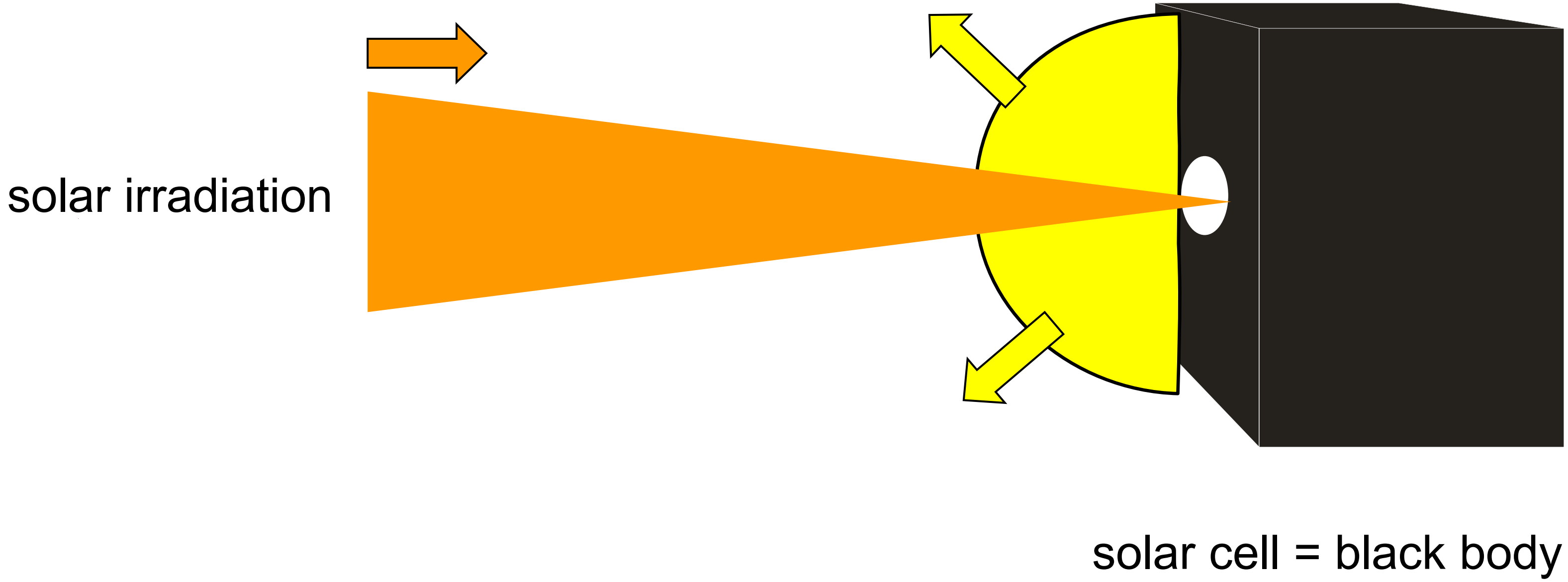
where $\Phi_{ph,\lambda}$ is the spectral photon flux of the incident light (e.g. AM1.5G spectrum).

Shockley-Queisser (SQ) efficiency limit

Step 2: Open-circuit voltage: Considerations 4, 5 & 6 will lead us to the maximum open-circuit voltage (V_{OC}) and fill factor (*FF*).

I. First, we consider the solar cell at thermal equilibrium (no external light on it and no voltage applied to it), which matches the situation of open circuit.

$$J_{em} = J_{ph}$$



Shockley-Queisser (SQ) efficiency limit

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Step 2: Open-circuit voltage: Considerations 4, 5 & 6 will lead us to the maximum open-circuit voltage (V_{OC}) and fill factor (FF).

I. First, we consider the solar cell at thermal equilibrium (no external light on it and no voltage applied to it), which matches the situation of open circuit.

$$J_{em} = J_{ph}$$

II. According to consider. 4 & 6, one absorbed photon generates one e-h-pair:

$J_{SC} = J_{ph}$ with the photogeneration current density J_{ph}.

III. According to consideration 5, we have only radiative recombination which can be described by Planktian black body radiation. So, for the emitted current density, we get:

$$J_{em} = q \int_{E_g}^{\infty} \Phi_{BB}(E_y) dE_y \left[\exp\left(\frac{qV_{OC}}{k_B T}\right) - 1\right]$$

$$J_{em} = J_0 \left[\exp\left(\frac{qV_{OC}}{k_B T}\right) - 1\right]$$

* Remember lecture 5.

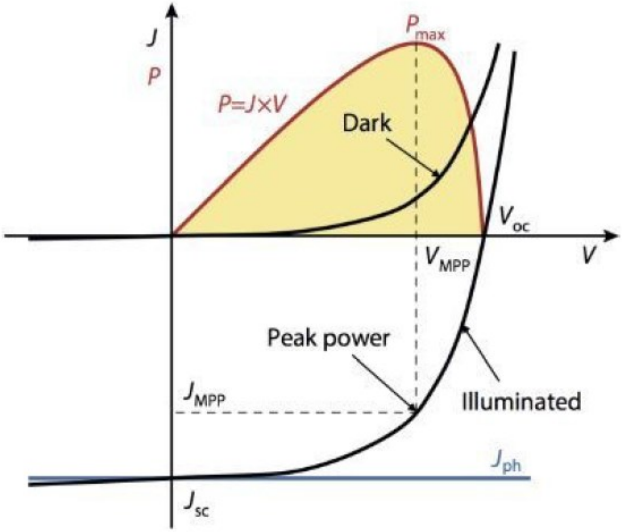
Shockley-Queisser (SQ) efficiency limit

Step 2: Spectral mismatch: Combining I, I & III, we can derive V_{OC}:

