"Solar Energy" WS 2014/2015

Lecture 12+13: Third Generation Photovoltaics

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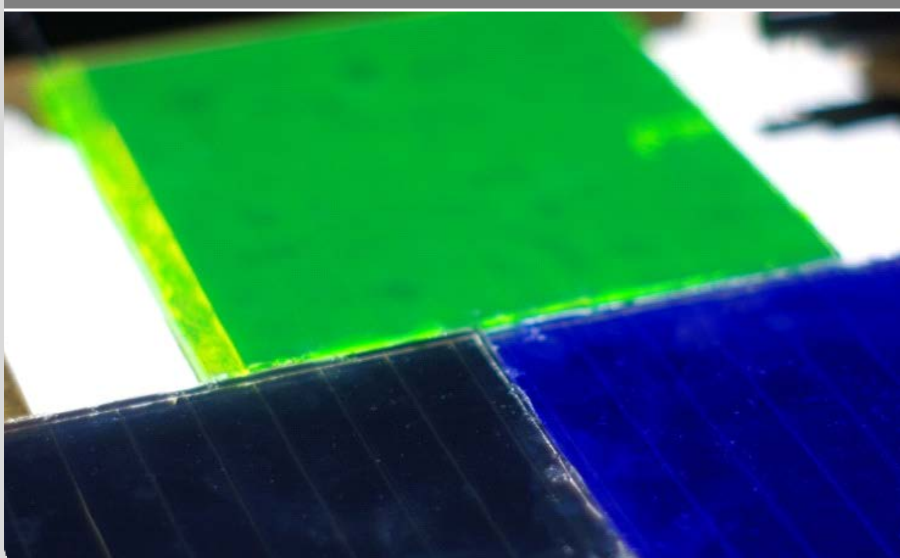
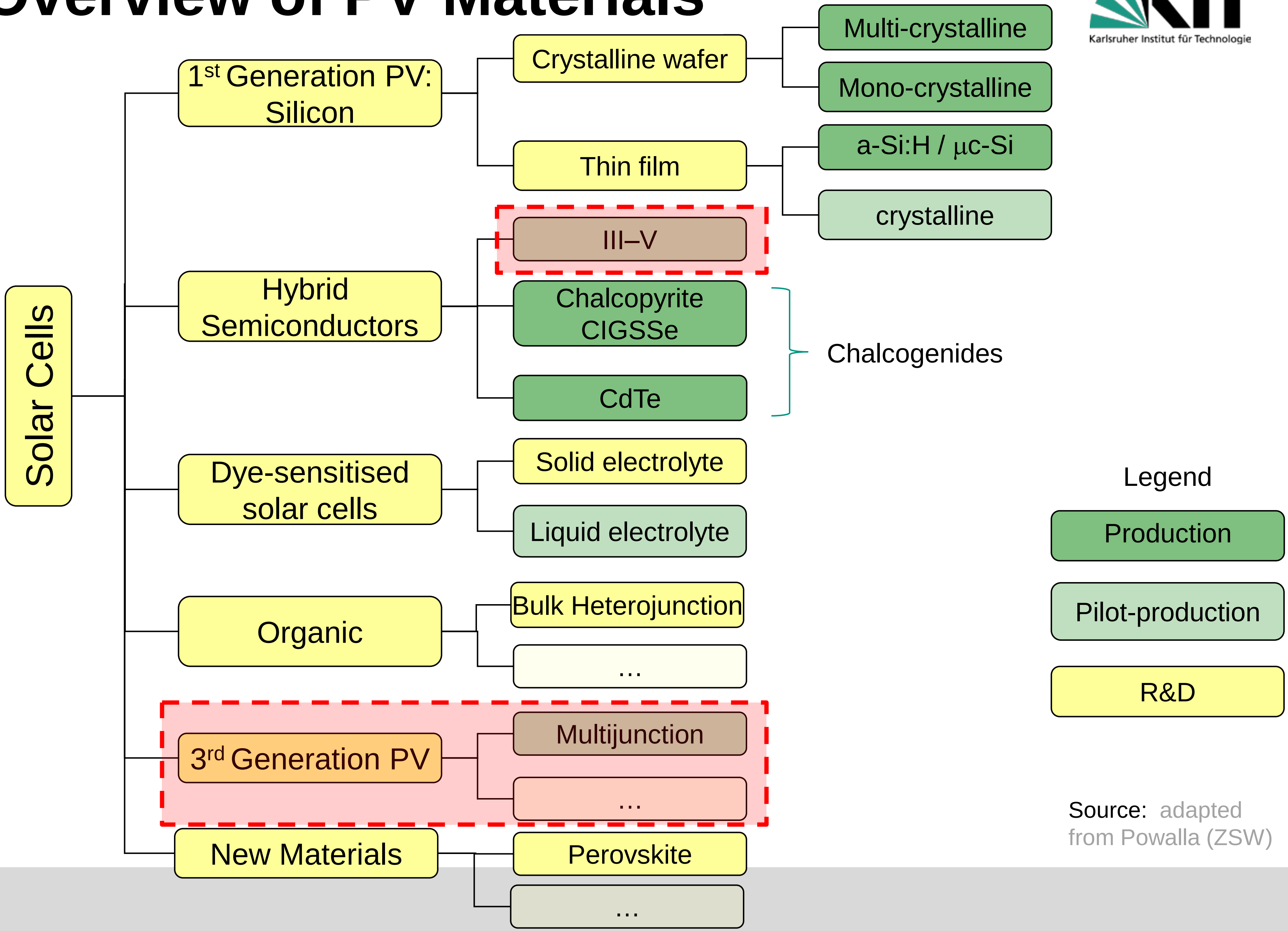


Overview of PV Materials

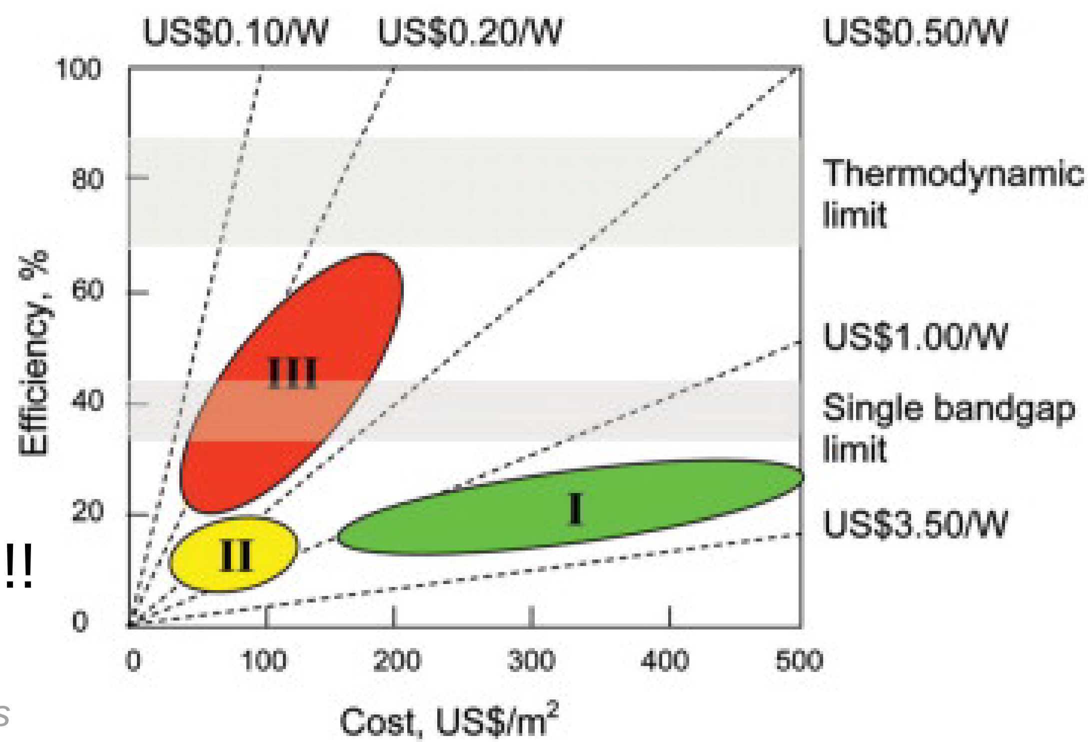


Source: adapted from Powalla (ZSW)

Generations of PV Technology

- 1st gen: wafer-based silicon
- 2nd gen: single junction thin films
- 3rd gen: strategies to overcome single-junction limits, e.g. tandem (multijunction) solar cells
- Originally defined back in late 90's by Martin Green (UNSW)
- But how does this look today?

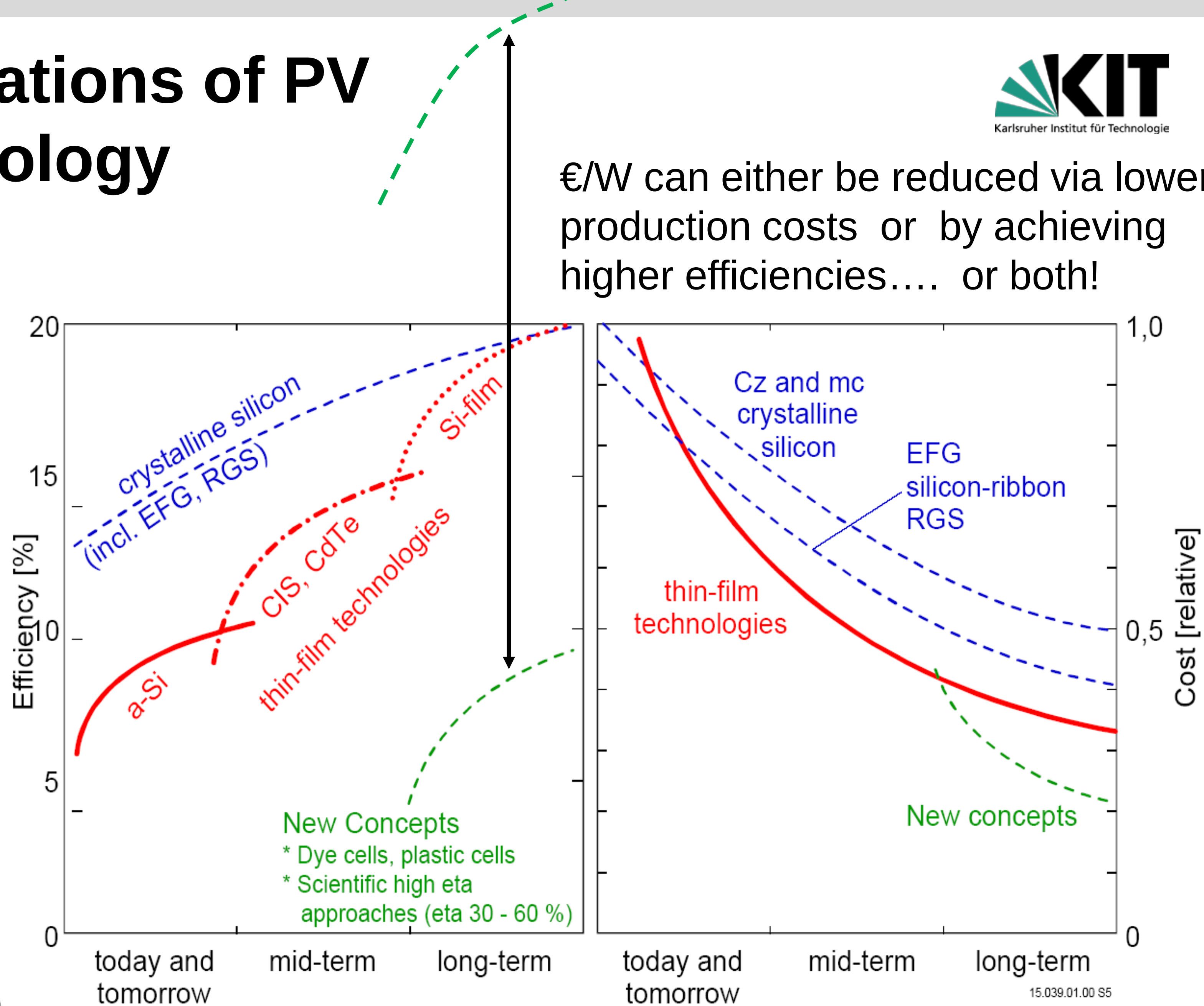
  I now occupies same space as II!!



Source: Martin Green, Univ. New South Wales

Generations of PV Technology

€/W can either be reduced via lower production costs or by achieving higher efficiencies…. or both!



Source:
W. Hoffmann, EPIA

Generations of PV Technology

- 1st gen: wafer-based silicon
- 2nd gen: single junction thin films
- 3rd gen: strategies to overcome single-junction limits, e.g. tandem (multijunction) solar cells

$\Rightarrow$ so what are the fundamental upper limits on solar energy conversion efficiency?

Fundamental PV Efficiency Limits

- Going back to thermodynamics: 1st and 2nd laws of thermodynamics as phrased by Rudolf 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”*.

- 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 $\Rightarrow$ less disorder $\Rightarrow$ smaller entropy
- 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
- In 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 $\dot{E}/\dot{T}$, if the transfer occurs in the presence of an infinitesimally small temperature differential.

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

Fundamental PV Efficiency Limits

- The most general efficiency limit for PV is the <u>Carnot limit</u>
- 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

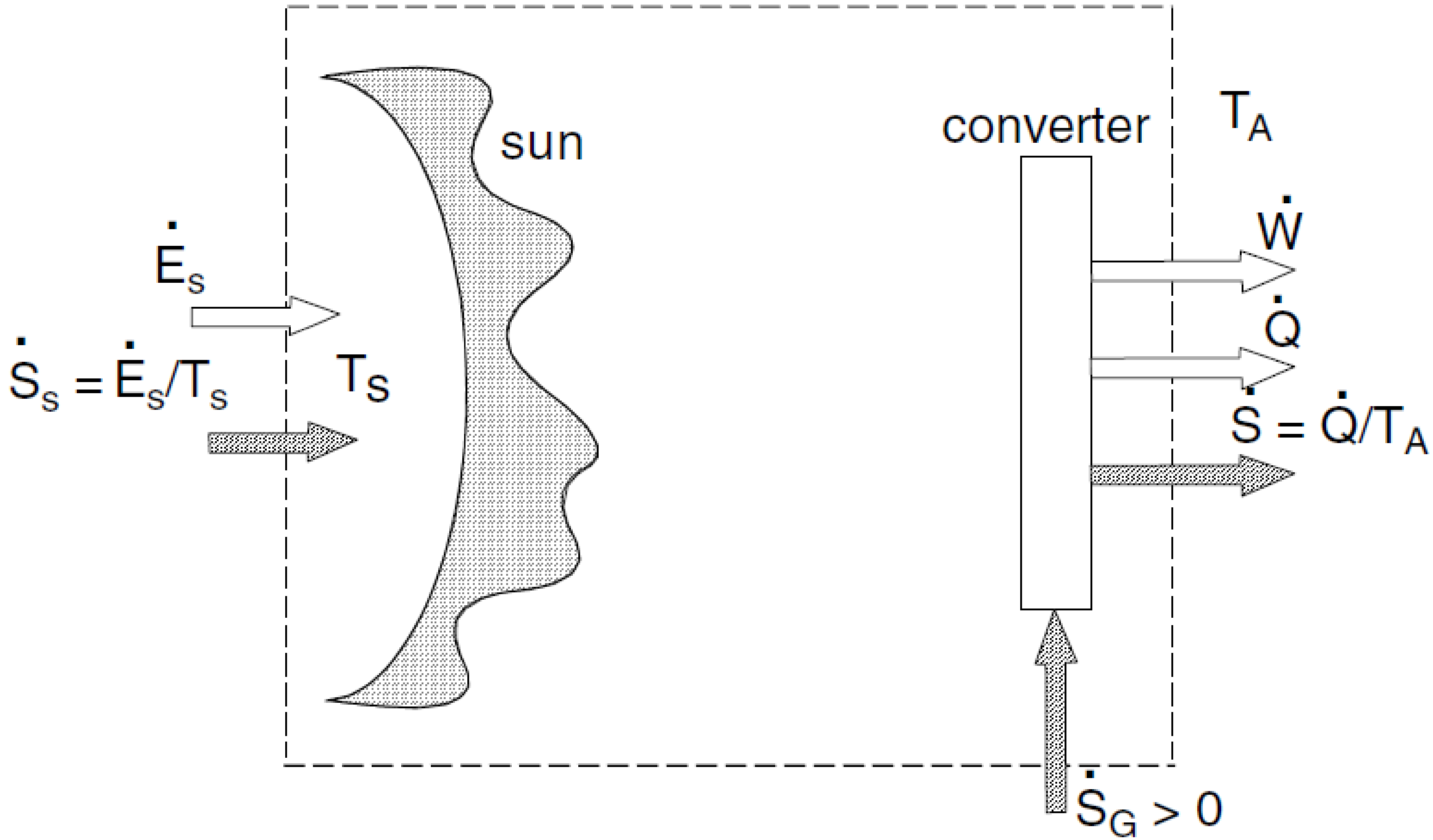


Fig. 3.1: System considered for calculating Carnot efficiency.

