The Shockley-Queisser Limit

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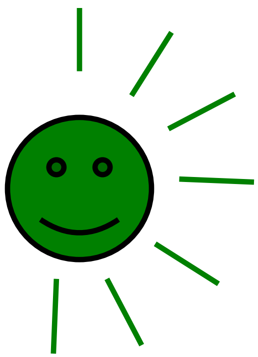
Outline

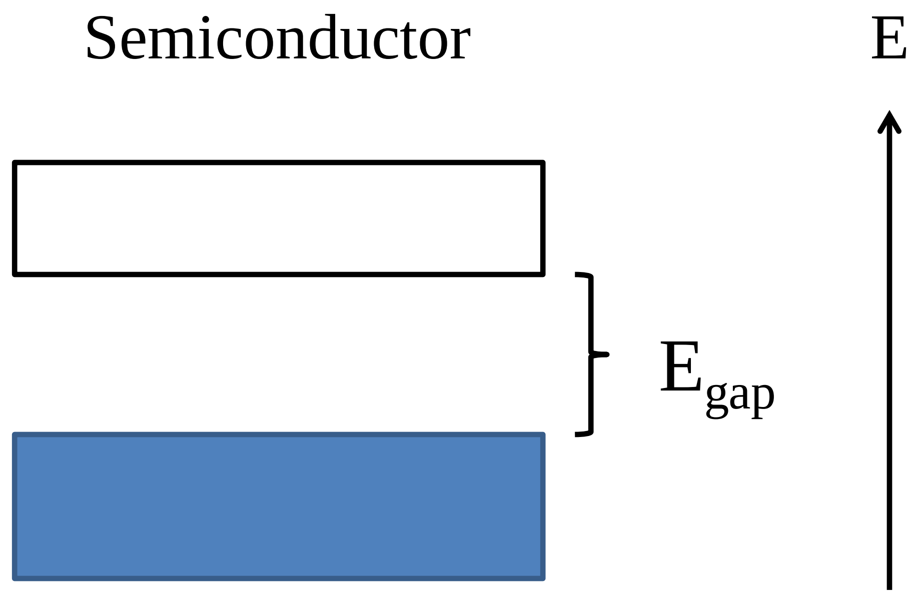
A. Loss factors
   1. Bandgap energy
   2. Geometric factor
   3. Recombination of electrons and holes