$$V_{OC} = \frac{k_B T}{q} \, ln\left[\frac{J_{SC}}{J_0} + 1\right]$$

Now, we can calculate the max. efficiency with

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

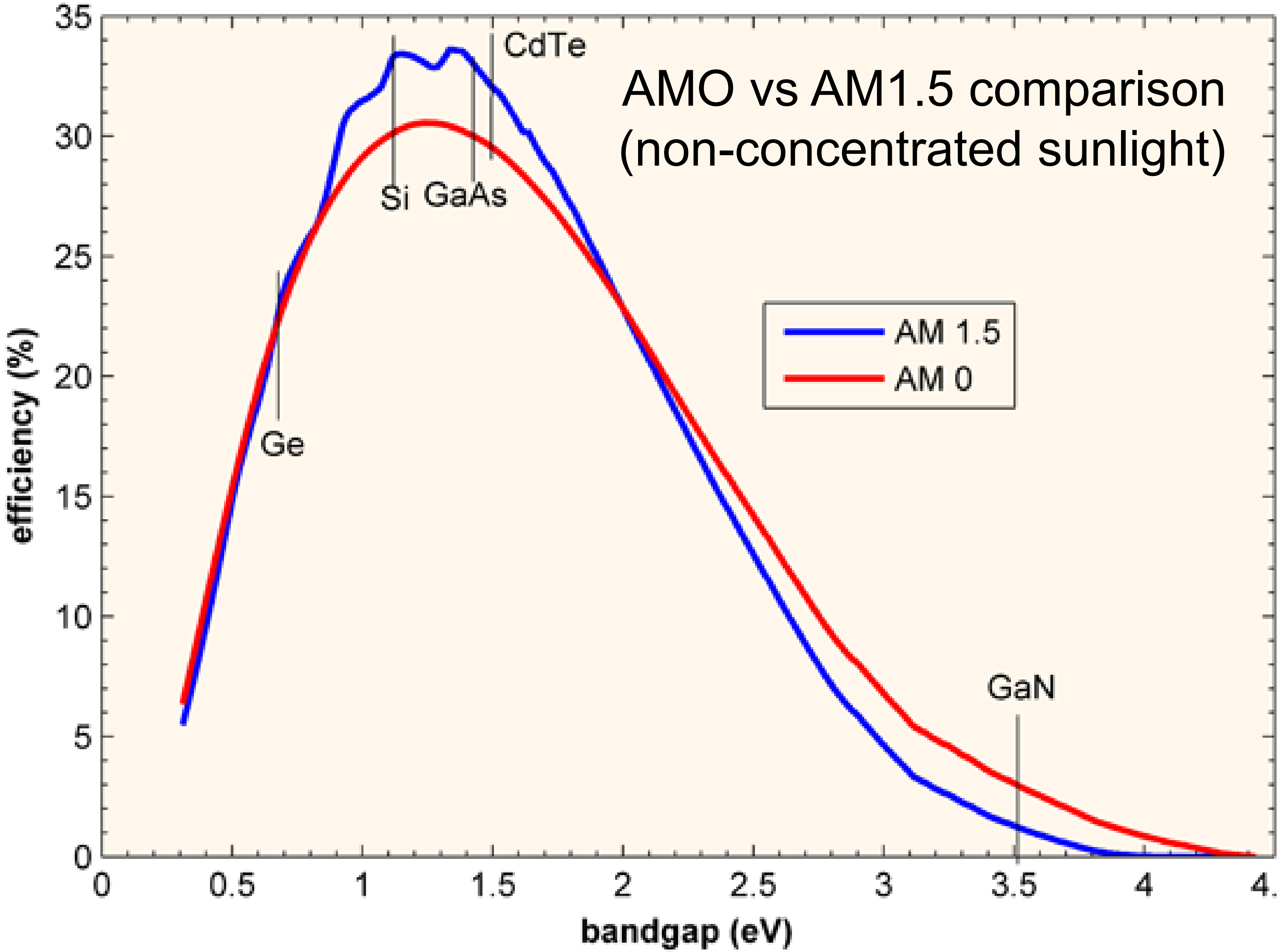


with the empirical optimum FF:

$$FF \approx \frac{qV_{OC}/k_B T - \ln(0.72 + qV_{OC}/k_B T)}{1 + qV_{OC}/k_B T}$$

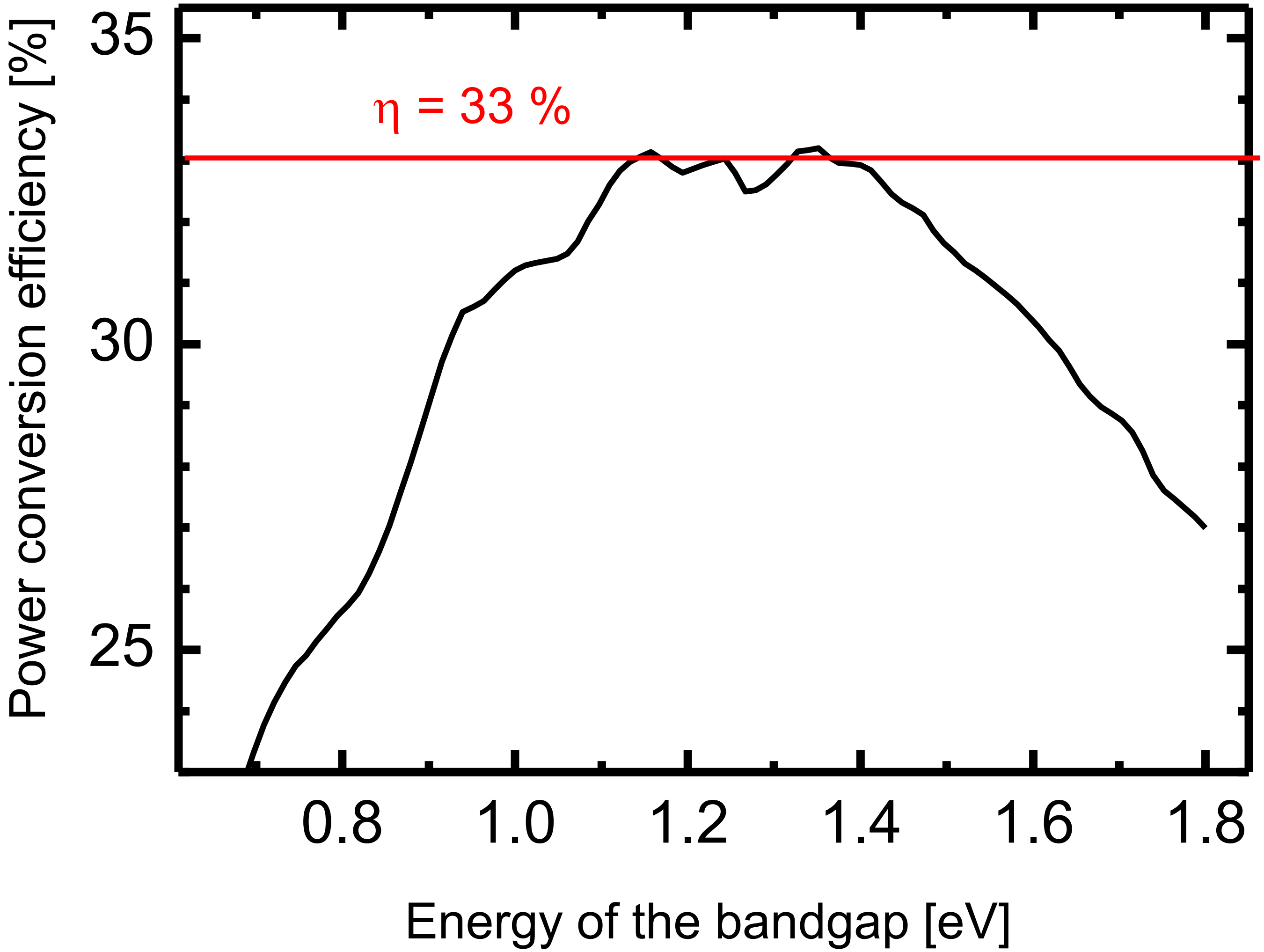
, which is very close to the real numerical max. PCE.

