Dye sensitized solar cells (2)

Basic Principles of Photovoltaics
Maximum power conversion of photovoltaic devices

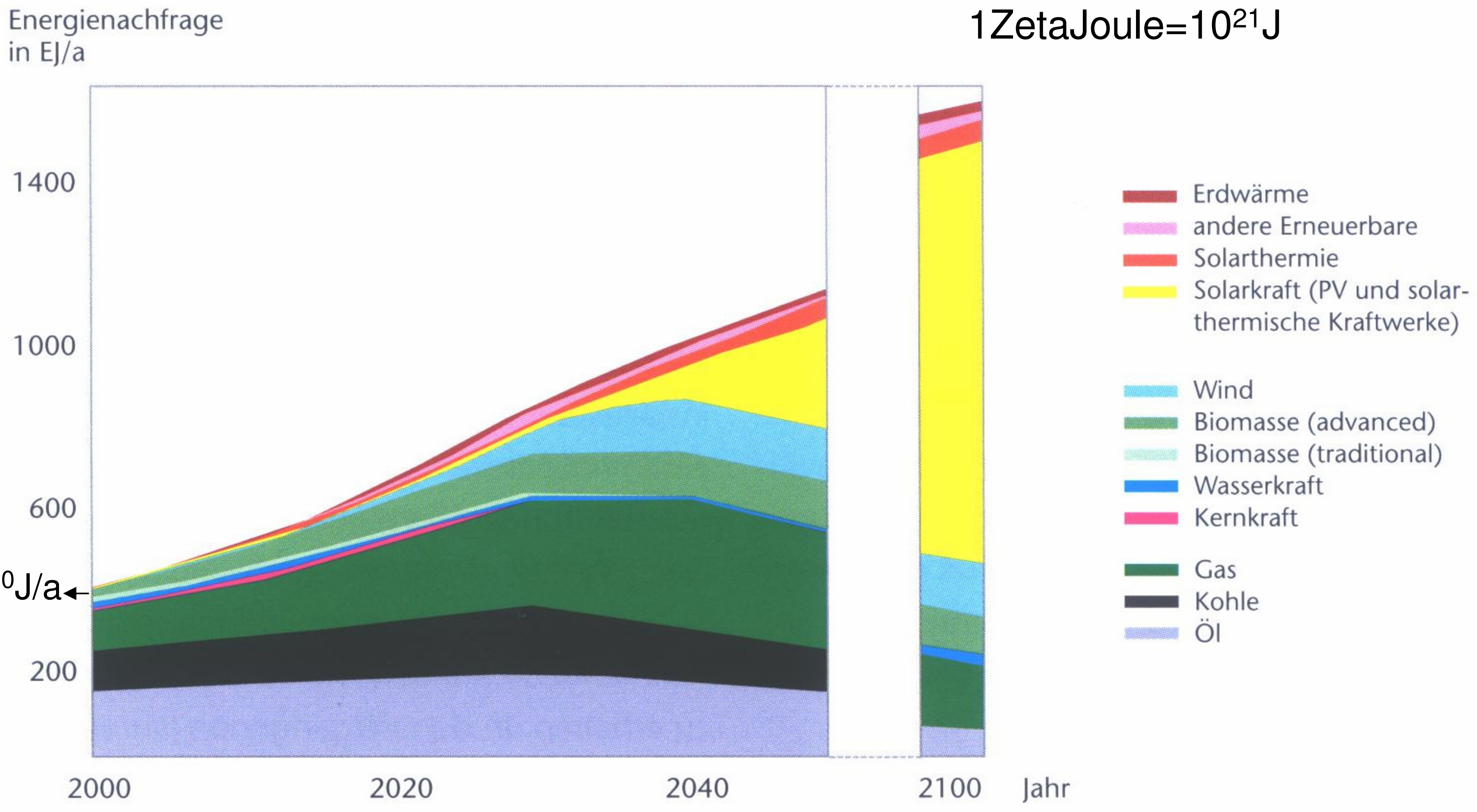
Ressources:
Peter Würfel, Physik der Solarzellen
Jenny Nelson, The Physics of Solar Cells
Thomas Dittrich, lecture notes

Energy demand

of a human	100 W to sustain biological life (2.4 kWh/day or 876 kWh/year) >3 kW to sustain comfortable life (>72 kWh/day or >26.28 MWh/year)
of mankind	more than $6x10^9$ individuals >$1.8x10^4$ GW to sustain comfortable life (18TW)
for comparison	energy in 100 g chocolate about 1 kWh energy in 1 l gazoline about 10 kWh power of one nuclear power plant about 1 GW

Scenario of worldwide energy demand

1EJ=1ExaJoule=10^{18}J
1ZetaJoule=10^{21}J



$3 \cdot 10^{20}$J/a ←

300 ExaJoule per year correspond about to 9 TW= 9000GW

The sun is a hot fire ball

spectrum of the black body radiation (Planck)
(energy flux as a function of the photon energy and of the temperature)

$$\frac{dJ_S(h\nu)}{d(h\nu)} = \frac{8\pi}{h^3c^2} \cdot \frac{(h\nu)^3}{\exp(\frac{h\nu}{k_B T_S}) - 1}$$

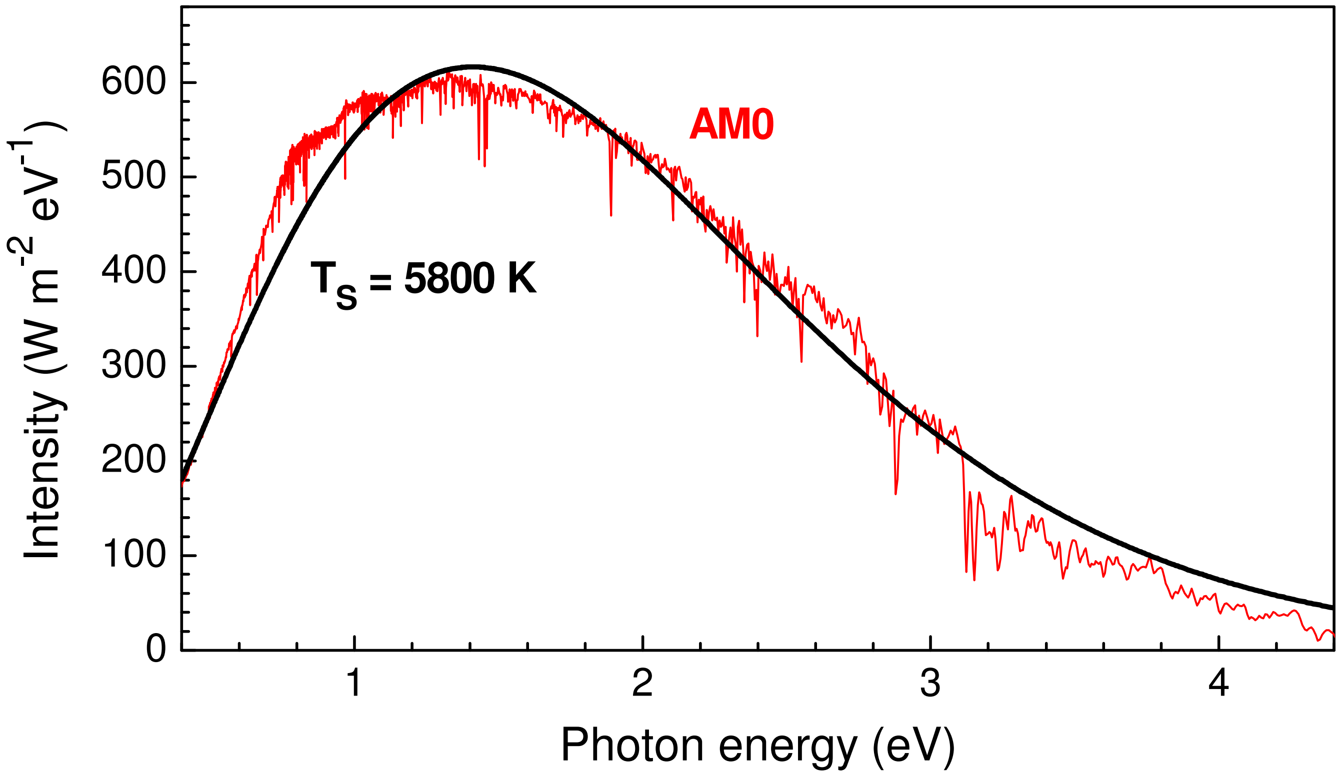
$$(h\nu)_{\max} = 2.82 \cdot k_B T$$

with
$h = 6.6\ 10^{-34}$ Js
$c = 3 \cdot 10^{8}$ m/s
$k_B = 1.38\ 10^{-23}$ J/K

By measuring the photon energy at the maximum of the sun spectrum T_s can be obtained.

temperature at the surface of the sun:

$T_S \approx 5800$ K


AM0
T_S = 5800 K
Intensity (W m^{-2} eV^{-1})
0
100
200
300
400
500
600
1
2
3
4
Photon energy (eV)

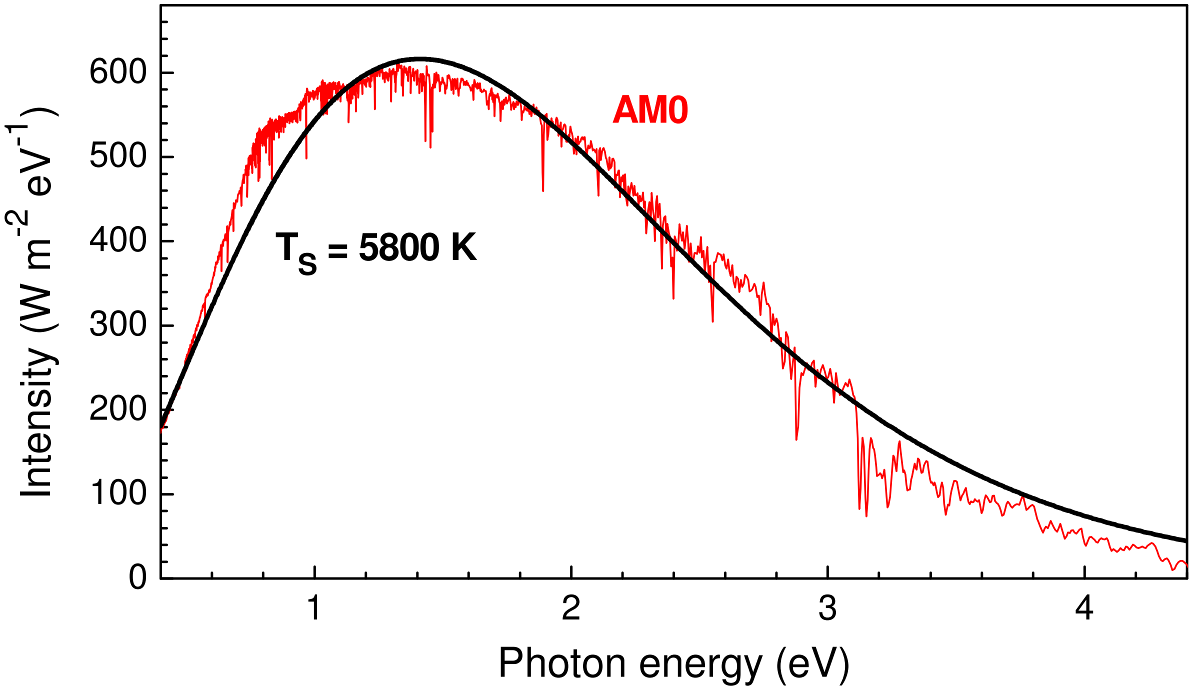
The unit of the photon flux

$$[d\Phi_S] = \frac{[dJ_S]}{[h\nu]} = \frac{W}{m^2 \cdot eV} \cdot \frac{1}{[e]V}$$

$$[d\Phi_S] = \frac{AV}{m^2 \cdot eV} \cdot \frac{1}{AsV}$$

$$[d\Phi_S] = \frac{1}{cm^2 \cdot eV \cdot s} = \frac{number\ of\ \ photons}{unit\ area \cdot energy\ unit \cdot time\ unit}$$

Energy flux spectrum and photon flux



for example:

$$dJ_S(1.2\,eV) \approx 550 \cdot \frac{W}{m^2 \cdot eV}$$

$$b_S(1.2\,eV) \approx \frac{550}{10^4 \cdot 1.2 \cdot 1.6 \cdot 10^{-19} \cdot cm^2 \cdot eV \cdot s}$$

$$b_S(1.2\,eV) \approx 3 \cdot 10^{17} \cdot \frac{1}{cm^2 \cdot eV \cdot s}$$

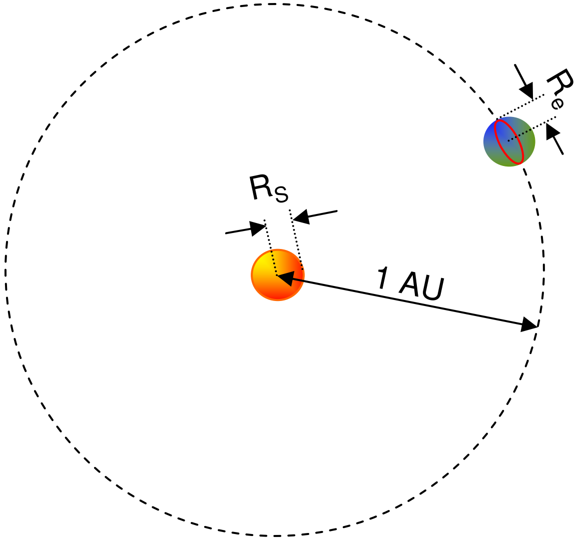
Power of the sun received on earth

Stefan-Boltzmann law $$I_S = \sigma \cdot T^4$$

power of the sun $$P_S = \sigma \cdot T^4 \cdot 4\pi \cdot R_s^2$$

power received on earth $$P_e = P_S \cdot \frac{\pi \cdot R_e^2}{4\pi \cdot (AU)^2}$$

with
$\sigma = 5.67\ 10^{-8}$ W/(m²K⁴)
$R_s = 7\ 10^5$ km
$R_e = 6.4\ 10^3$ km
AU = $1.5\ 10^8$ km