B. Overall efficiency

C. Optimum bandgap

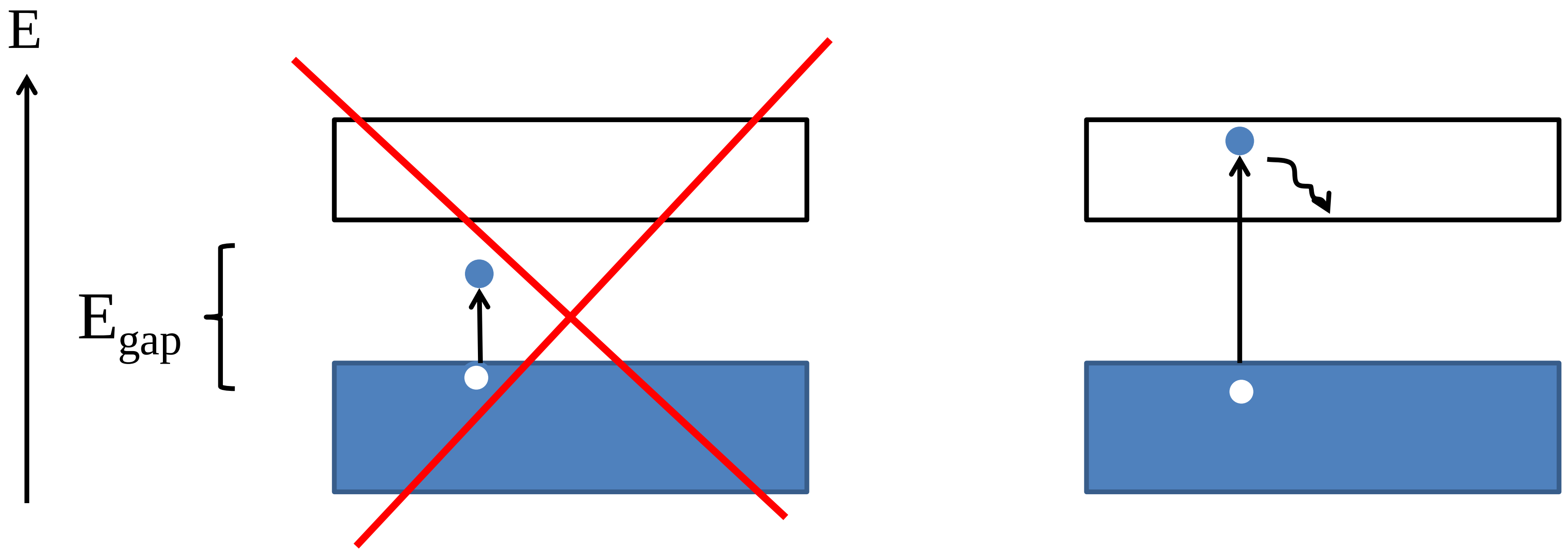
Photovoltaic Energy Conversion





- PV cells convert photon energy into electron energy.
  - These electrons carry a current and the resulting power can be extracted as electricity

Bandgap losses



- Photons with energy less than the bandgap cannot be absorbed by the solar cell.
  - Low energy photons contribute no energy
- Each absorbed photon can only contribute one electron to the conduction band.
  - High energy photons therefore only contribute a fraction of their energy

Bandgap loss efficiency factor

- Efficiency if the PV cell is affected only by bandgap losses

$$\eta_{bandgap}(\epsilon_{gap}, T_s) = \frac{\epsilon_{gap} Q_s}{p_s}$$

- ϵ_{gap}=bandgap energy; T_s=temperature of the sun; Q_s=number of absorbed photons (with $\epsilon < \epsilon_{gap}$) per unit area, per unit time; p_s=incident solar power per unit area

$$p_S = \int_0^{\infty} u(\epsilon, T_S)\, d\epsilon$$

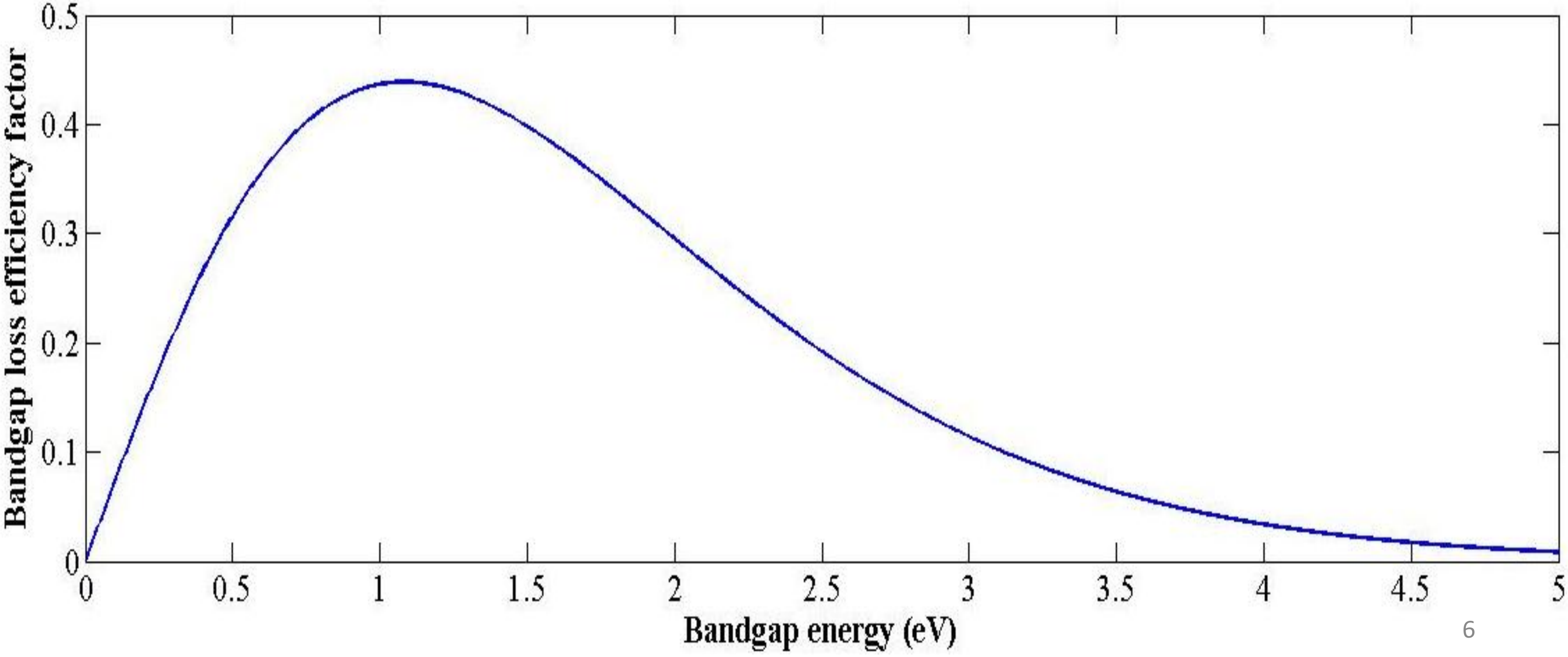
$$Q_S = \int_{\epsilon_{gap}}^{\infty} u_n(\epsilon, T_S)\, d\epsilon$$