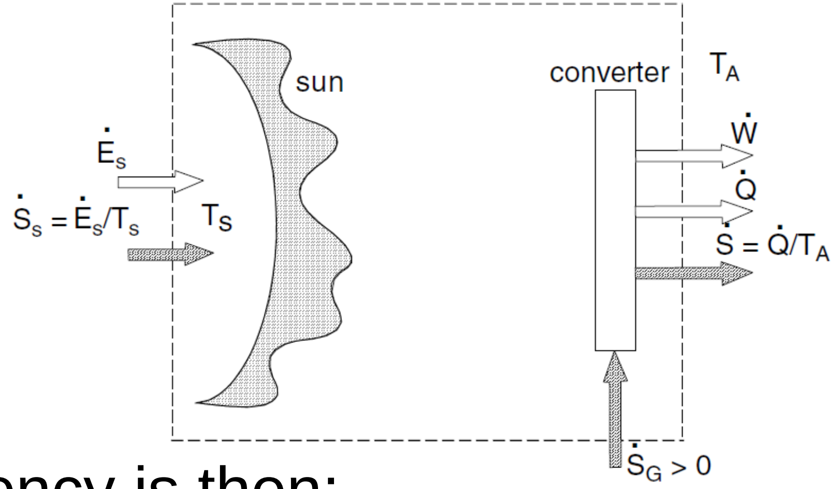
Source: Martin Green, "Third Generation Photovoltaics: Advanced Solar Energy Conversion", Springer 2003

Fundamental PV Efficiency Limits

- 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 its maximum value of 95% when $\dot{S}_G = 0$,
  $\Rightarrow$ Carnot efficiency for conversion of heat energy supplied to the sun's photosphere to terrestrial energy

Fundamental PV Efficiency Limits

- Interesting point: no information is required about converter itself $\Rightarrow$ natural question then is to whether there is 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

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- The Landsberg η limit considers a more restricted system
- Inputs are radiant energy and associated entropy fluxes from the sun plus the unavoidable entropy generation during the absorption and conversion processes
- Outputs are again work and heat fluxes, plus associated entropy flux. Additional outputs are the energy re-radiated by the converter $\dot{S}_C$ and associated entropy flux $\dot{E}_C$

$$\eta_L = 1 - \frac{4}{3}\frac{T_A}{T_S} + \frac{1}{3}\frac{T_A^4}{T_S^4} = 93.3\%$$

$$\text{for} \quad T_A = 300K$$

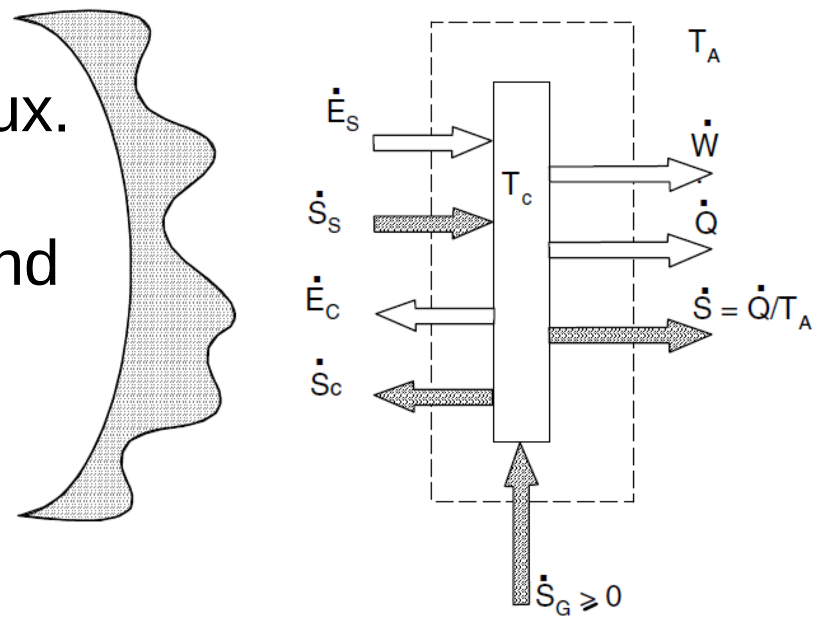


Fig. 3.2: System for calculating Landsberg efficiency limit.

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

Fundamental PV Efficiency Limits

- <u>Black body η limit</u> extends upon Landsberg analysis for reciprocal black-body absorbers $\Rightarrow$ 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

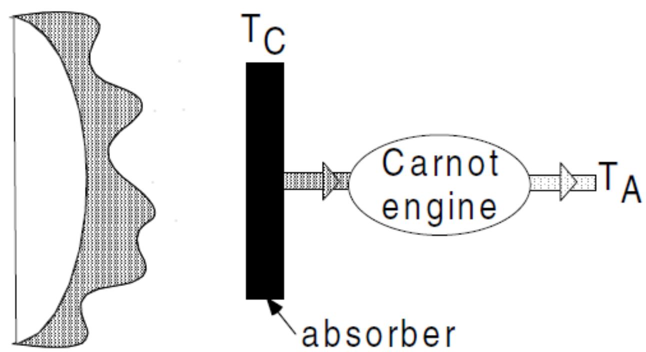
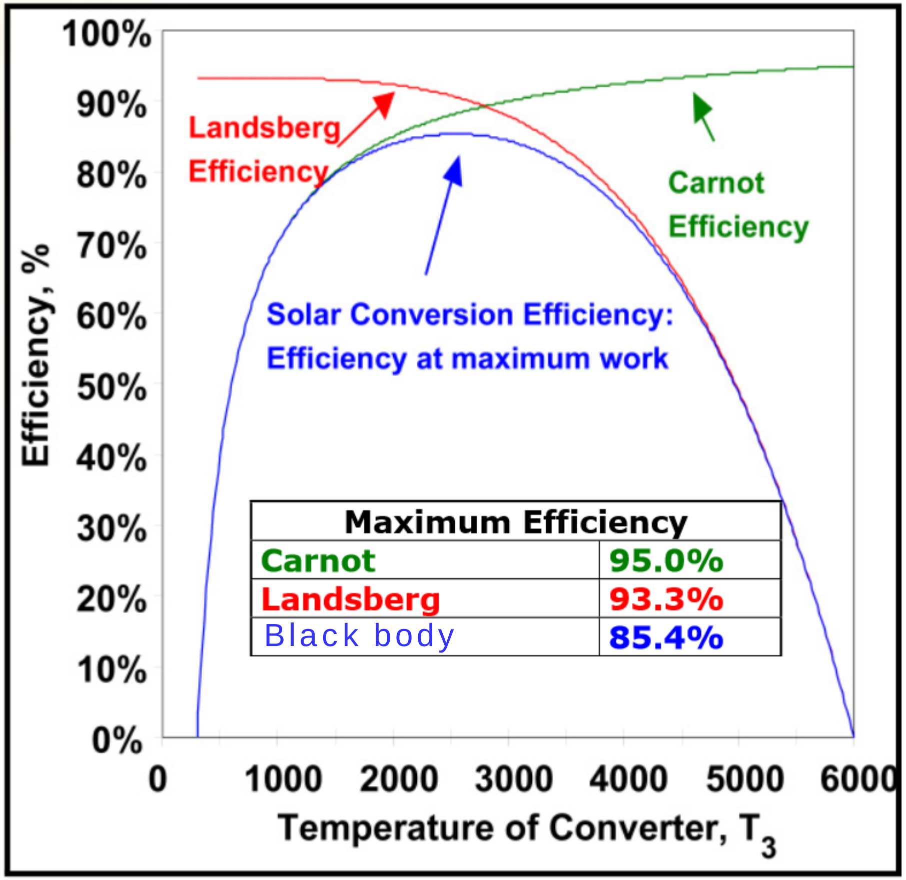


Fig. 3.3: Ideal solar thermal converter with sunlight absorbed by an absorber at temperature T_C, with heat extracted from this absorber converted to electricity by a Carnot converter.

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: adapted from Christiana Honsberg, http://www.energy.udel.edu/pdf/Honsberg_UDEI_Symposium.pdf

Fundamental PV Efficiency Limits

- Emission from a black-body at each photon energy is determined solely by *T*, but higher efficiency is possible if emission of light at each energy is optimised separately

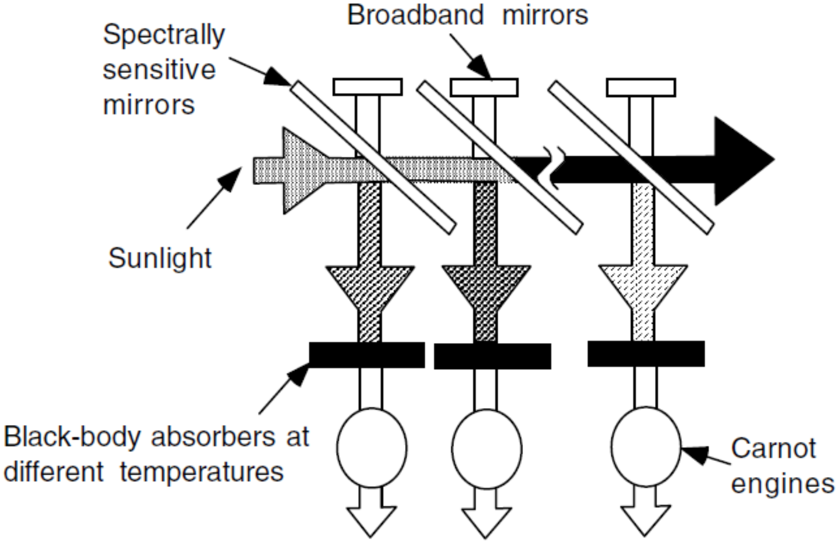


Fig. 3.4: Multicolour converter implemented using black-bodies and mirrors, both spectrally sensitive and broadband. The mirror arrangement shown ensures, in principle, that each black-body absorber both absorbs light over a narrow range of wavelengths, determined by the spectrally sensitive mirrors, and also has a nett emission over the same wavelength range.

$\Rightarrow$ η_{bb} = 86.8%, so PV has a slight advantage over solar thermal approaches

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

Fundamental PV Efficiency Limits

- Using tandem cell stacks, a conceptually equivalent geometry can be implemented much more elegantly

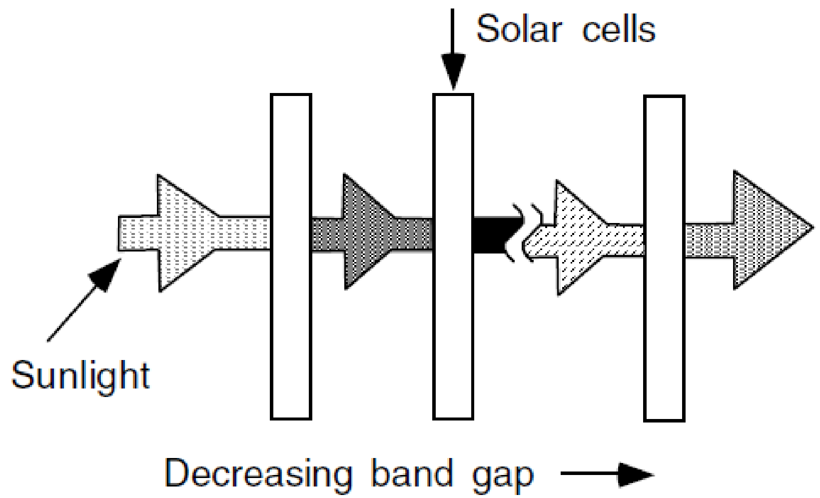


Fig. 3.6: Tandem cell stack giving the same limiting efficiency as the more complex system of Fig. 3.4.

- You have seen some practical implementations of this approach before (e.g. a-Si:H and OPV multi-junctions)

Fundamental PV Efficiency Limits

- Shockley-Queisser (SQ) efficiency limit for single *p-n* junction
- Starting point: an efficient solar cell needs to be an efficient absorber of solar photons and hence have properties related to a black-body, at least for $E > E_g$
    - Attributed all this radiation for $E > E_g$ to band-to-band recombination
    - Calculated the net rate of recombination in the cell taking into account photon recycling effects
    - Considered such a cell in thermal equilibrium (no external light on it and no voltage applied to it)

$\Rightarrow$ would have to be emitting Planckian black-body radiation at these energies

Fundamental PV Efficiency Limits

- SQ could now calculate the net recombination rate at any voltage $\Rightarrow$ leads to ideal solar cell equation with unity ideality factor (N = 1), area A and I_0 given by:

$$I_o = qA\dot{N}(E_G,\infty) \approx qA\left(\frac{2\pi kT}{h^3c^2}\right)\left[E_G{}^2 + 2(kT)E_G + 2(kT)^2\right]e^{-E_G/kT}$$

- Assumptions in this "detailed balance" approach:
  - i) The mobility μ is infinite $\Rightarrow$ collection of carriers no matter where they are generated
  - ii) Complete absorption of all photons above the band gap
  - iii) That $E_G >> kT$

Fundamental PV Efficiency Limits

- If sun is modelled as a black-body at temperature T_s
  $\Rightarrow$ *I–V* curve can be expressed as:

$$I = qAf_s\dot{N}(E_G,\infty,T_s) - qA\, f_c\dot{N}(E_G,\infty,T_c)(e^{qV/kT} - 1)$$

  where

  $f_s = 1$ for a system under maximum solar concentration (46200, calculated from $C_{ideal} \leq n^2/\sin^2\delta$ with angular diameter of the sun $\delta = 32$ arc minutes)

  $f_c = 1$ for a solar cell with maximum angular selectivity

- For the non-concentrating system analysed by SQ, the solar intercept fraction $f_s = 2.1646 \times 10^{-5}$ and $f_c = 1$

  $\Rightarrow$ peak efficiency of $\eta_{SQ} = 31.0\%$ for $E_G = 1.3$ eV for $T_S = 6000$ K and $T_C = 300$ K

Fundamental PV Efficiency Limits

For a concentrating system, $f_s = 1 \Rightarrow$ larger V_{oc} achieved $\Rightarrow$ increases the peak efficiency to 40.8% for E_G = 1.1 eV

