Energy Conversion by Semiconductor Devices

Jun-Ho YUM
junho.yum@epfl.ch

The History of Solar

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Solar technology isn't new. Its history spans from the 7th Century B.C. to today. We started out concentrating the sun's heat with glass and mirrors to light fires. Today, we have everything from solar-powered buildings to solar-powered vehicles.

Here you can learn more about the milestones in the historical development of solar technology, century by century, and year by year. You can also glimpse the future.

This timeline lists the milestones in the historical development of solar technology from the 7th Century B.C. to the 1200s A.D.

Byron Stafford, NREL / PIX10730

Byron Stafford, NREL / PIX06370

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Courtesy of Susan Sczepanski, NREL

The Anasazi cliff dwellings demonstrate passive solar design. (John Thornton, NREL / PIX03640)

7th Century B.C.
Magnifying glass used to concentrate sun's rays to make fire and to burn ants.

3rd Century B.C.
Greeks and Romans use burning mirrors to light torches for religious purposes.

2nd Century B.C.
As early as 212 BC, the Greek scientist, Archimedes, used the reflective properties of bronze shields to focus sunlight and to set fire to wooden ships from the Roman Empire which were besieging Syracuse. (Although no proof of such a feat exists, the Greek navy recreated the experiment in 1973 and successfully set fire to a wooden boat at a distance of 50 meters.)

20 A.D.
Chinese document use of burning mirrors to light torches for religious purposes.

1st to 4th Century A.D.
The famous Roman bathhouses in the first to fourth centuries A.D. had large south facing windows to let in the sun's warmth. For an example, see information on the http://www.hum.huji.ac.il/archaeology/zippori/RomanSeph.htm Zippori in the Roman Period from the Hebrew University of Jerusalem.

6th Century A.D.
Sunrooms on houses and public buildings were so common that the Justinian Code initiated "sun rights" to ensure individual access to the sun.

1200s A.D.
Ancestors of Pueblo people called Anasazi in North America live in south-facing cliff dwellings that capture the winter sun.

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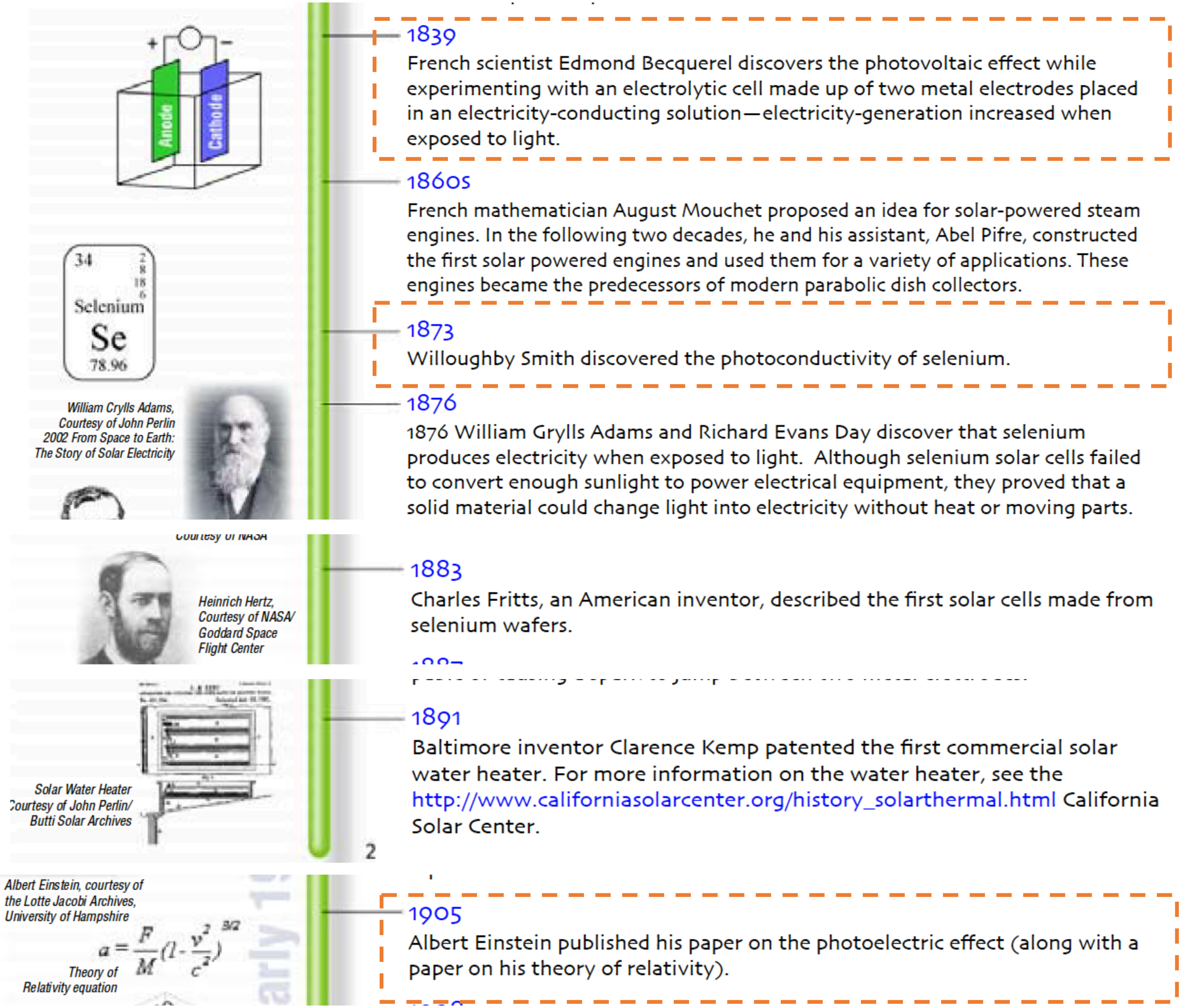

William Crylls Adams, Courtesy of John Perlin 2002 From Space to Earth: The Story of Solar Electricity

Courtesy of NASA

Heinrich Hertz, Courtesy of NASA/ Goddard Space Flight Center

Solar Water Heater Courtesy of John Perlin/ Butti Solar Archives

Albert Einstein, courtesy of the Lotte Jacobi Archives, University of Hampshire

$$a = \frac{F}{M}\left(1-\frac{v^2}{c^2}\right)^{3/2}$$

Theory of Relativity equation

1839
French scientist Edmond Becquerel discovers the photovoltaic effect while experimenting with an electrolytic cell made up of two metal electrodes placed in an electricity-conducting solution—electricity-generation increased when exposed to light.

1860s
French mathematician August Mouchet proposed an idea for solar-powered steam engines. In the following two decades, he and his assistant, Abel Pifre, constructed the first solar powered engines and used them for a variety of applications. These engines became the predecessors of modern parabolic dish collectors.

1873
Willoughby Smith discovered the photoconductivity of selenium.

1876
1876 William Grylls Adams and Richard Evans Day discover that selenium produces electricity when exposed to light. Although selenium solar cells failed to convert enough sunlight to power electrical equipment, they proved that a solid material could change light into electricity without heat or moving parts.

1883
Charles Fritts, an American inventor, described the first solar cells made from selenium wafers.

1891
Baltimore inventor Clarence Kemp patented the first commercial solar water heater. For more information on the water heater, see the http://www.californiasolarcenter.org/history_solarthermal.html California Solar Center.

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1905
Albert Einstein published his paper on the photoelectric effect (along with a paper on his theory of relativity).

- Jun-Ho YUM, junho.yum@epfl.ch

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U.S. Department of Energy
Energy Efficiency and Renewable Energy

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The Anasazi cliff dwellings demonstrate passive solar design. (John Thornton, NREL / PIX03644)

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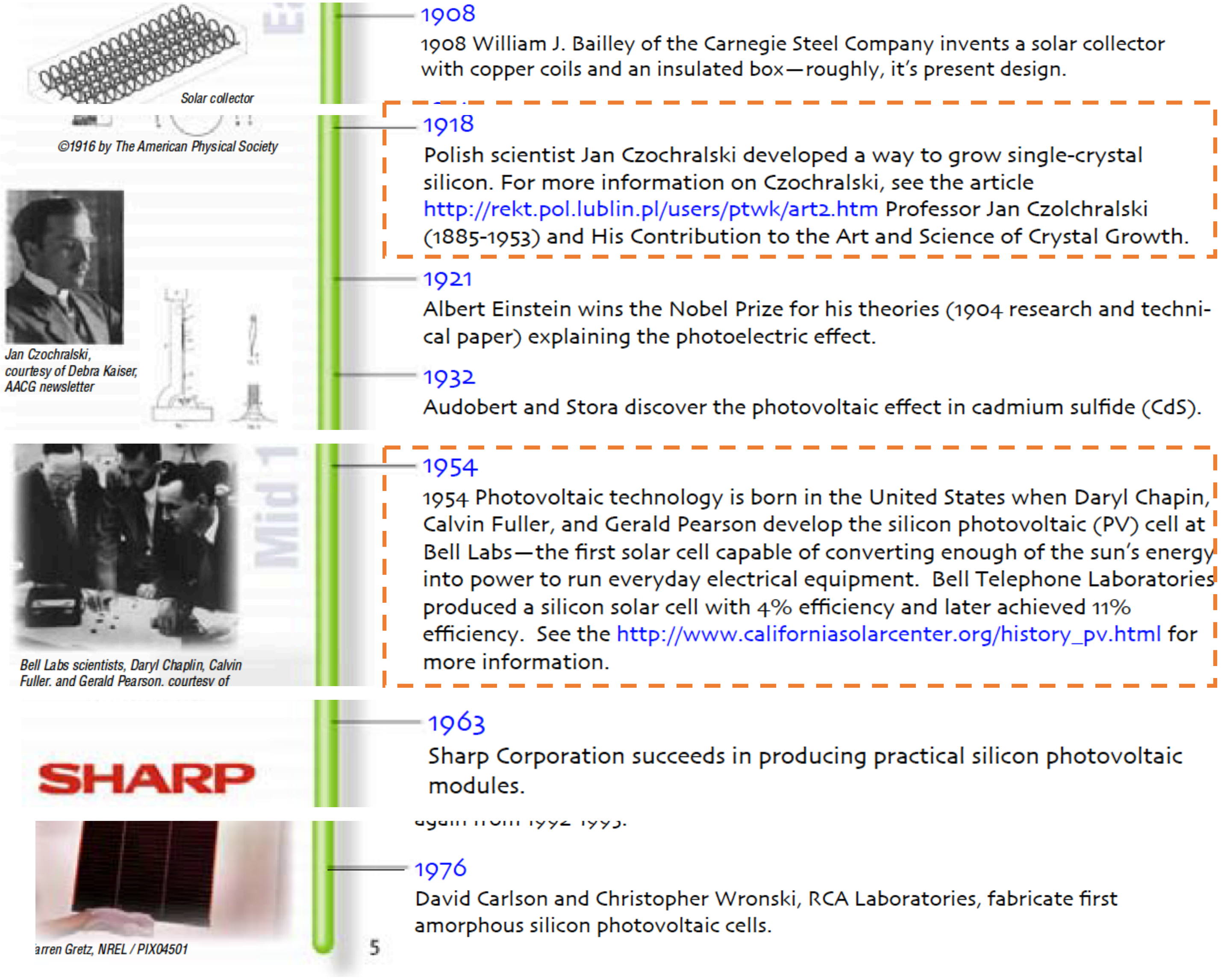
Solar collector

©1916 by The American Physical Society

Jan Czochralski, courtesy of Debra Kaiser, AACG newsletter

Bell Labs scientists, Daryl Chaplin, Calvin Fuller, and Gerald Pearson. courtesy of

arren Gretz, NREL / PIX04501

1908
1908 William J. Bailley of the Carnegie Steel Company invents a solar collector with copper coils and an insulated box—roughly, it's present design.

1918
Polish scientist Jan Czochralski developed a way to grow single-crystal silicon. For more information on Czochralski, see the article http://rekt.pol.lublin.pl/users/ptwk/art2.htm Professor Jan Czolchralski (1885-1953) and His Contribution to the Art and Science of Crystal Growth.

1921
Albert Einstein wins the Nobel Prize for his theories (1904 research and technical paper) explaining the photoelectric effect.

1932
Audobert and Stora discover the photovoltaic effect in cadmium sulfide (CdS).

1954
1954 Photovoltaic technology is born in the United States when Daryl Chapin, Calvin Fuller, and Gerald Pearson develop the silicon photovoltaic (PV) cell at Bell Labs—the first solar cell capable of converting enough of the sun's energy into power to run everyday electrical equipment. Bell Telephone Laboratories produced a silicon solar cell with 4% efficiency and later achieved 11% efficiency. See the http://www.californiasolarcenter.org/history_pv.html for more information.

1963
Sharp Corporation succeeds in producing practical silicon photovoltaic modules.

again from 1992-1995.

1976
David Carlson and Christopher Wronski, RCA Laboratories, fabricate first amorphous silicon photovoltaic cells.

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Photovoltaic effect

The **photovoltaic effect** is a process that generates voltage or electric current in a photovoltaic cell when it is exposed to sunlight. It is this effect that makes solar panels useful, as it is how the cells within the panel convert sunlight to electrical energy. The photovoltaic effect was first discovered in 1839 by Edmond Becquerel.