Shockley-Queisser (SQ) efficiency limit

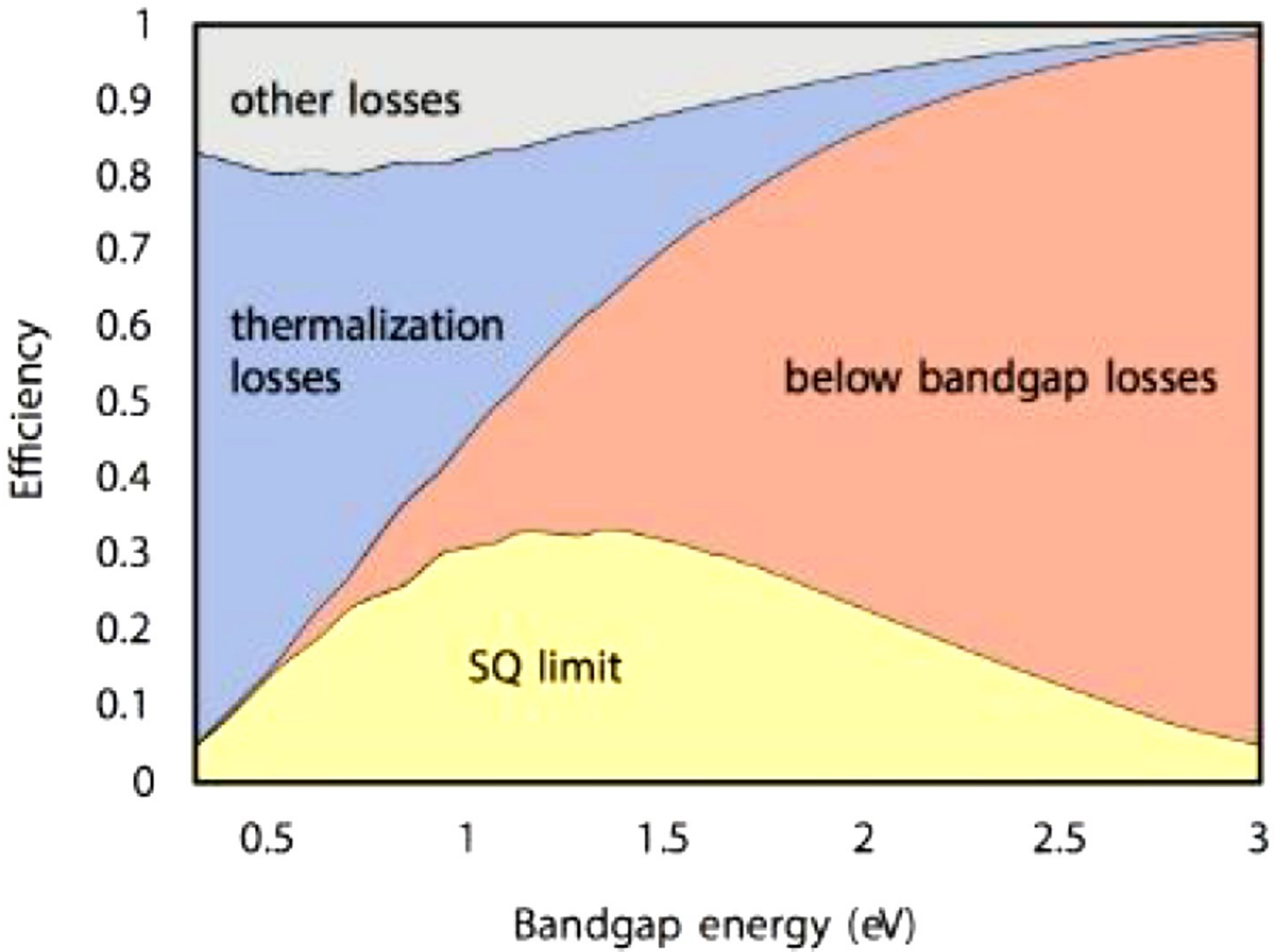


Source: http://www.pveducation.org/pvcdrom/solar-cell-operation/detailed-balance

Shockley-Queisser (SQ) efficiency limit



Shockley-Queisser (SQ) efficiency limit

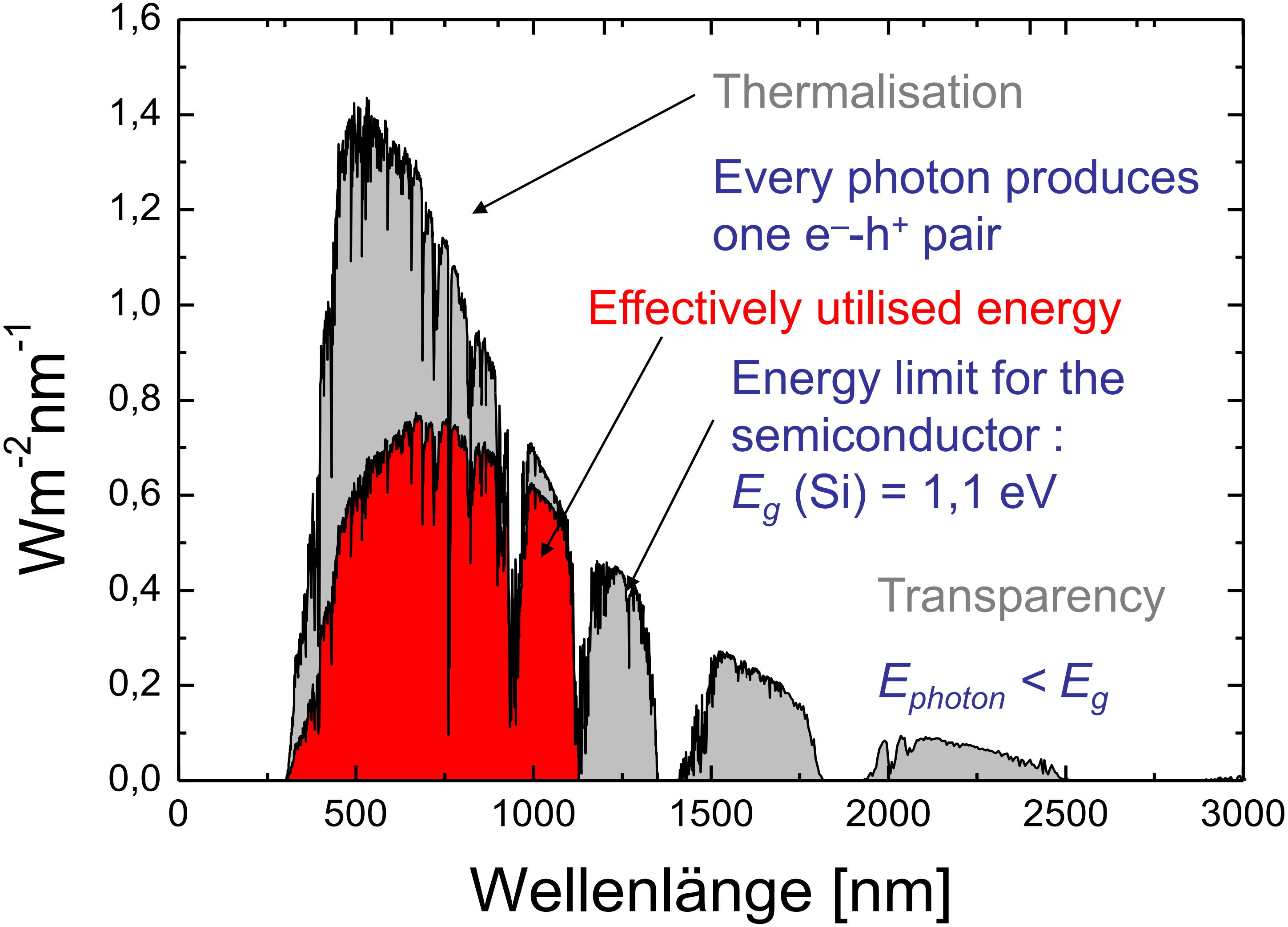


Quick Test

- What is the ultimate limit for any energy conversion process? Describe the derivation of this efficiency limit.
- What are the key assumptions for the Shockley Queisser limit?
- Explain the two key losses related to spectral mismatch.
- What is the max. PCE of a single junction solar cell assuming the AM1.5 spectrum?
- Why is radiative recombination considered for the SQ limit?
- What is the concept behind “detailed balance”?
- For which bandgap range is the maximum PCE according to the SQ limit larger than 30%
- List losses that reduce the power conversion efficiency of real solar cells compared to the Shockley Queisser limit.
  - Optical losses
  - Losses related to the bulk material characteristics
  - Contacts