- $u(\epsilon, T_S)$ is the solar blackbody spectrum converted into power per unit area
- $u_n(\epsilon, T_S)$ is the number of photon emitted per unit area

$$u_n(\epsilon, T_S) = u(\epsilon, T_S)/\epsilon$$

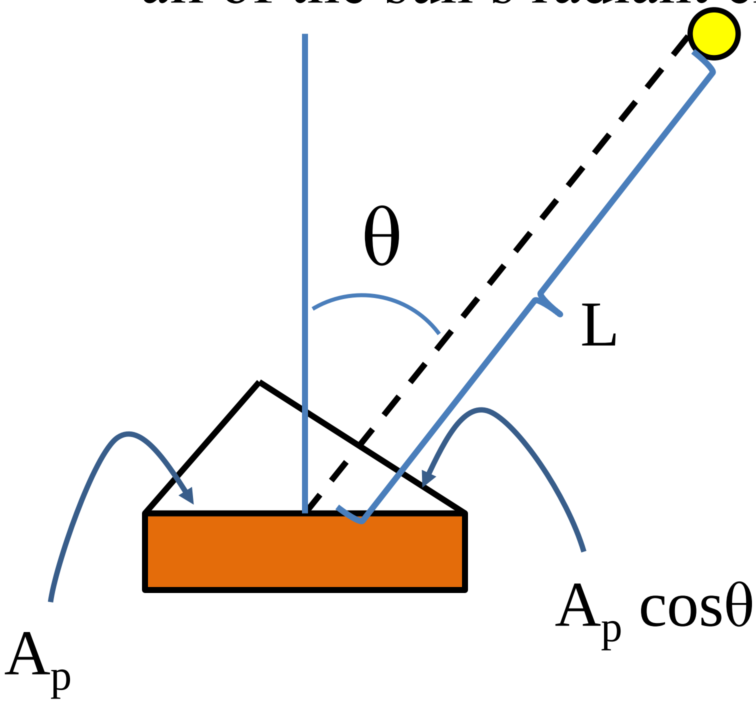
Bandgap loss efficiency as a function of bandgap

$$\eta_{bandgap}(\epsilon_{gap}, T_s) = \frac{\epsilon_{gap} \int_{\epsilon_{gap}}^{\infty} \frac{2\pi}{h^3 c^2} \frac{\epsilon^2}{e^{\epsilon/kT_s} - 1} d\epsilon}{\int_0^{\infty} \frac{2\pi}{h^3 c^2} \frac{\epsilon^3}{e^{\epsilon/kT_s} - 1} d\epsilon}$$



Geometric factor

- The solar cell is not at the surface of the sun, so it can't absorb all of the sun's radiant energy.