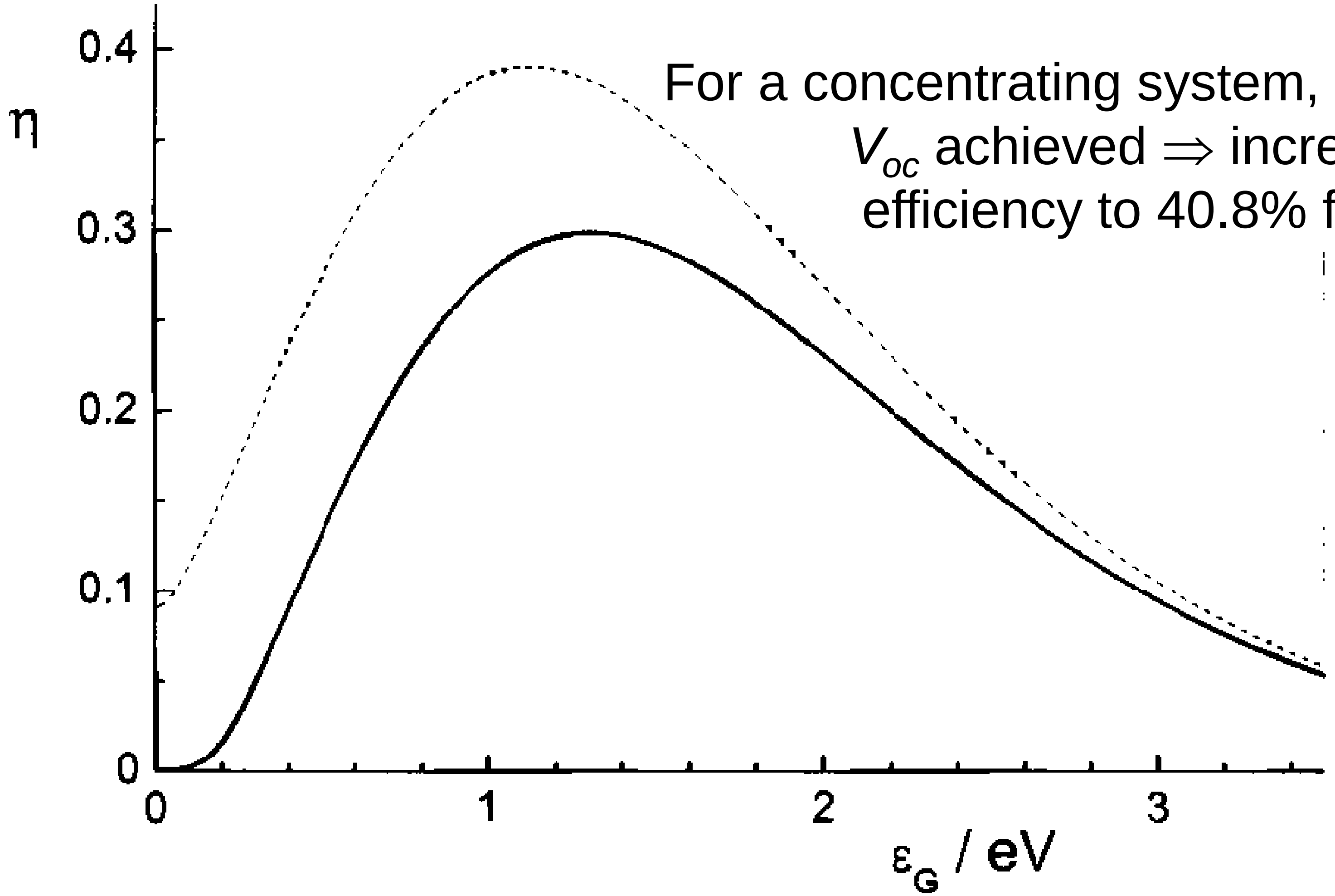


Figure 7.2: Efficiency of solar cells with radiative recombination only as a function of their energy gap for the *AM*0 spectrum, non-concentrated (solid line) and for full concentration (dashed line).

Source: Peter Würfel, "Physics of Solar Cells", Wiley 2005

Fundamental PV Efficiency Limits

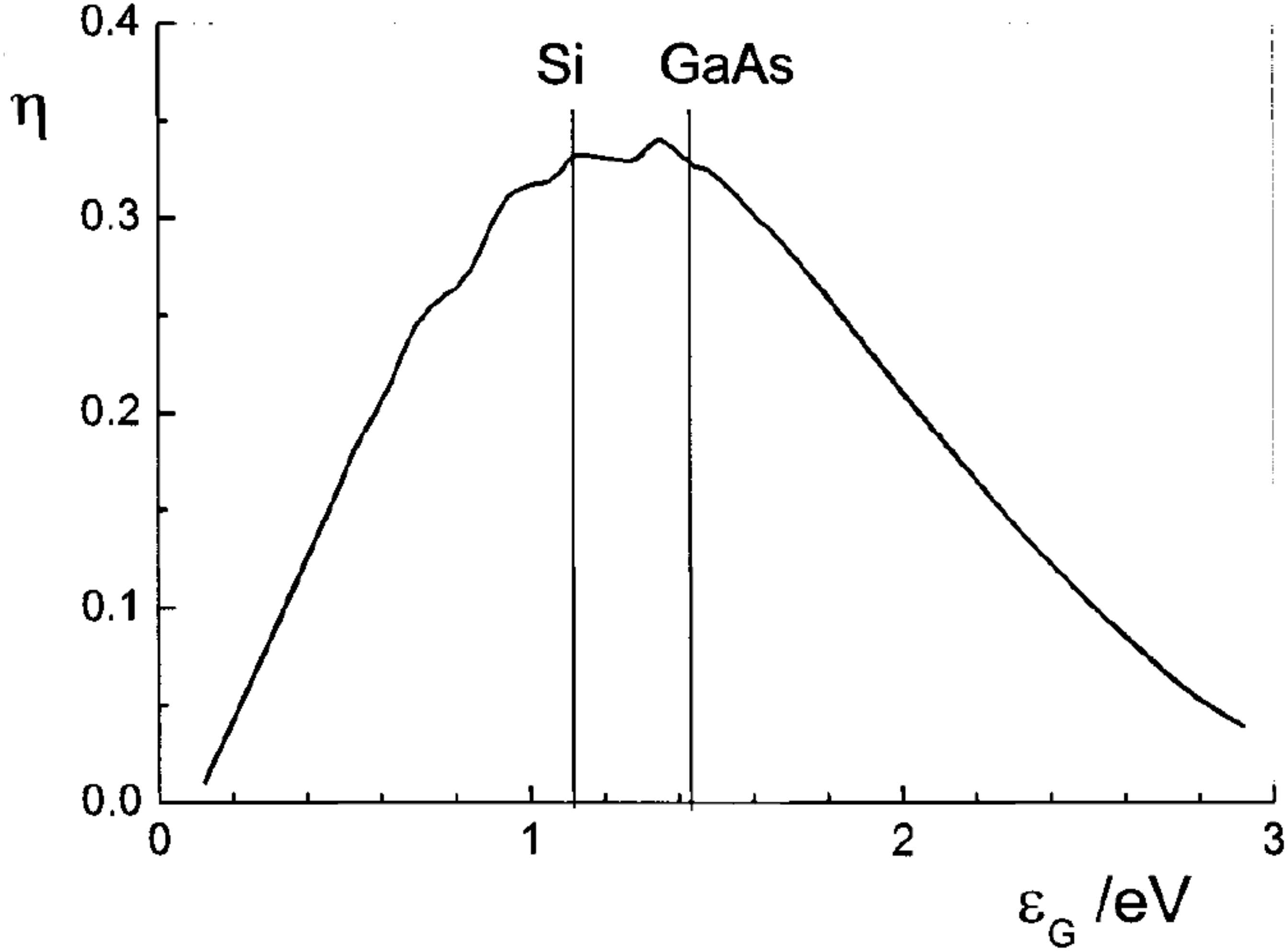
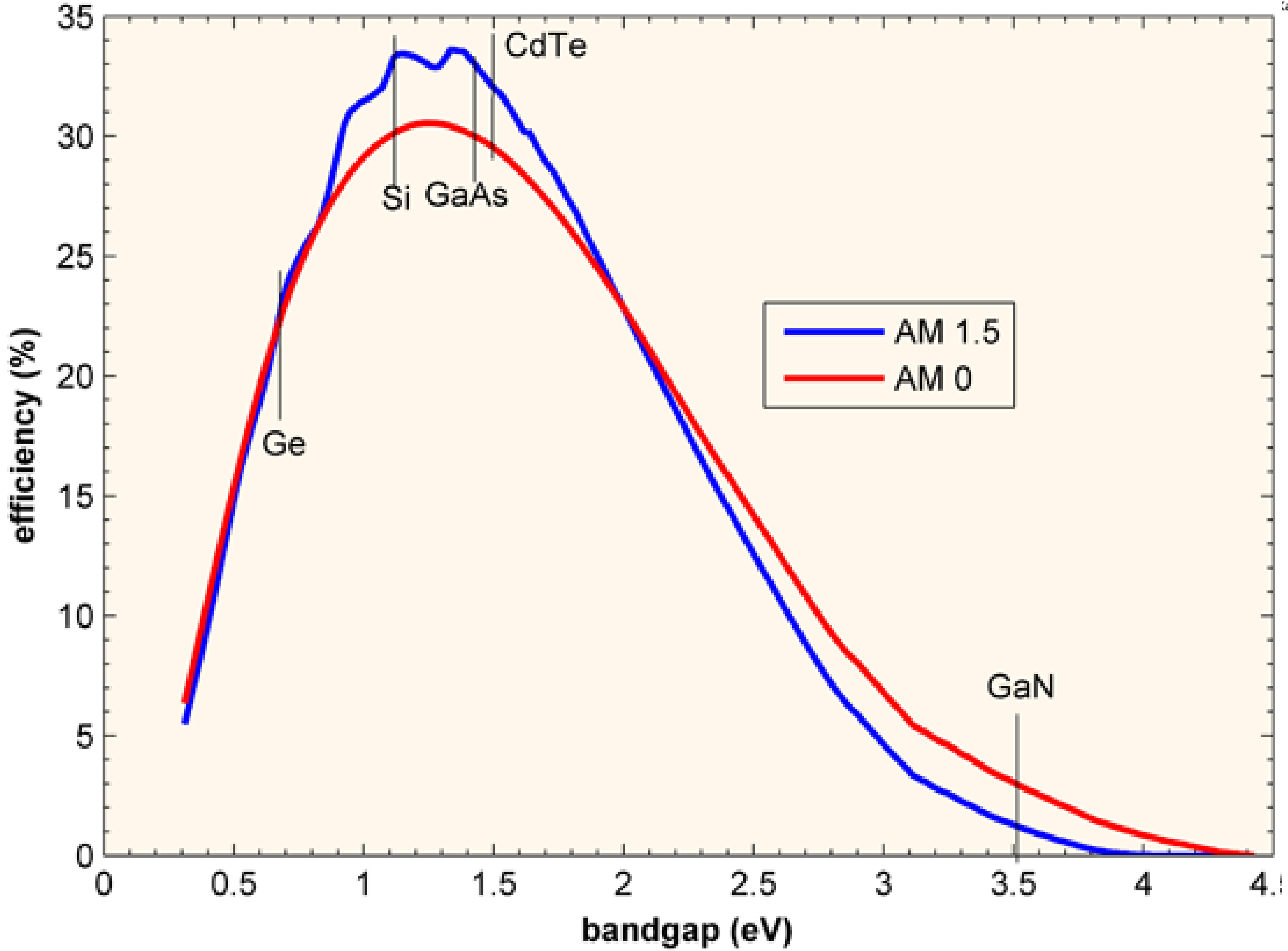


Figure 7.3: Efficiency of solar cells with radiative recombination only as a function of the energy gap for the *AM* 1.5 spectrum.

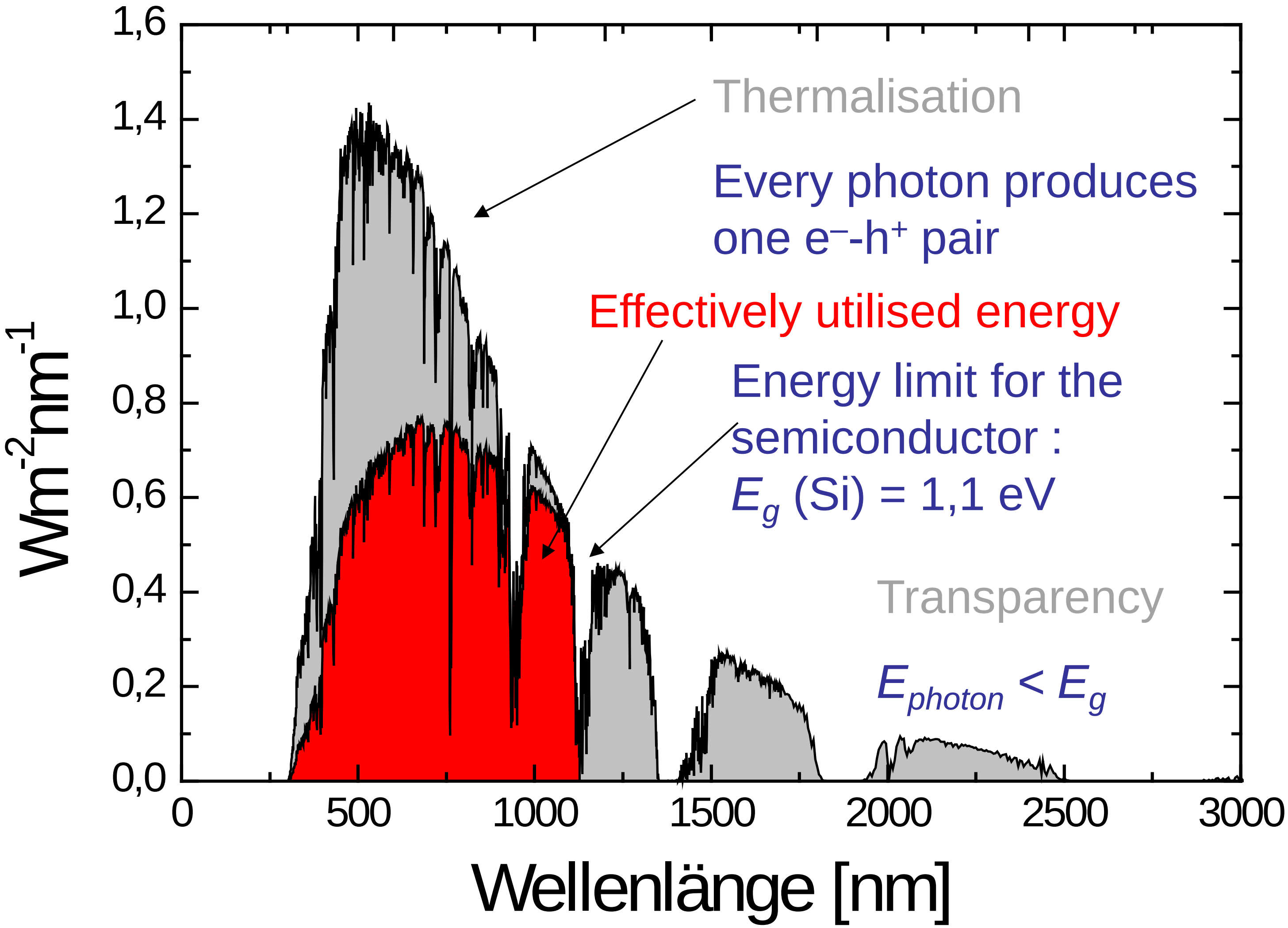
Source: Peter Würfel, "Physics of Solar Cells", Wiley 2005

Fundamental PV Efficiency Limits



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

Die Absorption der „Sonnenphotonen“



Tandem Solar Cells

Table 5.1: Limiting efficiencies and optimal bandgaps for a range of tandem cell designs (Marti and Araujo 1996; Brown 2002).