PART II: THIRD GENERATION CONCEPTS

Effective Utilisation of Solar Photons



Concept #1: Multijunction Solar Cells

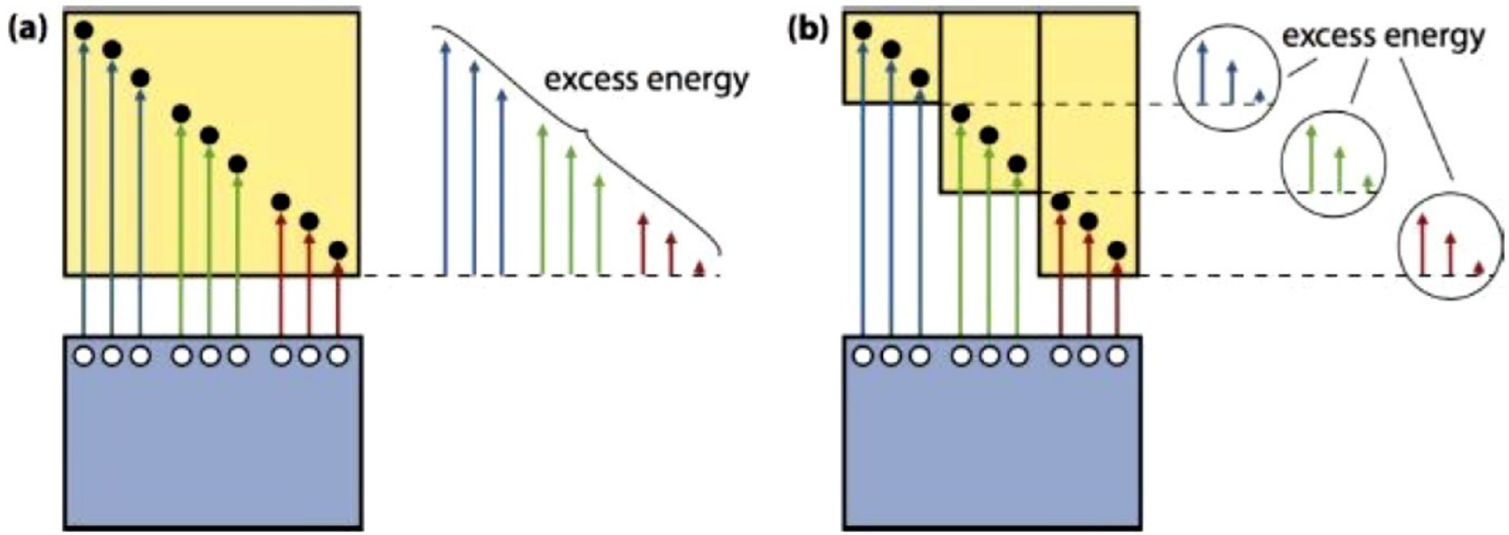


Figure 10.9: Illustrating the lost excess energy in (a) a single-juntion; and (b) a multi-junction solar cell.

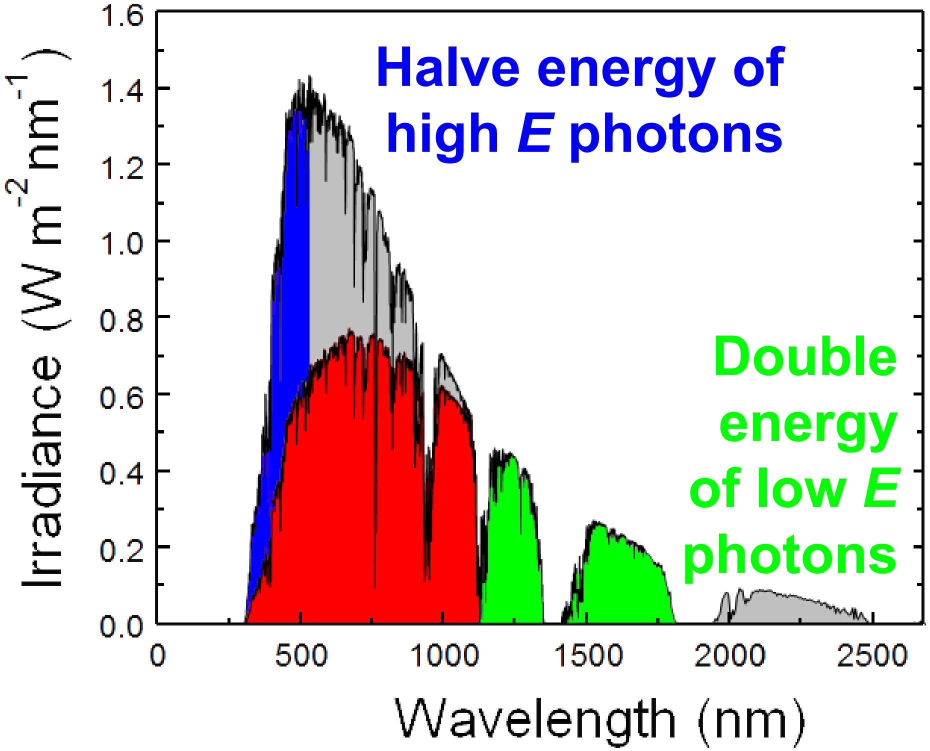
⇒ Next lecture!

Multijunction Solar Cells are yet the only commercially relevant 3rd generation PV concept.

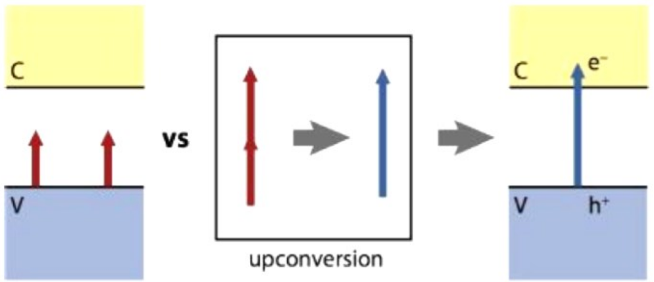
Source: textbook

Concept #2: Spectral Conversion (Recapitulation)

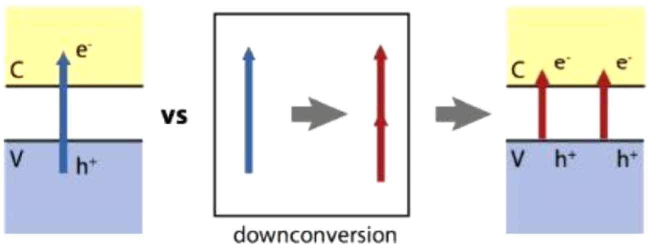
- Use of **luminescent materials** to change wavelengths of sunlight
- Address thermalisation and transparency losses
- Still rely on a single-junction solar cell