$P_e \approx 1.8\ 10^8$ GW

more than 1000…10000 times
the energy demand of mankind

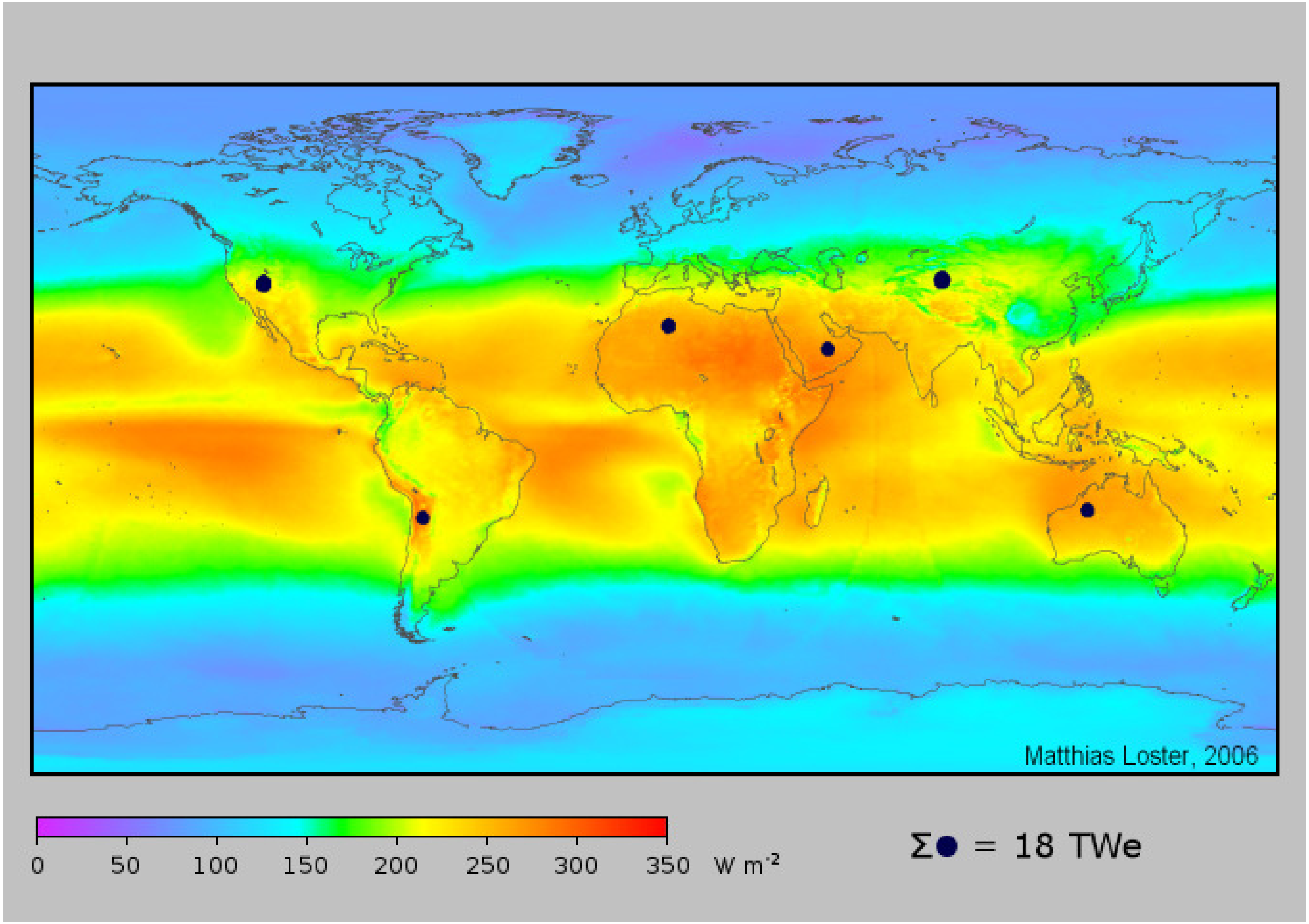
At present mankind needs about 9000GW

The solar constant

energy flux of sun light to the earth normalized to the area of 1 m²

$$J_S = \frac{P_s}{4\pi \cdot (AU)^2}$$

J_S = 1.353 kW/m²


Matthias Loster, 2006
0
50
100
150
200
250
300
350
W m^{-2}
Σ● = 18 TWe

Annual average solar irradiance

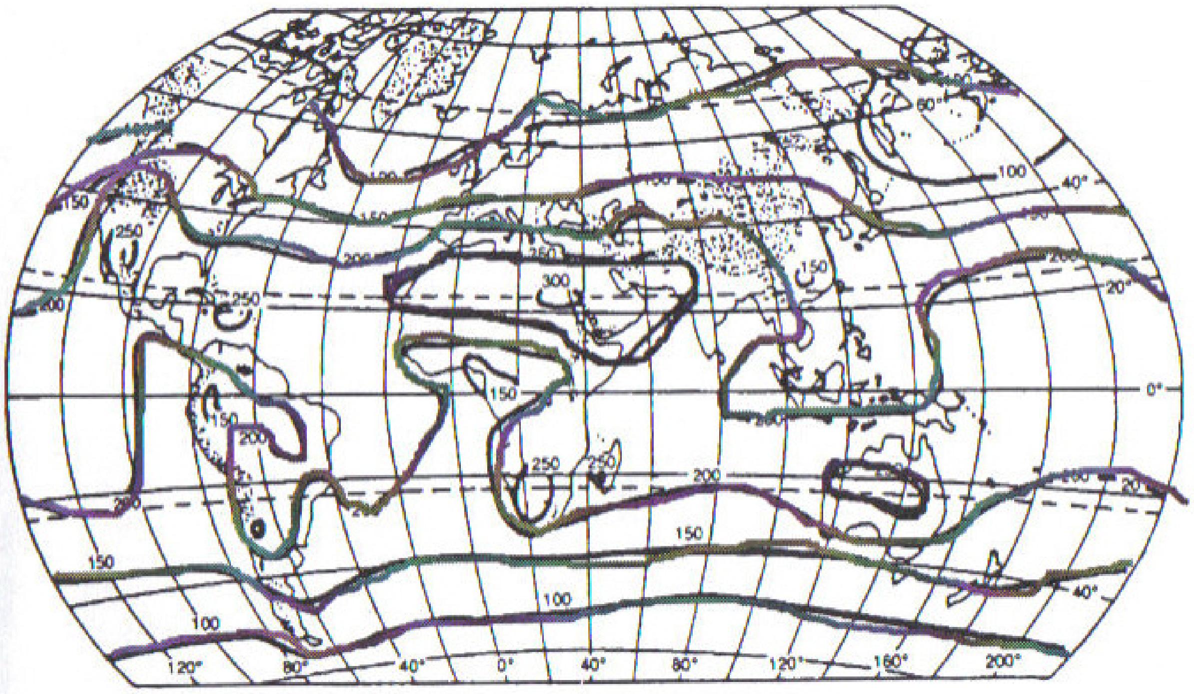
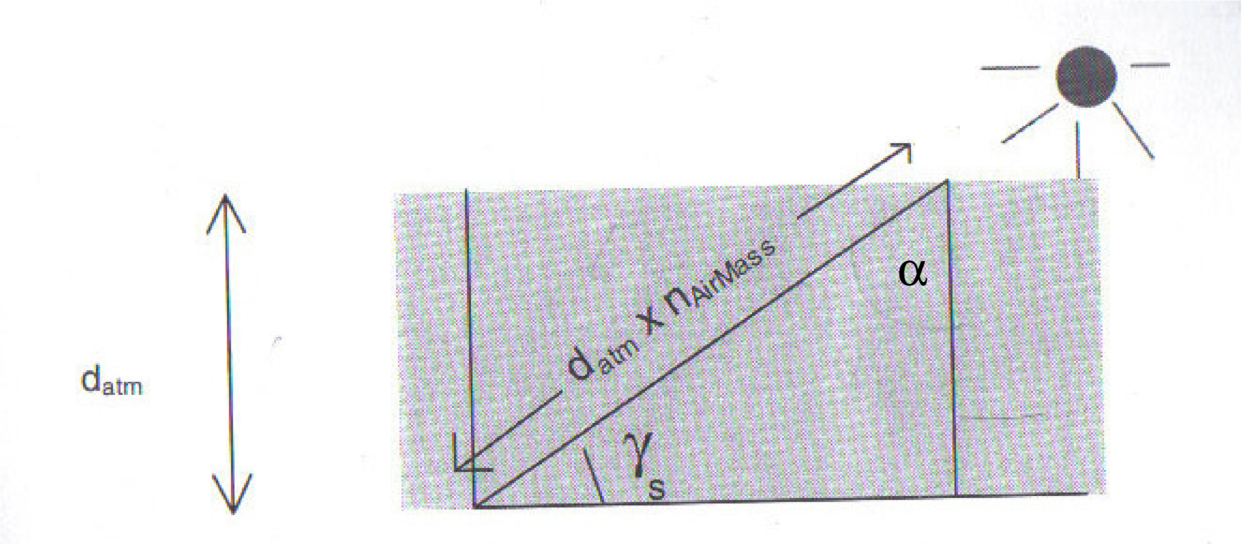


Fig. 2.3. Global distribution of annual average solar irradiance. The values on the irradiance contours are given in W m^{-2}.

Global average: Extraterrestial $\langle J_E \rangle = 1/4 \cdot 1353 W/m^2 = 338 W/m^2$
CH: $115 W/m^2$
Saudi-Arabien: $285 W/m^2$

*

Air Mass: AM1.5, AM1.0….



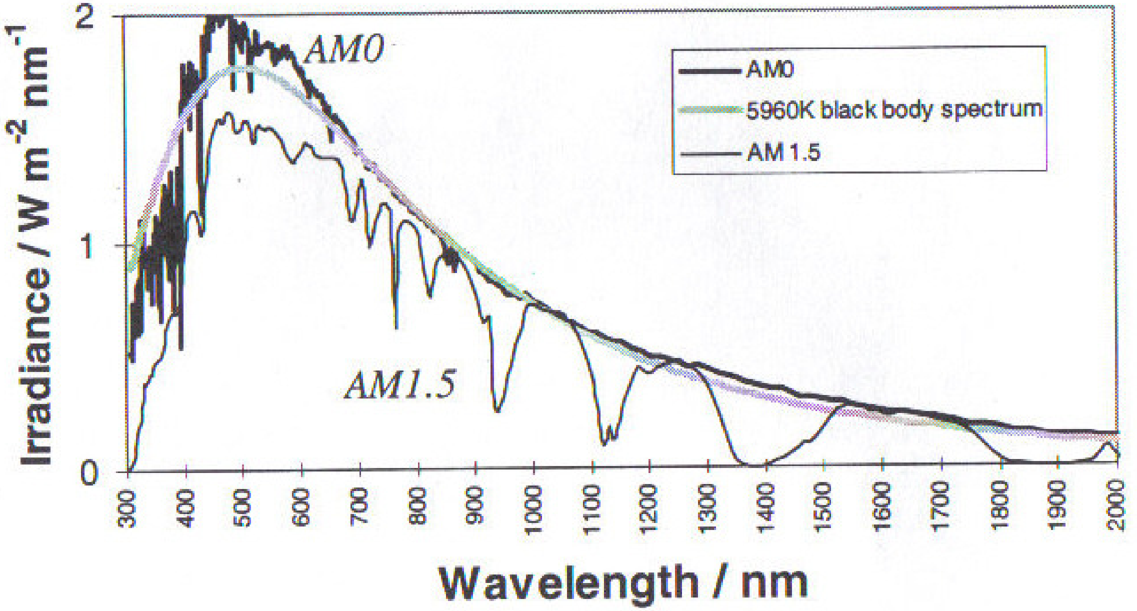
$n_{\text{air mass}} = 1 / \sin(\gamma_s)$

$\gamma_s = 41.8^{\circ} \Rightarrow n_{\text{air mass}} = 1.5$

Alternatively: $n_{\text{air mass}} = 1 / \cos(\alpha)$

Definition: For convenience AM1.5 is defined as 1000W/m² integrated irradiance
(Typical experimental values at 42º are 900W/m²)
AM0: Extraterrestial; AM1.0: equator

Solar spectrum



-Comparison of AM0 (extraterrestial) with black body radiation of T=5960K and AM 1.5

-Dips in spectrum at 900, 1100, 1400 and 1900nm (H_2O) and at 1800 and 2600nm (CO_2)