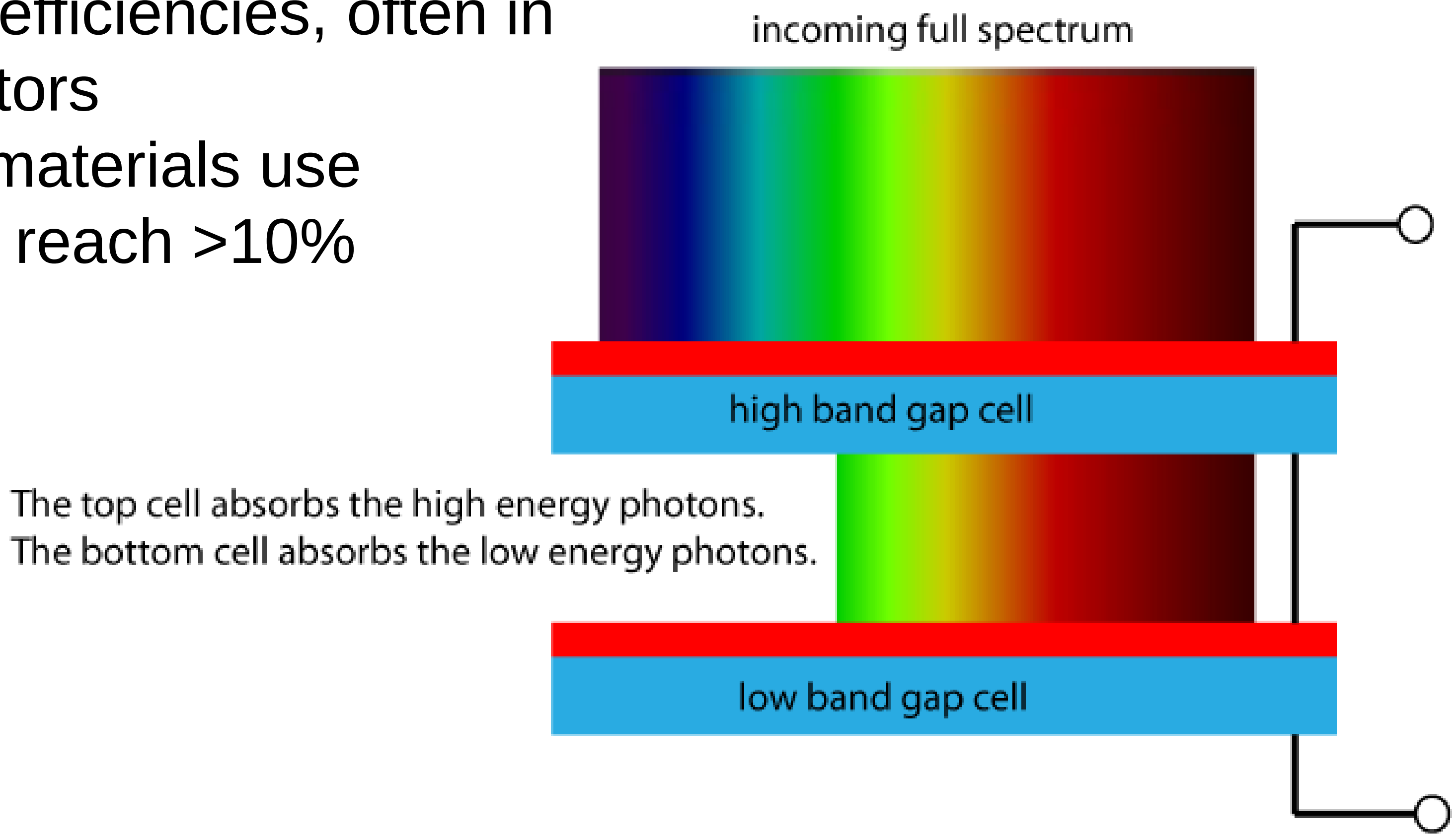
No. of Cells	Description	Optimal Bandgaps (eV)						Effic %
		E1	E2	E3	E4	E5	E6	
1	Diffuse	1.31						31.0
	Direct	1.11						40.8
2	Diffuse, series connected	0.97	1.70					42.5
	Diffuse, unconstrained	0.98	1.87					42.9
	Direct, series connected	0.77	1.55					55.5
	Direct, unconstrained	0.77	1.70					55.9
3	Diffuse, series connected	0.82	1.30	1.95				48.6
	Diffuse, unconstrained	0.82	1.44	2.26				49.3
	Direct, series connected	0.61	1.15	1.82				63.2
	Direct, unconstrained	0.62	1.26	2.10				63.8
4	Diffuse, series connected	0.72	1.10	1.53	2.14			52.5
	Diffuse, unconstrained	0.72	1.21	1.77	2.55			53.3
	Direct, series connected	0.51	0.94	1.39	2.02			67.9
	Direct, unconstrained	0.52	1.03	1.61	2.41			68.8
5	Diffuse, series connected	0.66	0.97	1.30	1.70	2.29		55.1
	Diffuse, unconstrained	0.66	1.07	1.50	2.03	2.79		56.0
	Direct, series connected	0.44	0.81	1.16	1.58	2.18		71.1
	Direct, unconstrained	0.45	0.88	1.34	1.88	2.66		72.0
6	Diffuse, series connected	0.61	0.89	1.16	1.46	1.84	2.41	57.0
	Diffuse, unconstrained	0.61	0.96	1.33	1.74	2.26	3.00	58.0
	Direct, series connected	0.38	0.71	1.01	1.33	1.72	2.31	73.4
	Direct, unconstrained	0.40	0.78	1.17	1.60	2.12	2.87	74.4
∞	Diffuse (unconstrained, series connected, 2-terminal)							68.2
	Direct (unconstrained, series connected, 2-terminal)							86.8

Tandem cells can achieve η up to 86.8% for an infinite number of cells!

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

Tandem Solar Cells

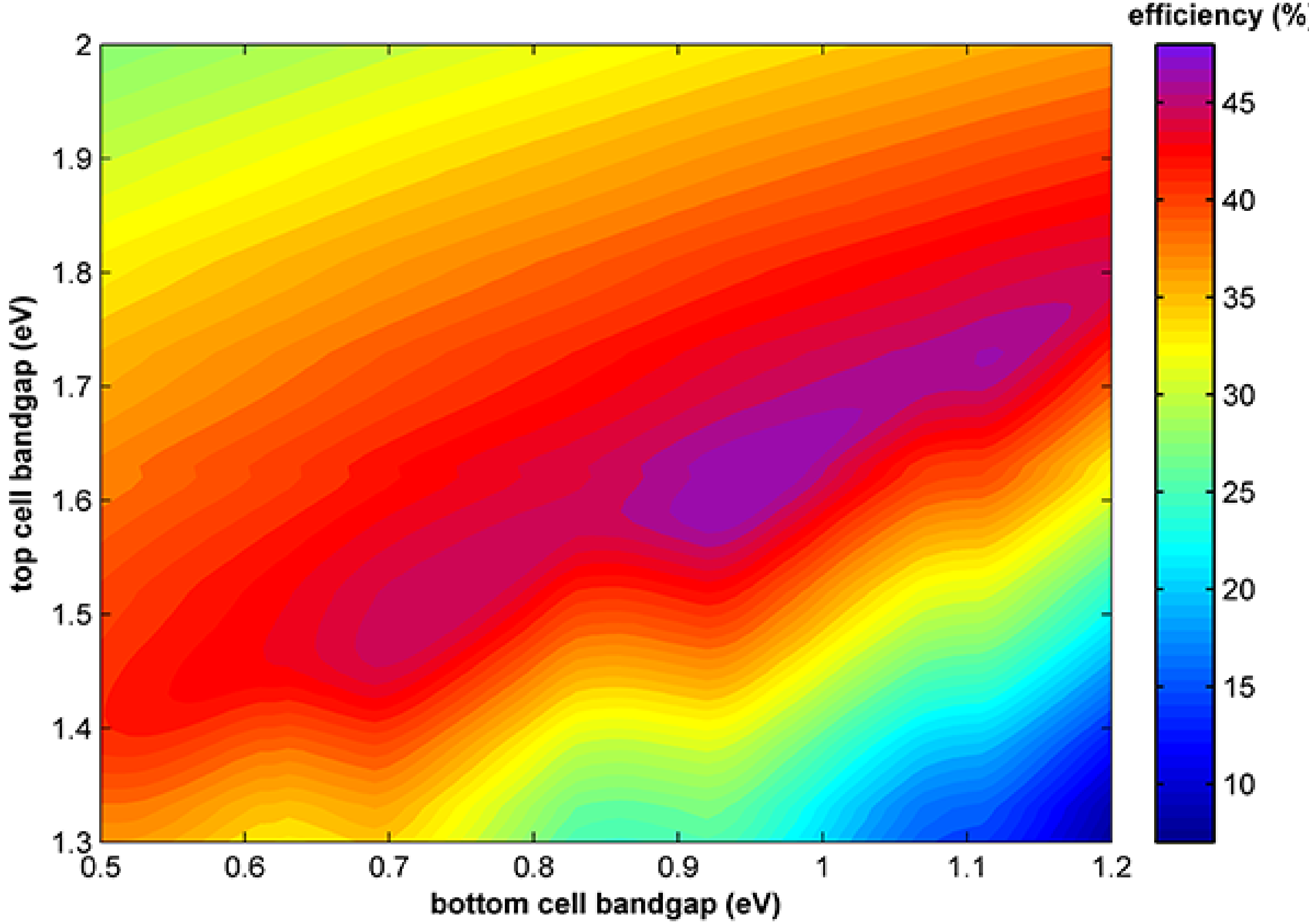
- Multiple materials used for tandems ⇒ primarily III-V and alloys from the a-Si-C-Ge system
- III-V materials used to achieve ultra-high efficiencies, often in concentrators
- Low cost materials use tandem to reach >10%