Upconversion



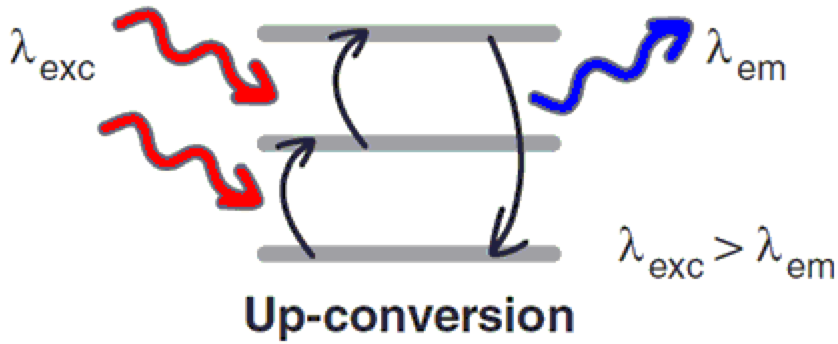
Downconversions



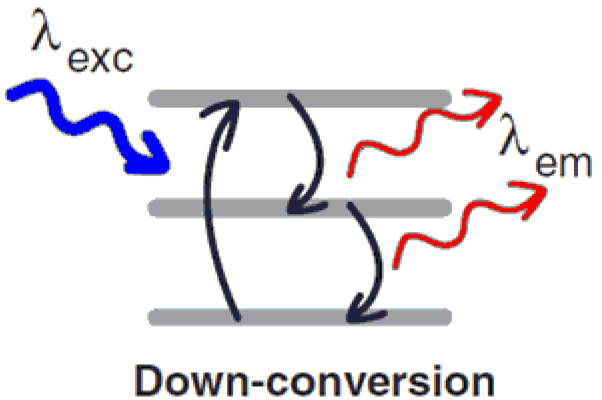
Concept #2: Spectral Conversion (Recapitulation)

[=>See lecture 14: Luminescent materials for PV]

- Up-conversion (UC) of 2 low-energy photons to give 1 higher-energy photon
  $\Rightarrow$ addresses sub-bandgap losses



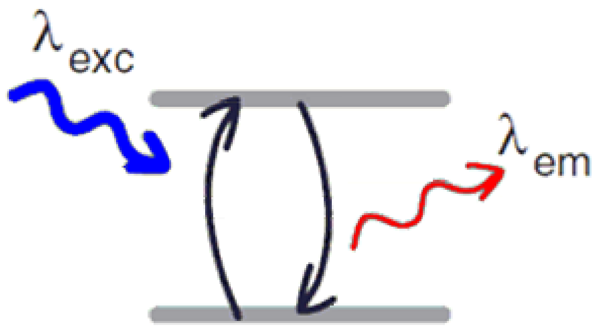
- Down-conversion (DC) a.k.a. quantum cutting, is where 1 high-energy photon is 'cut' into 2 lower-energy photons
  $\Rightarrow$ addresses lattice thermalisation losses



Concept #2: Spectral Conversion (Recapitulation)

[=>See lecture 14: Luminescent materials for PV]

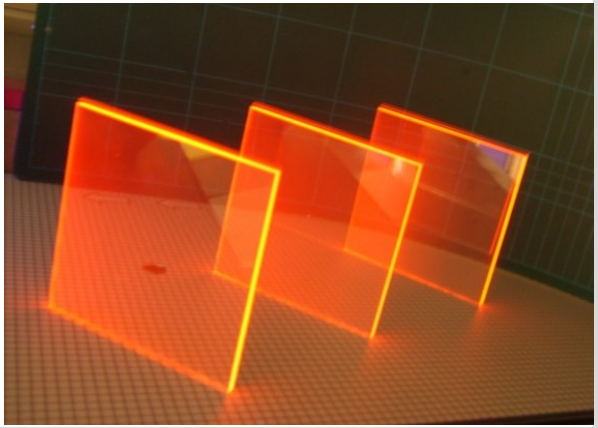
- Luminescent down-shifting: standard photoluminescence (Stokes) process



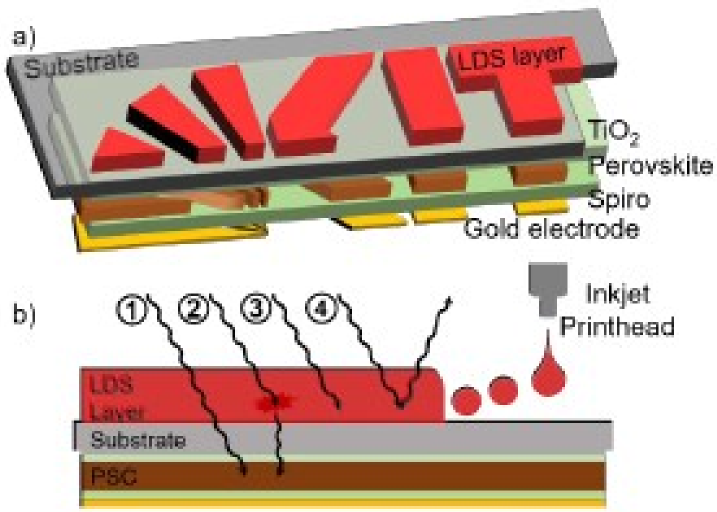
- Doesn't address thermalisation or sub-bandgap losses, but:

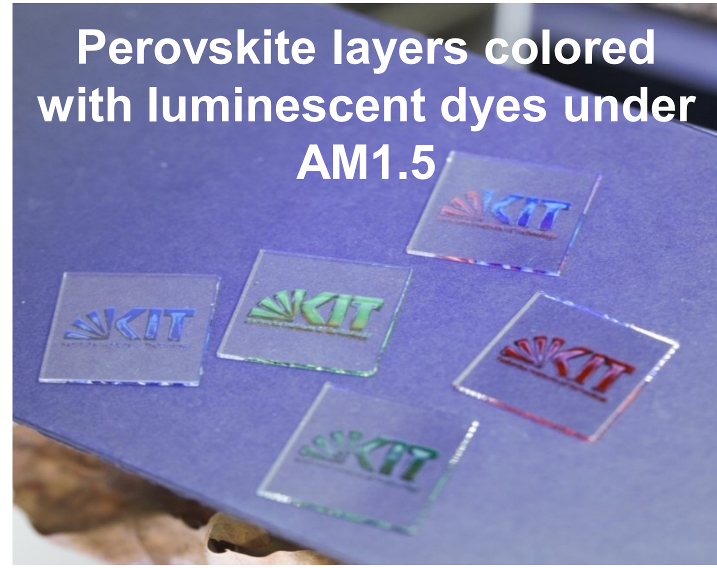
⇒ can still enhance performance of solar cells with poor external quantum efficiency (EQE)

⇒ waveguiding of PL is principle behind the luminescent solar concentrator (LSC)