Temperature on earth from energy balance

$I_{atm} \rightarrow 0$

Energy flux from sun to earth

$$I_s = J_s \cdot \pi \cdot R_e^2$$

Black body radiation from earth into free space

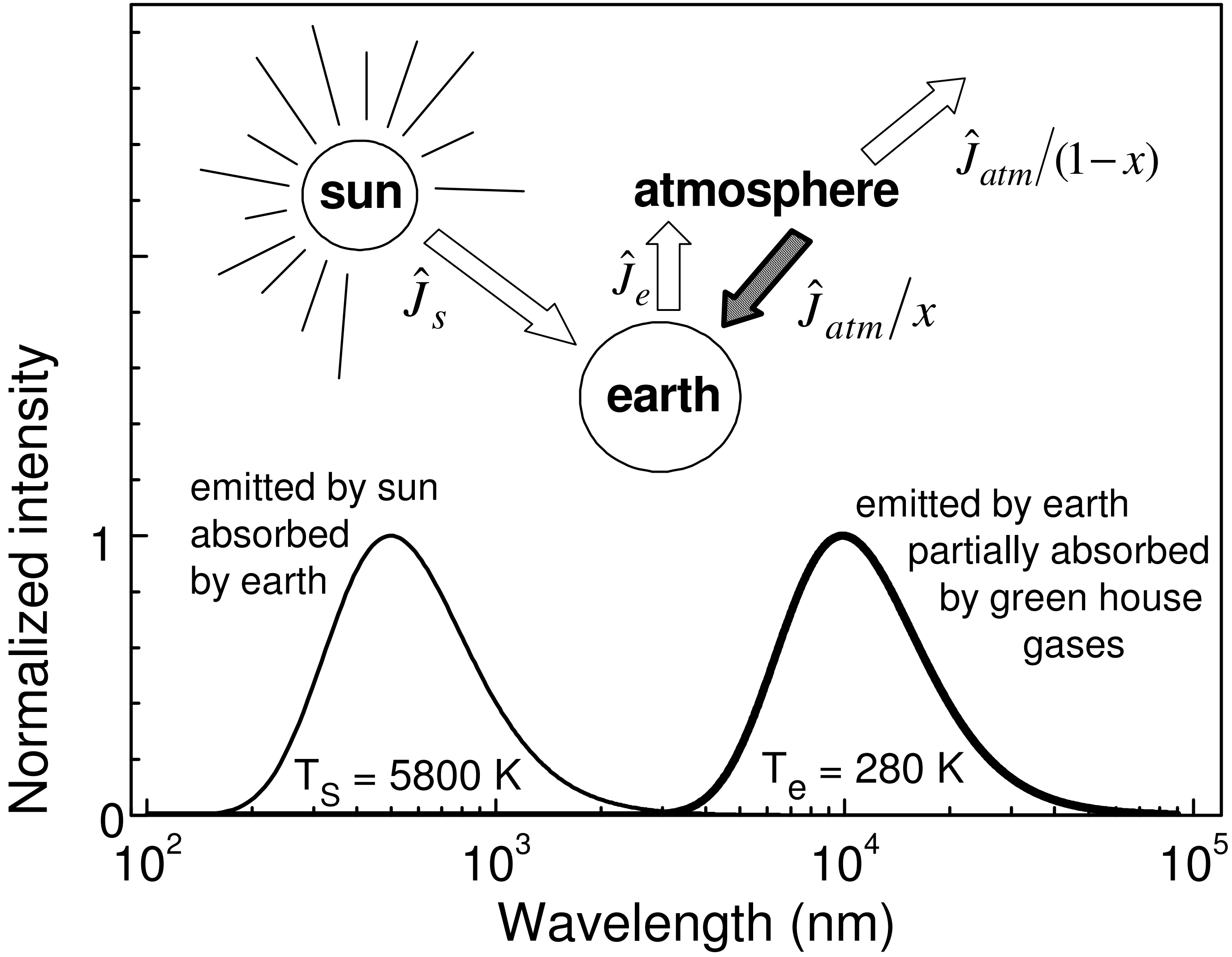
$$I_e = \sigma \cdot T_e^4 \cdot 4\pi \cdot R_e^2$$

with
$\sigma = 5.67\ 10^{-8}$ W/(m^{2}K^4)
$J_s = 1.35$ kW/m^2

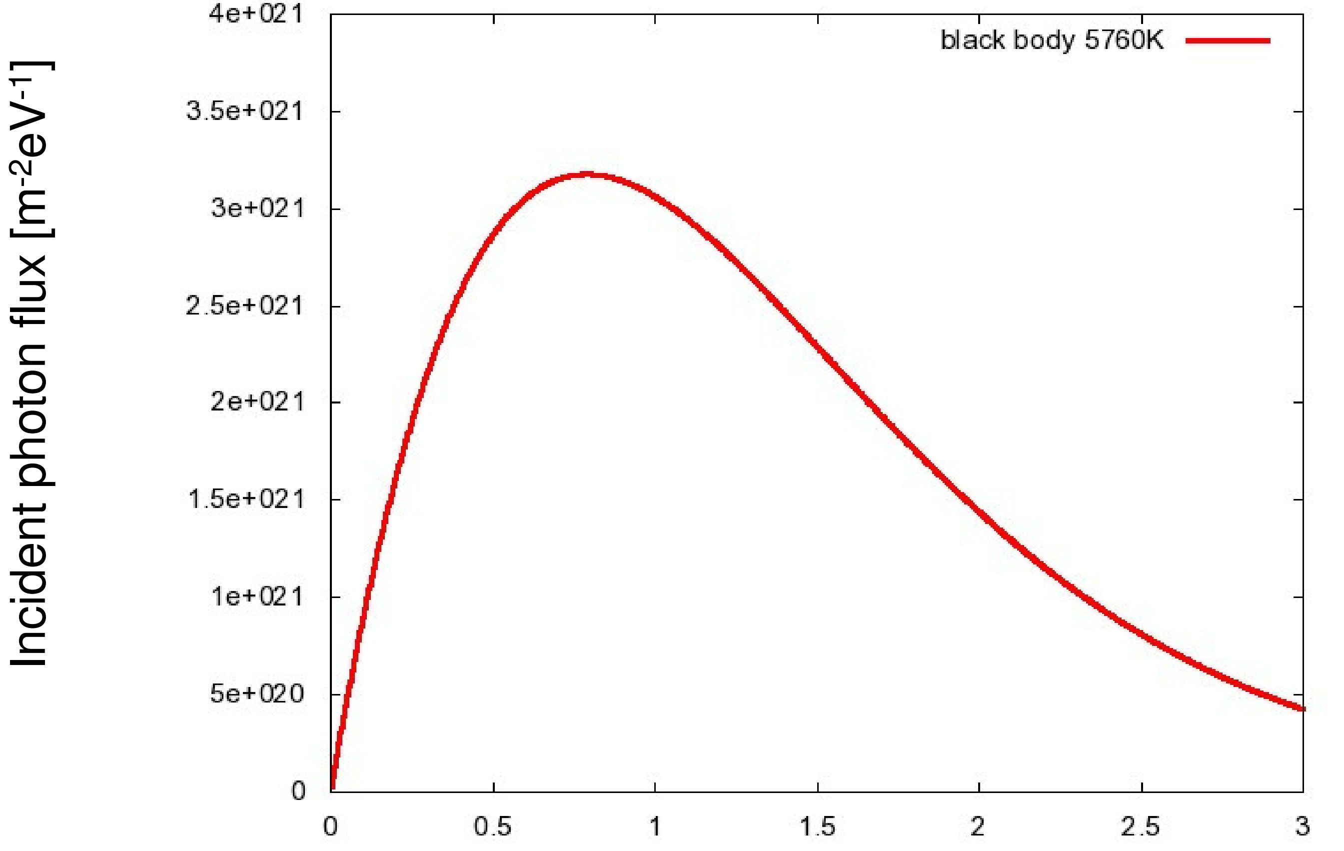
Balance

$$I_e = I_s$$

$$\Rightarrow T_e = \sqrt[4]{\frac{J_s \cdot \pi \cdot R_e^2}{\sigma \cdot 4\pi \cdot R_e^2}} \approx 277\,K$$


sun
$\hat{J}_s$
atmosphere
$\hat{J}_e$
$\hat{J}_{atm}/x$
$\hat{J}_{atm}/(1-x)$
earth
emitted by sun absorbed by earth
emitted by earth partially absorbed by green house gases
T_S = 5800 K
T_e = 280 K
Normalized intensity
1
0
10^2
10^3
10^4
10^5
Wavelength (nm)

Black body radiation at 5760K



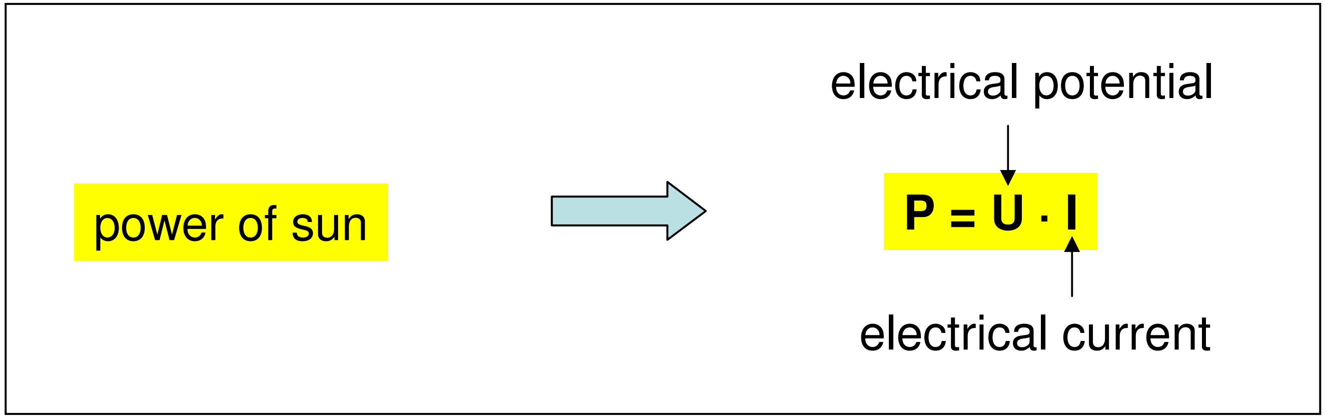
$$b_s(E) = \frac{2F_s}{h^3c^2}\left(\frac{E^2}{e^{E/k_BT_s} - 1}\right)$$

*

$F_s=6.8\cdot10^{-5}$
(corresponds to the sun-earth geometry)

The solar cell

electronic device converting solar power directly into electrical power



power of sun

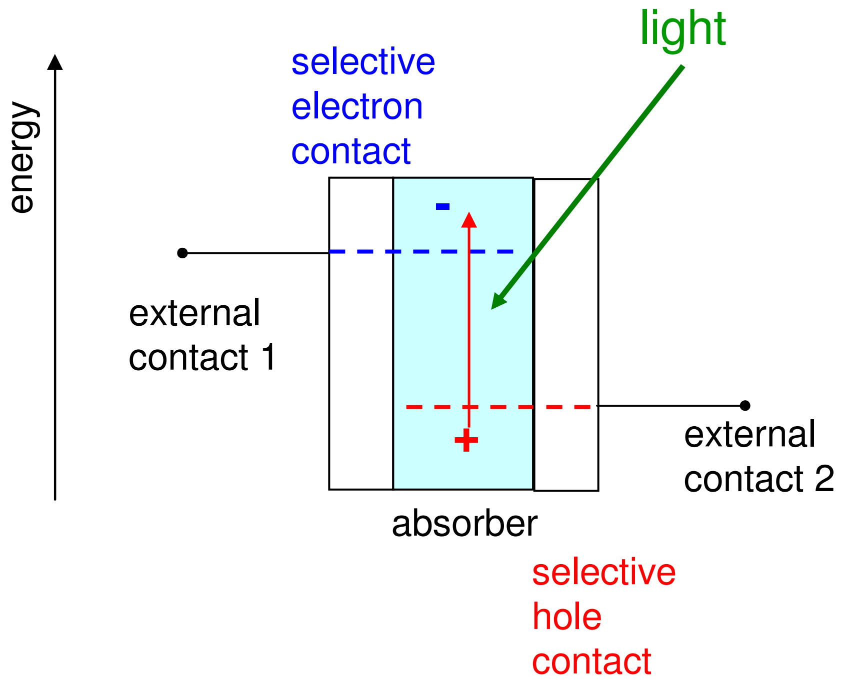
electrical potential

$P = U \cdot I$

electrical current

A solar cell absorbs light and conducts electrons and
holes to separate electron and hole collecting contact.

A major characteristic is the energy conversion efficiency.