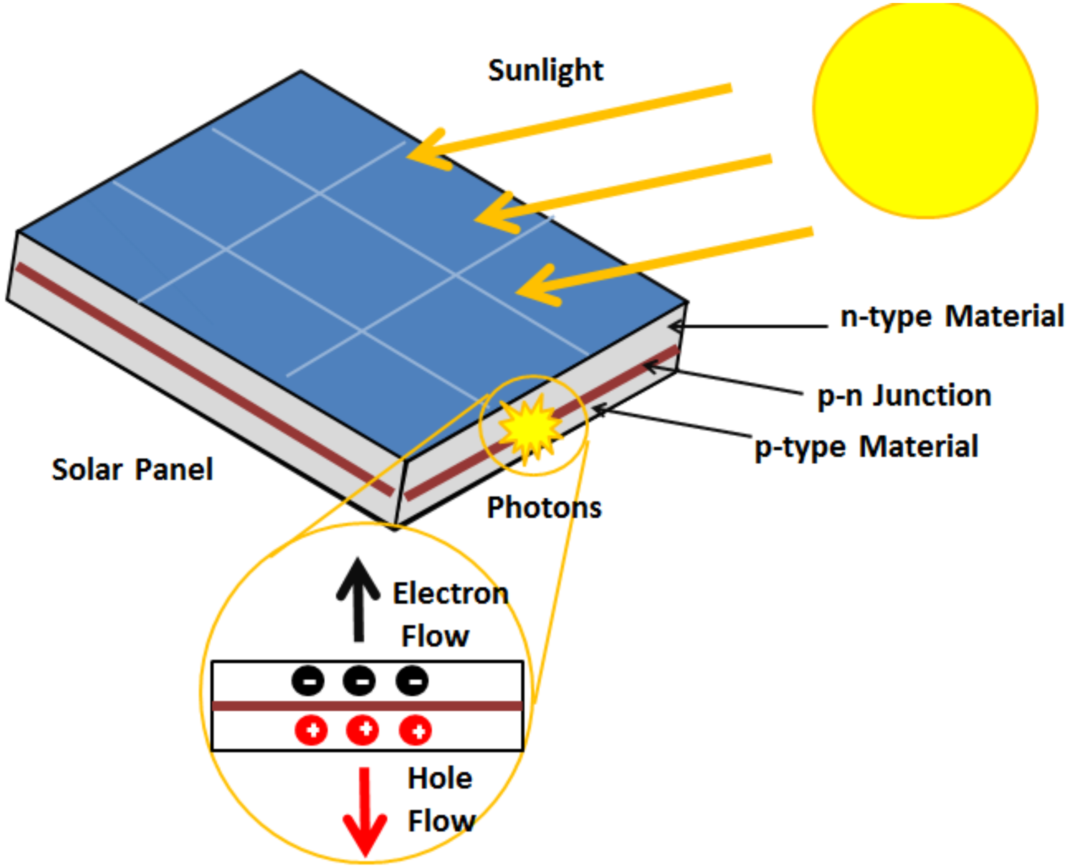

Image taken from https://energyeducation.ca/encyclopedia/Photovoltaic_effect

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Photoelectric effect vs Photovoltaic effect

Photoelectric effect is the **emission of electrons** from the surface of a substance in response to incident light	Photovoltaic effect is the process (e.g. in pn junction) produce **an electrical voltage** under illumination
Electrons are emitted	**Electrons are not emitted**
An electric current is **not** generated	**An electric current is generated**
Occurs when the energy provided by photons is enough to overcome the electron binding energy (W_F)	Occurs when the energy provided by photons is enough to overcome the potential barrier of excitation (band gap)

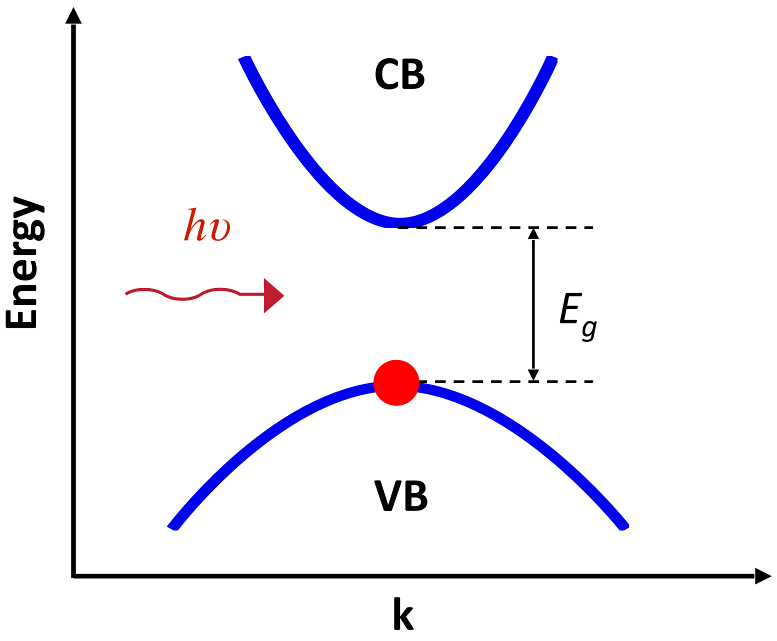
- Jun-Ho YUM, junho.yum@epfl.ch

Light Absorption by Semiconductors

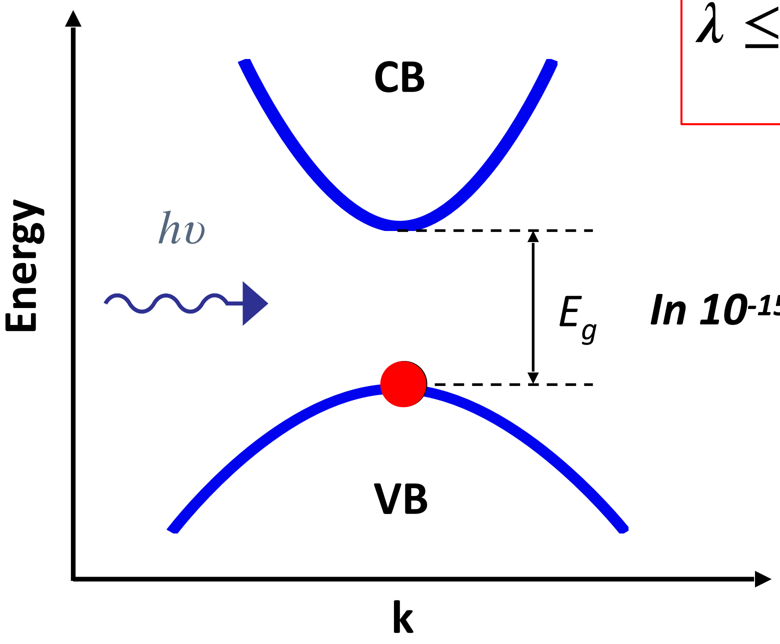
$$\nu = \frac{c}{\lambda} \geq \frac{E_g}{h}$$

$$\lambda \leq \frac{hc}{E_g}$$

$h\nu < E_g$

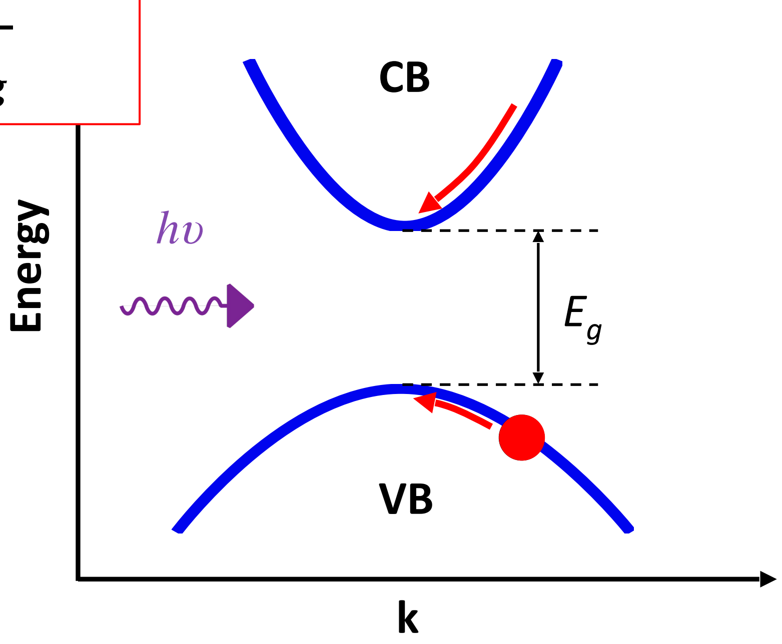


$h\nu = E_g$



In 10^{-15} s

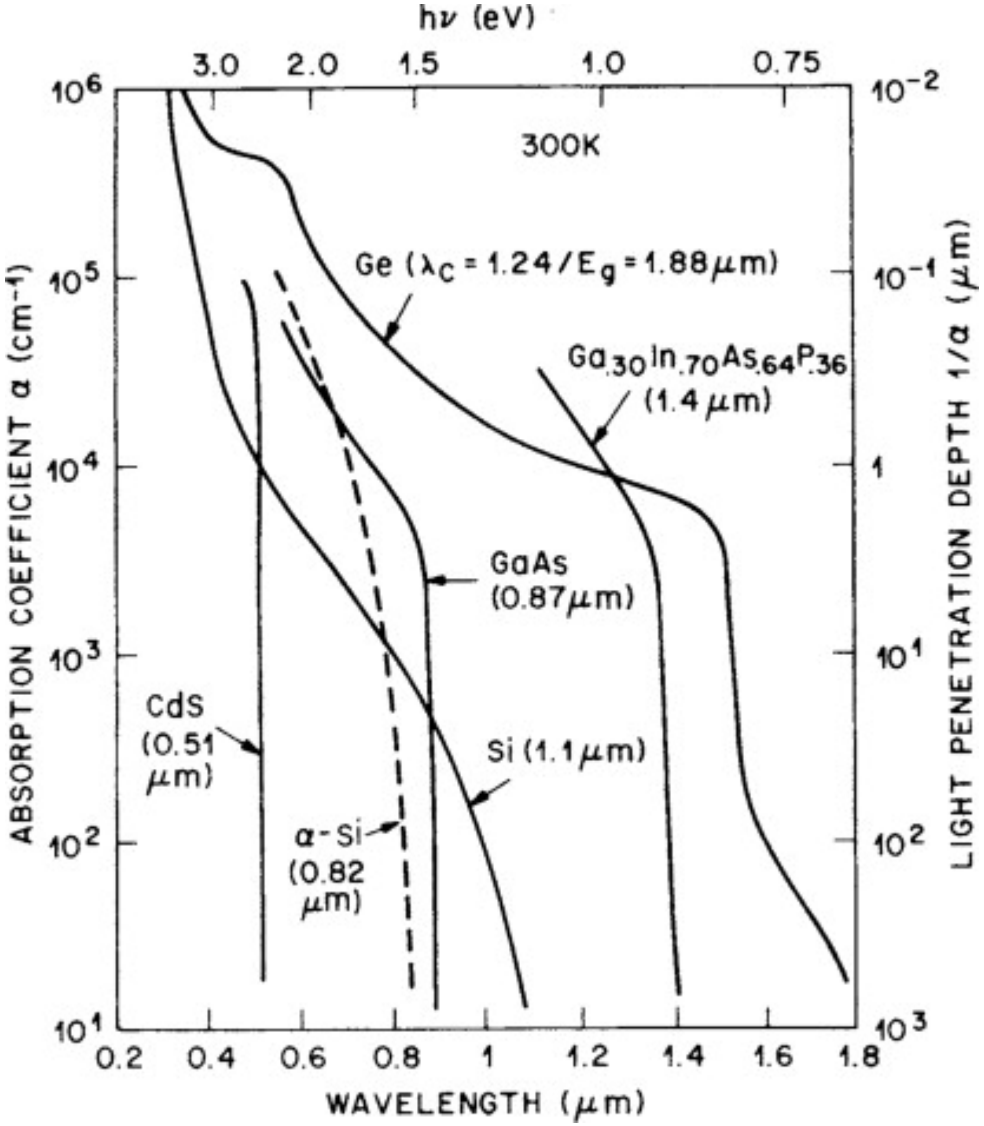
$h\nu > E_g$



- Photons are absorbed by the SC and create electron-hole pairs when the photon energy is equal and greater than the band gap of the SC.
- If the photon energy is much greater than the band gap, the excess energy ($h\nu - E_g$) is lost due to the ultrafast relaxation of carriers, e.g. 10^{-14} to 10^{-11} sec (thermalization or vibrational relaxation).

Light Absorption by Semiconductors

- **Absorption** of photons with energy $\geq E_g$
- Loss: **Transmission, Reflection**
- When an object is exposed to radiation, some of the incident radiation is absorbed (***A***), some are scattered (***R***), and some are transmitted, Transmittance (***T***). (***A*** **+** ***T*** **+** ***R*** **= 1**)
- Absorption coefficient α: Absorption coefficient characterizes the efficiency of a material in absorbing optical power.
- Absorption depth is the inverse of absorption coefficient, describing how deeply light penetrates into a SC.
- Direct gap transitions are much more efficient than indirect transitions and results in much higher α.