Luminescence Dyes also can serve purpose of colouration





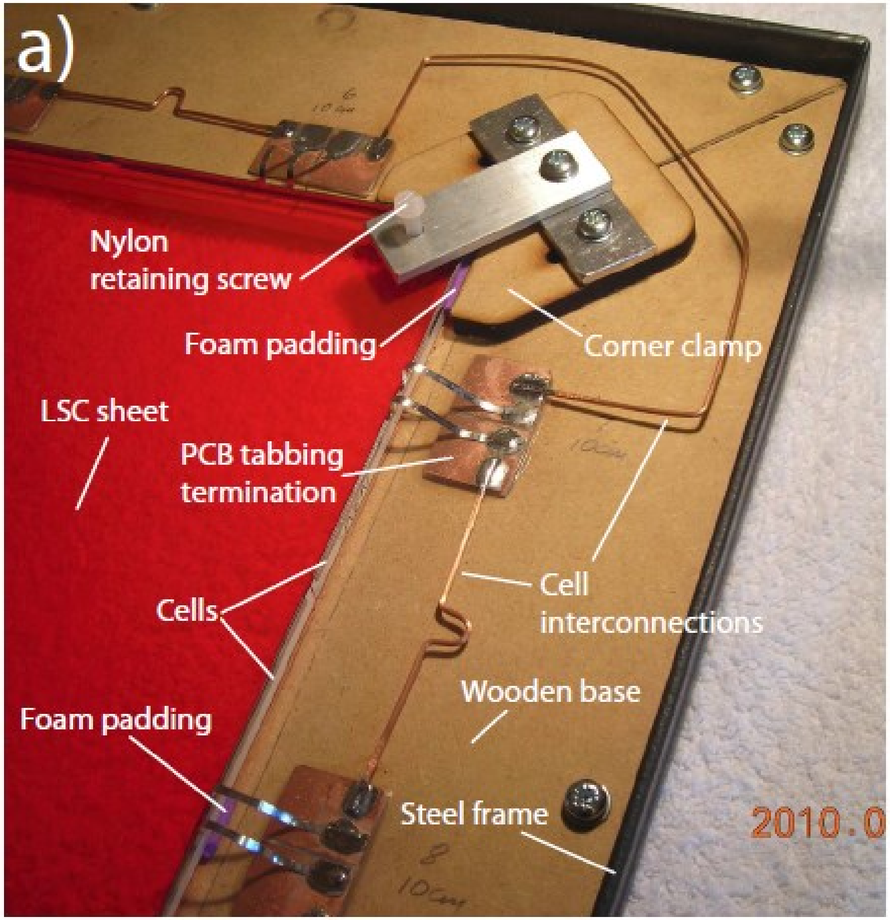
- Top: Inkjet printing of luminescent dyes
- Bottom: Inkjet printed perovskite PV

=> **Colored Perovskite PV**

Source: Shape and Color Flexibility for Inkjet Printed Perovskite Photovoltaics, S. Schlisske, et al. ACS Applied Energy Materials (2018)

Luminescent Solar Concentrators

- Large areas possible (60cm × 60cm, h = 2%)



<u>LSC materials</u>:
- cast PMMA
- 400ppm Lumogen Red300
- 10**cm** × **0.3cm c-Si solar cells**

Source: Wilson, PhD thesis (2010)

Concept #3: Intermediate band solar cell

- Way of addressing sub-bandgap transparency losses

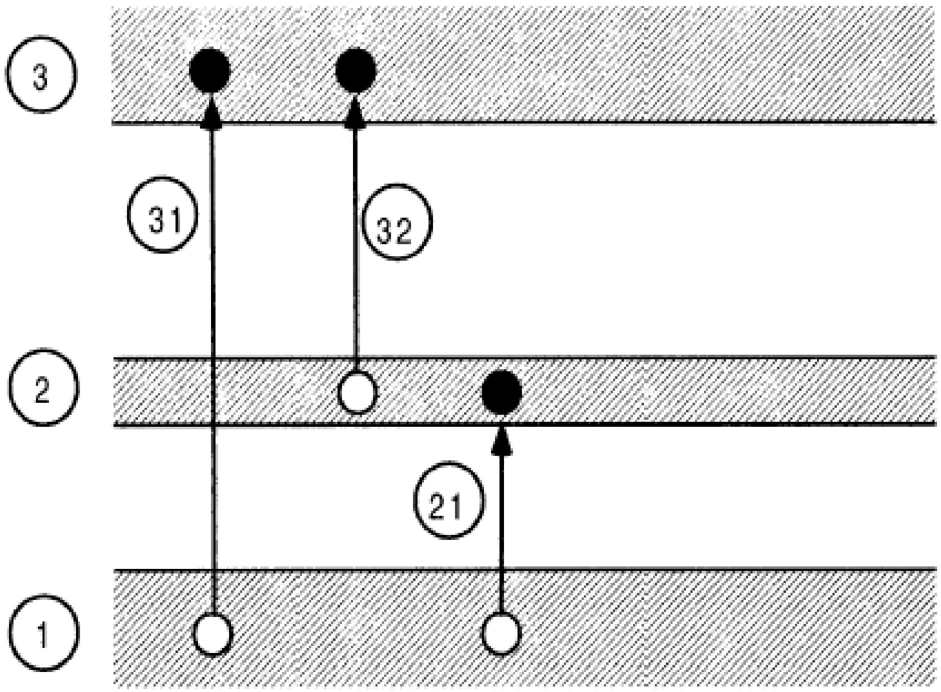


Fig. 8.3: 3-band solar cell. The lower- and upper-most bands are valence and conduction bands, while the intermediate band is considered to be an impurity band.

Source: Martin Green, "Third Generation Photovoltaics: Advanced Solar Energy Conversion", Springer 2003

Concept #3: Intermediate band solar cell

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- High efficiencies again possible with three bands….

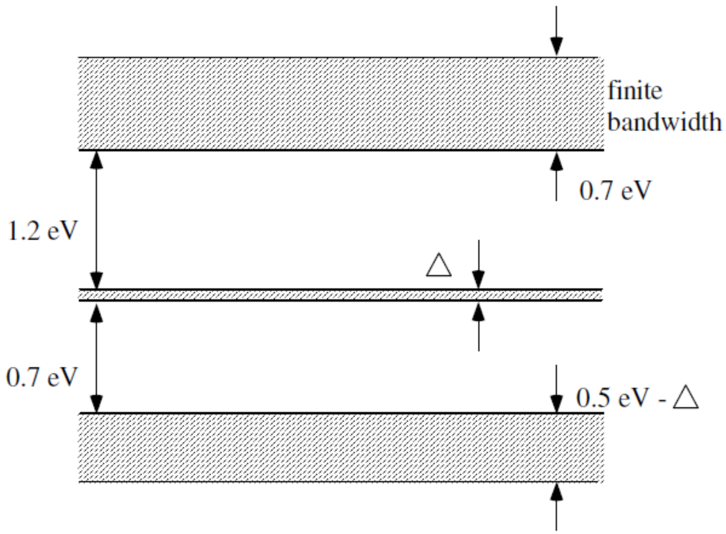


Fig. 8.6: Optimally designed 3-band cell with photon selectivity ensured by finite bandwidth for each of the 3 bands involved.