energy

selective
electron
contact

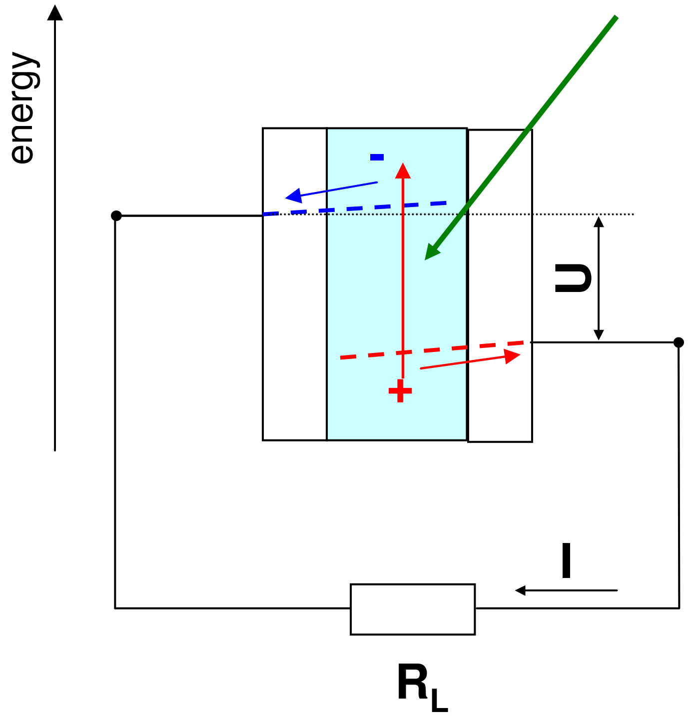
light

external
contact 1

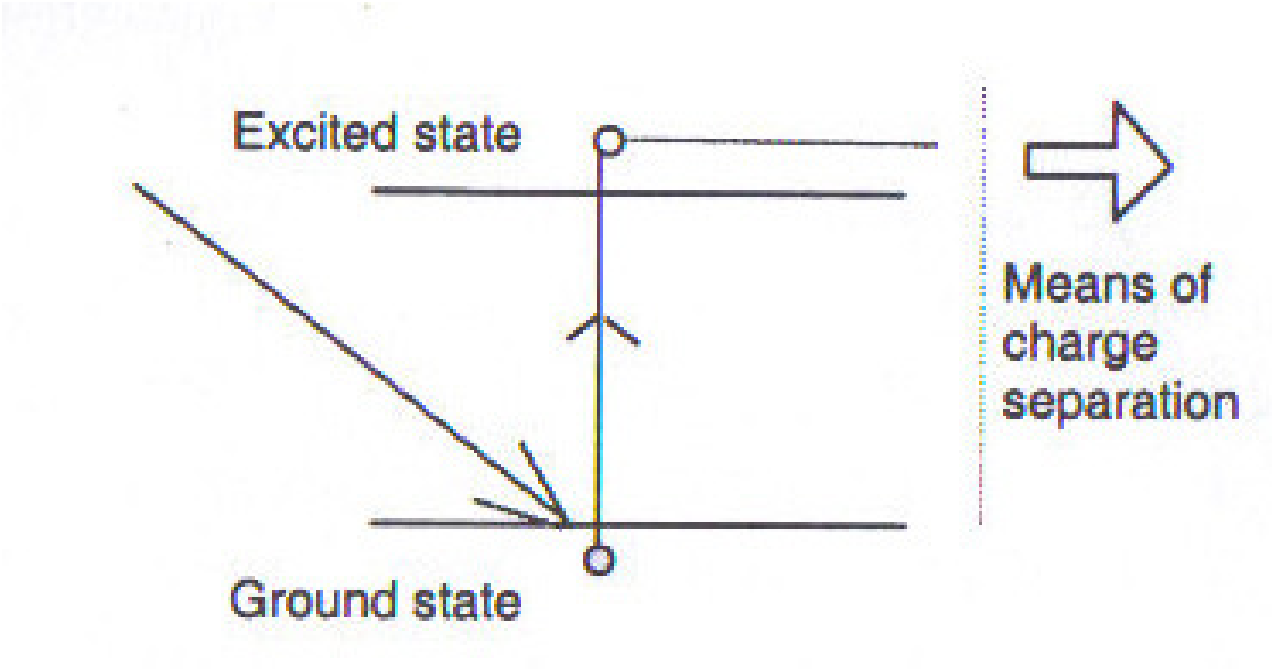
external
contact 2

absorber

selective
hole
contact


energy
-
+
U
I
R_L

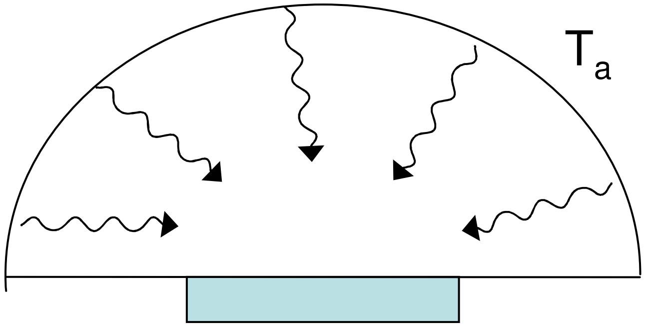
Excitation and charge separation



Photon creates electron-hole pair, which is separated by an asymmetric potential. Charge separation prevents relaxation to its initial state.

Cell in the dark: Absorption of thermal photons

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



b_a : incident photon flux
h: Planck‘s constant
c: speed of light
k_B: Boltzmann constant
E: Energy
Thermal photons are absorbed from the environment of Temperature T_a
F_a: geometry factor; $F_a=\pi$ for hemisphere

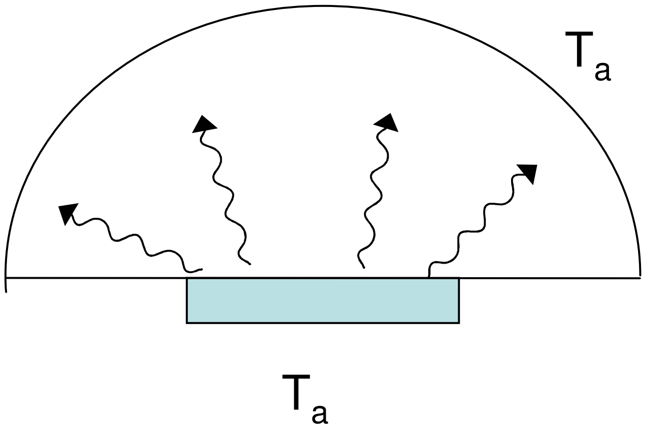
The equivalent current density j_{abs} absorbed from the ambient:

$$j_{abs}(E) = q\left(1-R(E)\right)a\left(E\right)\frac{2F_a}{h^3c^2}\left(\frac{E^2}{E^{E/k_BT_a}-1}\right)$$

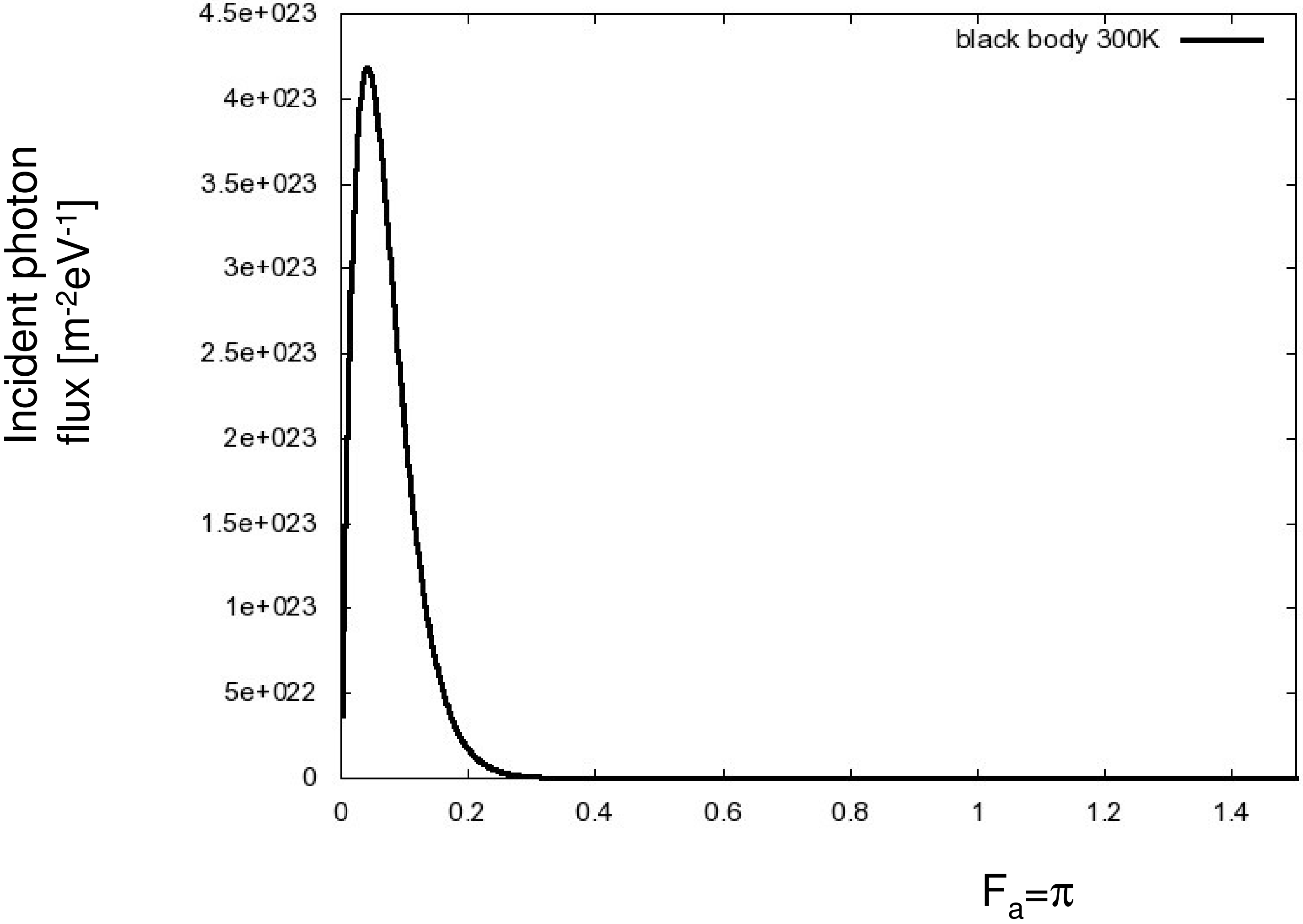
Cell in the dark: Emission of thermal photons

$$j_{rad}(E) = q\big(1 - R(E)\big)\varepsilon\big(E\big)\frac{2F_a}{h^3c^2}\left(\frac{E^2}{E^{E/k_BT_a} - 1}\right) = q\big(1 - R(E)\big)\varepsilon\big(E\big)b_a(E)$$

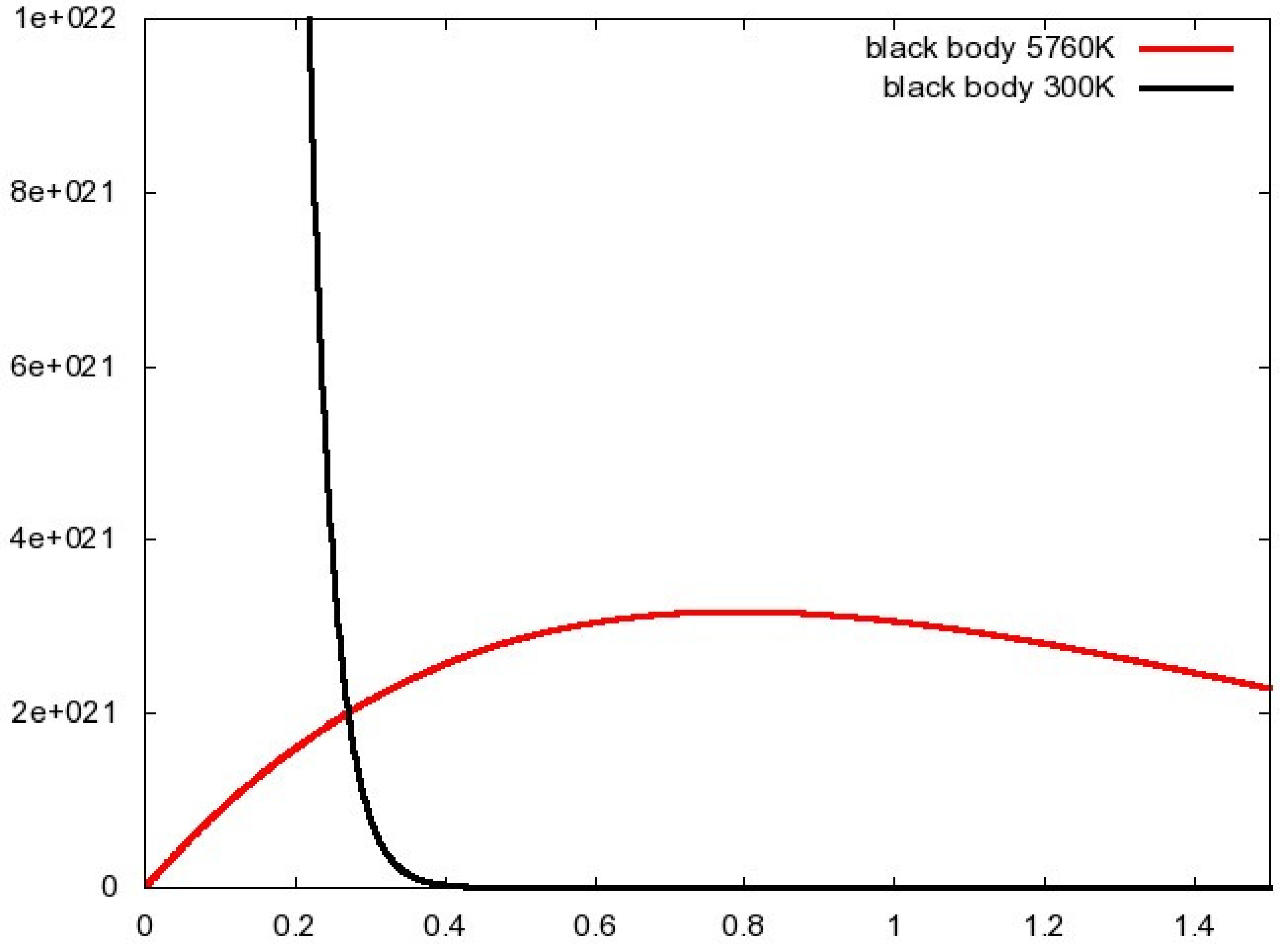
In equilibrium: Kirchoff‘s law ε(E)=a(E)



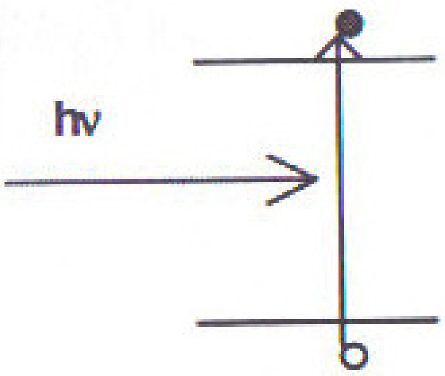
Black body radiation at 300K



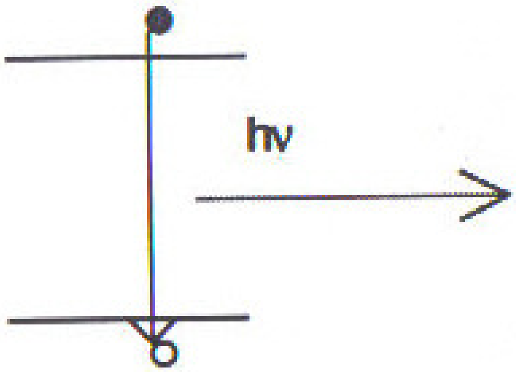
Comparison of black body radiation at 300K and 5760K



Absorption and spontaneous emission



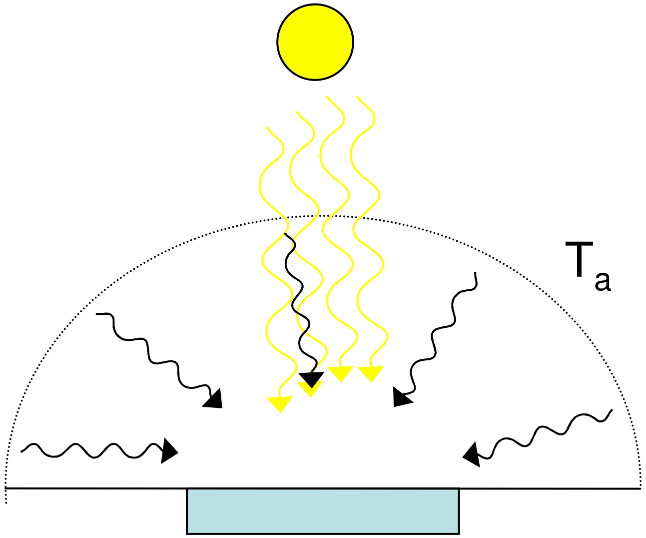
absorption



spontaneous emission

Under illumination (absorption)