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Beer-Lambert Law

- **Lambert's law**: the decrease in light intensity due to the thickness of the absorbing medium at any point is directly proportional to the light intensity.

$$-\frac{dI}{dl} \propto I$$

dI: the slight decrease in light intensity when passing a small distance dl

I: the intensity of monochromatic light just before entering the medium

$$-\frac{dI}{dl} = \alpha I$$

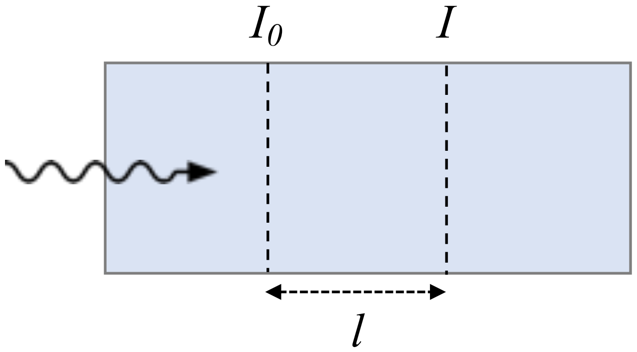
α: absorption coefficient (cm^{-1})

$$-lnI = \alpha l + C$$

At $l = 0, I = I_0$ → $C = -lnI_0$

$$-ln\left(\frac{I}{I_0}\right) = \alpha l \rightarrow I = I_0\exp(-\alpha l) \quad \text{or} \quad \log\left(\frac{I}{I_0}\right) = -\alpha' l$$

where α' : extinction coefficient = $\alpha/2.303$



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- **Beer-Lambert's law**: Extended by Beer, the decrease in light intensity due to not only the thickness of the absorbing medium but also the concentration of the solution.

$$-\frac{dI}{dl} \propto c \quad \rightarrow \quad \log\left(\frac{I}{I_0}\right) = -\varepsilon c l$$

ε = molar extinction coefficient (Lmol^{-1}cm^{-1})

c = concentration (M)

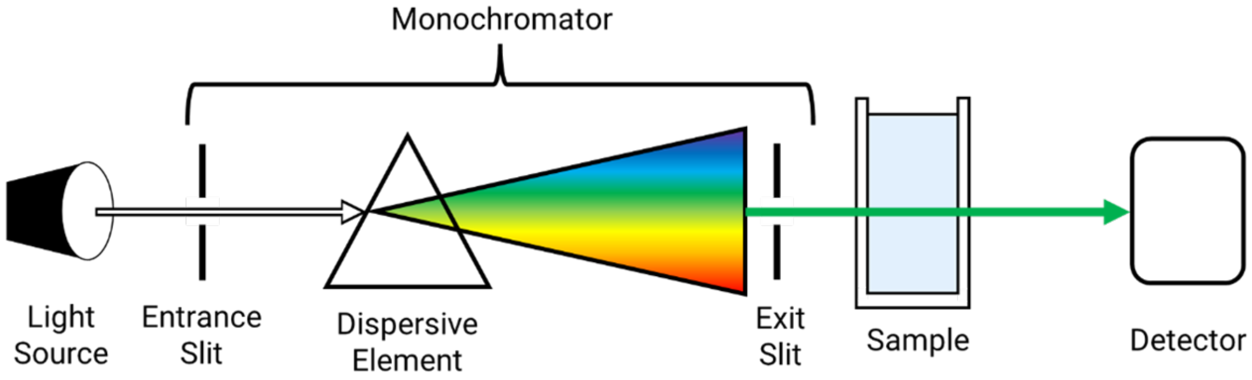
l is the path length (cm)

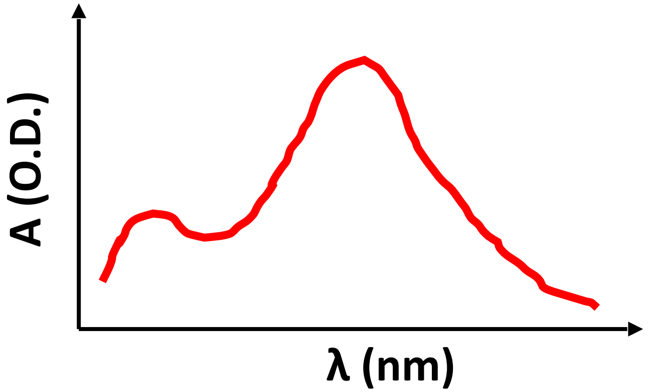
Molar extinction coefficient: It measures the probability of electronic transitions.

Jun-Ho YUM, junho.yum@epfl.ch

Absorbance and Transmittance

- Absorbance (***A***) known as optical density (OD): the quantity of light absorbed by a sample.
- Transmittance (***T***): the quantity of light that passes through a sample.
- Tool: UV-vis-NIR spectroscopy





$$T = \frac{I}{I_0} \quad or \quad T(\%) = 100 \times T$$

$$A = -\log(\frac{I}{I_0}) = -\log(T) = \log(\frac{1}{T})$$

Beer-Lambert's law

- Jun-Ho YUM, junho.yum@epfl.ch

Absorbance, Transmittance, and Absorptance

From absorbance definition

The relative loss of intensity (absorptance): $1 - T = 1 - \frac{I}{I_0} = 1 - 10^{-A}$

$$\mathrm{A} = -\log(\frac{I}{I_0})$$

Example 1) Find the relative amount of light that gets absorbed by the sample (**absorptance**) if the absorbance of the sample is **2** at a particular wavelength.

$$1 - 10^{-A} = 1 - \frac{1}{100} = 0.99 \quad (with\ A = 2)$$

99% of the light is absorbed and 1% of light is transmitted.

Absorbance (OD)	Transmittance (%)	(Absorptance)
0	100%	0%
1	10%	90%
2	1%	99%
3	0.1%	99.9%
5	0.001%	99.999%

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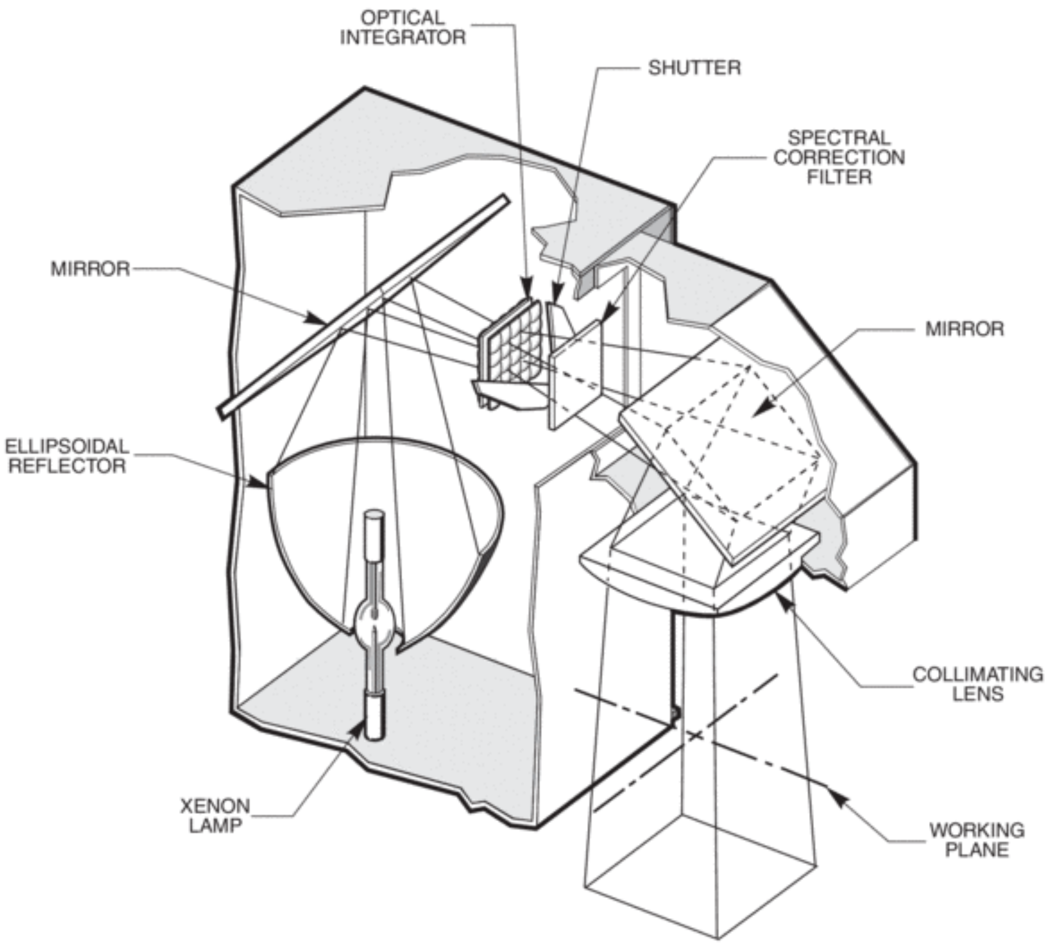
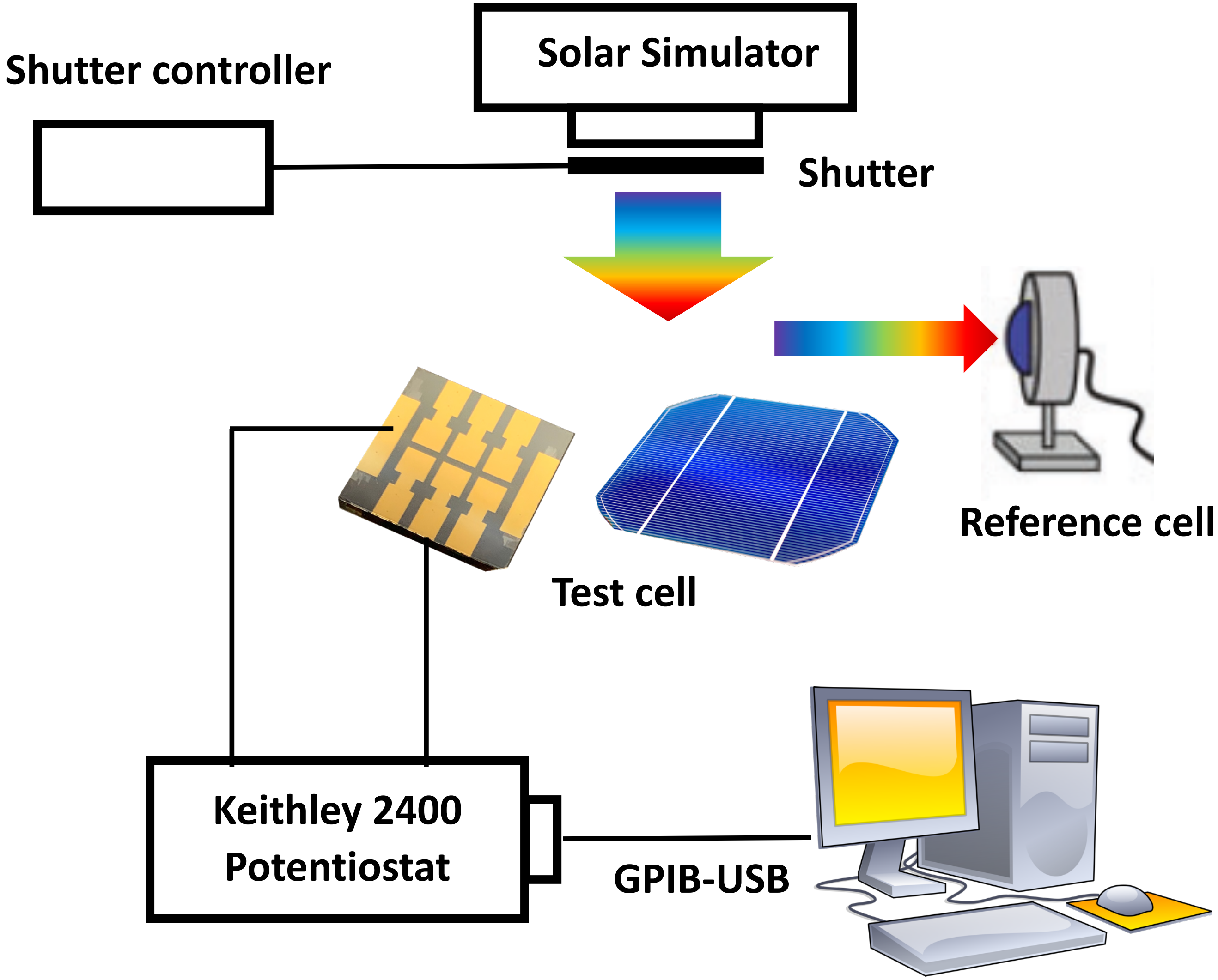
Solar Cell Test Setup: Solar Simulator





Solar Simulator

Shutter controller

Shutter

Reference cell

Test cell

Keithley 2400 Potentiostat

GPIB-USB

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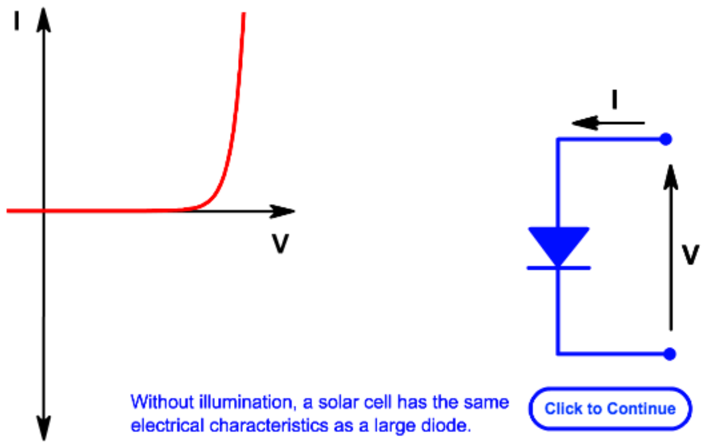
IV curve

The IV curve of a solar cell = the superposition of the IV curve of the solar cell diode in the dark with the light-generated current.

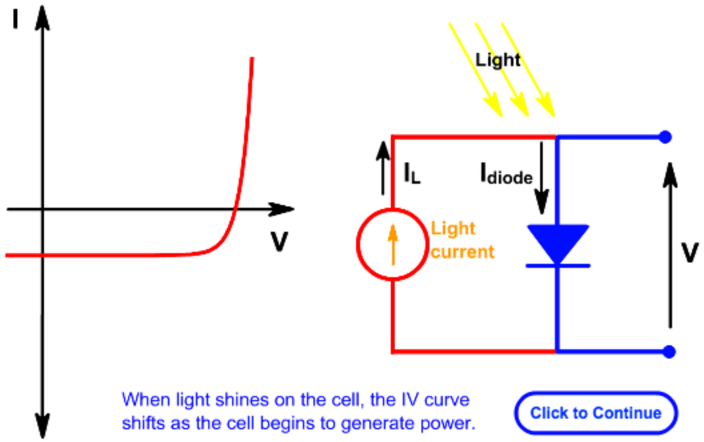
$$I = I_L - I_D(V) = I_L - I_0\left[\exp\left(\frac{eV}{nk_BT}\right) - 1\right]$$

I_L = Light generated current

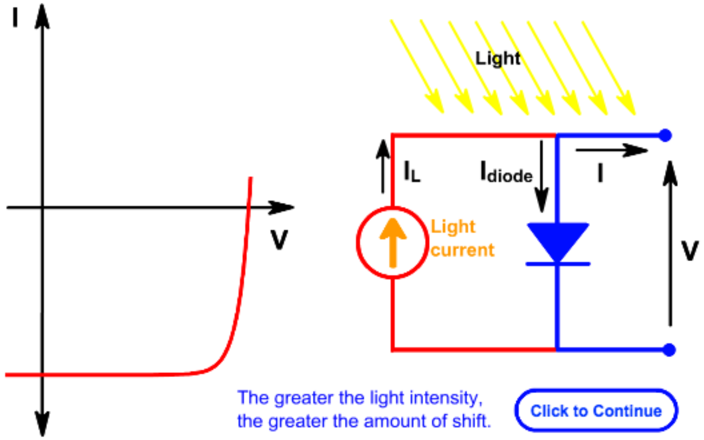
I_D = Dark current



Without illumination, a solar cell has the same electrical characteristics as a large diode.



When light shines on the cell, the IV curve shifts as the cell begins to generate power.