Source: *http://pveducation.org/pvcdrom/solar-cell-operation/tandem-cells*

Tandem Solar Cells

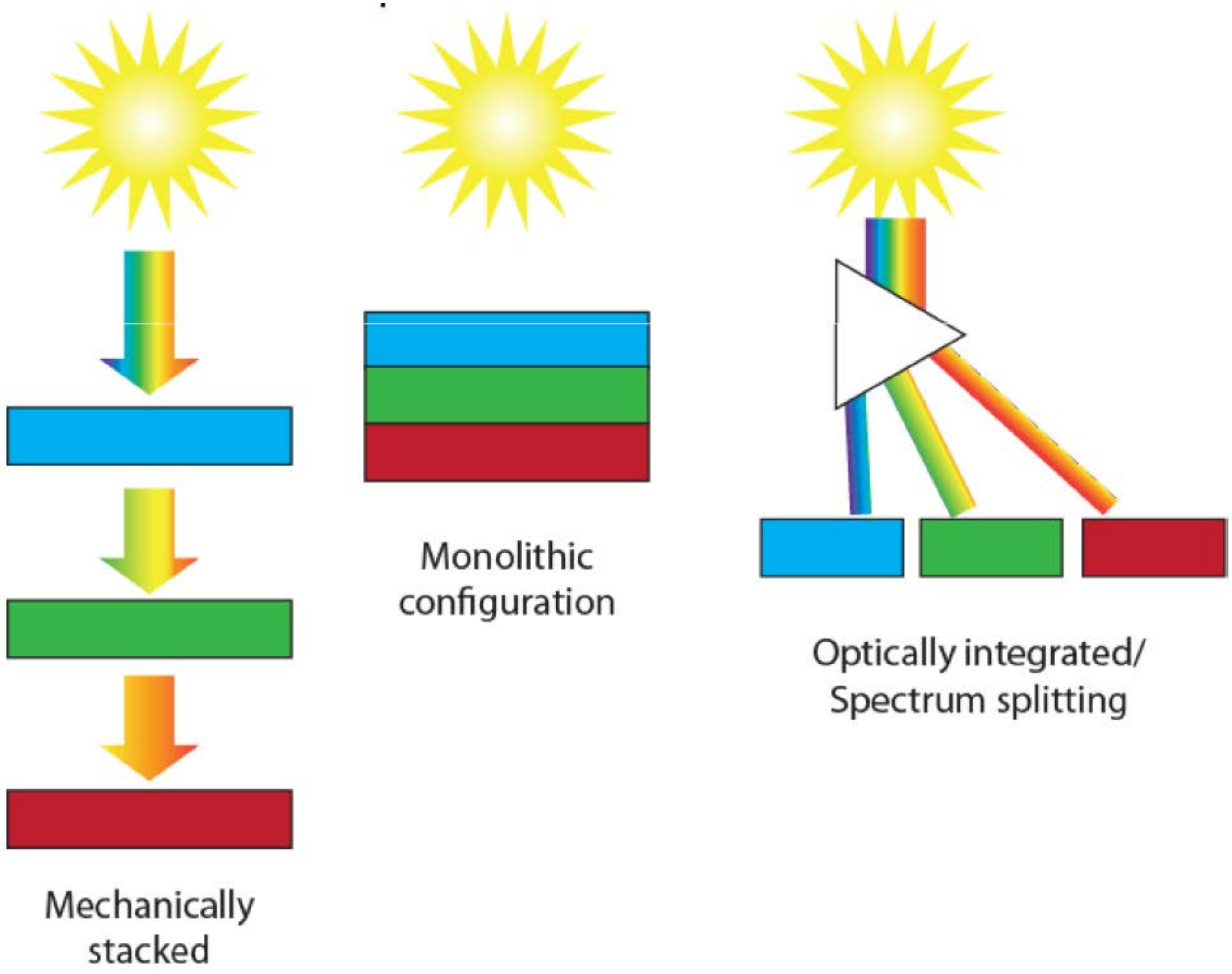
- Ideal bandgaps for double junction



Source: http://pveducation.org/pvcdrom/solar-cell-operation/tandem-cells

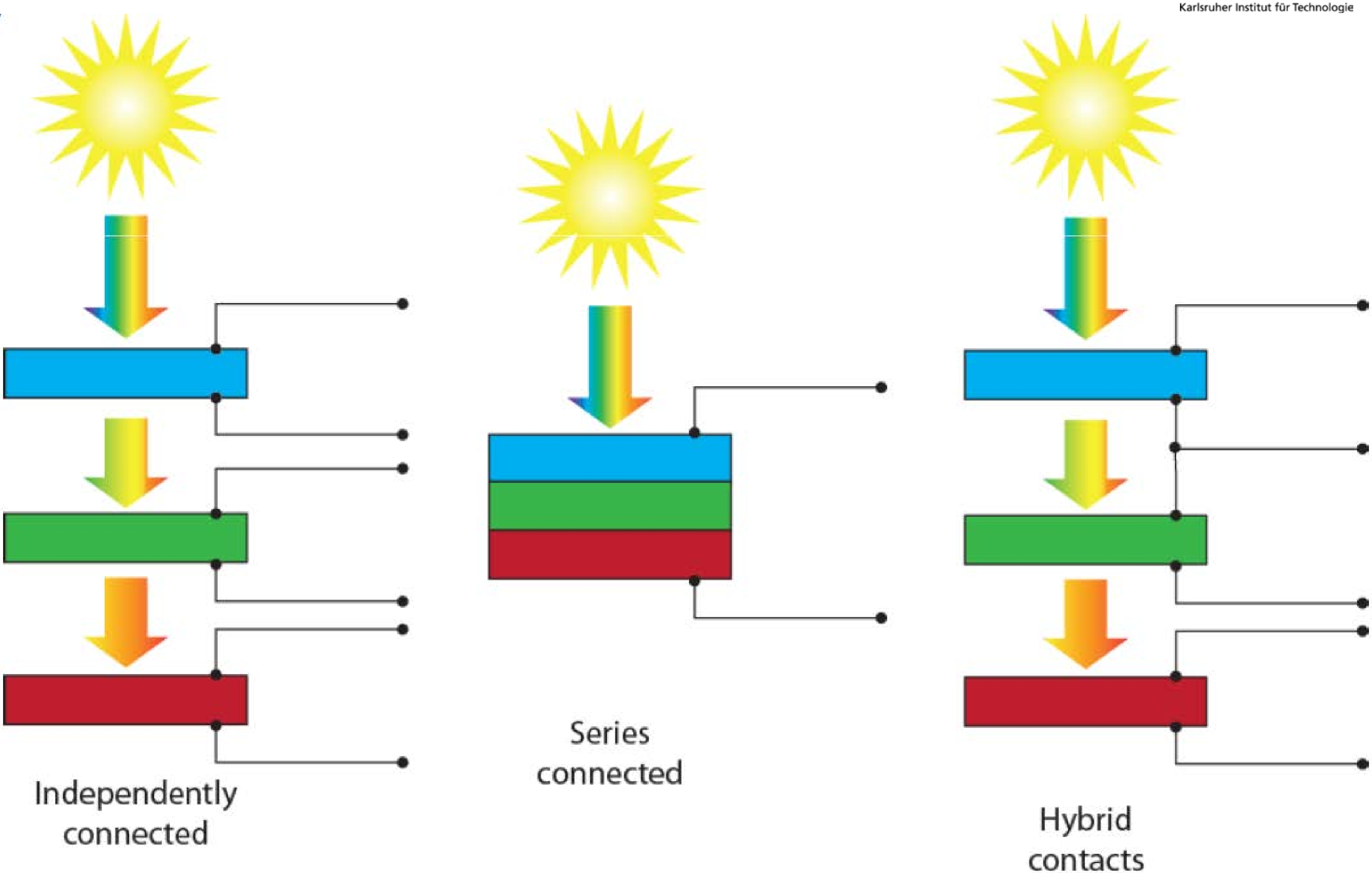
Tandem Solar Cells

- Many configurations for optically integrated or spectrum split devices



Source: *Christiana Honsberg, ASU, "Tandem Solar Cells"*

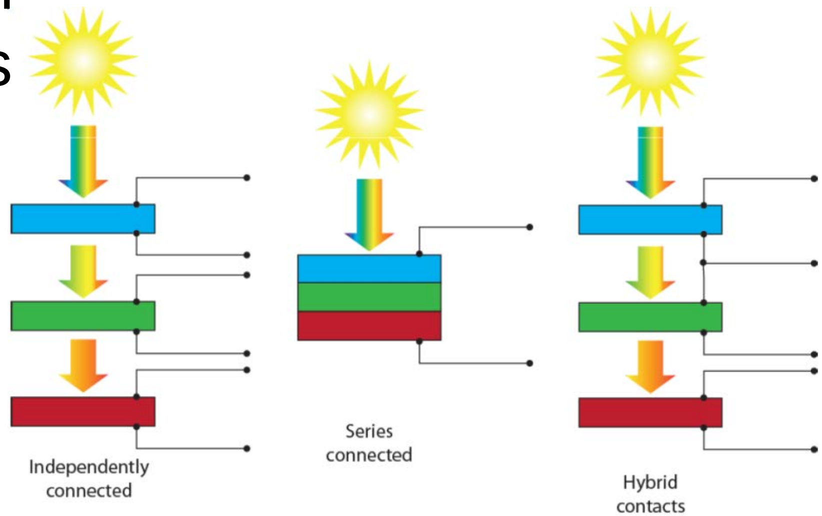
Tandem Solar Cells



Source: *Christiana Honsberg, ASU, "Tandem Solar Cells"*

Tandem Solar Cells

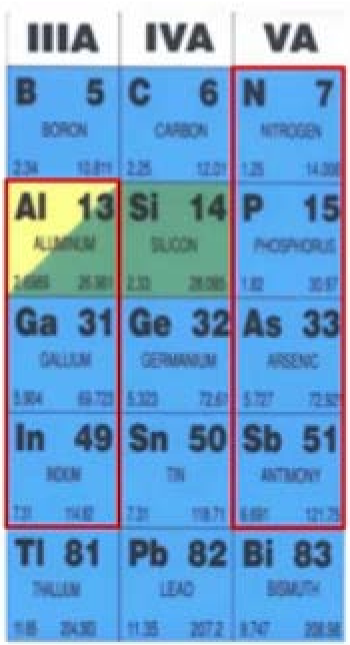
- Electrical interconnection impacts the theoretical efficiency (small effect), optimum materials, and device design
- Approaches other than series connected introduce additional cost and complexity into power electronics (and also typically solar cell design), so monolithic, series connected devices are most commonly implemented
- Series connected requires current matching and places substantial constraints on tandem efficiency by limiting the materials that can be used
- Other approaches not used in practice

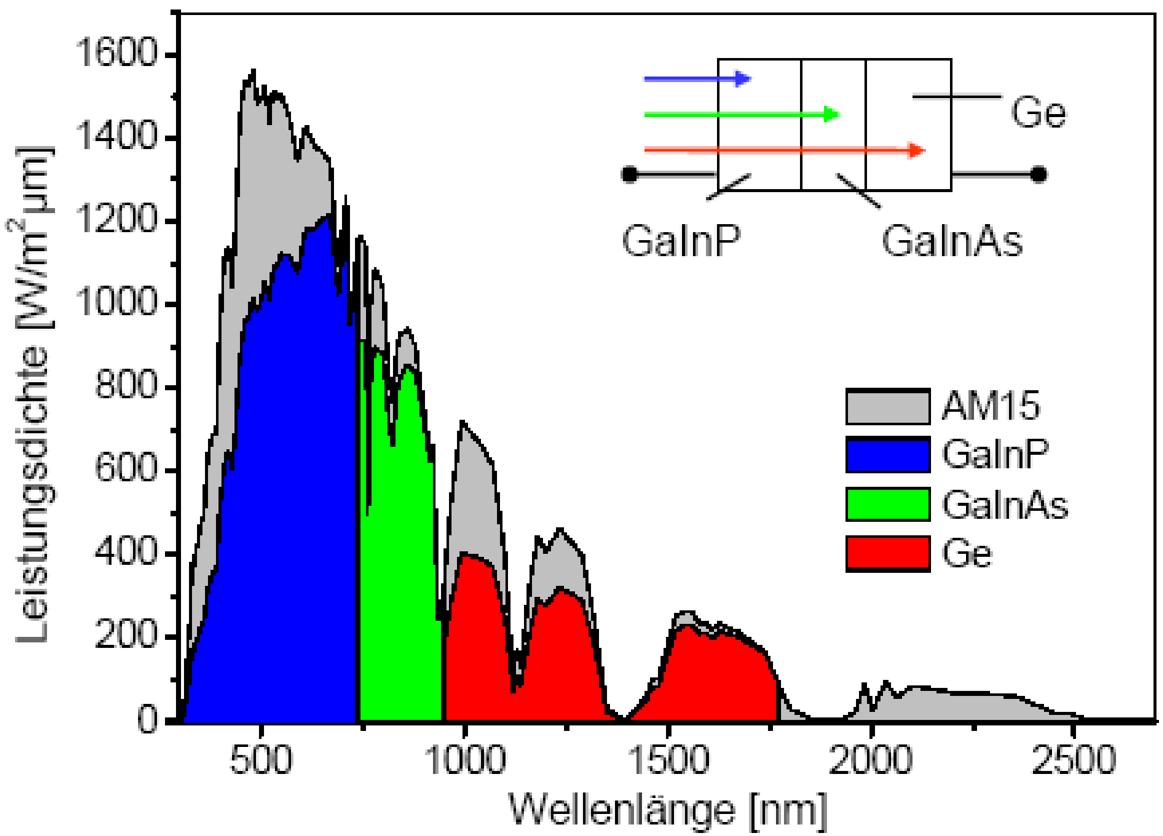


Source: Christiana Honsberg, ASU, "Tandem Solar Cells"

Tandem Solar Cells

- Minimise lattice thermalisation and transparency losses – example of GaInP / GaInAs / Ge triple-junction solar cell





Source: *Andreas Bett, Fraunhofer ISE*

Tandem Solar Cells

- Realising high efficiency requires nearly ideal solar cells of desired bandgaps $\Rightarrow$ each has high minority carrier lifetime
- Major design constraint are:
  - Series connection $\Rightarrow$ lowest maximum power current limits the overall power
  - Closely lattice matched solar cell materials $\Rightarrow$ high material quality which in turn means materials must be closely lattice matched
  - Overall, tandems highly dependant on material availability and quality.
- Design constraints impact number of solar cells in stack, theoretical efficiency of tandem, and (through material quality) fraction of theoretical efficiency achieved

Tandem Solar Cells

Karlsruher Institut für Technologie

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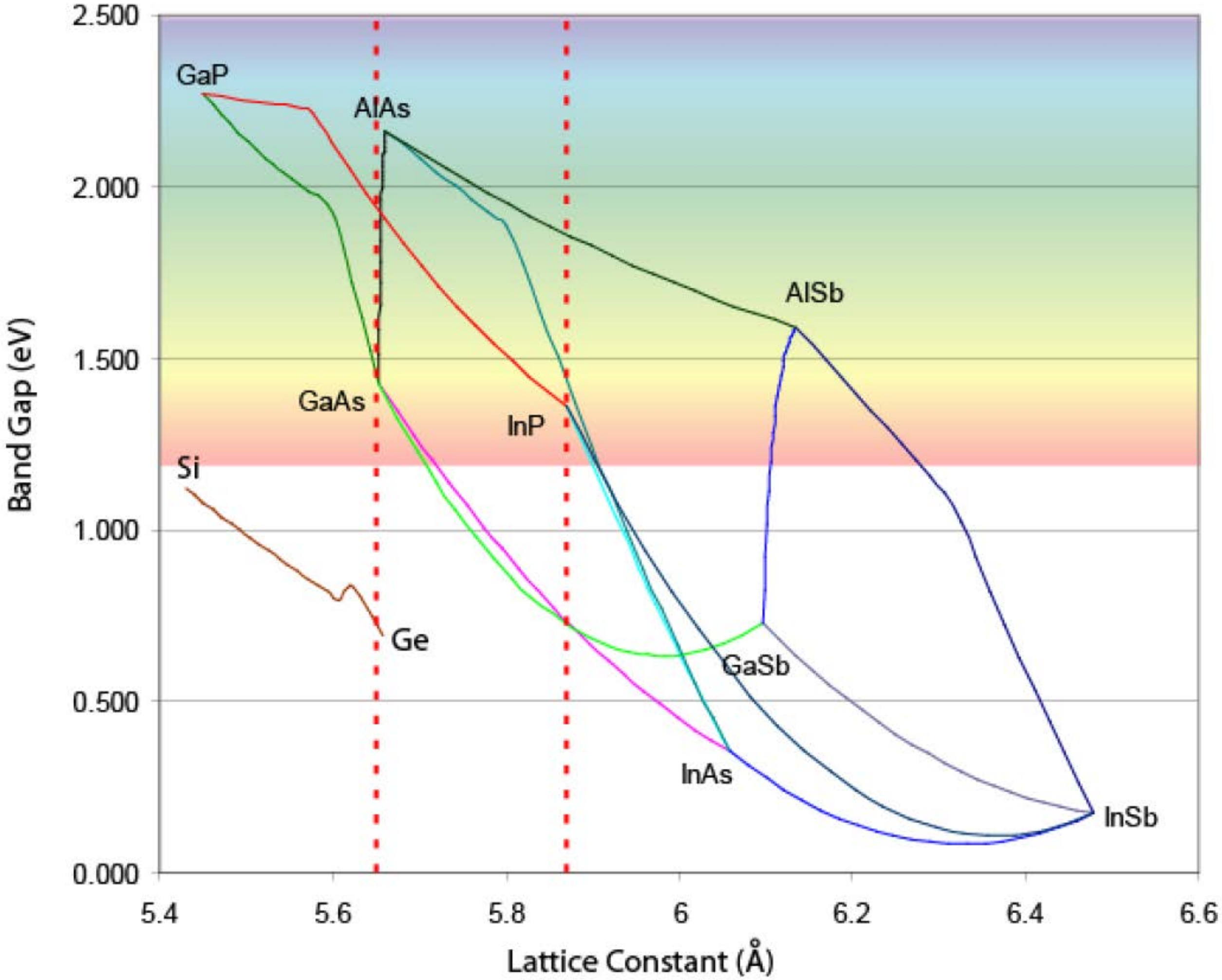
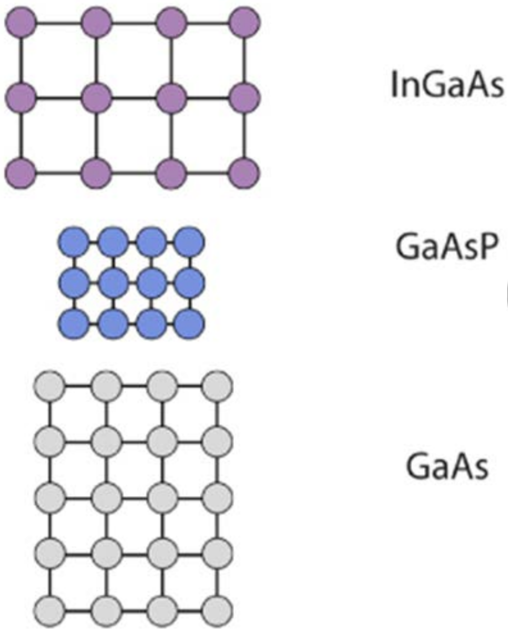
Tandem Solar Cells

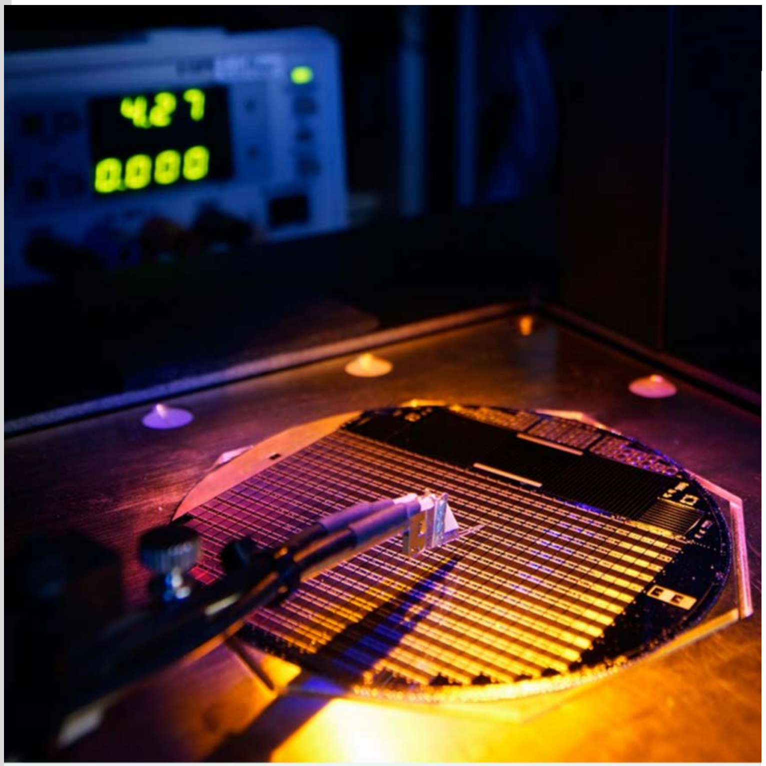




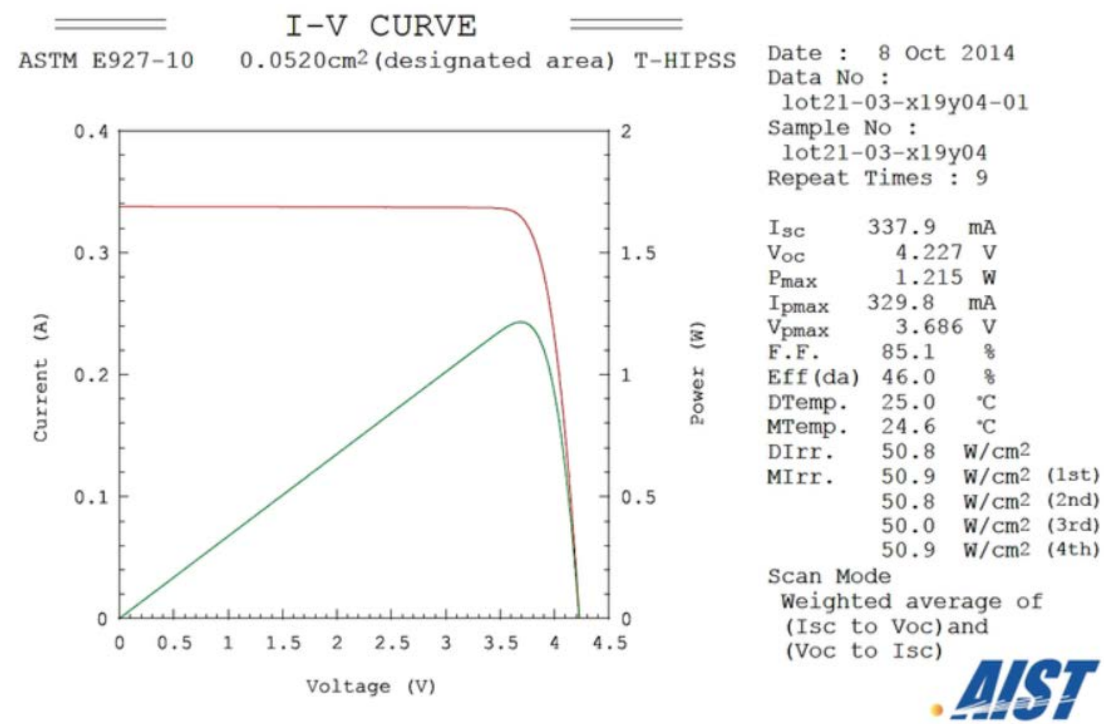
Source: *Christiana Honsberg, ASU, "Tandem Solar Cells"*

Tandem Solar Cells

- New world record of 46% efficient solar cell (4 junctions) on 1st Dec – by Soitec and CEA-Leti, France, together with the Fraunhofer Institute for Solar Energy Systems



New record solar cell on a 100 mm wafer yielding approximately 500 concentrator solar cell devices.