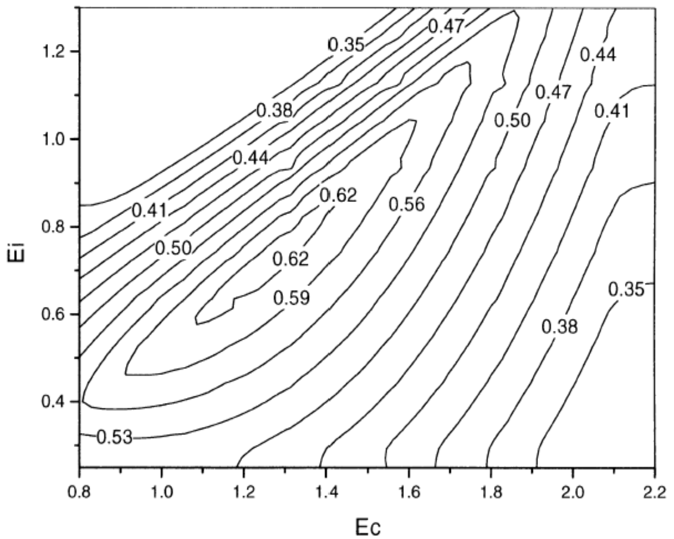


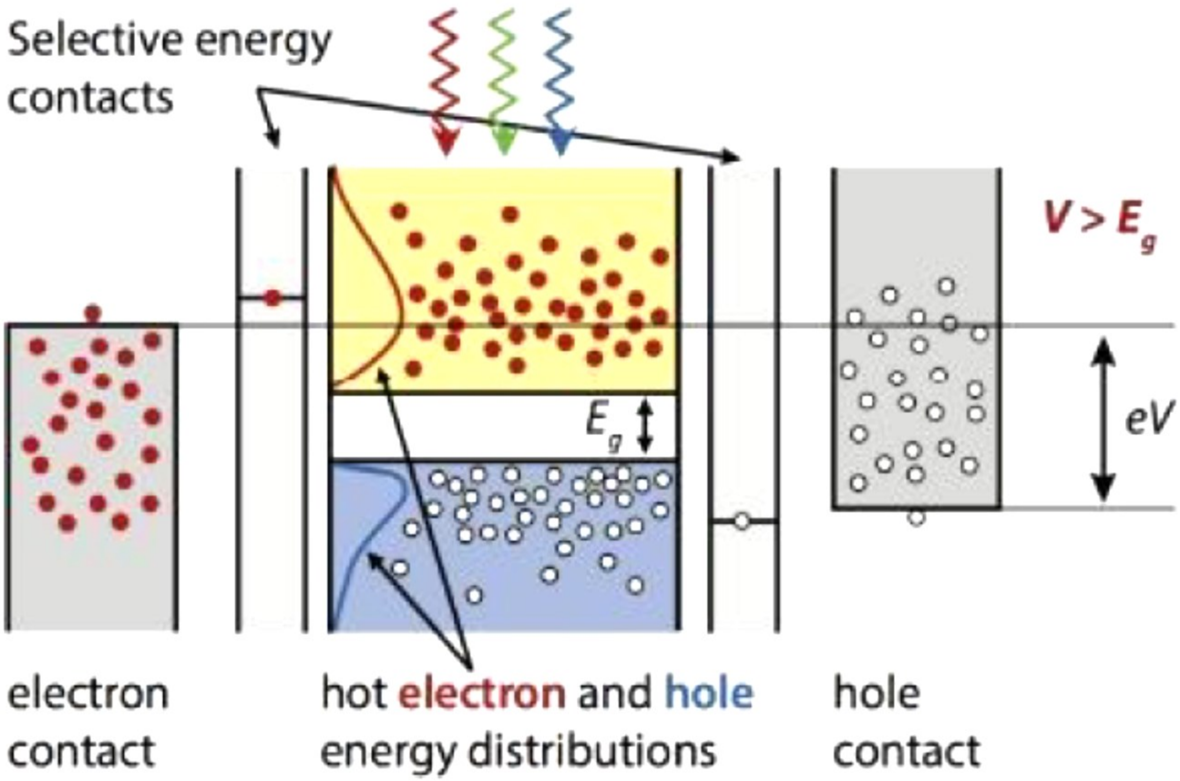
Fig. 8.5: Limiting efficiency of a 3-band cell as a function of the two lower threshold energies (Corkish 1999). (T_s = 6000 K, T_c = 300 K).

- Only possible if a concept is considered that avoids recombination via the intermediate band (spin selelctivity or similar) => not solved!

Source: *Martin Green, "Third Generation Photovoltaics: Advanced Solar Energy Conversion", Springer 2003*

Concept #4: Hot Carrier Solar Cells

- How to achieve this??
- One idea (Würfel): use a wide bandgap semiconductor with narrow conduction and valence bands



Source: Textbook

Concept #4: Hot Carrier Solar Cells

- Different approach: extract excess energy from high-energy charge carriers energy they thermalize back down to band edges

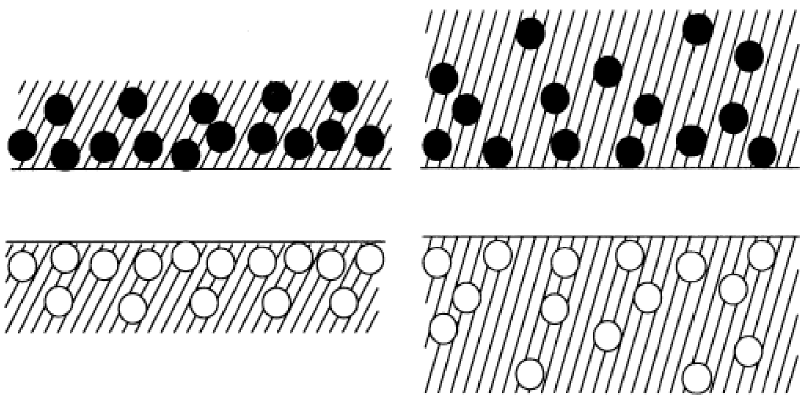


Fig. 6.1: Normally carriers thermalise with the lattice as in (a). In hot carrier cells, e energy is stored in a hot carrier distribution, as shown in (b).

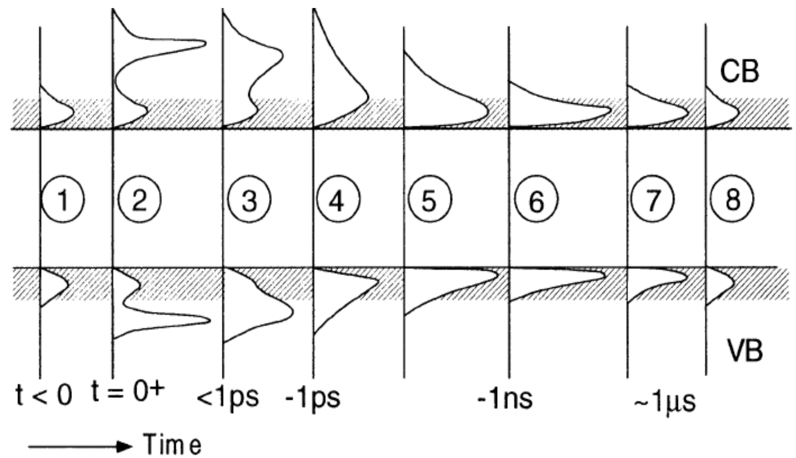


Fig. 6.2: Time evolution of electron and hole distributions in a semiconductor subject to a short, high intensity, monochromatic pulse of light from a laser: (1) Thermal equilibrium before pulse; (2) "coherent" stage straight after pulse; (3) carrier scattering; (4) thermalisation of "hot carriers"; (5) carrier cooling; (6) lattice thermalised carriers; (7) recombination of carriers; (8) return to thermal equilibrium.