The greater the light intensity, the greater the amount of shift.

From PV education

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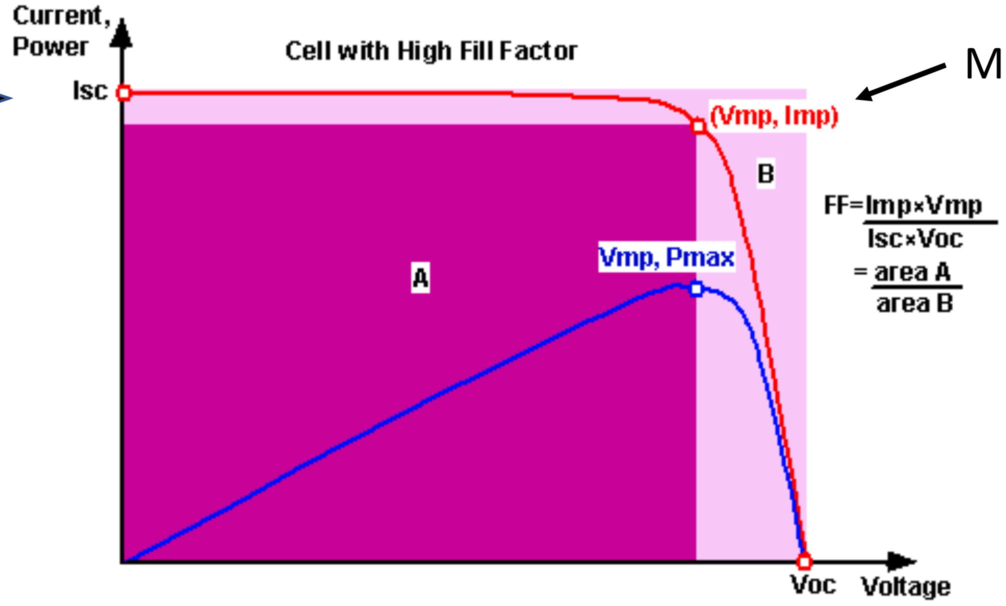
IV curve: I_{SC} V_{OC} and MPP

At $\boldsymbol{V = 0}$, the condition is defined as the **short-circuit condition**: **short−circuit current** ($\boldsymbol{I_{sc}}$)



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Maximum power point (MPP)

$\boldsymbol{I_{mp}, V_{mp}}$

At $\boldsymbol{I = 0}$, the condition is defined as the **open-circuit condition**:
open−circuit voltage ($\boldsymbol{V_{OC}}$)

$$V_{OC} = \frac{nk_BT}{e}\ln(\frac{I_L}{I_0} + 1)$$

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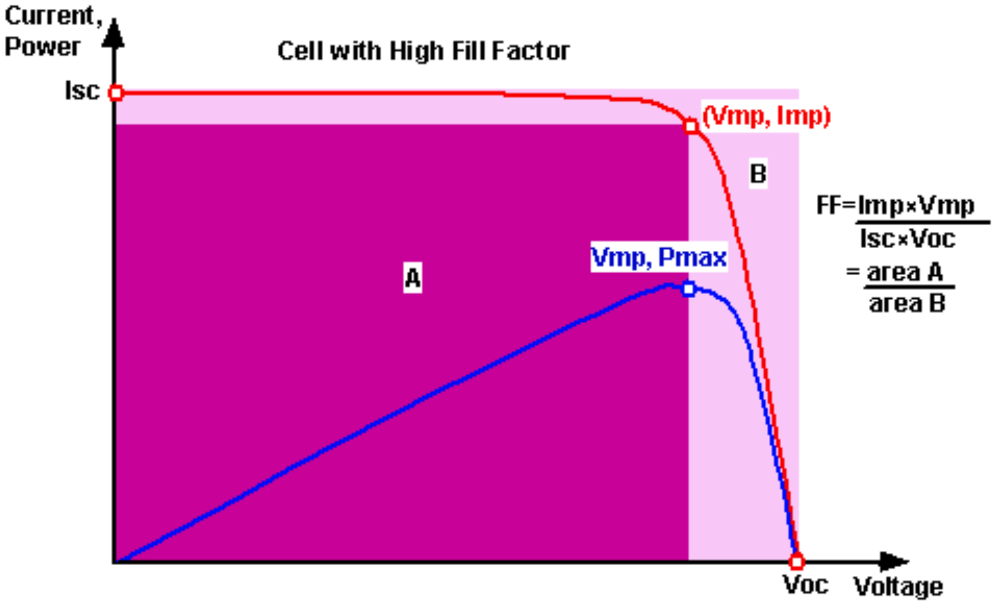
IV curve: Fill Factor and PCE

Fill Factor (FF) is a parameter which determines the maximum power from a solar cell.

$$FF = \frac{P_{mp}}{V_{OC} \times I_{SC}} = \frac{V_{mp} \times I_{mp}}{V_{OC} \times I_{SC}}$$



From PV education

- Terrestrial solar cells are measured under **AM1.5G** conditions (**1000 W/m²**) and at a temperature of **25°C**.
- Solar cells intended for space use are measured under AM0 conditions (1367 W/m²).
- A solar cell with a conversion efficiency of 100% is theoretically impossible.

$$Power\ conversion\ efficiency\ (\%) = \eta = \frac{Generated\ electrical\ power\ (W)}{Incident\ light\ power\ (W)} \times 100$$

$$\frac{P_{mp}}{P_{inc}} = \frac{V_{OC} \times I_{SC} \times FF}{P_{inc}(W)} = \frac{V_{OC} \times J_{SC} \times FF}{P_{inc}(W/m^2)} \qquad with\ J_{SC} = I_{SC}/A$$

- Jun-Ho YUM, junho.yum@epfl.ch

Loss Processes in Solar Cells

Intrinsic losses

Unavoidable

- Optical loss
- Transmission loss
- Thermalization loss
- Carnot loss
- Emission loss
- Boltzmann loss

Extrinsic losses

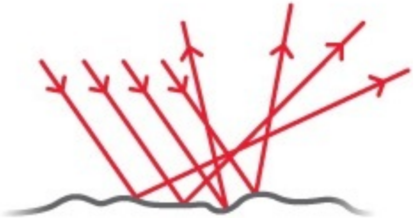
Avoidable

- Non-radiative loss
- Series resistance loss
- Shunt resistance loss
- Parasitic absorption loss

- The optical loss by reflection from the cells.
- The transmission loss by the non-absorption of photons with energy below the bandgap.
- A strong interaction between excited carriers and lattice phonons introduces a thermalization loss as carriers cool to the bandgap edge.

Specular reflection

Diffuse reflection



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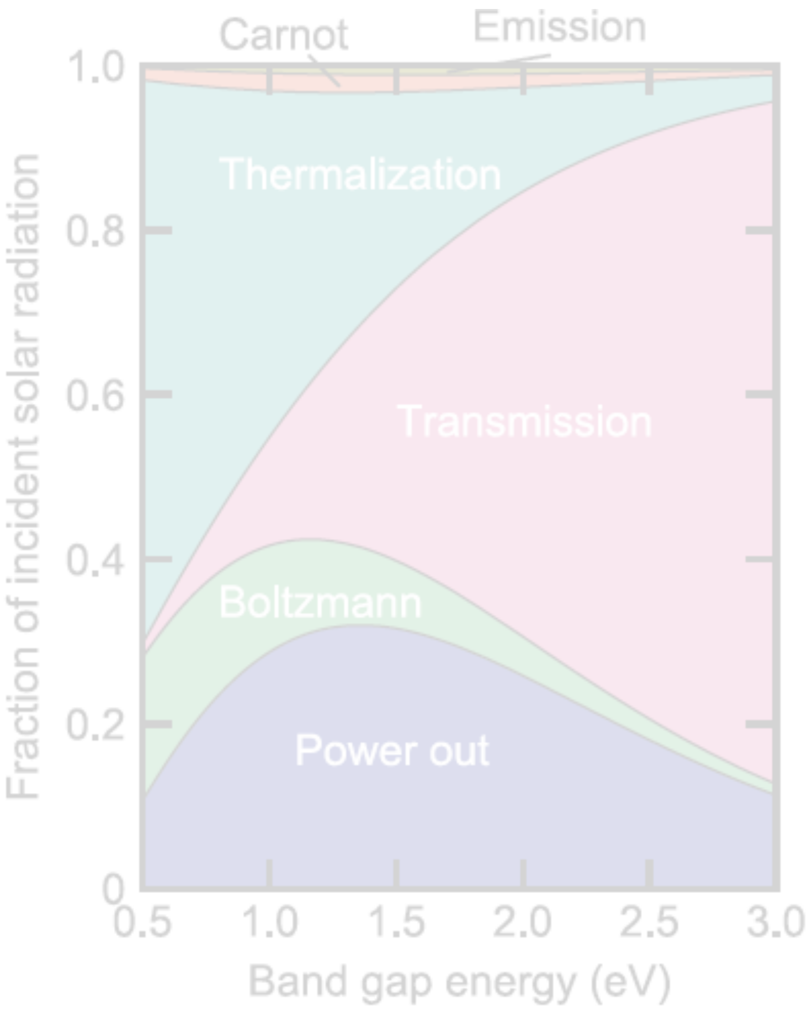
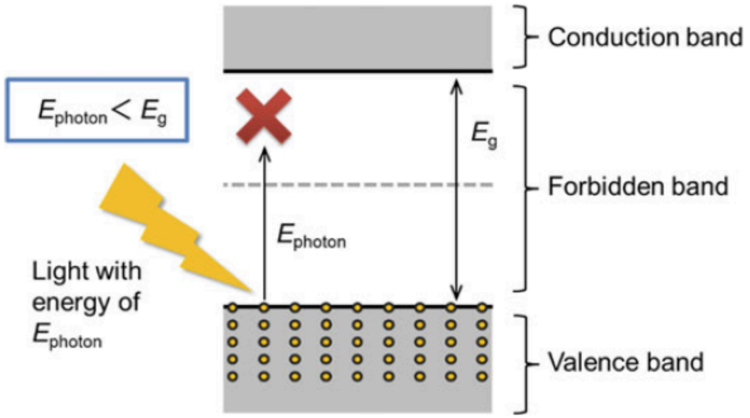
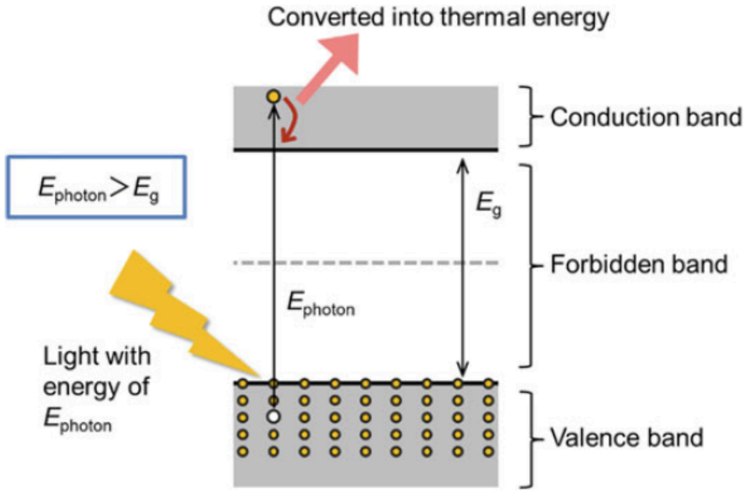
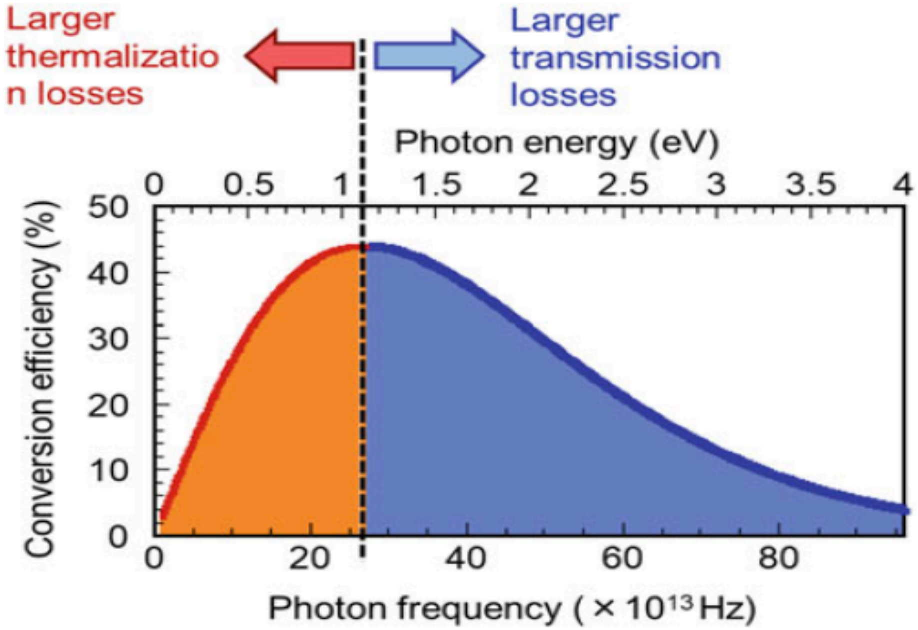


Transmission loss



Thermalization loss





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- Work loss in the heat engine with heat flowing from a hot reservoir (the Sun) to a cold reservoir (the atmosphere).
- The emission loss originates from the photon emission of the cells as a result of radiative recombination.
- Inequality of absorption and emission angles results in an entropy generation.