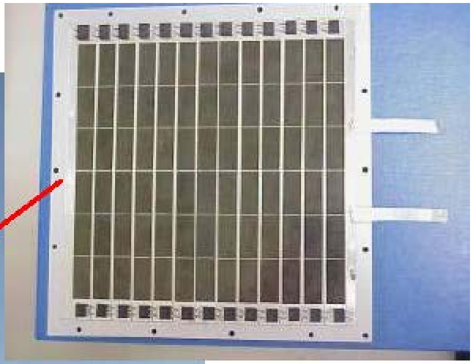


IV characteristics of the new 4-junction solar cell with an efficiency of 46% at 50.8 W/cm2 which corresponds to a concentration ration of 508 times the solar AM1.5d (ASTM E927-10) spectrum.

Source: http://www.ise.fraunhofer.de/en/press-and-media/press-releases/press-releases-2014/new-world-record-for-solar-cell-efficiency-at-46-percent

Tandem Solar Cells

- Such high efficiency solar cells are used in high concentration, two-axis tracking systems
- High concentration means small area (and lower cost) needed for solar cells
- Trade-off between the costs of i) solar cell and ii) balance of the systems (BoS) components



Source: *Christiana Honsberg, ASU, "Tandem Solar Cells"*

Hot Carrier Solar Cells

- Idea: extract excess energy from high-energy charge carriers energy they thermalise back down to band edges

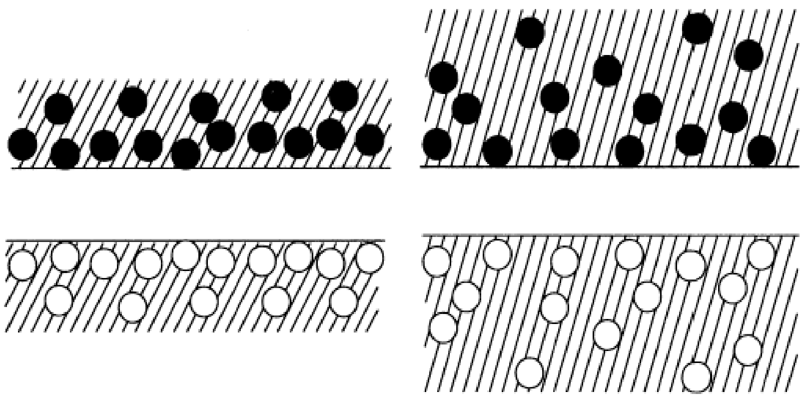


Fig. 6.1: Normally carriers thermalise with the lattice as in (a). In hot carrier cells, energy is stored in a hot carrier distribution, as shown in (b).

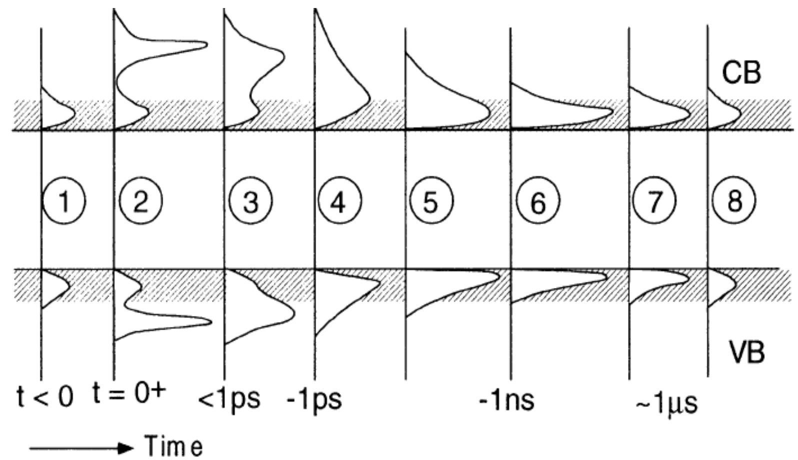


Fig. 6.2: Time evolution of electron and hole distributions in a semiconductor subject to a short, high intensity, monochromatic pulse of light from a laser: (1) Thermal equilibrium before pulse; (2) "coherent" stage straight after pulse; (3) carrier scattering; (4) thermalisation of "hot carriers";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

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

Hot Carrier Solar Cells

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

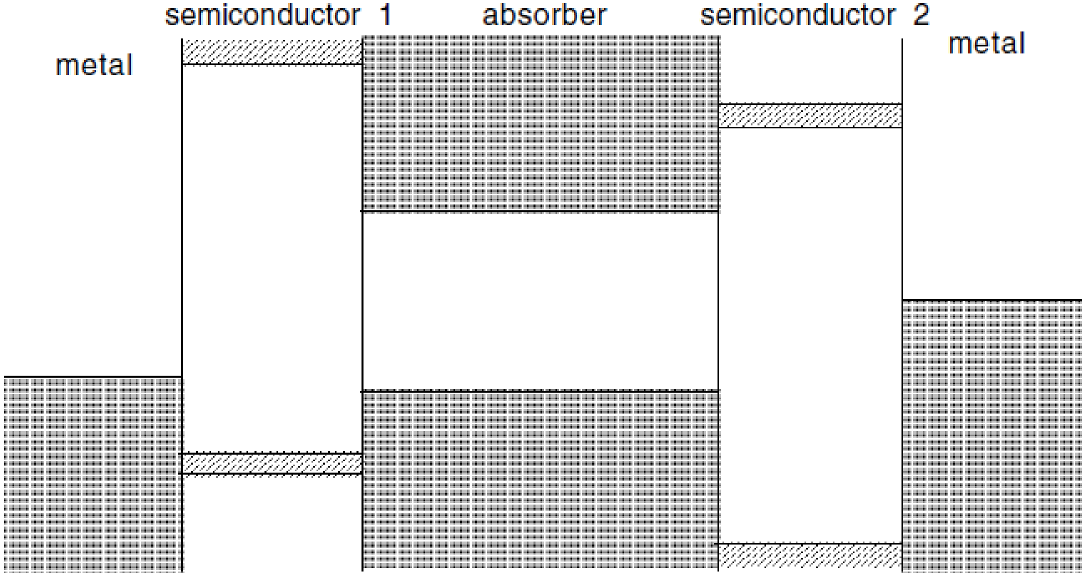


Fig. 6.3: Selective energy contacts to hot carrier cell based on wide bandgap semiconductors with narrow valence (left) and conduction (right) bands.

- Maybe also possible using quantum dots

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

Hot Carrier Solar Cells

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

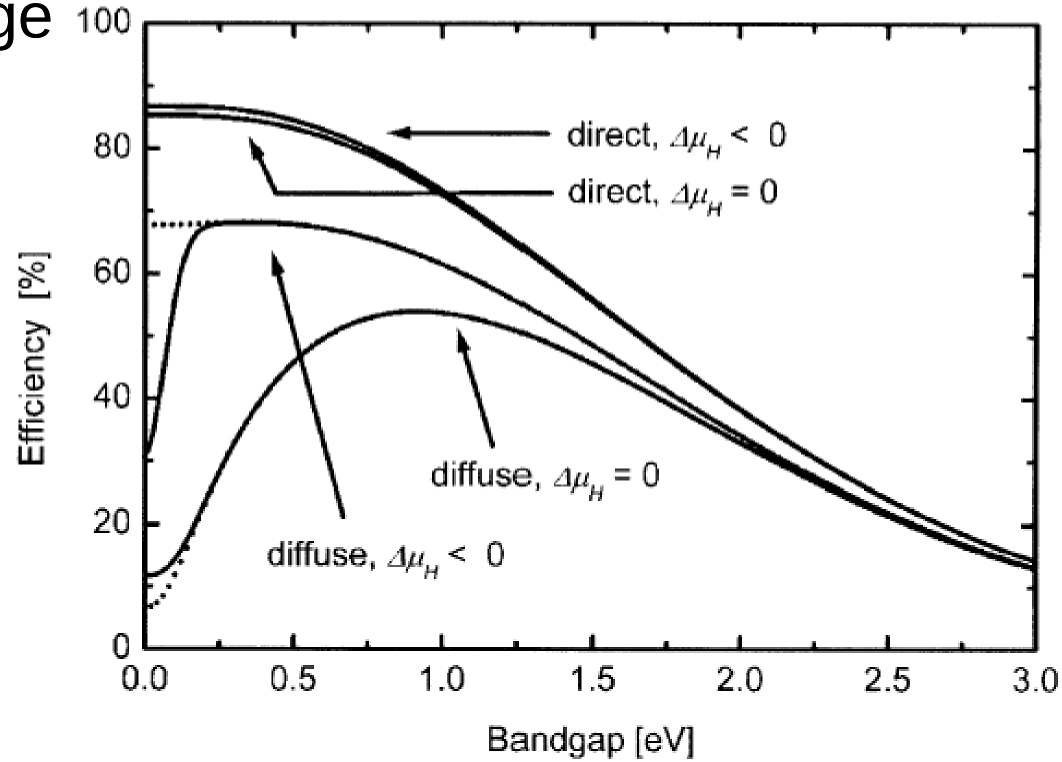


Fig. 6.7: Limiting efficiency of a hot carrier cell for direct and diffuse sunlight. The curves labelled $\Delta\mu_H < 0$ show the unconstrained case while the curves labelled $\Delta\mu_H = 0$ shows the case where there are high levels of interaction between hot electrons and holes.

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

Impact Ionisation

- Idea: to generate more than one e^{-}-h^{+} pair per high energy photon ⇒ quantum efficiency can now be >100%!

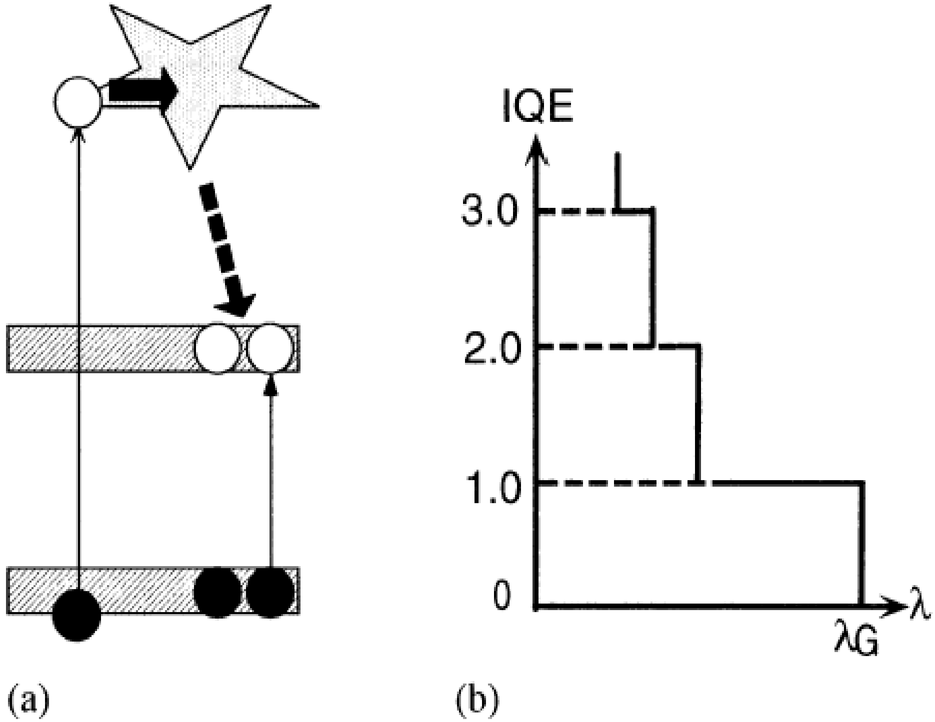


Fig. 7.1: (a) Schematic of the impact ionisation process whereby one energetic photon creates multiple electron-hole pairs; (b) Energetically feasible internal quantum efficiency, where λ_G is the wavelength corresponding to the threshold energy for electron-hole pair creation.

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

Impact Ionisation

- If impact ionization occurs, we must also consider the reverse process Auger recombination
- Main point: all of the absorbed energy remains in the electronic system and the thermal losses are very small

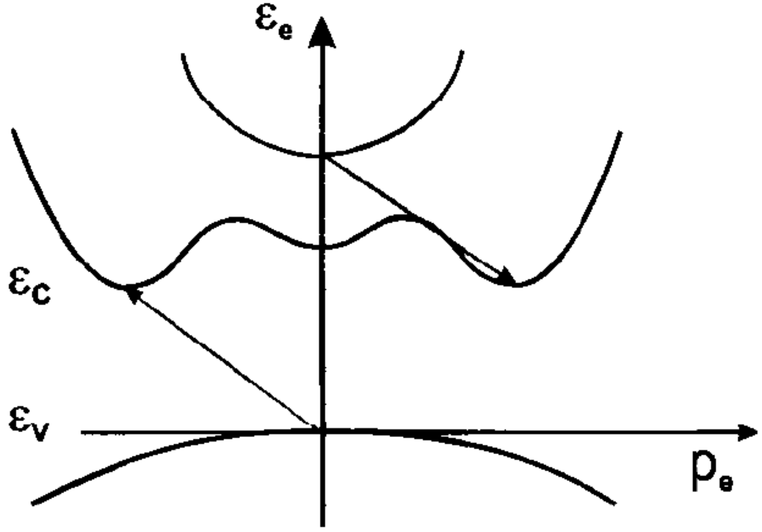


Figure 8.8: Transition of an electron from a higher band to the minimum of the conduction band by impact ionization in an indirect semiconductor, resulting in the additional generation of an electron and a hole at the band edges.

Source: Peter Würfel, "Physics of Solar Cells", Wiley 2005

Impact Ionisation

- Again, very high efficiencies theoretically possible, even for unconcentrated sunlight (lower curve)

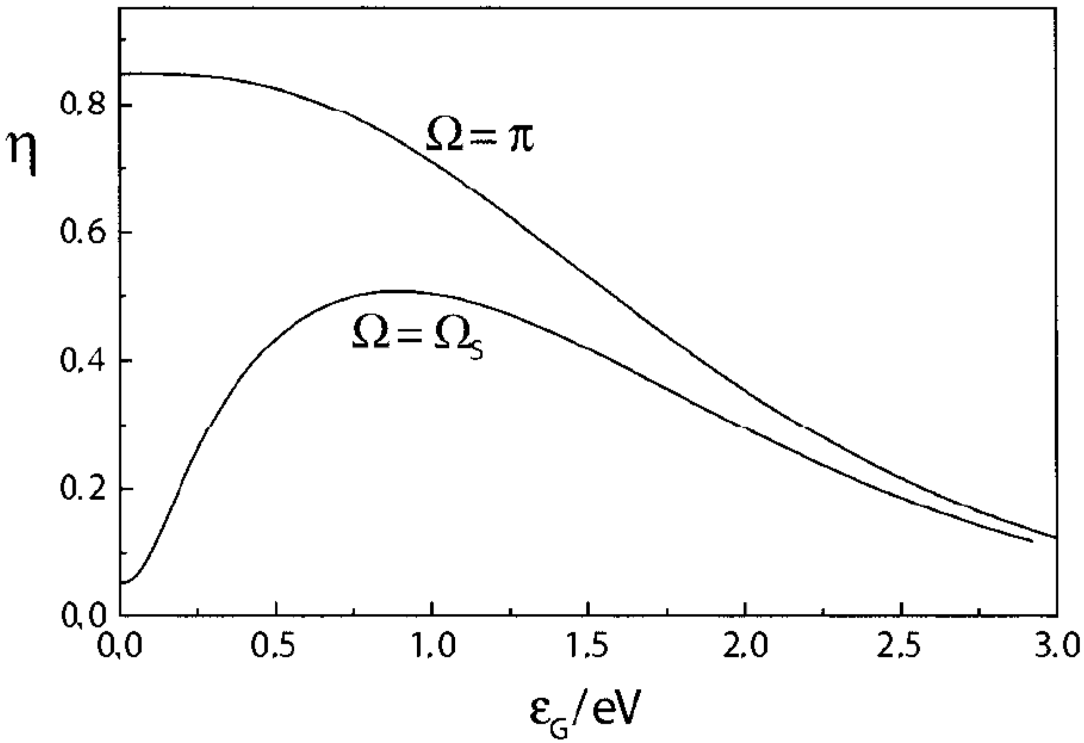


Figure 8.10: Efficiency for a hot carrier cell with impact ionization for non-concentrated incident solar radiation with $\Omega = \Omega_S$ and for maximum concentration with $\Omega = \pi$.