- Hot carriers may be able to travel 10nm before they thermalize

Source: Martin Green, "Third Generation Photovoltaics: Advanced Solar Energy Conversion", Springer 2003

Concept #4: Hot Carrier Solar Cells

- Efficiency potential is high, but research still at a very fundamental stage

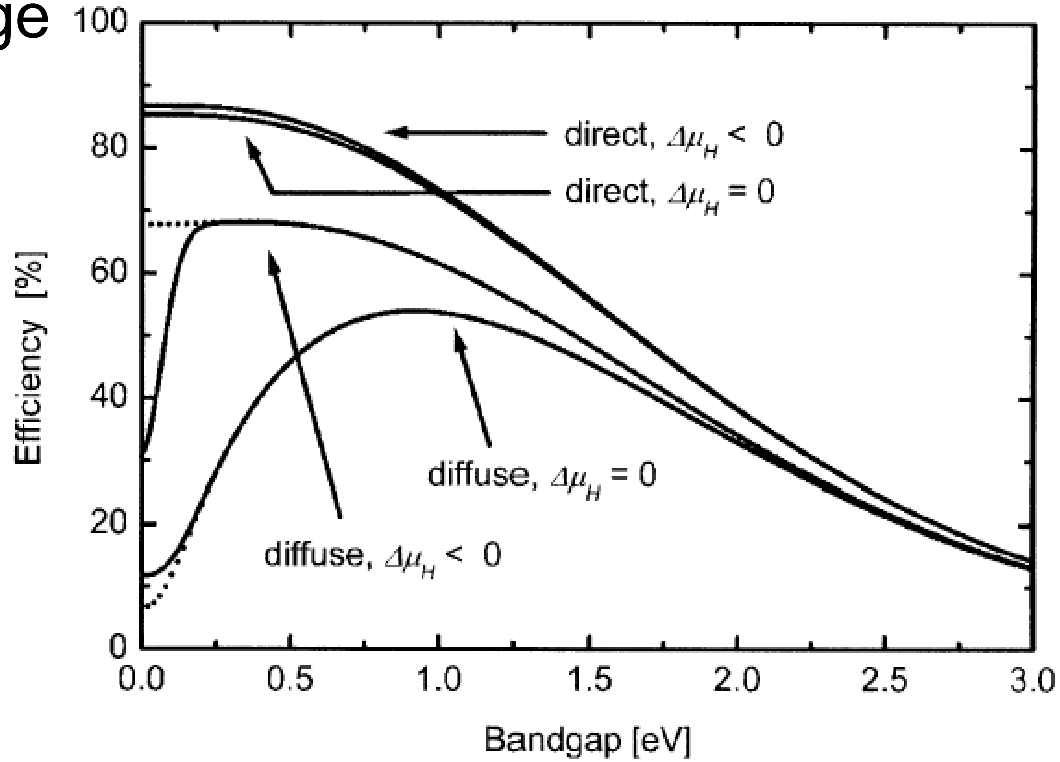


Fig. 6.7: Limiting efficiency of a hot carrier cell for direct and diffuse sunlight. The curves labelled $\Delta\mu_H < 0$ show the unconstrained case while the curves labelled $\Delta\mu_H = 0$ shows the case where there are high levels of interaction between hot electrons and holes.

Source: Martin Green, "Third Generation Photovoltaics: Advanced Solar Energy Conversion", Springer 2003

Concept #4: Hot Carrier Solar Cells

- How to achieve this??
- One idea (Würfel): use a wide bandgap semiconductor with narrow conduction and valence bands

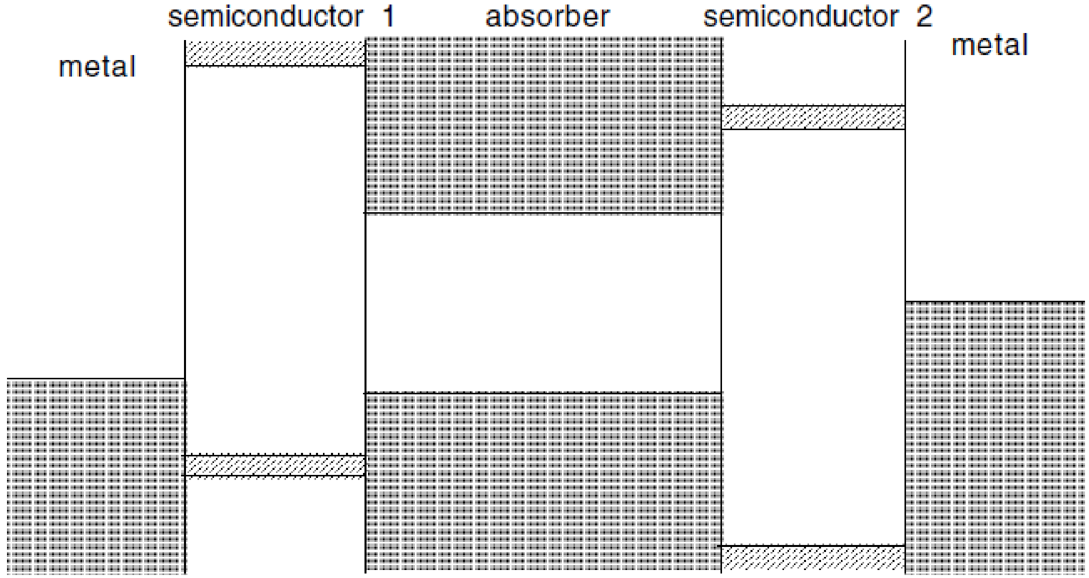


Fig. 6.3: Selective energy contacts to hot carrier cell based on wide bandgap semiconductors with narrow valence (left) and conduction (right) bands.

- Maybe also possible using quantum dots

Source: *Martin Green, "Third Generation Photovoltaics: Advanced Solar Energy Conversion", Springer 2003*

Quick Test Part on 3rd Gen. Concept #1: Multijunction Photovoltaics

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For more details please see also the next lecture 17 on multijiunction photovoltaics.

Quick Test Part on 3rd Gen. Concept #2: Spectral Conversion

- Explain the principle behind (i) UC, (ii) DC, (iii) LDS, and (iv) LSC.
- Which fundamental loss is addressed by (i) UC, (ii) DC, and (iii) LDS, respectively?
- What are the challenges hampering the deployment of (i) UC, (ii) DC, or (iii) LDS?

For more details please see also the lecture on luminescent materials.

Quick Test Part on 3rd Gen. Concept #3: Intermediate band solar cell

- Explain the working principle of an intermediate band solar cell.
- Which fundamental loss is addressed in an hypothetical intermediate band solar cell?

Quick Test Part on 3rd Gen. Concept #4: Hot Carrier Solar Cell

- Explain the working principle of a hot carrier solar cell.
- Which fundamental loss is addressed in an hypothetical intermediate band solar cell?

Questions ?