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

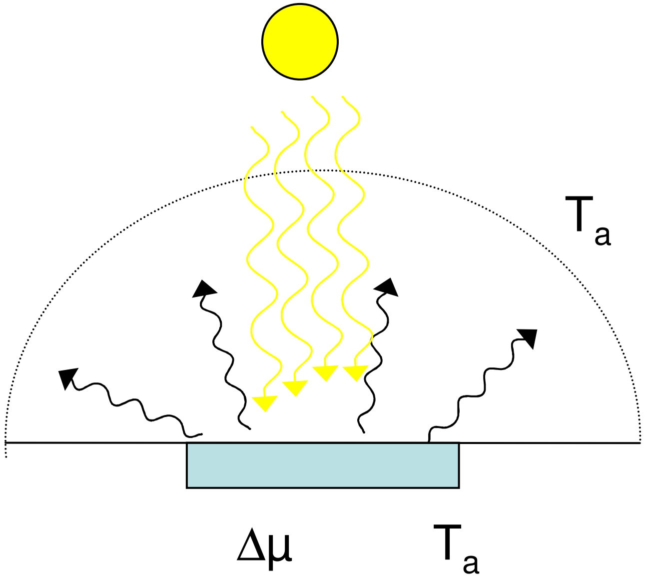


Ts: Temperature of the sun
$F_s = \pi \sin^2\theta_s = \pi / 4.6 \cdot 10^4$
$\theta_s = 0.26º$

$$j_{abs}(E) = q(1 - R(E))a(E)(b_s(E) + (1 - F_s / F_a)b_a(E))$$

Under illumination (emission)

Depends on the Δμ . When electrons are at raised energy, relaxation is more frequent: Generalized Planck’s radiation law:



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

$$j_{rad}(E) = q\big(1-R(E)\big)\varepsilon\big(E\big)b_e(E,\Delta\mu)$$

Net current density under illumination

Under the assumption that ε(E)=a(E) and Δμ=const across the cell

$$j_{abs}(E) - j_{rad}(E) = q\left(1 - R(E)\right)a\left(E\right)(b_s(E) + (1 - F_s / F_a)b_a(E) - b_e(E, \Delta\mu))$$

Net absorption:

$$j_{abs-net}(E) = q\left(1 - R(E)\right)a\left(E\right)(b_s(E) - \frac{F_s}{F_a} b_a(E))$$

Net Emission
Radiative recombination

$$j_{rad-emission}(E) = q\left(1 - R(E)\right)a\left(E\right)(b_e(E, \Delta\mu) - b_e(E, 0))$$

Photocurrent

$$J_{sc} = q\int_0^\infty \eta_c(E)\left(1-R(E)\right)a\left(E\right)(b_s(E) - \frac{F_s}{F_a}b_a(E))dE \approx q\int_0^\infty \eta_c(E)\left(1-R(E)\right)a\left(E\right)(b_s(E)dE$$

η_C: probability that electron is collected

cf.

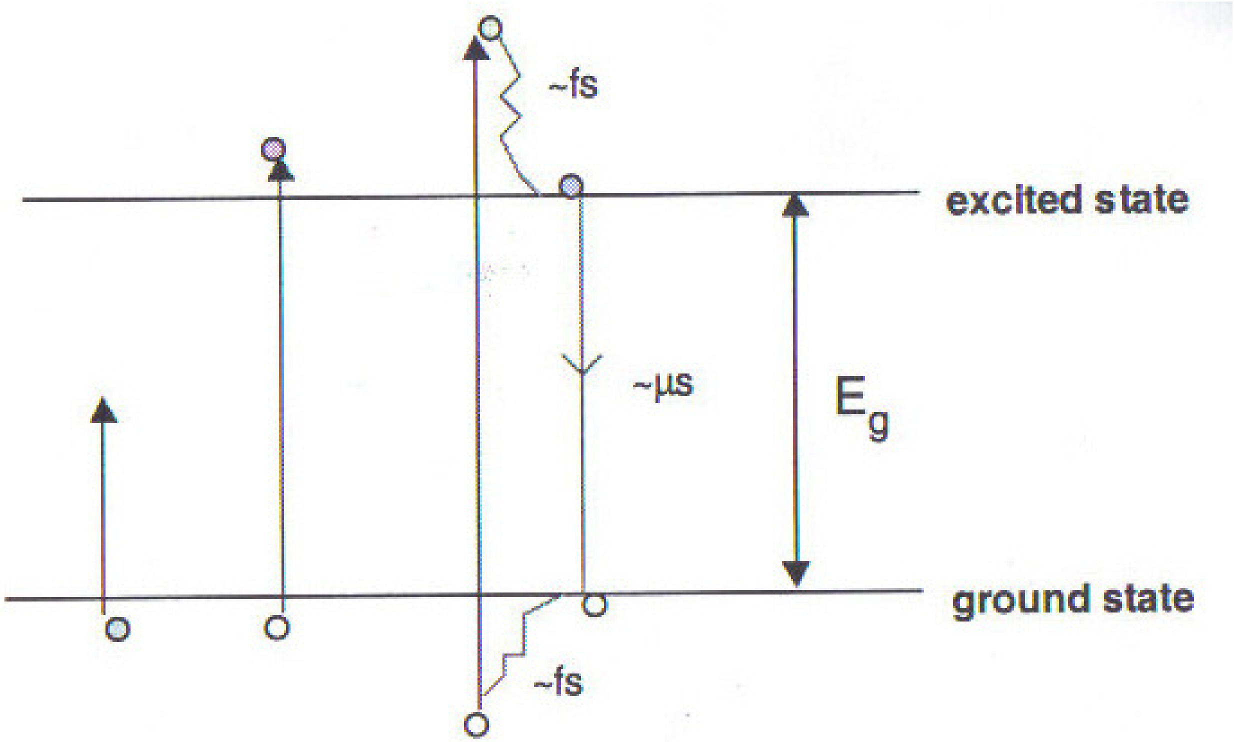
$$J = q\int_0^\infty QE(E)\cdot b_s(E)dE$$

Quantum efficiency: $QE(E)= \eta_C(E)(1-R(E))a(E))$

For non-reflecting material: $R(E)=0$ and perfect charge separation $\eta_C=1$:

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

Two band photoconverter



Photons with $E>>E_g$ have the same effect like electrons with $E=E_g$
Photocurrent is rather proportional to photon flux and not photon energy
But photons with $E<E_g$ can not create electron hole pairs

Dark current

Assumption:
-only loss process is radiative relaxation of electrons through spontaneous emission
-No non-radiative losses due to scattering at defects in the material

$$J_{dark} = q\int_0^{\infty} \left(1 - R(E)\right) a\left(E\right) (b_e(E, \Delta\mu) - b_e(E,0)) dE$$

where $\Delta\mu = qV$

Dark current is related to emitted flux, which is increased with increasing voltage

Net cell current density

$$J(V) = J_{sc} - J_{dark}(V) = q\int_{0}^{\infty}\left(1 - R(E)\right)a\left(E\right)\left(b_{s}(E) - (b_{e}(E,\Delta\mu) - b_{e}(E,0))\right)dE$$

incoming flux

emitted flux

For step-like absorption (E>E_g):

$$J(V) = J_{sc} - J_{dark}(V) = q\int_{E_g}^{\infty} b_{s}(E) - (b_{e}(E,\Delta\mu) - b_{e}(E,0))dE$$

J(V) depends strongly on voltage:

$$J(V) = J_{sc} - J_{0}\left(e^{qV/k_{B}T} - 1\right)$$

at V=V_{oc} the total emitted flux balances the absorbed flux

Limiting efficiency

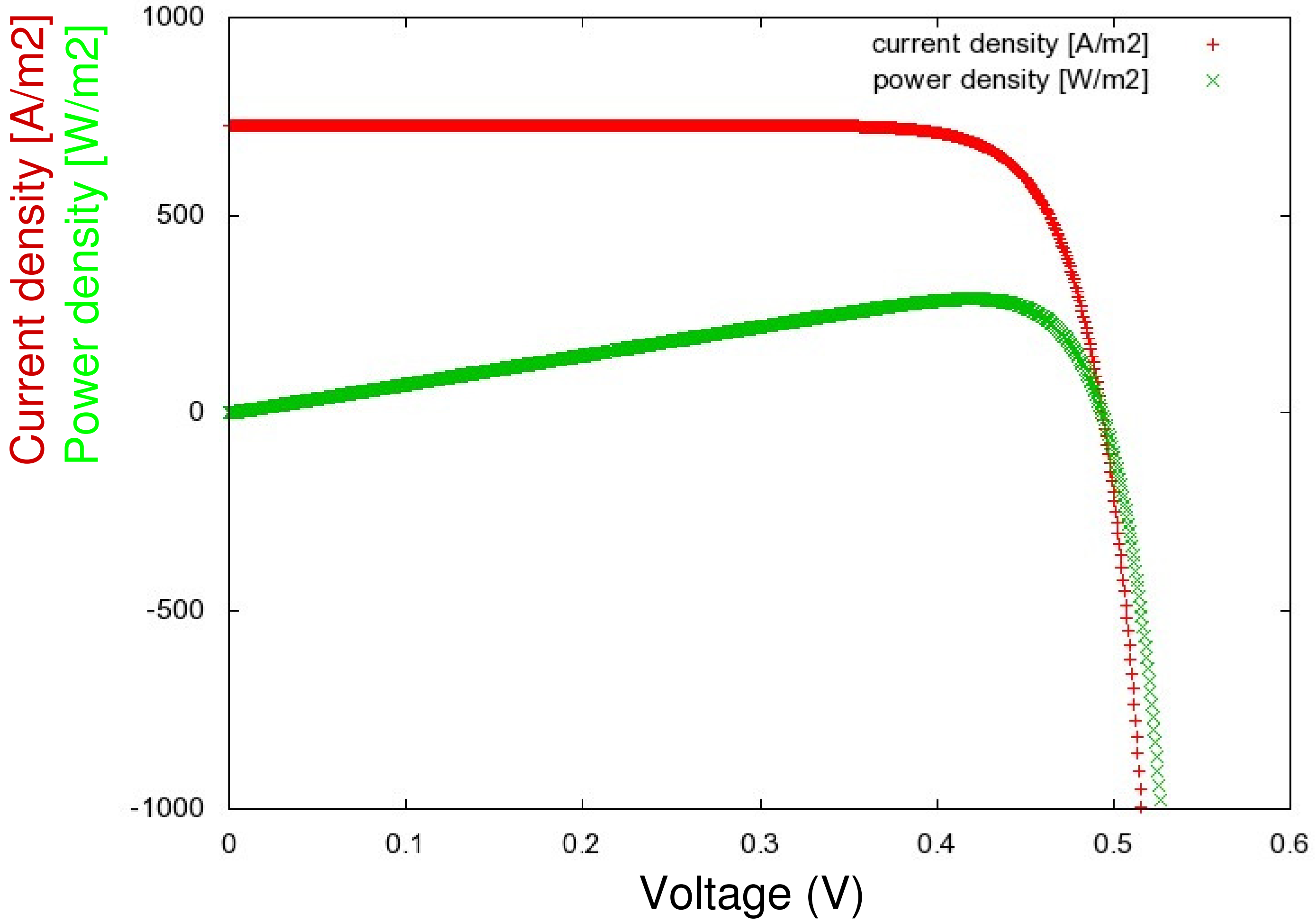
Incident power: $P_s = \int_0^\infty E \cdot b_s(E) dE$

Output power: P = V J(V)
(assumption no Ohm‘s losses)

Power conversion efficiency: $$\eta = \frac{VJ(V)}{P_s}$$

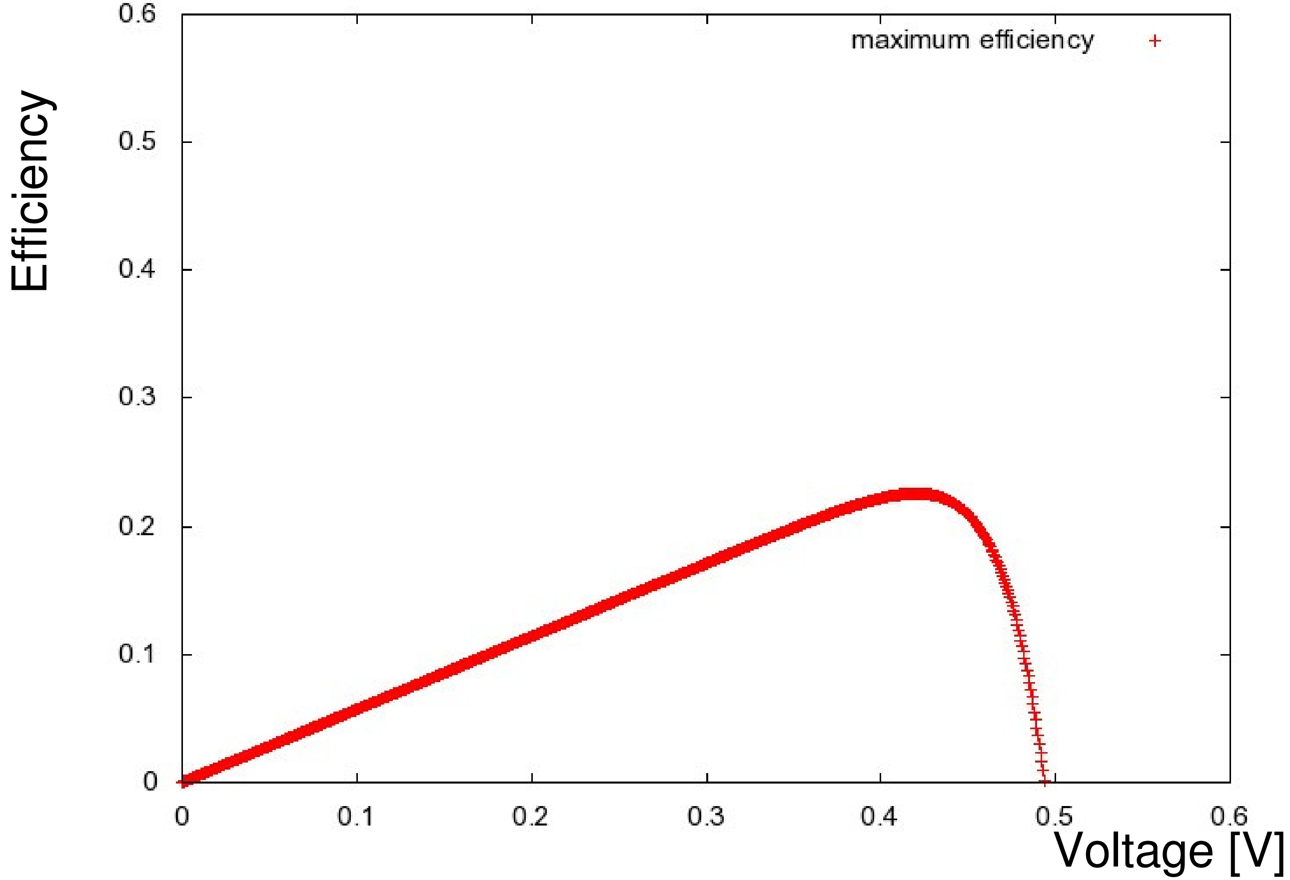
Maximum efficiency is achieved when: $$\frac{d}{dV}\left(J(V)V\right) = 0$$