Source: Peter Würfel, "Physics of Solar Cells", Wiley 2005

Two-Step Absorption

- Way of addressing sub-bandgap transparency losses
  $\Rightarrow$ impurity photovoltaic (IPV) device

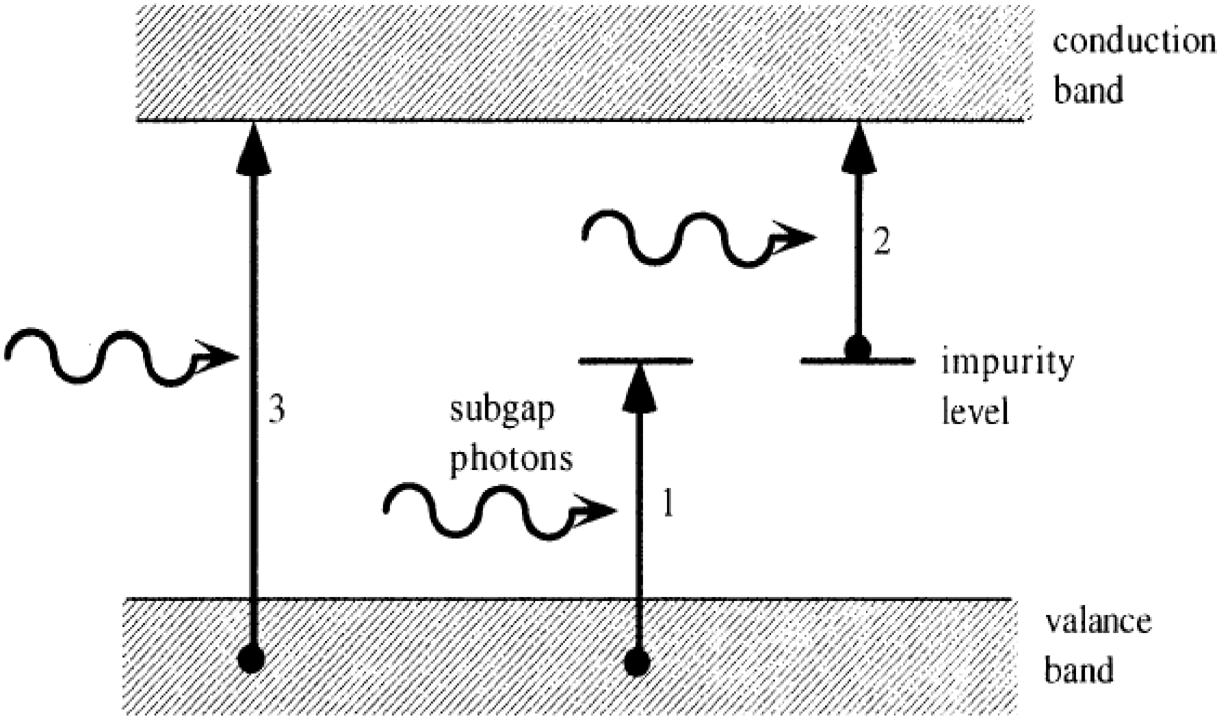


Fig. 8.1: Impurity photovoltaic effect where electron-hole pairs are generated by sub-bandgap photons (Keevers and Green 1994).

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

Two-Step Absorption

- Way of addressing sub-bandgap transparency losses
  $\Rightarrow$ intermediate band solar cell

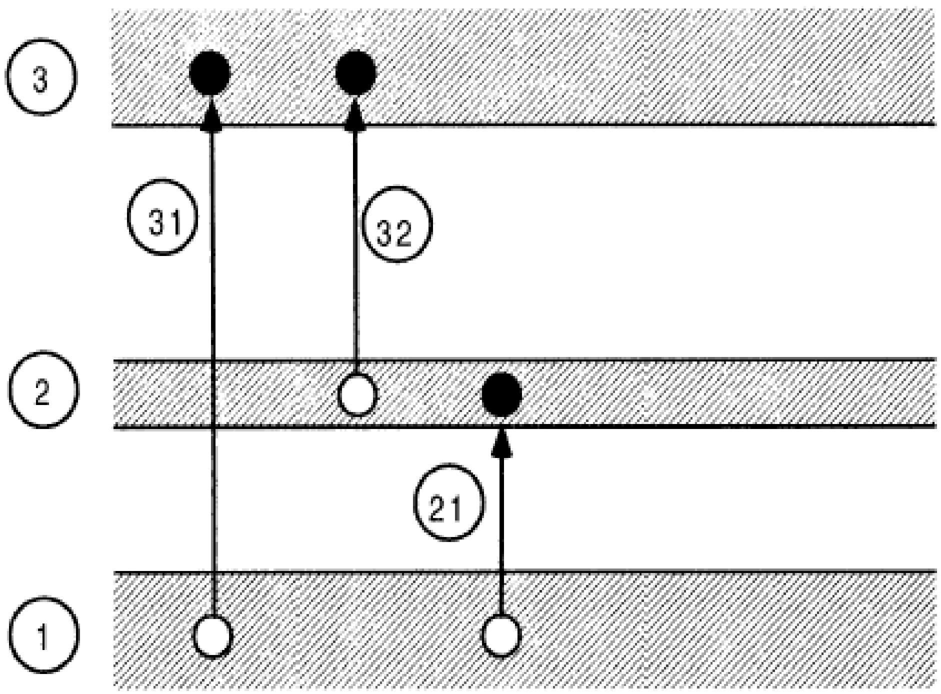


Fig. 8.3: 3-band solar cell. The lower- and upper-most bands are valence and conduction bands, while the intermediate band is considered to be an impurity band.

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

Two-Step Absorption

- High efficiencies again possible with three bands….

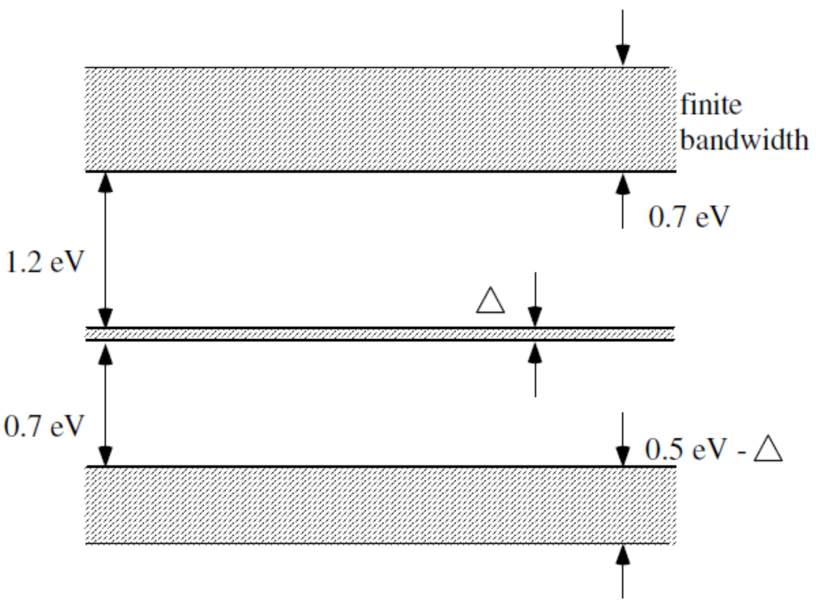


Fig. 8.6: Optimally designed 3-band cell with photon selectivity ensured by finite bandwidth for each of the 3 bands involved.

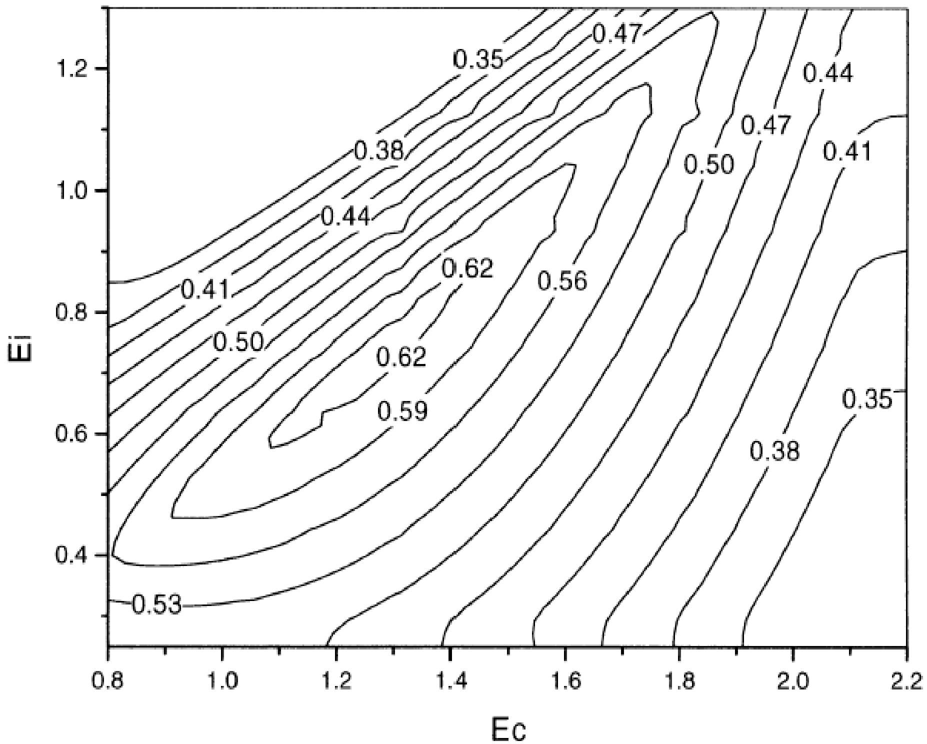


Fig. 8.5: Limiting efficiency of a 3-band cell as a function of the two lower threshold energies (Corkish 1999). (T_s = 6000 K, T_c = 300 K).

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

Two-Step Absorption

- Way of addressing sub-bandgap transparency losses
  $\Rightarrow$ impurity photovoltaic (IPV) device

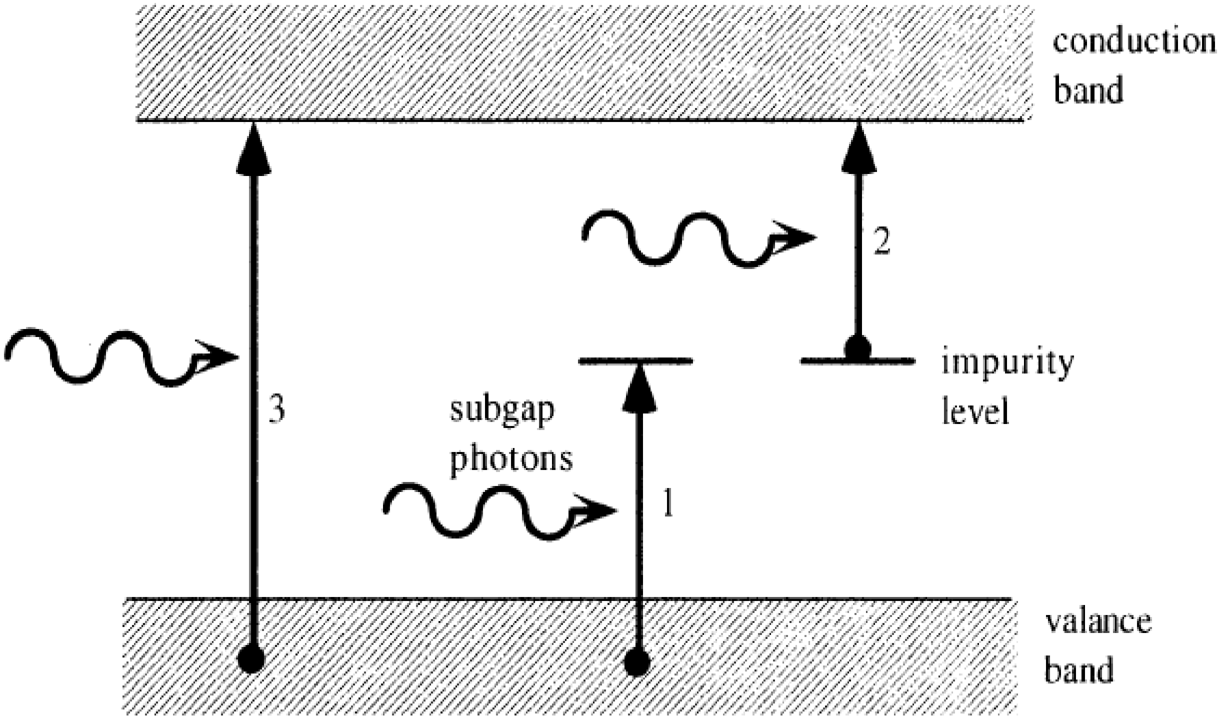


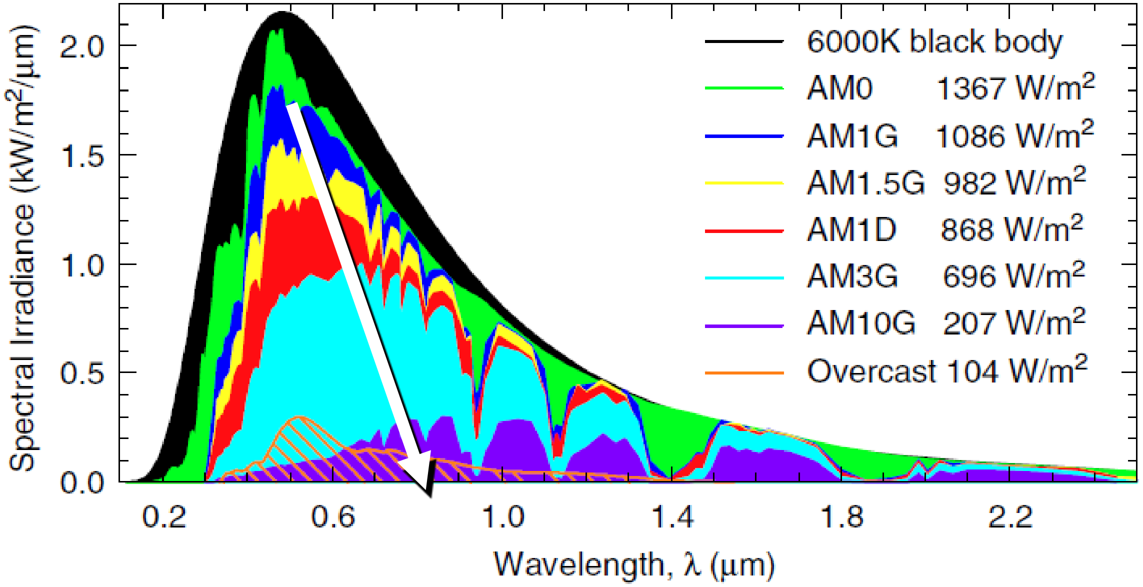
Fig. 8.1: Impurity photovoltaic effect where electron-hole pairs are generated by sub-bandgap photons (Keevers and Green 1994).