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- Shunt resistance loss
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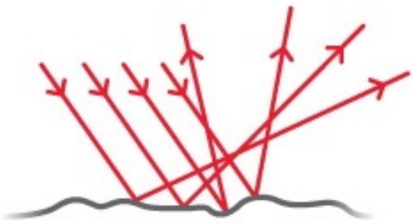

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Reversible Carnot Engine

$$\eta_c = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

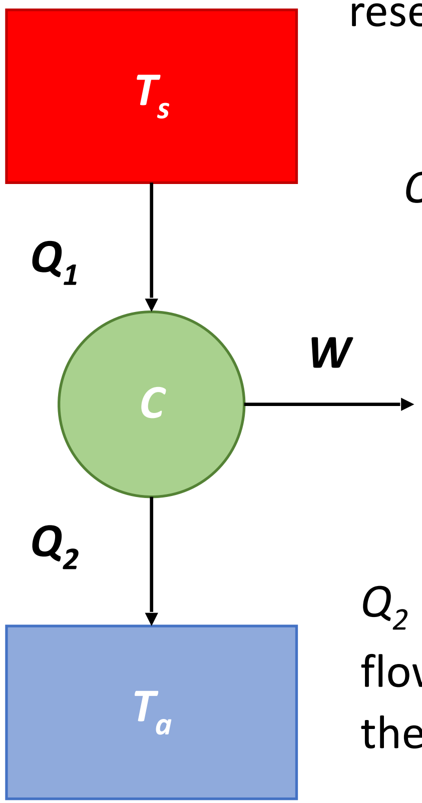
For a reversible engine, the total entropy is conserved, $S = S_1 - S_2 = 0$,

$$\frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0$$

$$\eta_c = 1 - \frac{T_2}{T_1} = 1 - \frac{T_a}{T_s}$$

T_s = 6,000 K and $T_a = 300$ K
η_c = 0.95, an upper limit of solar converters

Carnot loss



T_s is the high temperature reservoir, the sun

Q_1 is the incident solar energy

W is the work delivered to a load in the form of electrical energy, $W = Q_1 - Q_2$

Q_2 is the amount of energy flowing from the converter to the heat sink

T_a is the low temperature reservoir, the ambient atmosphere

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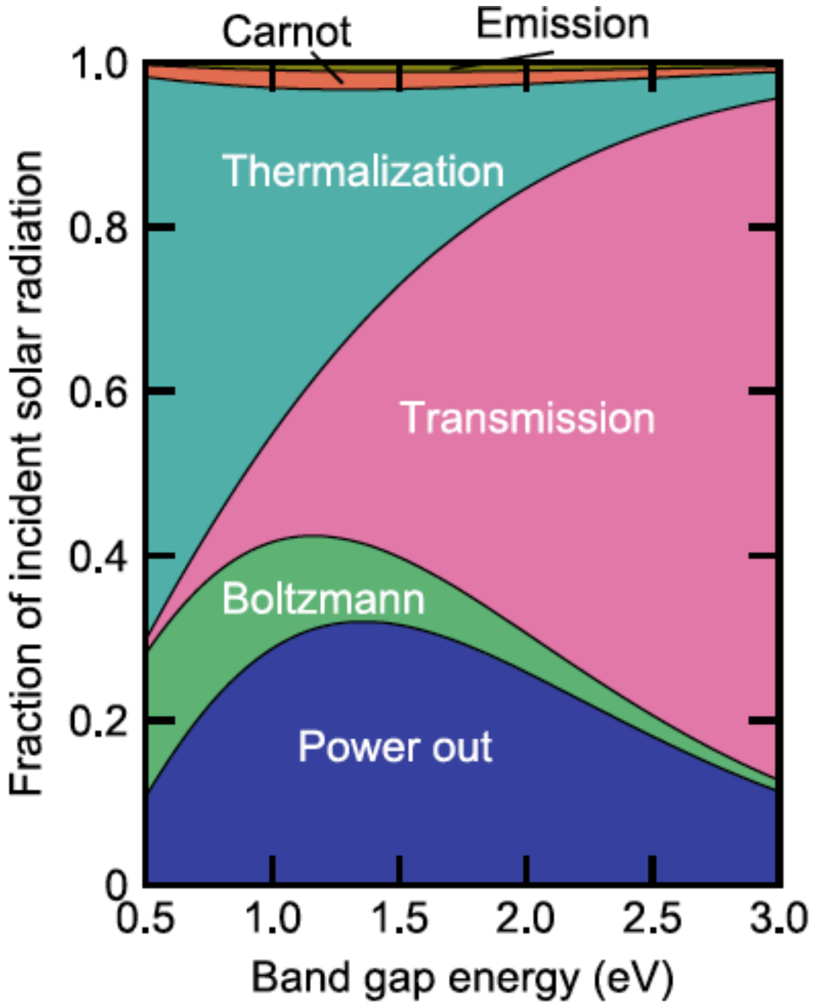
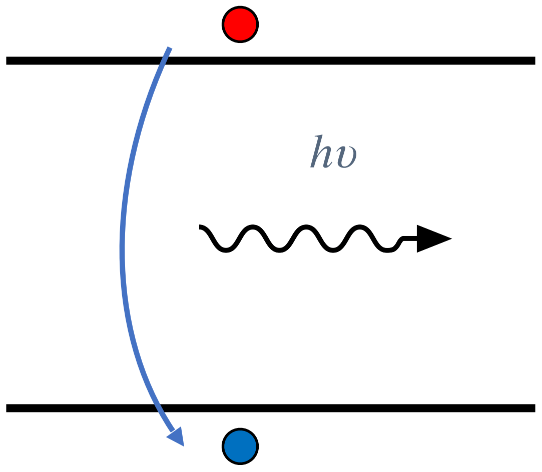
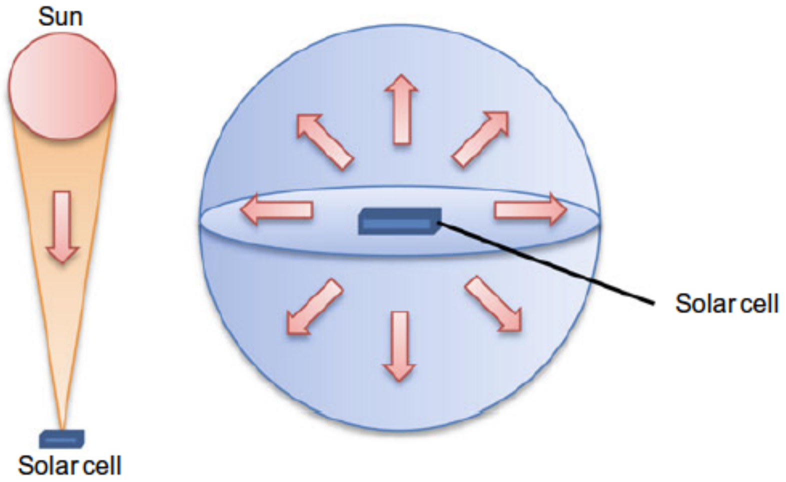
Loss Processes in Solar Cells



Emission loss



Boltzmann loss: Incident solar energy with the solid angle but the solar cell emits light into the emission solid angle of 2π.



$$\Delta S = kln(2\pi) - kln(\Omega_{se})$$

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- Boltzmann loss

Extrinsic losses

Avoidable

- Non-radiative loss
- Series resistance loss
- Shunt resistance loss
- Parasitic absorption loss

- Non-radiative recombination (NRR) losses originating from different mechanisms: Shockley-Read-Hall (SRH) recombination, Auger recombination, Recombination at Interface, etc.

  External radiative efficiency (*ERE*) is the ratio of radiatively recombined carriers against all recombined carriers.

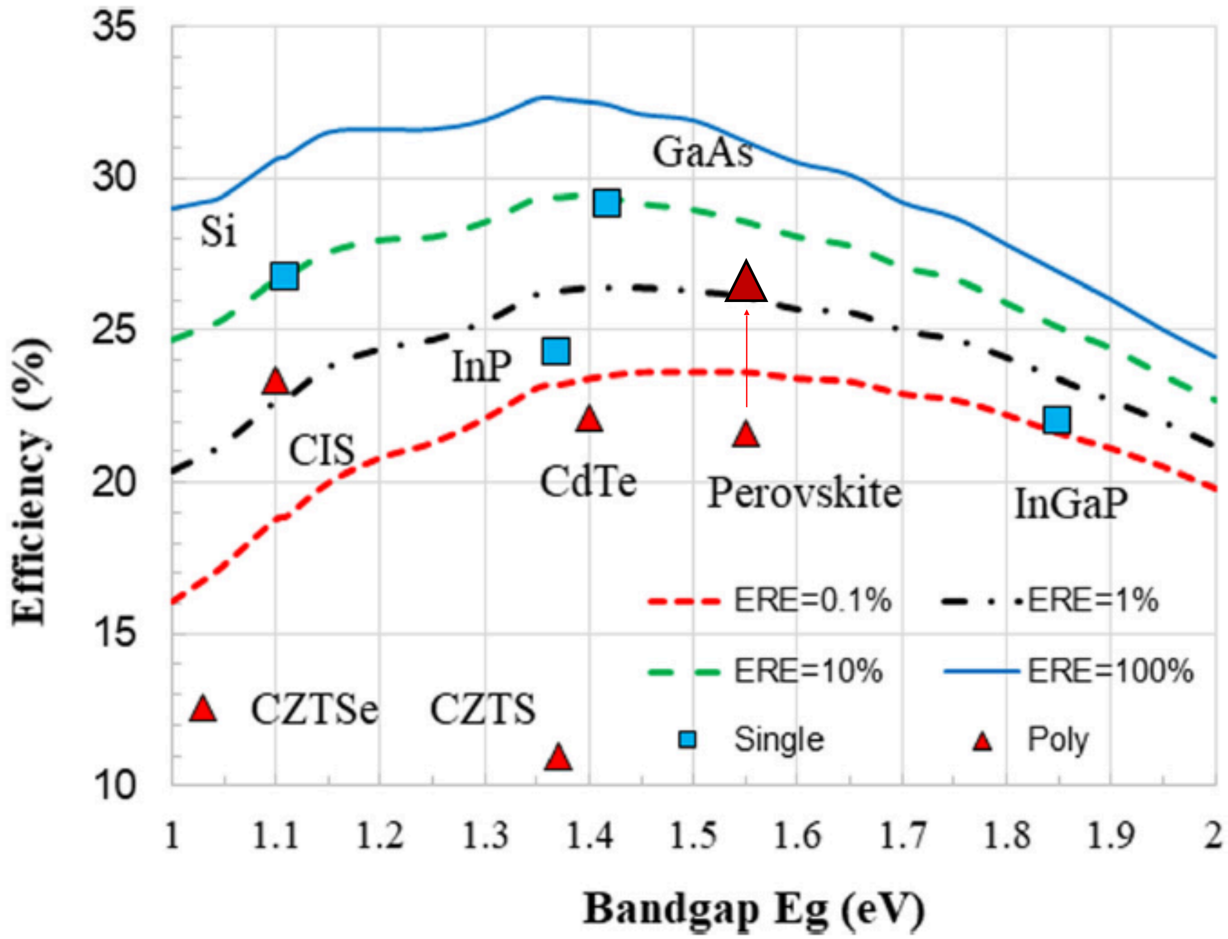
  $$ERE = J_{rad}/(J_{rad} + J_{nrad})$$

  Therefore the rest fraction of the recombinations (1 – *ERE*) refers to the non-radiative recombinations.

  ERE = 1 (100%) at Shockley-Queisser limit
- The series resistance in solar cells.
- The shunt resistance in solar cells.
- Parasitic absorption by solar cell component (non active).

- Jun-Ho YUM, junho.yum@epfl.ch

Efficiency and ERE



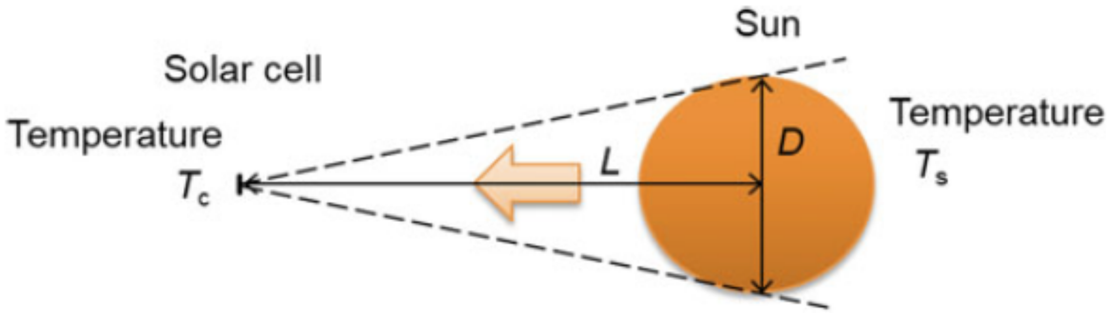
$$ERE = J_{rad}/(J_{rad} + J_{nrad})$$

Yamaguchi et al., J. Appl. Phys. 129, 240901 (2021)

- Jun-Ho YUM, junho.yum@epfl.ch

Detailed balance limit of Efficiency of p-n Junction Solar Cells

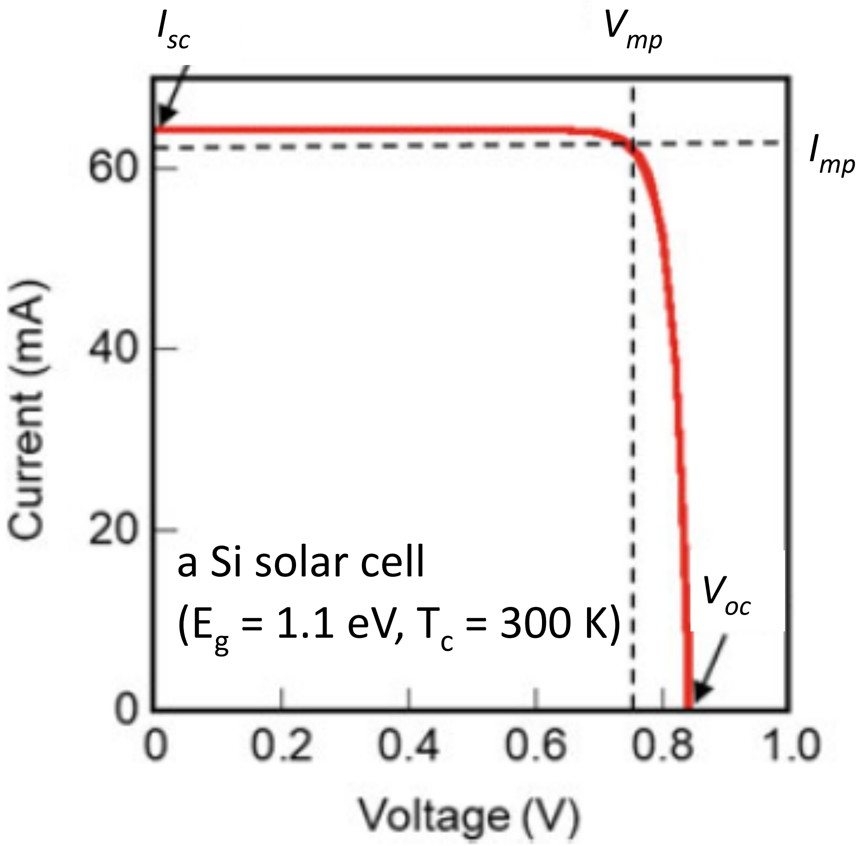
The balance between the carrier generation and recombination that occurs under the particular condition (maximum power point) for maximum extractable electrical power was considered.