Maximum current and power densities with E_g=0.7eV



E_g=0.7V T_s=5760K T_a=300K P_S=1275W/m2

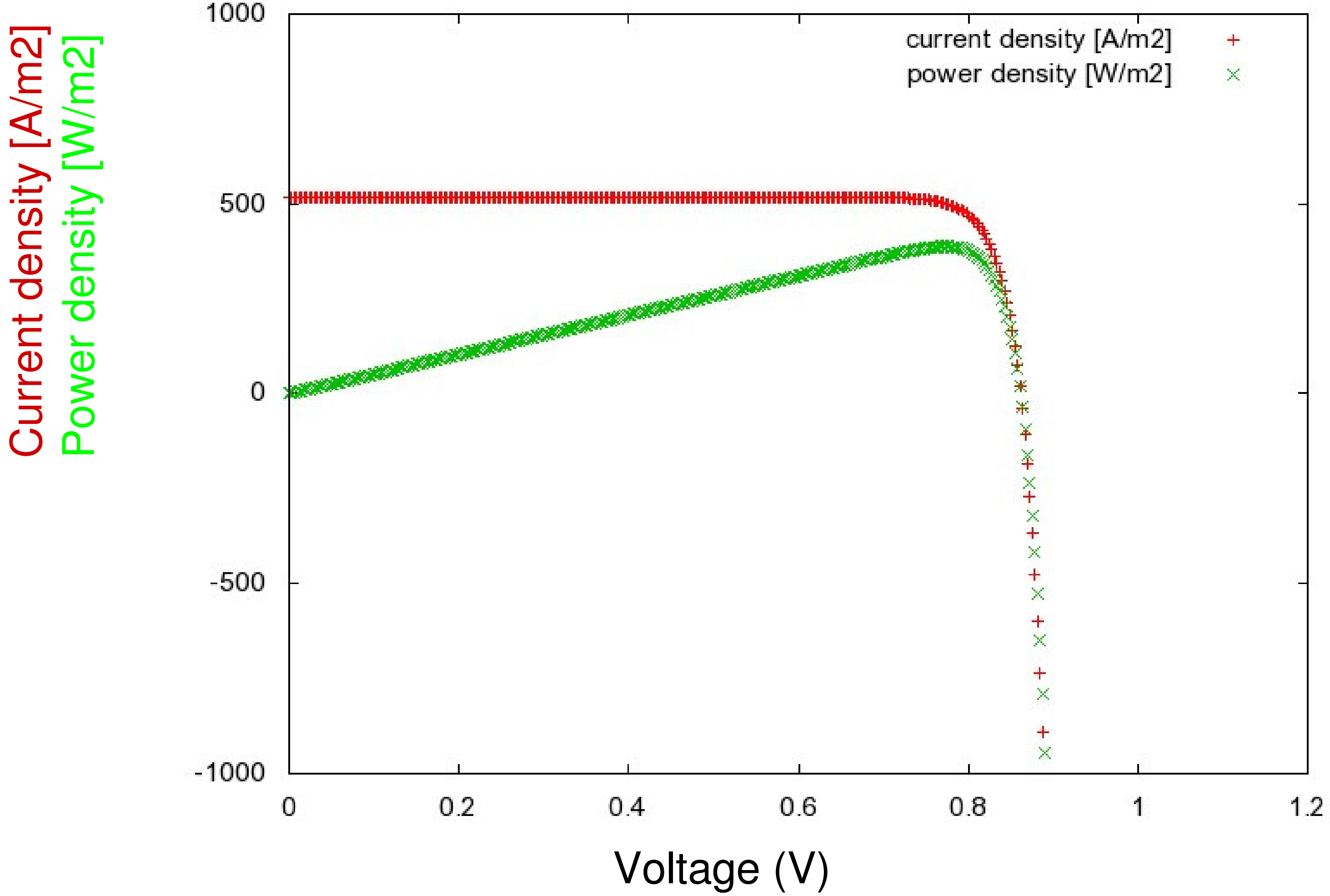
Maximum efficiency for E_g=0.7eV



$$\eta = \frac{VJ(V)}{P_s}$$

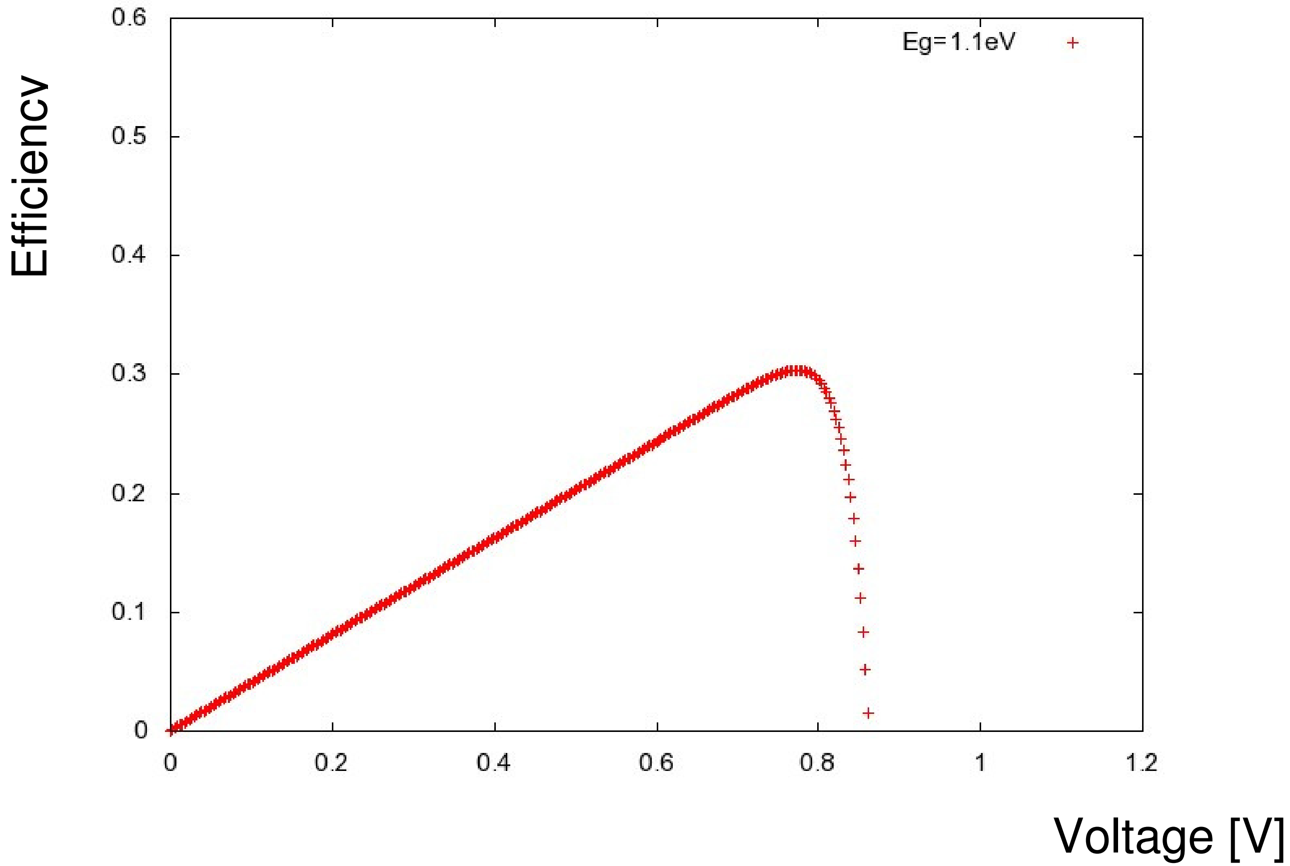
Best performance at V_m=0.45V with 22.5%

Maximum current and power densities with E_g=1.1eV



E_g=0.7V T_s=5760K T_a=300K P_S=1275W/m2

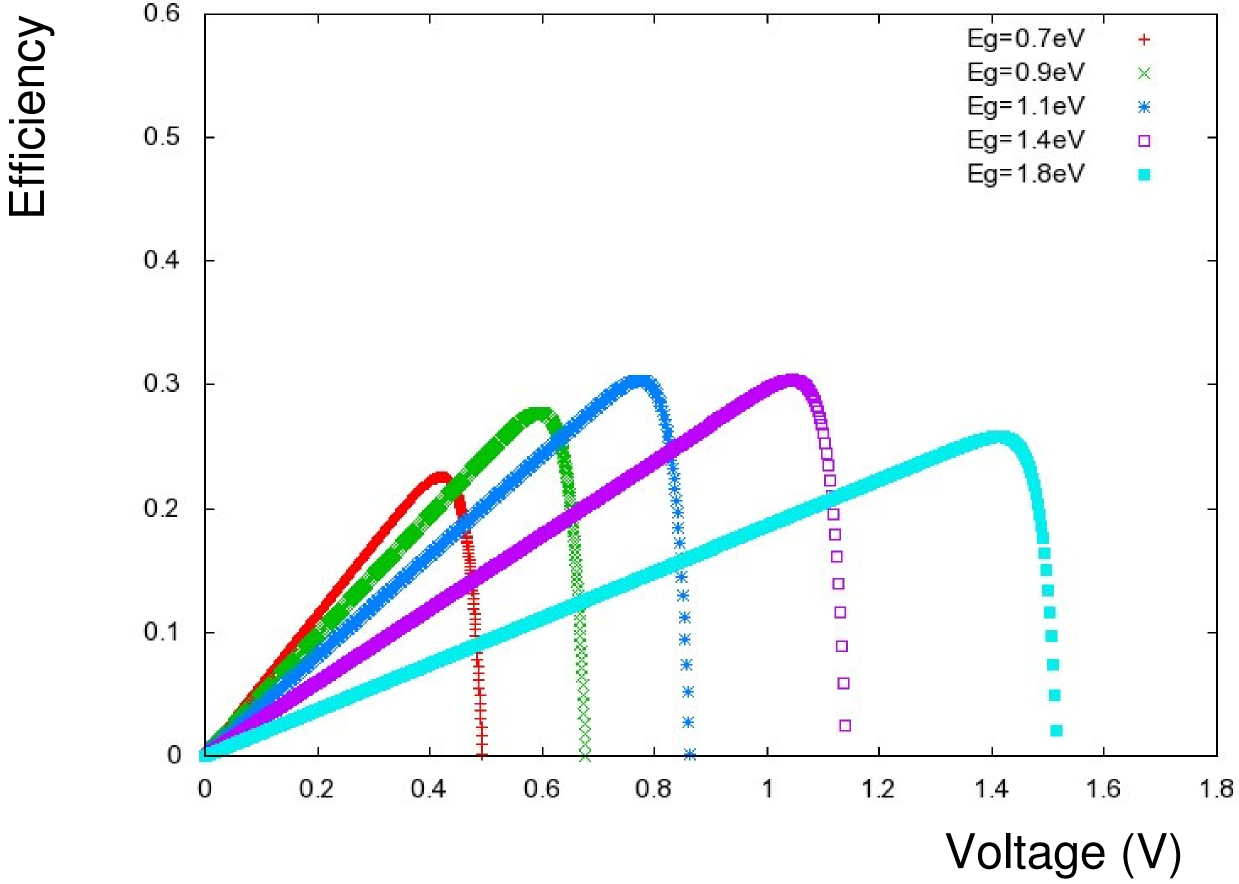
Maximum efficiency for E_g=1.1eV



$$\eta = \frac{VJ(V)}{P_s}$$

Best performance at V_m=0.77V with 30%

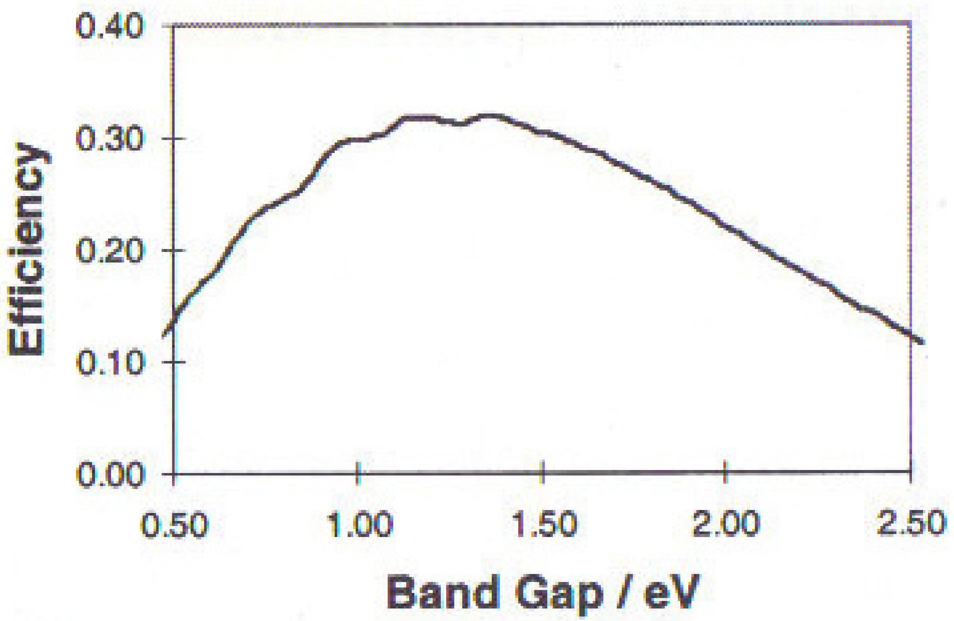
Maximum efficiency for different band gaps