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

Briefly back to Tandems

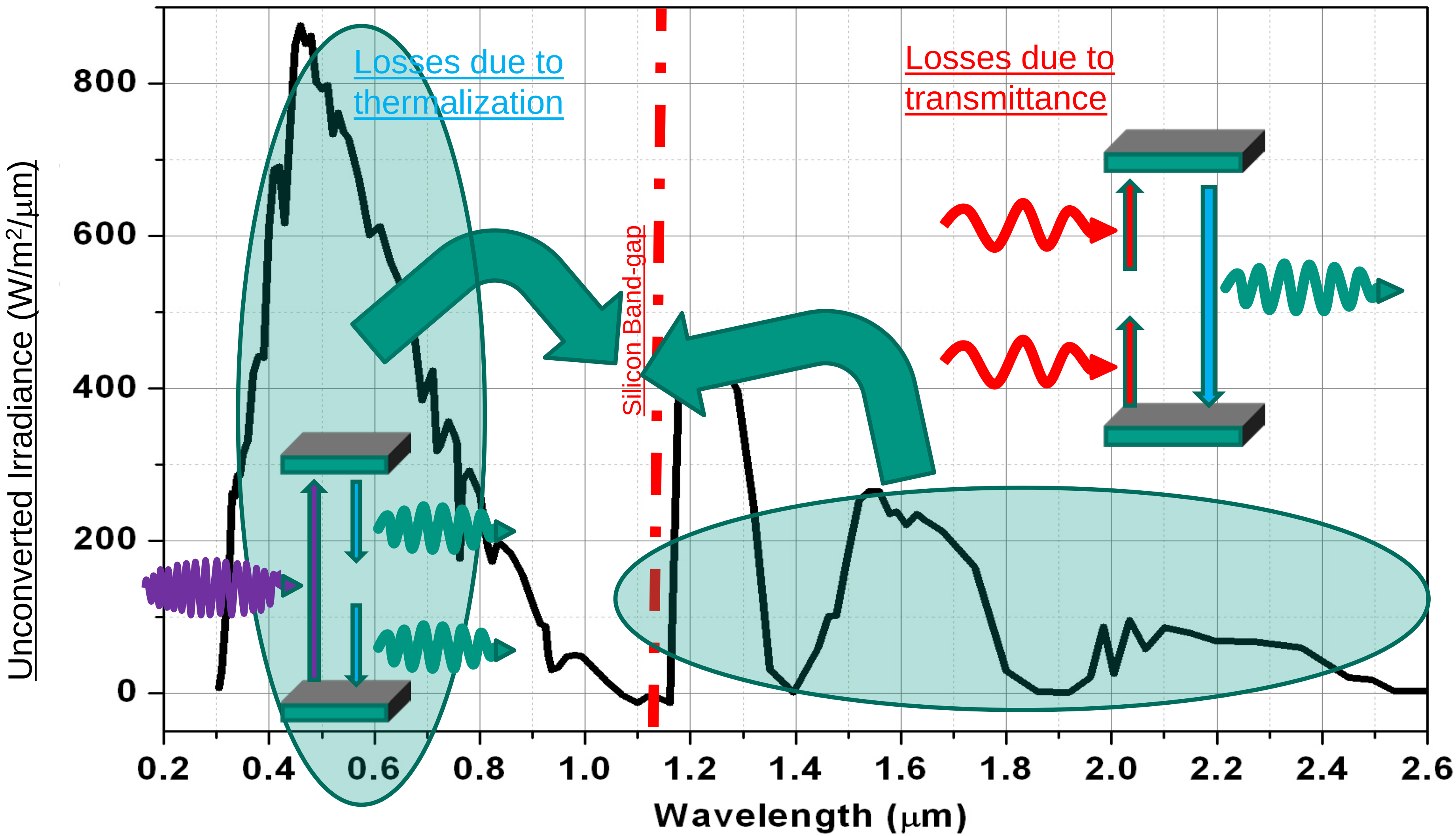
Disadvantages

- ✗ Solar cells connected in series ⇒ current matching problem with varying AM
- ✗ Best suited for non-varying sunlight ⇒ space
- ✗ Price... also best suited for space?



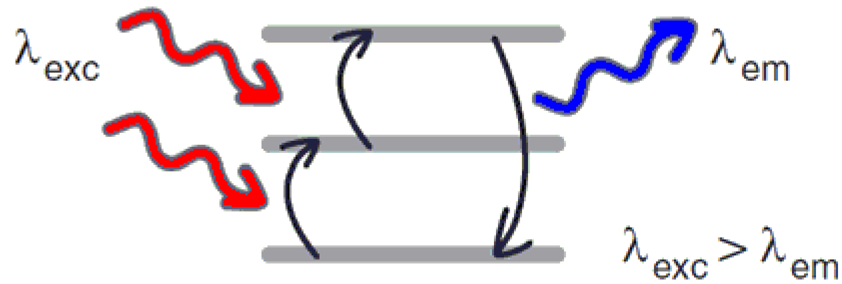
⇒ *What can be achieved with spectral conversion?*

Spectral Conversion

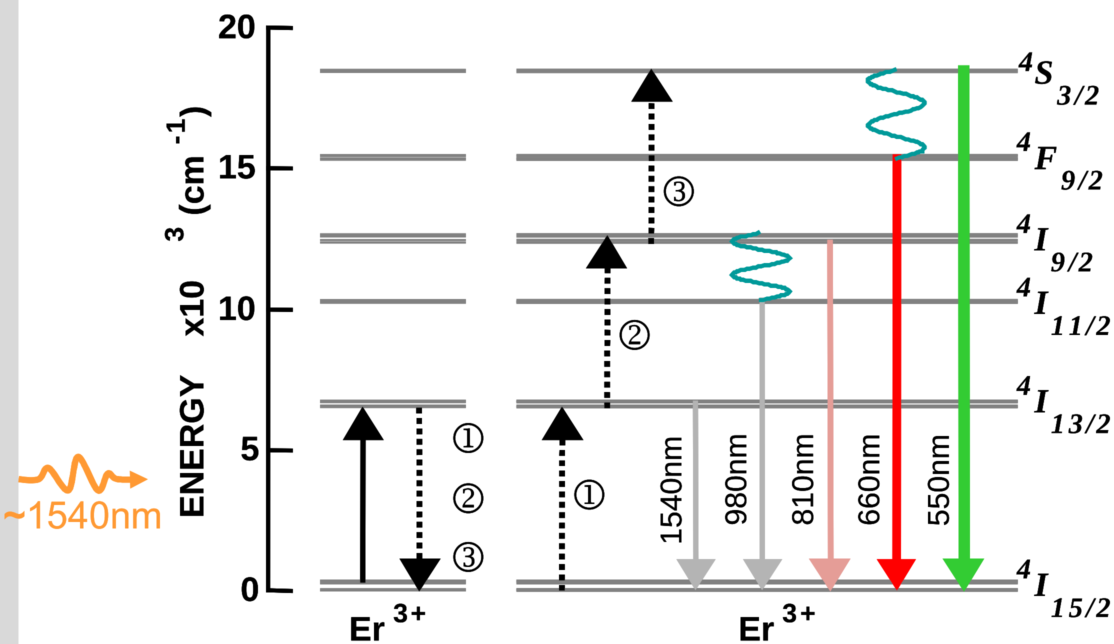


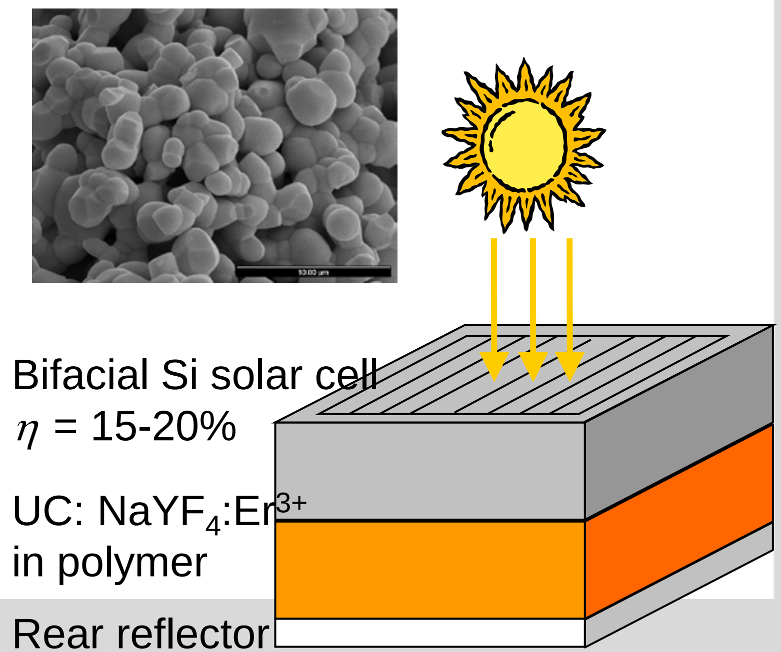
Up-Conversion

Up-conversion of 2 low-E photons to give 1 higher-E photon ⇒ overcomes sub-bandgap losses BUT additional recombination paths not introduced



Up-conversion

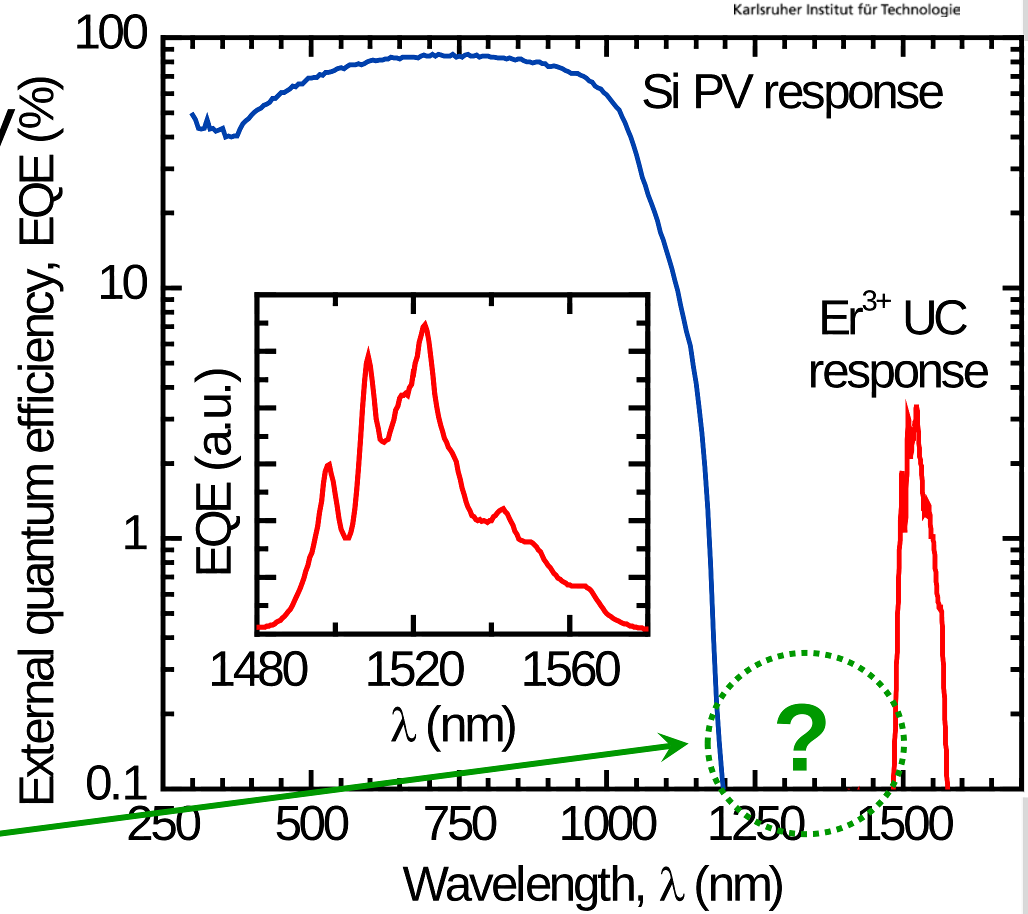




[Shalav, Richards, et al., APL 86 (2005) 103505]

Si-based Up-Conversion Devices

2005 UNSW:
Best EQE of 3.4% UC-PV device with $[Er^{3+}] = 20\%$

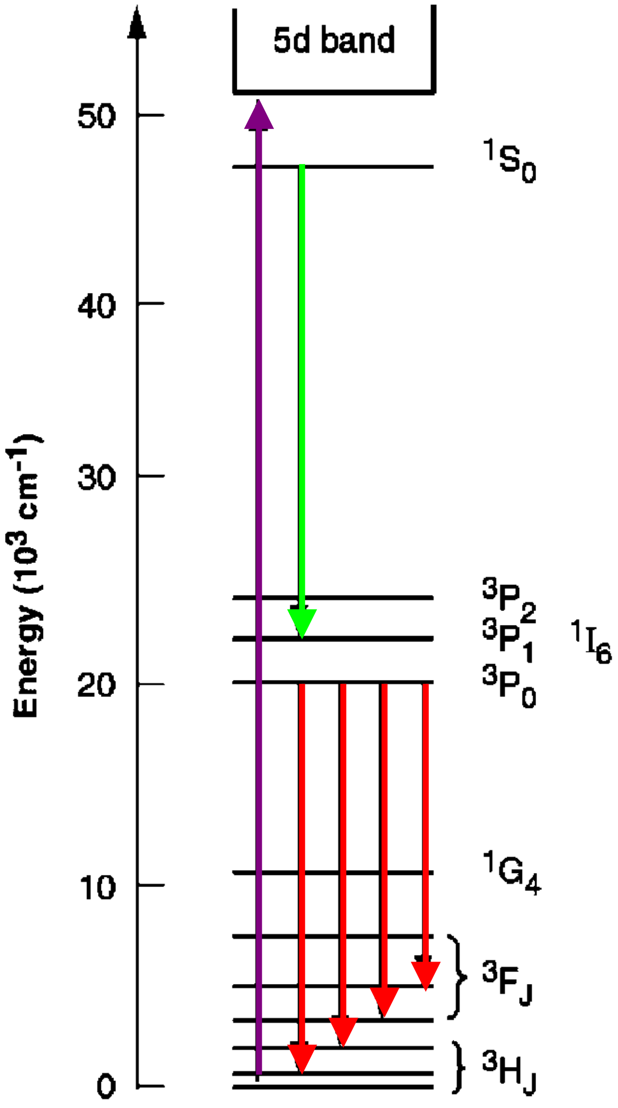


Challenge how to i) improve EQE as well as ii) harvest 1200 – 1500nm light?

*[Shalav, Richards, et al., Appl. Phys. Lett. 86 (2005) 103505
Richards, Shalav, IEEE Trans. Elec. Dev. 54 (2007) 2679 – 2684
Shalav, Richards, Green, Sol.En.Mat.Sol.Cell 91 (2007) 829–842]*

Down-Conversion

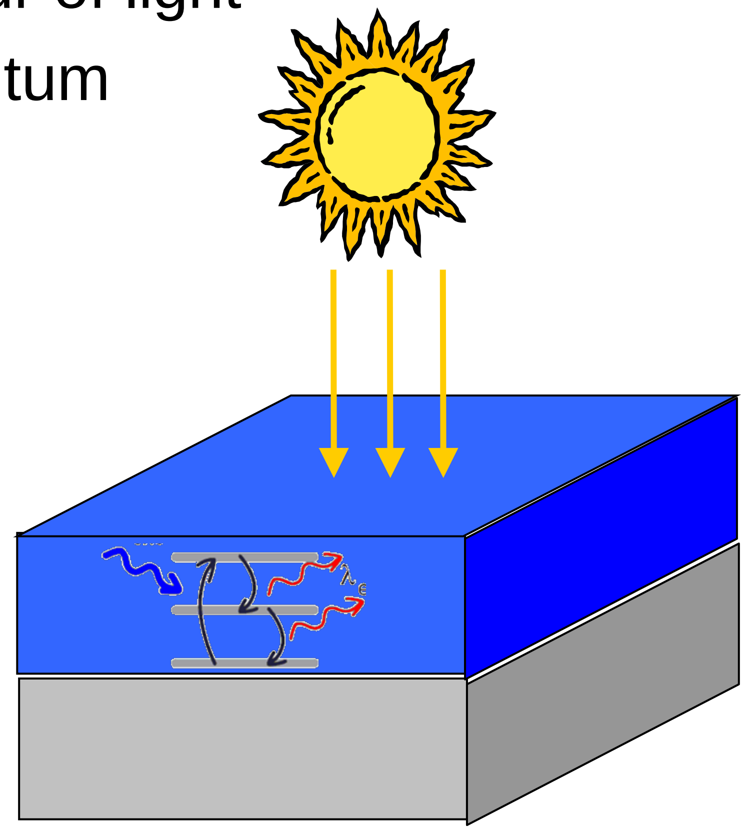
- DC already used in other industries
- While fluorescent lamp phosphors based on Pr^{3+} ion achieve quantum yields of 140%, several challenges remain for PV:
  - No deep UV light in solar spectrum!
  - Lanthanide ions are weak absorbers $\Rightarrow$ current layers would be ~1cm thick



[adapted from Ronda, J. Alloys Comp. 225 (1995) 534]

Down-Conversion

- But for PV there are some advantages:
  - DC is linear process
  - Don't care about colour of light
- Can we realise 200% quantum efficiencies…??



[Richards, Sol.En.Mat.Sol.Cells 90 (2006) 1189]