- The solar cell has a finite temperature T_c and also emits black-body radiation = the solar cell is surrounded by a black body with T_c.
- Consider electron-hole pairs generated by the radiation of the black body with T_c.
- The probability t_c for an electron-hole pair by the incident photons larger than E_g is set to 100%, $t_c = 1$.
- All photogenerated electrons and holes thermalize to the band edges.
- All the photogenerated charge carriers are collected at short-circuit condition = unlimited mobility.
- The radiation absorbed by the cell is equal to the radiation emitted ($R_{abs} = R_{emit}$) = non-radiative recombination is not taken into account.

Detailed balance limit of Efficiency of p-n Junction Solar Cells

$$IV = I_0 V\left[exp(\frac{V_{oc}}{V_c}) - exp\left(\frac{V}{V_c}\right)\right]$$



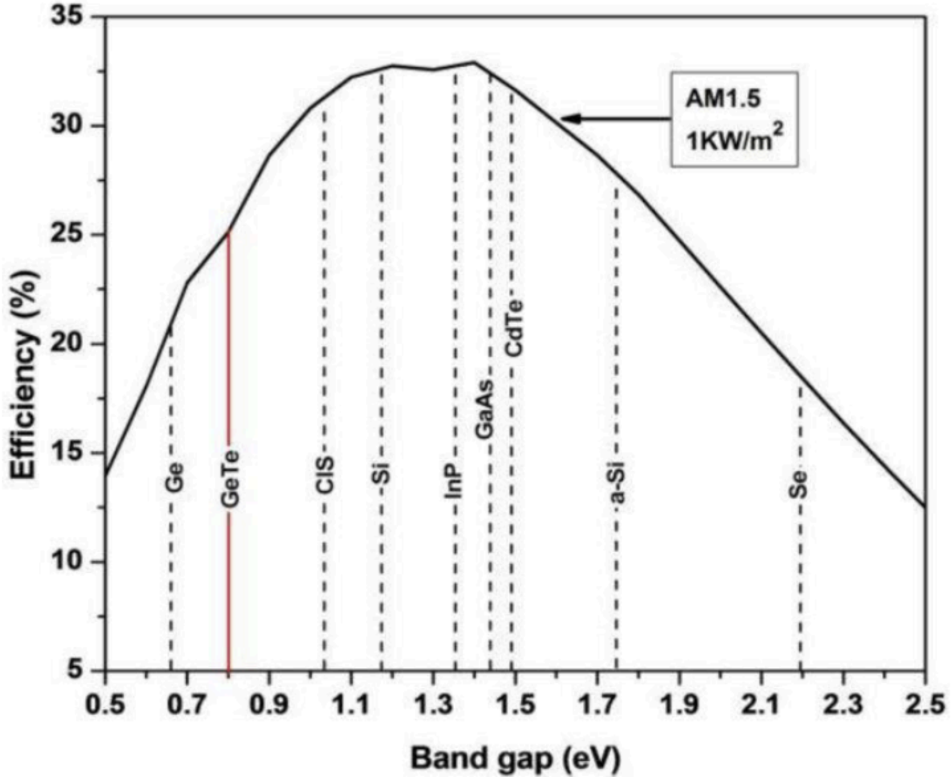
a Si solar cell

(E_g = 1.1 eV, T_c = 300 K)

Shockley-Queisser (S-Q) limit

33.7% with E_g = 1.34 eV

32% with Si E_g = 1.12 eV



Detailed balance limit of Efficiency of p-n Junction Solar Cells

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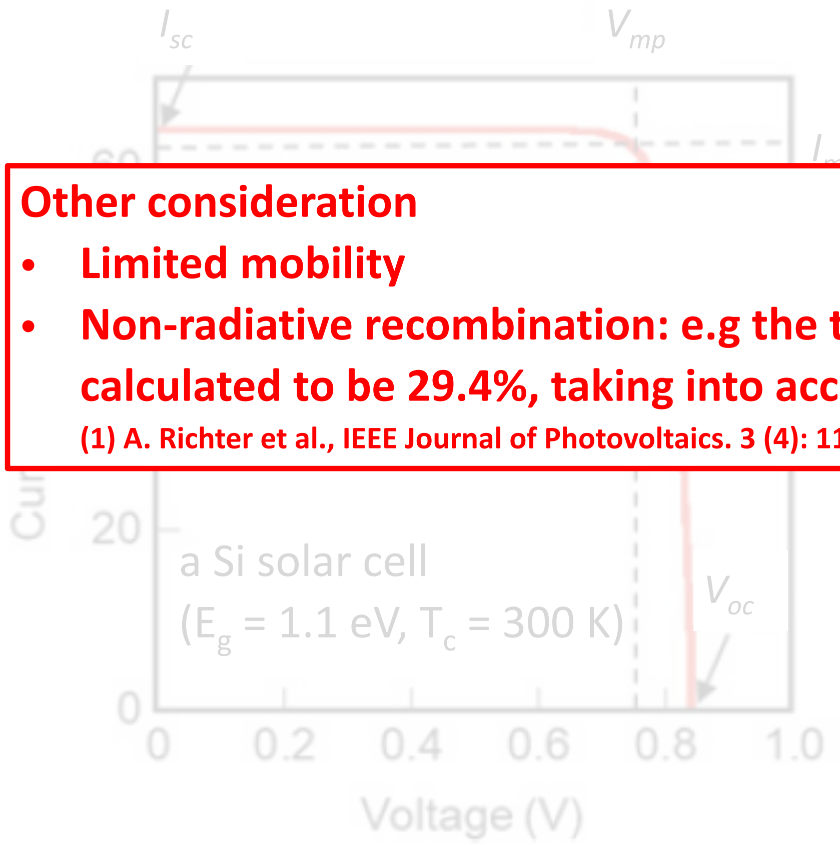

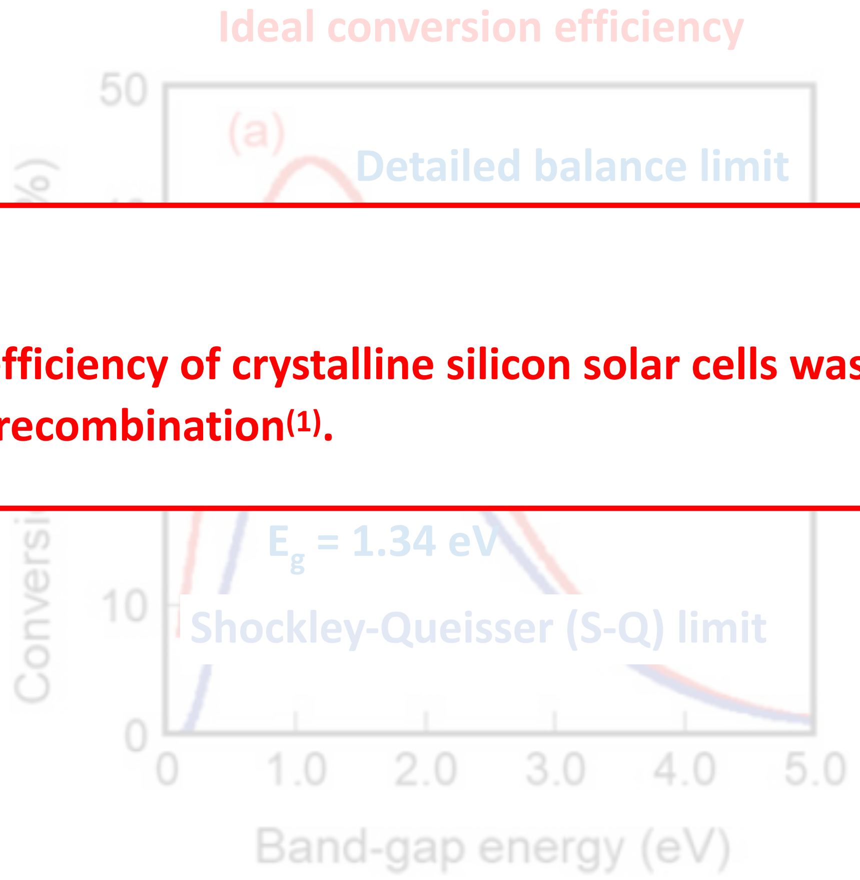

Other consideration

- **Limited mobility**
- **Non-radiative recombination: e.g the theoretical efficiency of crystalline silicon solar cells was calculated to be 29.4%, taking into account Auger recombination(1).**

(1) A. Richter et al., IEEE Journal of Photovoltaics. 3 (4): 1184–1191 (2013)

Ideality Factor

$$I = I_L - I_0\left[\exp\left(\frac{eV}{nk_BT}\right) - 1\right] \approx I_L - I_0\left[\exp\left(\frac{eV}{nk_BT}\right)\right]$$

n = A measure of how closely the diode follows the ideal diode equation.

Ideality factor depends on recombination type.

Recombination type	n	Description
band to band (low level injection)	1	Recombination limited by minority carrier.
SRH, band to band (high level injection)	2	Recombination limited by both carrier type.
Junction (depletion region)	2	Two carriers limit recombination.
Auger	2/3	Two majority and one minority carriers required.

- Jun-Ho YUM, junho.yum@epfl.ch

Ideality Factor

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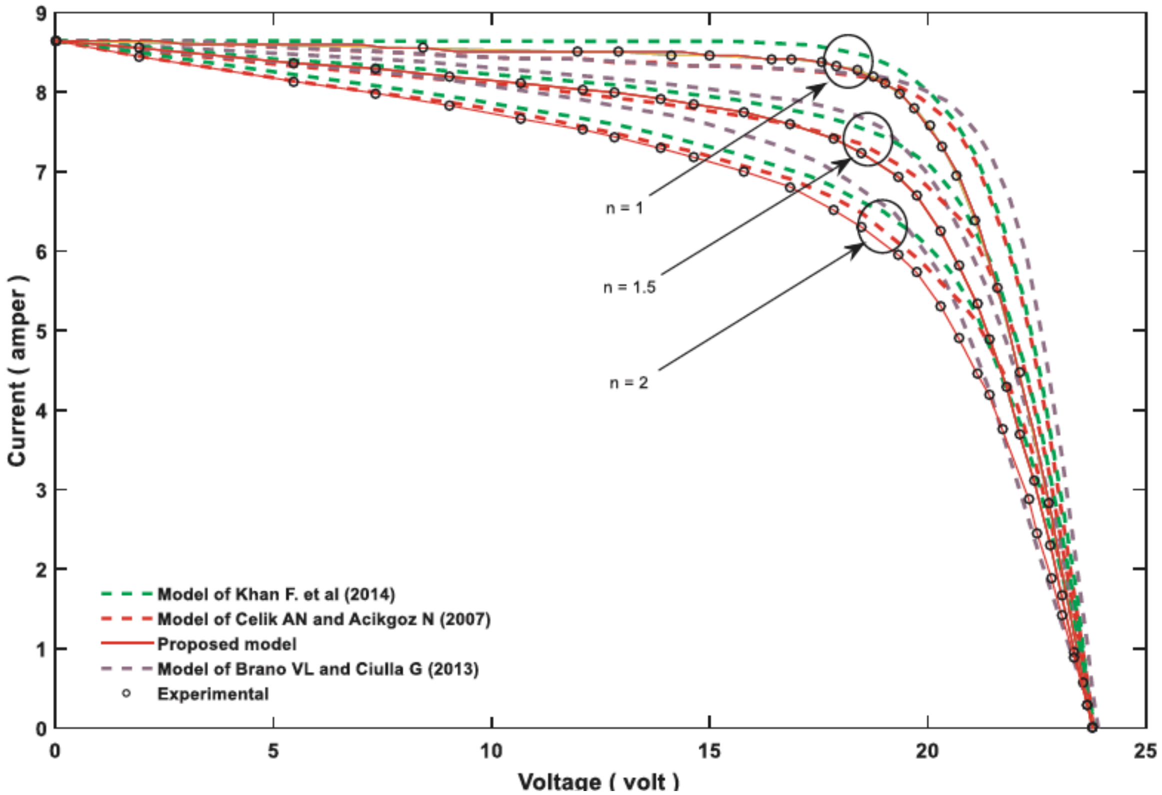


From A. Humada et al., *Solar Energy,* 190. 742 – 760 (2020)

- Jun-Ho YUM, junho.yum@epfl.ch

Parasitic Resistances

Real cells: Resistance of the contacts and leakage currents through the cell and/or around the sides of the device.

Series resistance (R_{series}): it arises from the resistance of the cell material to current flow, particularly through the front surface to the contacts and from resistive contacts. It is a particular problem at high current densities, i.e. under concentrated light. A **low R_{series}** is desired!

Shunt resistance (R_{shunt}): It arises from the leakage of the current through the cell, e.g. defects or cracks, causing power loss by diverting current. It is a problem with poorly rectifying devices. A **high R_{shunt}** is desired!