$$\eta = \frac{VJ(V)}{P_s}$$

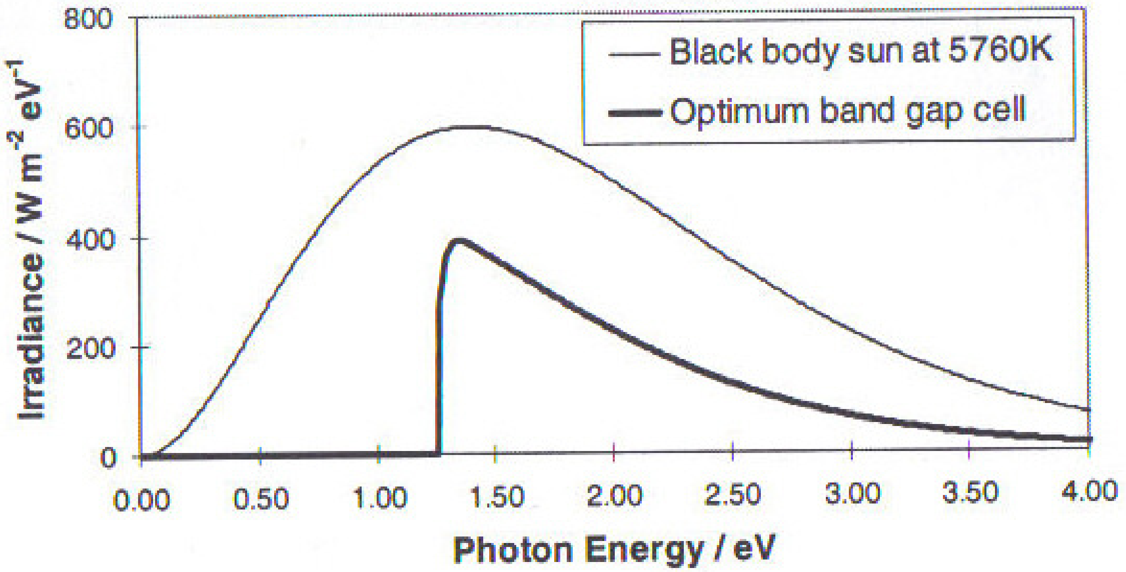
E_g=0.7-1.8V T_s=5760K T_a=300K P_S=1275W/m2

Limiting efficiency for a single band gap cell in AM 1.5



Optimum of a single band gap cell is 33% at 1.4eV

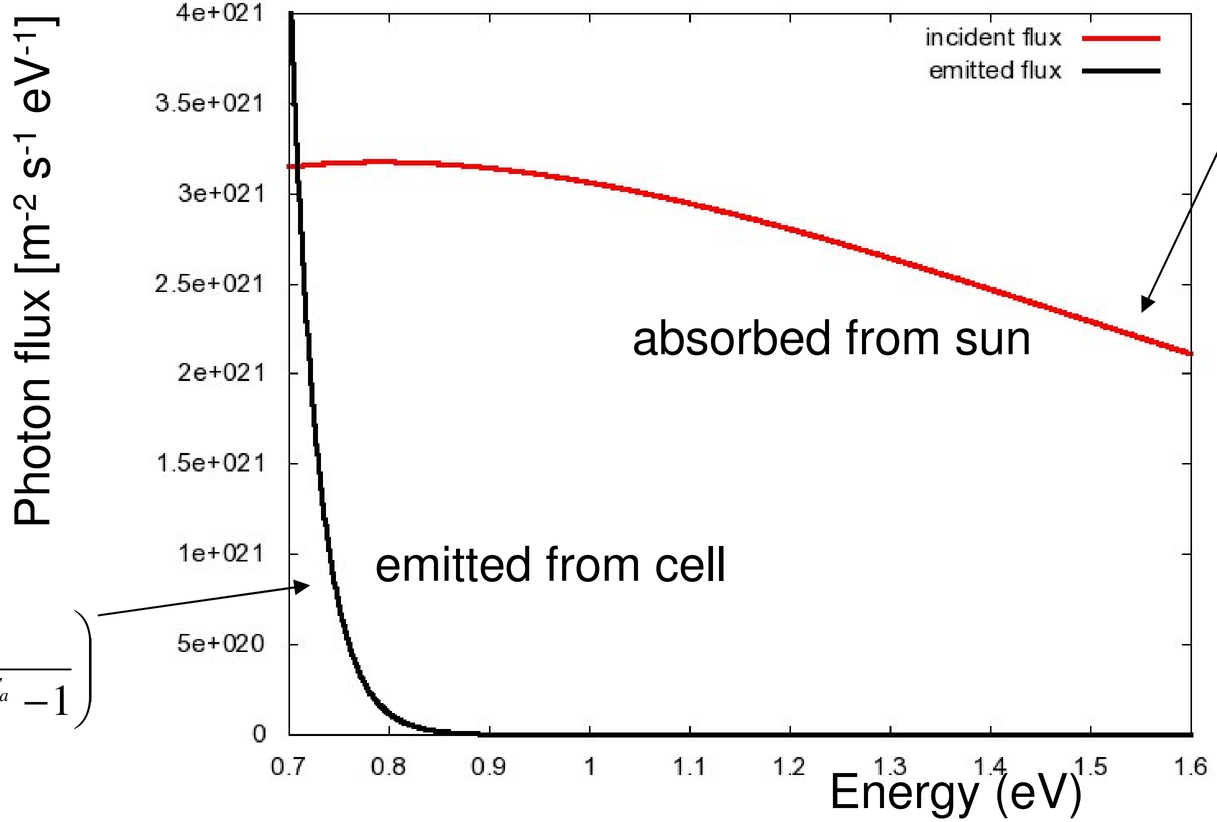
Power spectrum of a black body at 5760K and power available to a optimum band gap cell



Photons with E<Eg are not used
Photons with E>>E_g have the same effect as E=E_g

Comparison of Photon Fluxes ($V<V_{oc}$)

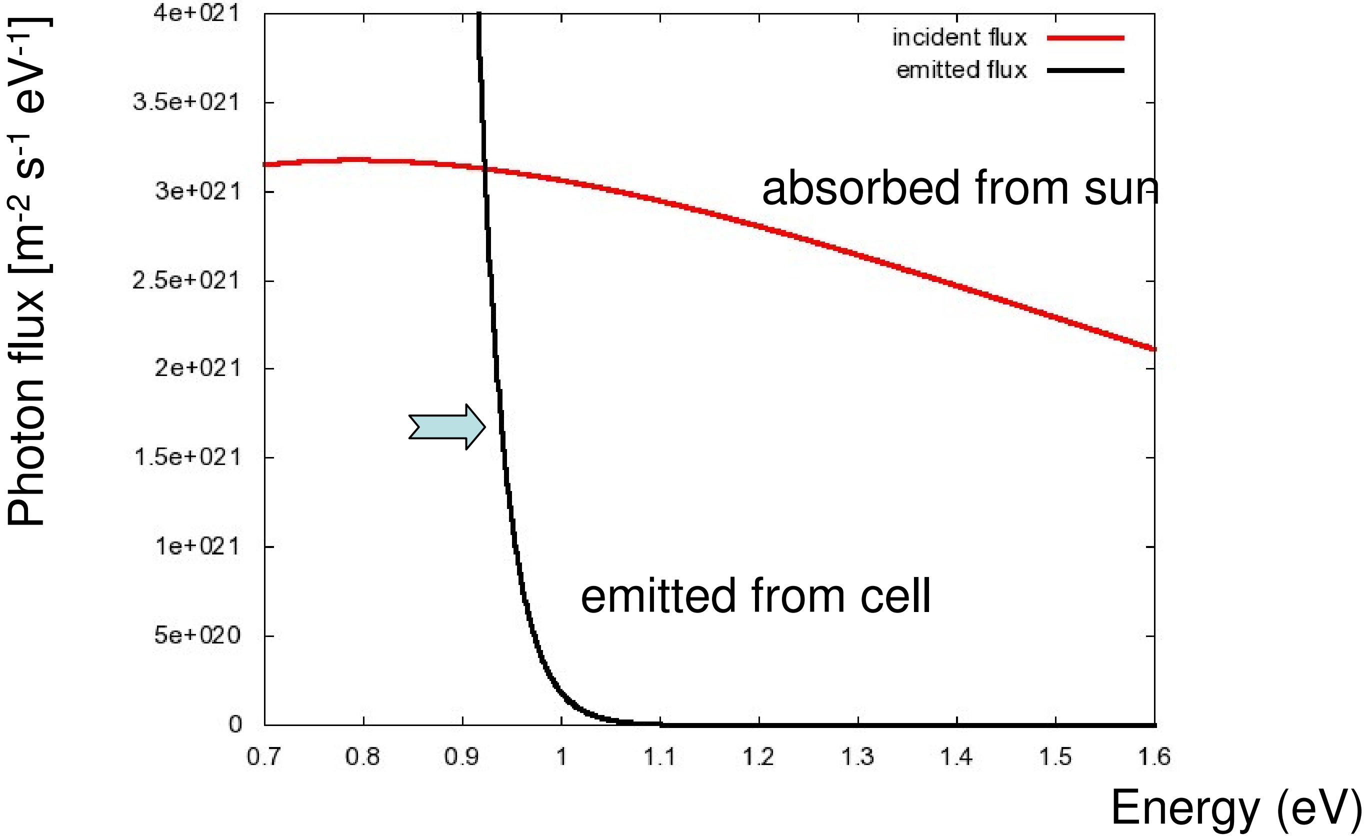
$$b_s(E)=\frac{2F_s}{h^3c^2}\left(\frac{E^2}{E^{E/k_BT_s}-1}\right)$$



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

$V=0.4V$ $E_g=0.7V$ $T_s=5760K$ $T_a=300K$ $P_S=1275W/m^2$

Comparison of Photon Fluxes (V>Voc)



$V=0.6V$ $E_g=0.7V$ $T_s=5760K$ $T_a=300K$ $P_S=1275W/m^2$

Requirements for ideal photoconverter

- Energy gap E_g
- All incident radiation with $E>E_g$ is absorbed
- Each photon creates one electron-hole pair
- Excited pairs do not recombine, except radiatively, as required by the the balance
- Charges are completely separated
- Charges are transported without losses

Energy gap E_g

The optimum band gap for AM1.5 of 1.4eV with 33%

III-V-semiconductors: GaAs 1.42eV (2009: 26% achieved)
InP 1.35eV
but expensive

Silicon 1.1eV would give a maximum efficiency of 30% (2009: 24.7%)
Cheap and high quality crystals available, but energy intensive production

CdTe and $CuInGaSe_2$ are developed and have low energy production costs (2009: 19.9%)

Other parameters

Light absorption: Almost perfect absorption with E>Eg is achieved
for layer thicknesses of 10-100 microns

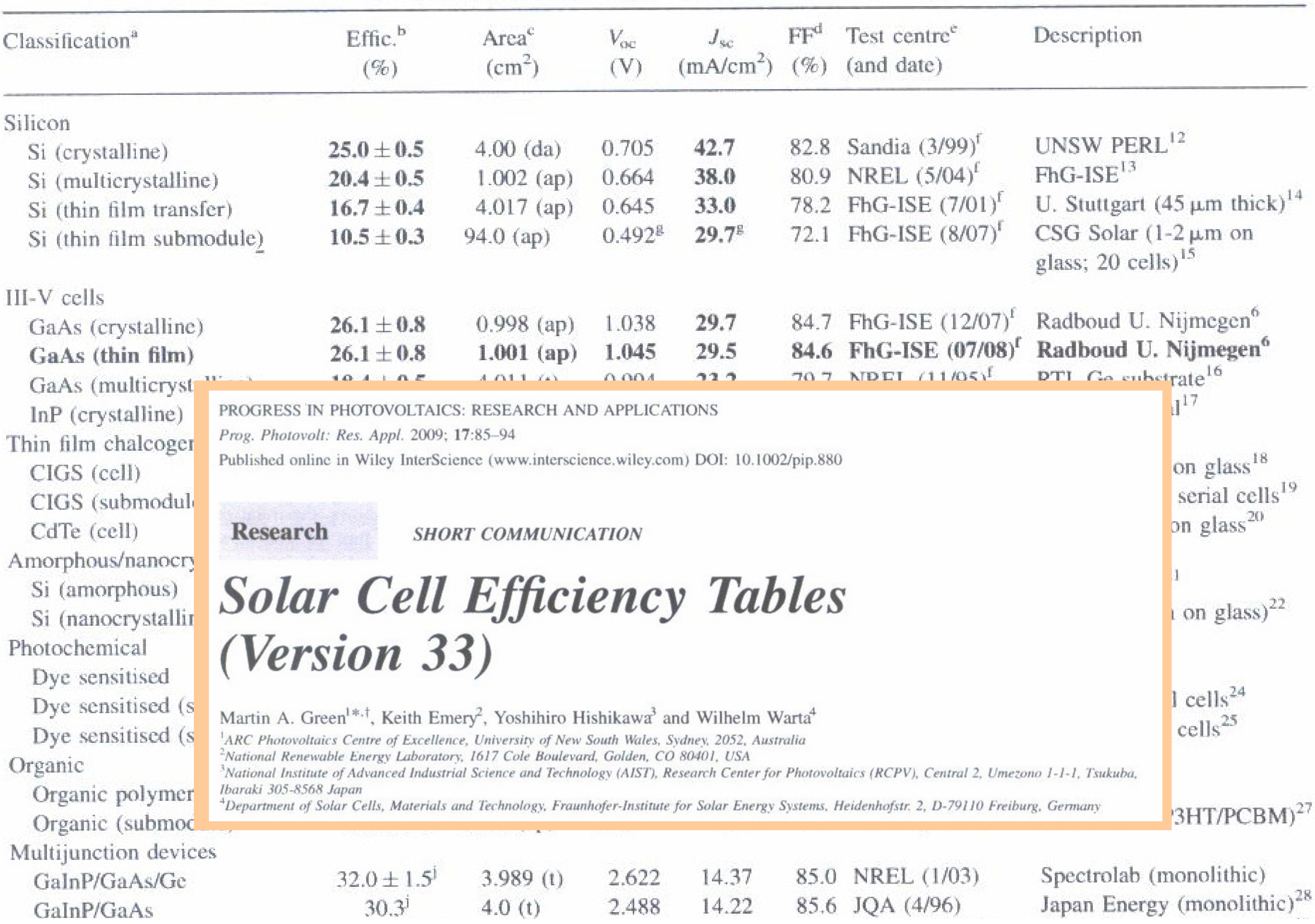
Charge separation: Asymmetry is realized with pn-junctions
(either highly doped layers of same materials or different materials)
Junction quality is of central importance. (especially large areas)