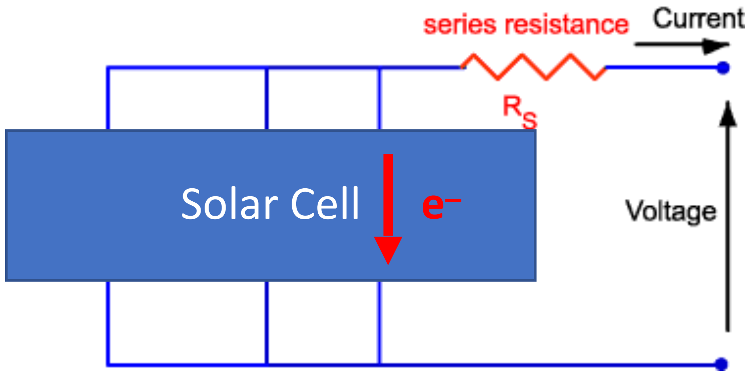
The diode equation becomes:

$$I = I_L - I_0\left[\exp\left(\frac{e(V + IR_{series})}{nk_BT}\right) - 1\right] - \frac{V + IR_{series}}{R_{shunt}}$$

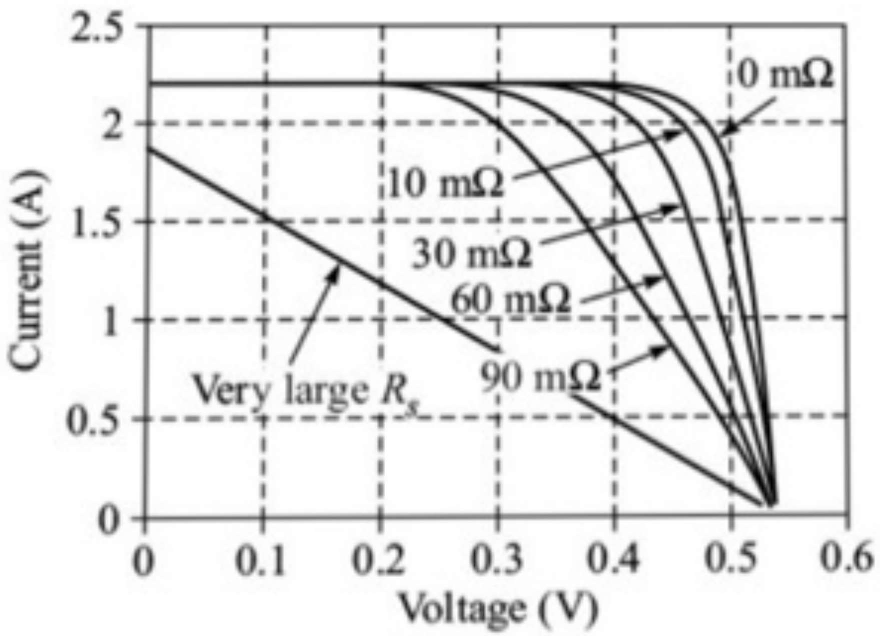
- Jun-Ho YUM, junho.yum@epfl.ch

Series Resistance and Shunt Resistance

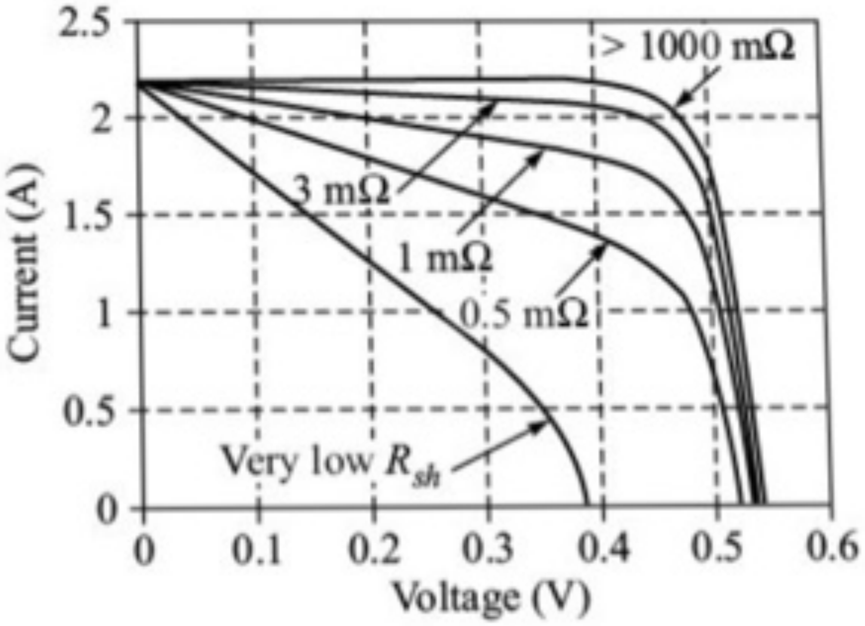
Resistive effects, series resistance (R_{series}) and shunt resistance (R_{shunt}) in solar cells reduce the efficiency of the solar cell by dissipating power in the resistances, mainly the **fill factor**.



The effect of R_{series}



The effect of R_{shunt}



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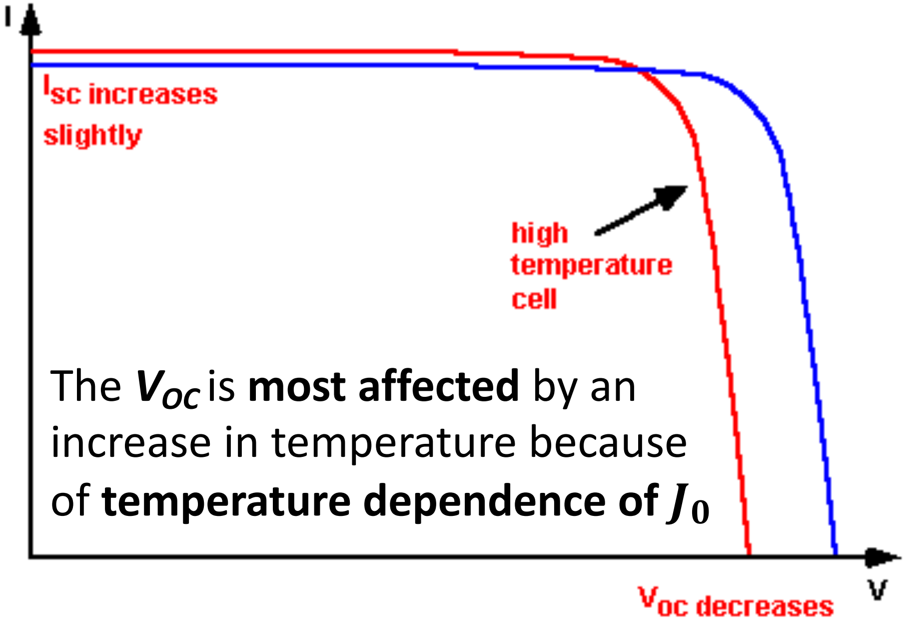
Effect of Temperature

$$\frac{1}{J_{SC}}\frac{dJ_{SC}}{dT} \approx 0.0006\ per\ ^{\circ}\mathrm{C}\ for\ Si$$

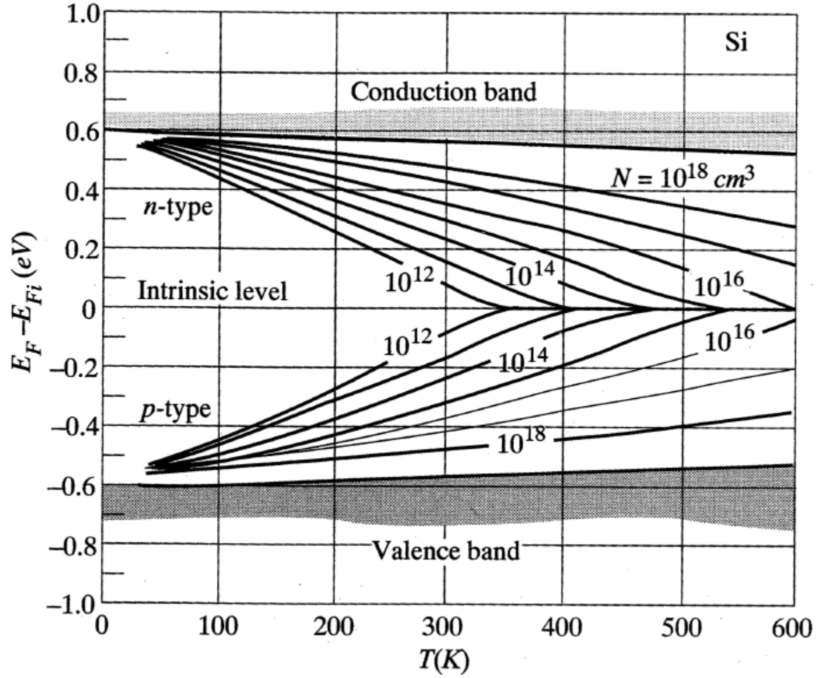
$$(0.06\%\ per\ ^{\circ}\mathrm{C})$$



The V_{OC} is **most affected** by an increase in temperature because of **temperature dependence of J_0**

$$\frac{dV_{OC}}{dT} \approx -2.2mV\ per\ ^{\circ}\mathrm{C}\ for\ Si$$

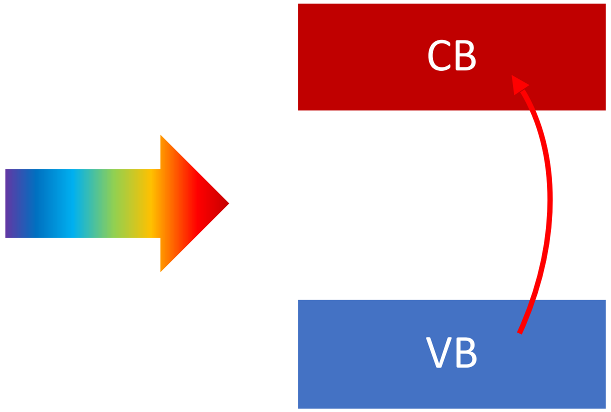
An increase in temperature → Reduced Band Gap of SC



$$V_{OC} = \frac{nk_BT}{e}\ln\left(\frac{I_L}{I_0}+1\right) \qquad J_0 = e\left(\frac{D_e n_{P0}}{L_e}+\frac{D_h p_{N0}}{L_h}\right) = e n_i^2\left(\sqrt{\frac{D_e}{\tau_e}}\frac{1}{N_A}+\sqrt{\frac{D_h}{\tau_h}}\frac{1}{N_D}\right)$$

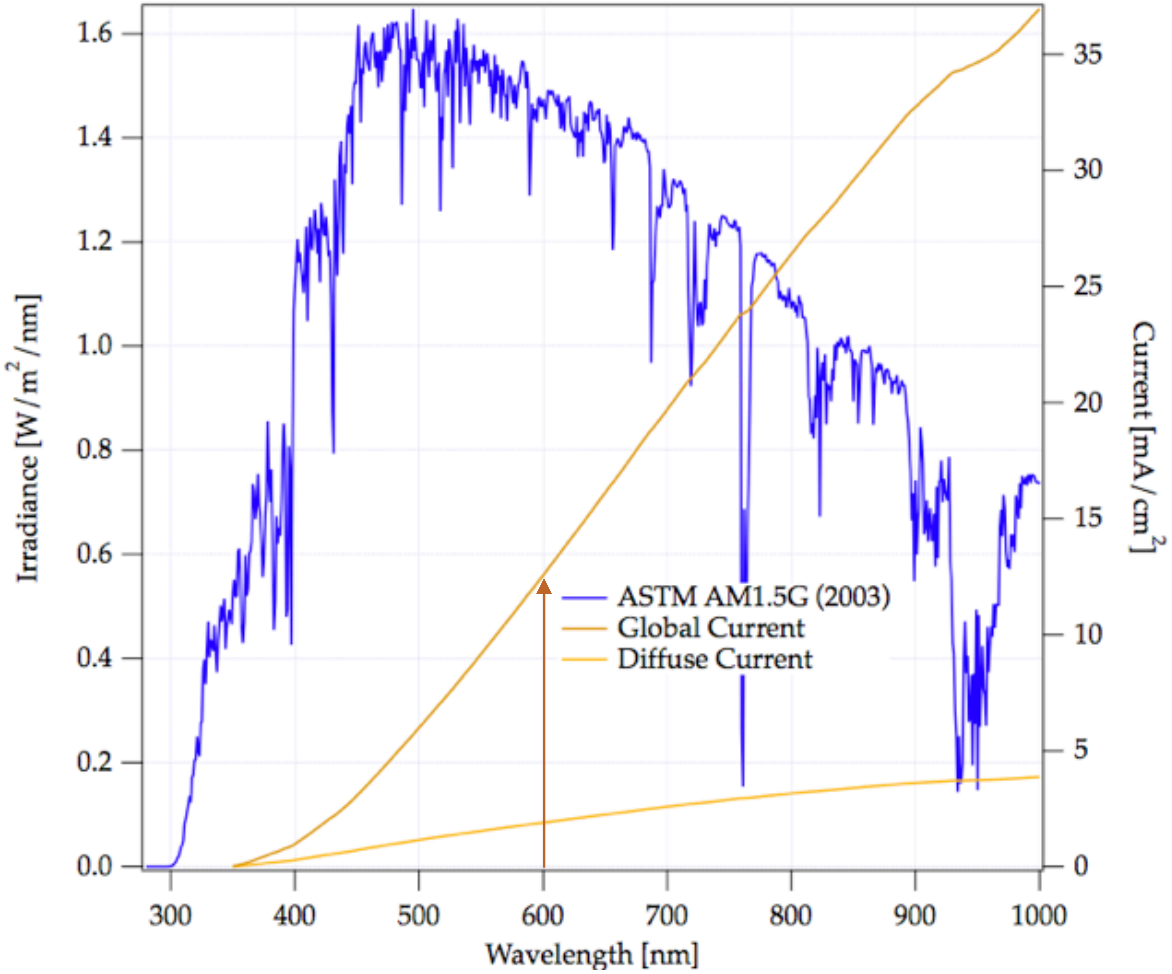
- Jun-Ho YUM, junho.yum@epfl.ch

Semiconductors in Solar Cell



- **Light management:**
  - **Thickness**
  - **Band gap**
  - **Light management by scattering or reflection**

- **Carrier management:**
  - **Charge separation**
  - **Charge collection**



2.1 eV

- Jun-Ho YUM, junho.yum@epfl.ch

IPCE and APCE

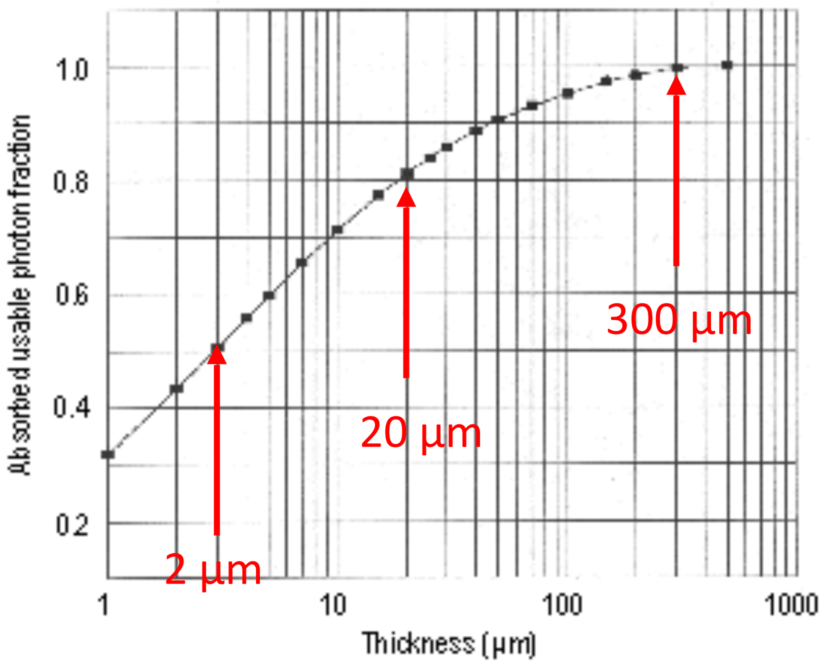
Incident Photon-to-Current Conversion Efficiency (IPCE) or External Quantum Efficiency (EQE) =

$$\frac{Collected\ electrons\ at\ a\ given\ wavelength}{Photons\ in\ at\ a\ given\ wavelength} = \frac{J_{SC}/q}{P_{in}/h\nu} = \frac{J_{SC}(A/cm^2)}{P_{in}(W/cm^2)} \times \frac{1240}{\lambda(nm)} \times 100$$

Absorbed Photon-to-Current Conversion Efficiency (APCE) or Internal Quantum Efficiency (IQE):

$$\frac{Collected\ electrons\ at\ a\ given\ wavelength}{Absorbed\ photons\ at\ a\ given\ wavelength} = \frac{EQE}{1-R-T} = \frac{EQE}{LHE} \approx \frac{EQE}{1-10^{-A}}$$

LHE = Light harvesting efficiency



Ex) While 100% of the light is absorbed by a 300 µm Si wafers, this falls off to 80% in a 20 µm thin layers and 50% in a 2 µm thin layers.

1. IQE = 100% and 2 µm Si —> EQE = 50%
2. IQE = 50% and 300 µm Si —> EQE = 50%
3. IQE = 100% and 300 µm Si —> EQE = 100%

IQE is determined by charge management, e.g. charge separation/collection.

EQE involves both charge management and light management.

- Jun-Ho YUM, junho.yum@epfl.ch

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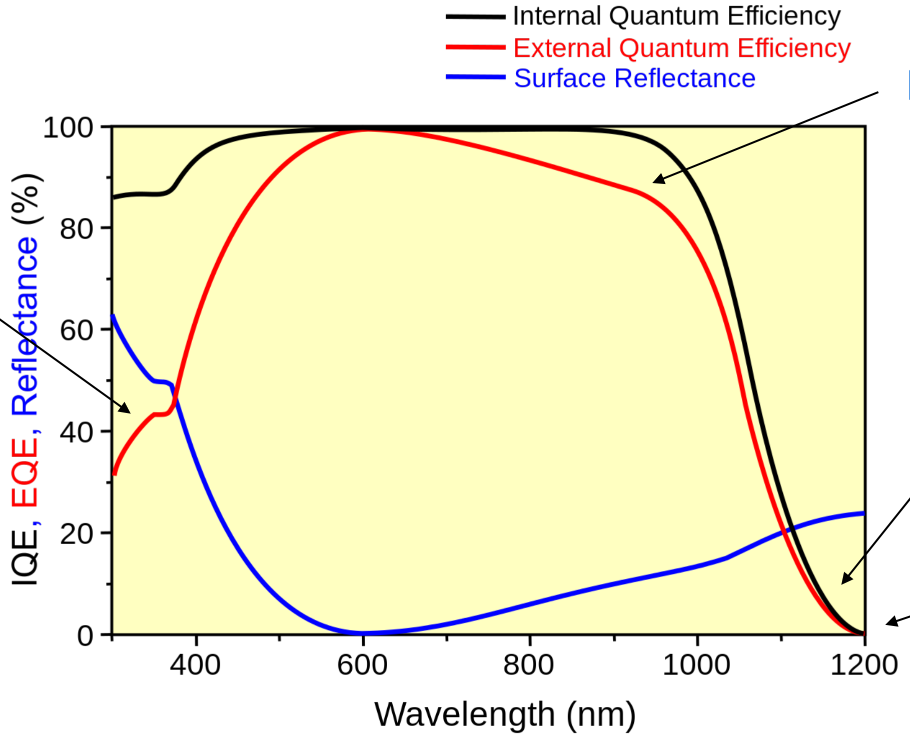
LHE = Light harvesting efficiency

Reflection, Parasitic absorption, front surface recombination

Blue: light management

Organe: charge management



Reflection, limited diffusion length

Reduced absorption, rear surface recombination, low diffusion length

No light is absorbed below the band gap

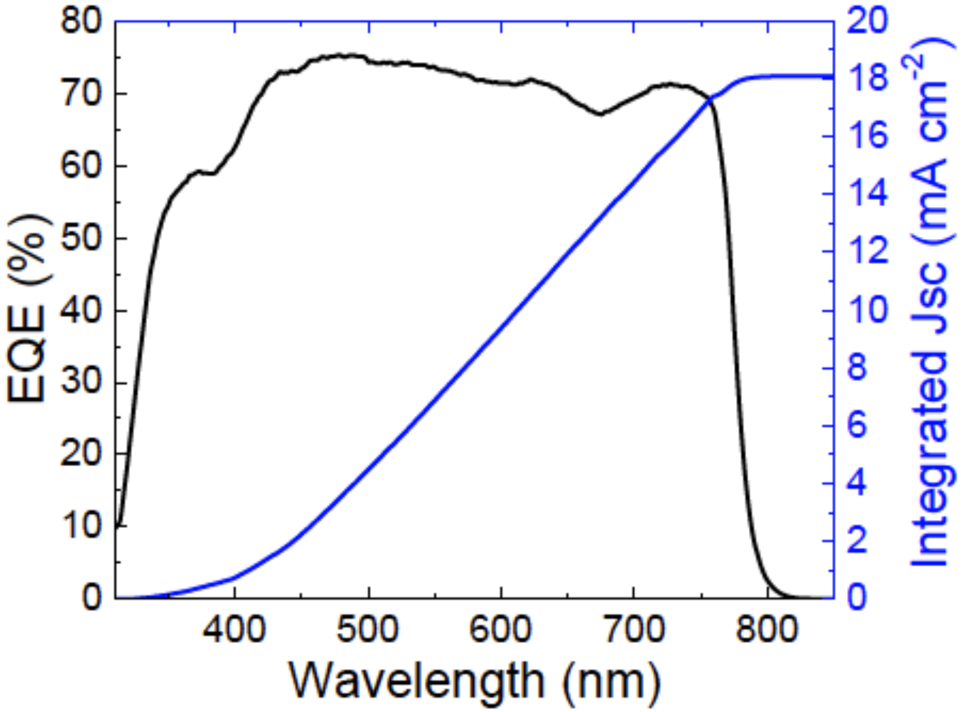
IPCE and J_{SC}

When the EQE is integrated overall all wavelength, it will return J_{SC}

$$\frac{Collected\ electrons\ at\ a\ given\ wavelength}{Photons\ in\ at\ a\ given\ wavelength} = \frac{J_{SC}/q}{P_{in}/h\upsilon}$$

$$J_{SC} = q\int_{\lambda_1}^{\lambda_2} EQE(\lambda)\Phi^{AM1.5}d\lambda$$

$\Phi^{AM1.5}$: Spectral photon flux



From C. Perini et al., *J. Mater. Chem. A,* 8. 25283 – 25289 (2020)

- Jun-Ho YUM, junho.yum@epfl.ch

Solar Cell Test Setup: EQE

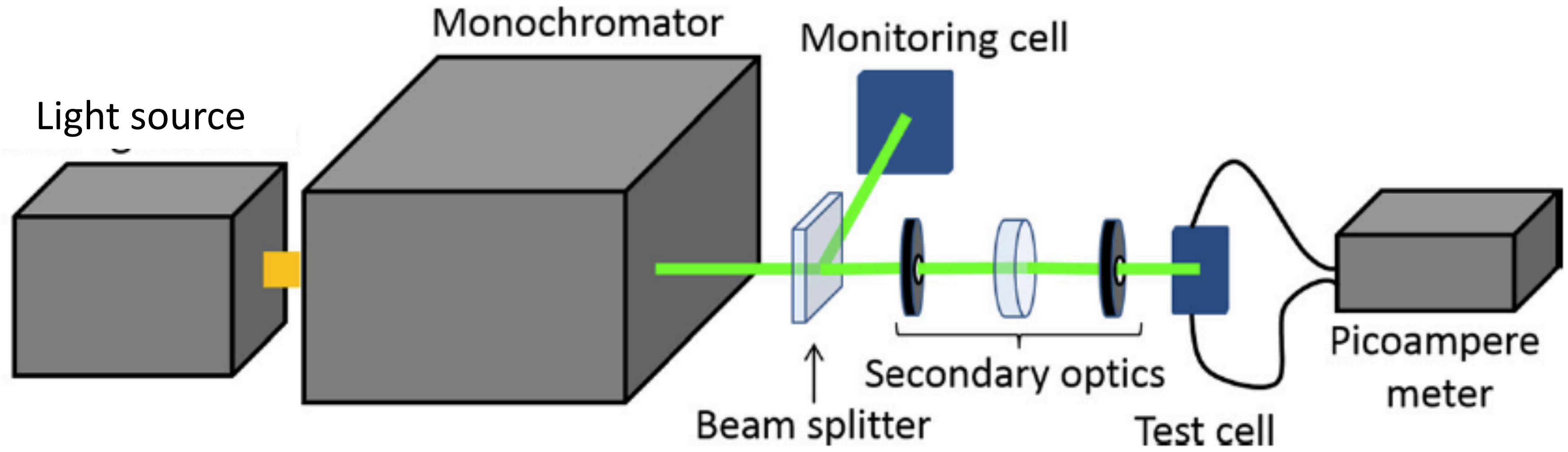


Image from Leyre *et al.,* J. Renewable Sustainable Energy *7*, 043130 (2015)

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Solar Cell Test Setup: EQE

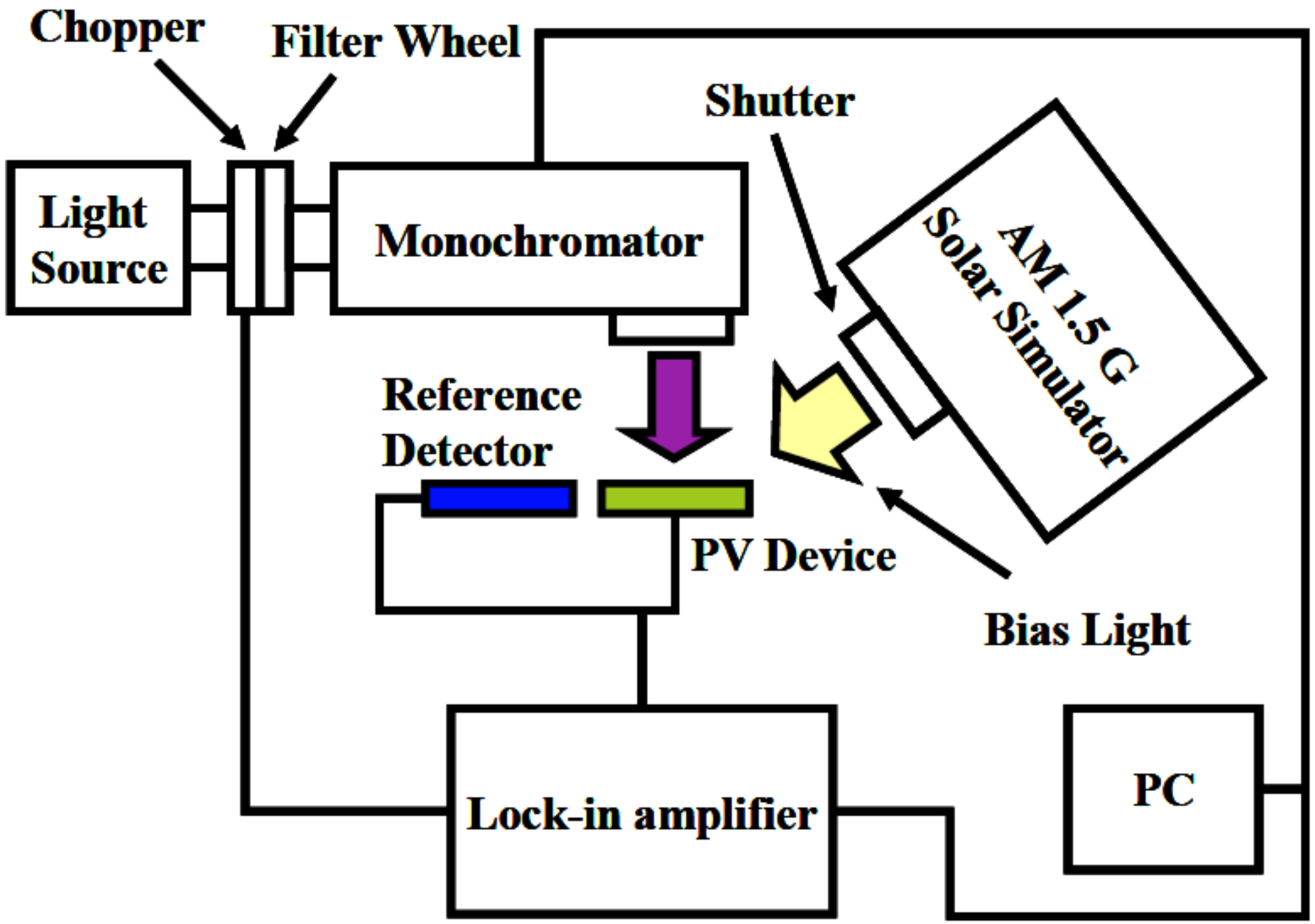

Image from C-F Lin *et al.,* Int. J. Mol. Sci., 12, 476-505 (2011)

- Jun-Ho YUM, junho.yum@epfl.ch