Lossless transport:
Good Ohmic contacts, low resistance material for conduction (serial resistance),
No leakage current (parallel resistance)

Optimum load resistance:
Should be optimized to match best operating point
For most applications rather arrays than individual cells are to be optimized

Reasons for losses

- Reflection at front surface
- Non-radiative recombination of carriers
  (defect sites trap charges, which subsequently recombine)
- Voltage drop due to series resistance $\Delta\mu \neq qV$



Classification[a]	Effic.[b] (%)	Area[c] (cm^2)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF[d] (%)	Test centre[e] (and date)	Description
Silicon							
Si (crystalline)	**25.0 ± 0.5**	4.00 (da)	0.705	**42.7**	82.8	Sandia (3/99)[f]	UNSW PERL[12]
Si (multicrystalline)	**20.4 ± 0.5**	1.002 (ap)	0.664	**38.0**	80.9	NREL (5/04)[f]	FhG-ISE[13]
Si (thin film transfer)	**16.7 ± 0.4**	4.017 (ap)	0.645	**33.0**	78.2	FhG-ISE (7/01)[f]	U. Stuttgart (45 μm thick)[14]
Si (thin film submodule)	**10.5 ± 0.3**	94.0 (ap)	0.492[g]	**29.7**[g]	72.1	FhG-ISE (8/07)[f]	CSG Solar (1-2 μm on glass; 20 cells)[15]
III-V cells							
GaAs (crystalline)	**26.1 ± 0.8**	0.998 (ap)	1.038	**29.7**	84.7	FhG-ISE (12/07)[f]	Radboud U. Nijmegen[6]
GaAs (thin film)	**26.1 ± 0.8**	**1.001 (ap)**	**1.045**	**29.5**	**84.6**	**FhG-ISE (07/08)**[f]	**Radboud U. Nijmegen**[6]
GaAs (multicryst	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	RTI, Ge substrate[16]
InP (crystalline)							l[17]
Thin film chalcoger							
CIGS (cell)							on glass[18]
CIGS (submodul							serial cells[19]
CdTe (cell)							on glass[20]
Amorphous/nanocry							
Si (amorphous)							
Si (nanocrystallir							on glass)[22]
Photochemical							
Dye sensitised							
Dye sensitised (s							l cells[24]
Dye sensitised (s							cells[25]
Organic							
Organic polymer							
Organic (submoc							3HT/PCBM)[27]
Multijunction devices							
GaInP/GaAs/Ge	32.0 ± 1.5[j]	3.989 (t)	2.622	14.37	85.0	NREL (1/03)	Spectrolab (monolithic)
GaInP/GaAs	30.3[j]	4.0 (t)	2.488	14.22	85.6	JQA (4/96)	Japan Energy (monolithic)[28]

PROGRESS IN PHOTOVOLTAICS: RESEARCH AND APPLICATIONS
Prog. Photovolt: Res. Appl. 2009; **17**:85–94

Research *SHORT COMMUNICATION*

Solar Cell Efficiency Tables (Version 33)

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Ways to improve

- Concentrators
- Tandem cells
- Organic cells with a variety of band gaps

Types of solar cells with regard to technology

Concentrator systems

Ge / $In_xGa_{1-x}As$ / $In_xGa_{1-x}P$
world record: **41.6%**
module efficiency: 28%
system efficiency: 23%

direct sun light is demanded

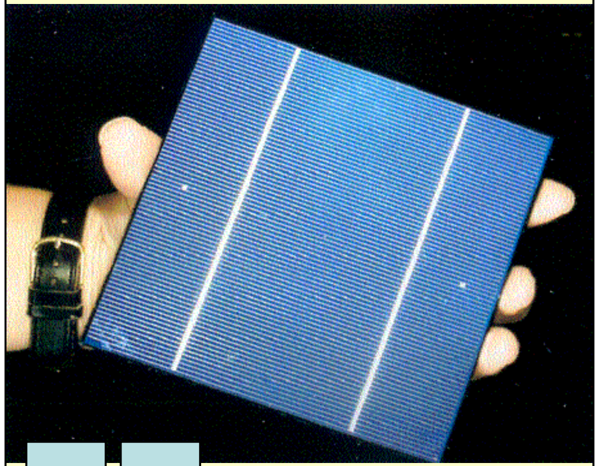
need for optical tracking

Si-wafer-based

c-Si, mk-Si
world record : 24.7%
module efficiency : 18%

energy intensive production of Si (very high purity needed)

dominant on market



Thin film

a-Si:H, nc-Si, CdTe, $Cu(In,Ga)(S,Se)_2$
nanostructured solar cells
organic solar cells
world record :
19.9% $Cu(In,Ga)Se_2$

integrated series connection

largest cost reduction potentials

Material mit Bandgaps

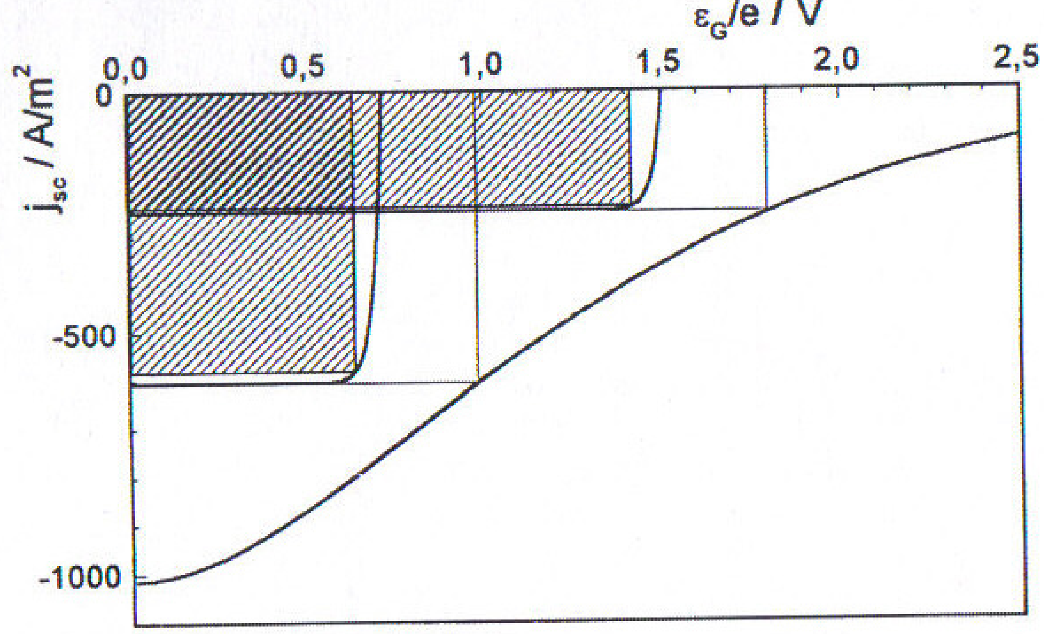


Abb. 8.2 Kennlinien von zwei Solarzellen mit Bandabstand ε_{G1} = 1.8 eV und ε_{G2} = 0.98 eV

Theoretische Effizienz von Tandemzellen

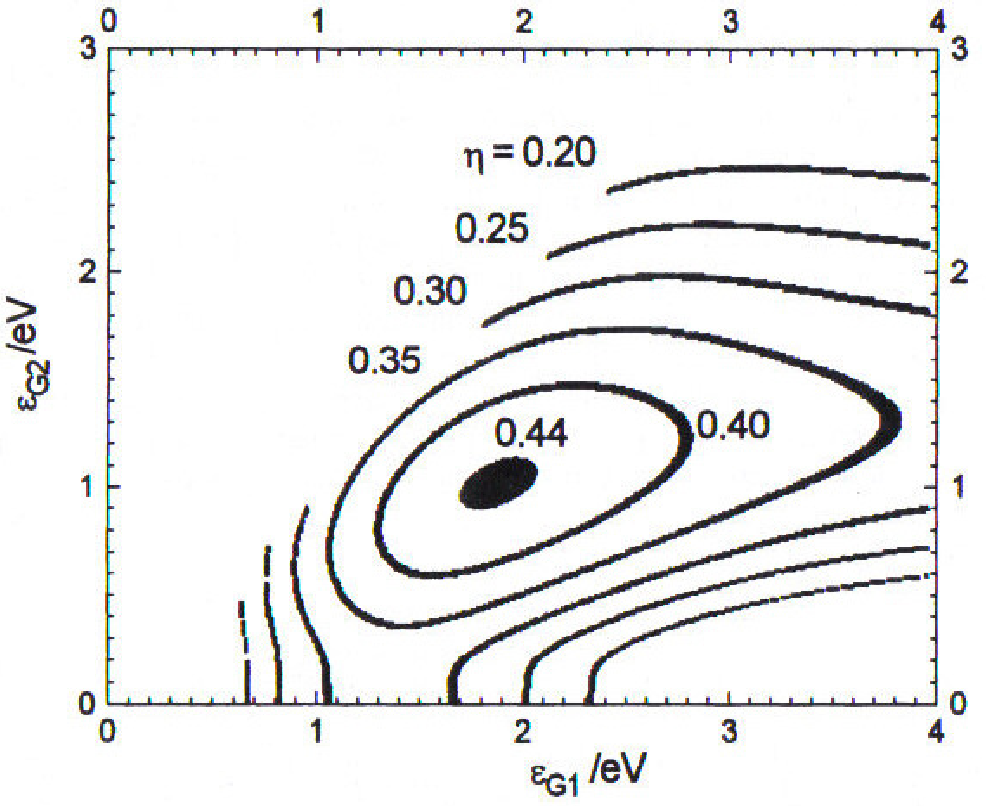
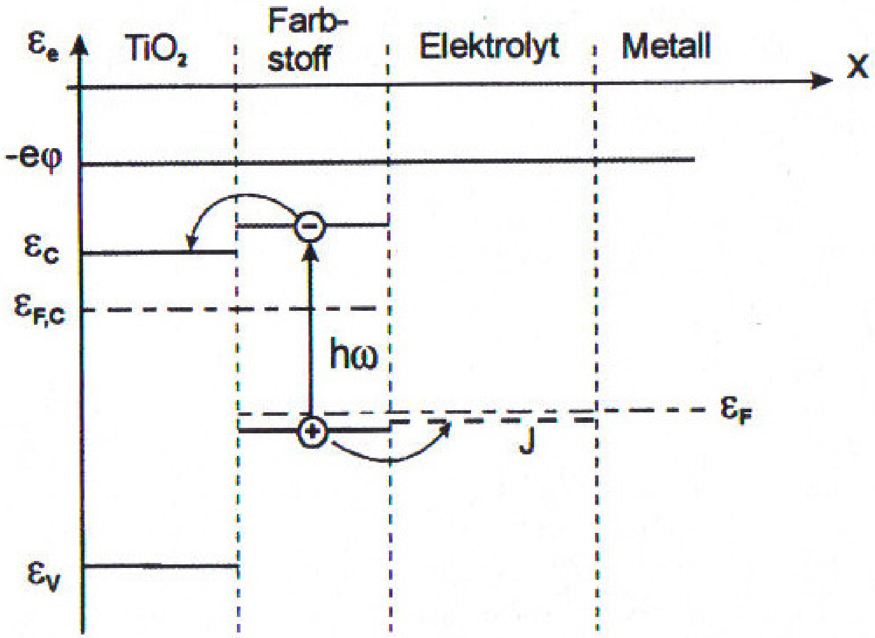


Abb. 8.3 Wirkungsgrad für zwei Tandemsolarzellen mit den Bandabständen ε_{G1} und ε_{G2} bei Addition ihrer Energieströme für das *AM*0-Spektrum

DSSC



Farbstoffsolarzelle, in der die Elektron-Loch Paare in dem Farbstoff Rutheniumbipyridil erzeugt werden. Die Elektronen fließen nach links über den n-Leiter TiO_2 ab, die Löcher nach rechts über Jod-Ionen, mit denen der Elektrolyt Acetonitril dotiert ist.

Farbstoff kann an Sonnenspektrum angepasst werden ⇒ verbesserter Wirkungsgrad
Probleme: Transport der Elektronen und Löcher zu den Elektroden ⇒ dünne Schicht
Absorption durch monomolekulare Schicht ist gering ⇒ Dickere Schichten