Power incident on the PV cell (P_{inc}):

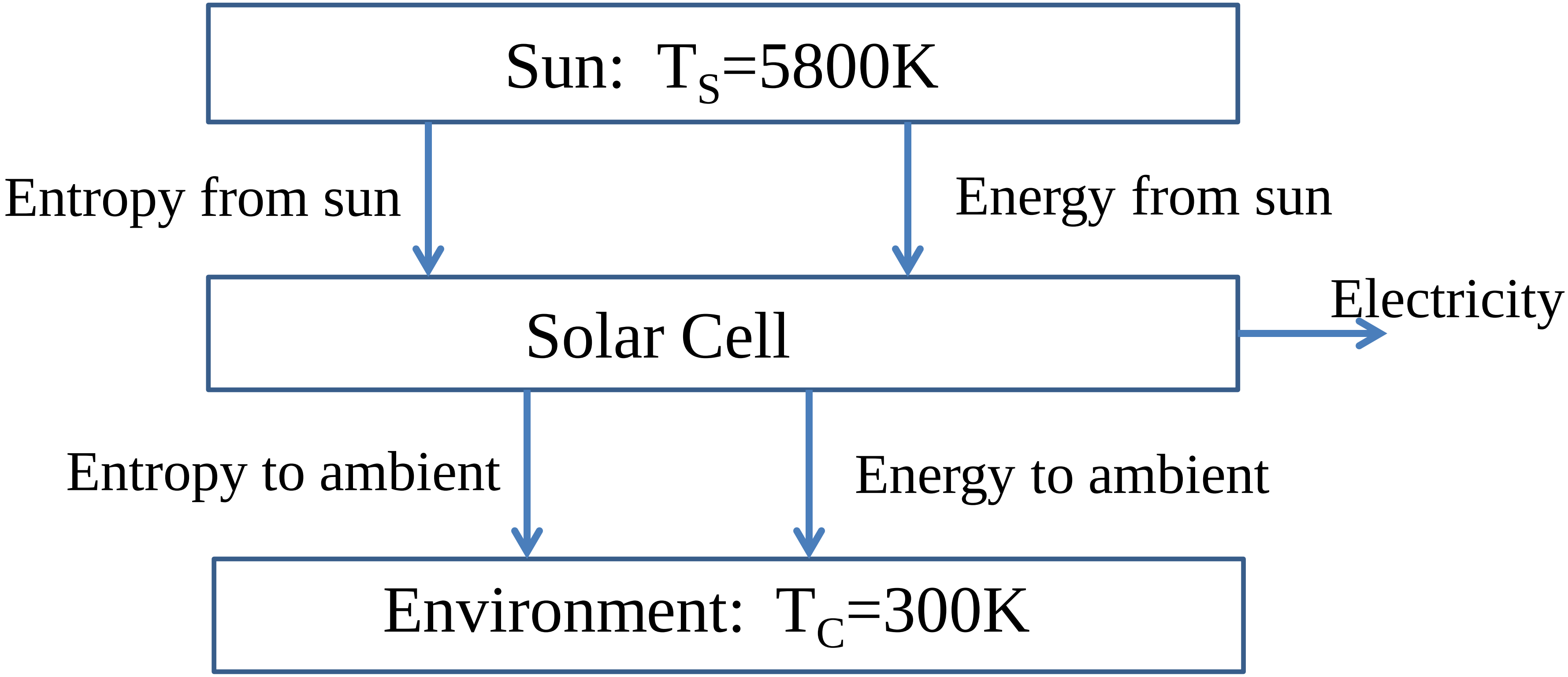
$$P_{inc} = p_s A_s \left(\frac{A_p \cos\theta}{4\pi L^2} \right) = p_s A_p f_\omega$$

Use the same geometric factor to recalculate F_S, the number of absorbed photons:

$$F_s = Q_s A_p f_\omega$$

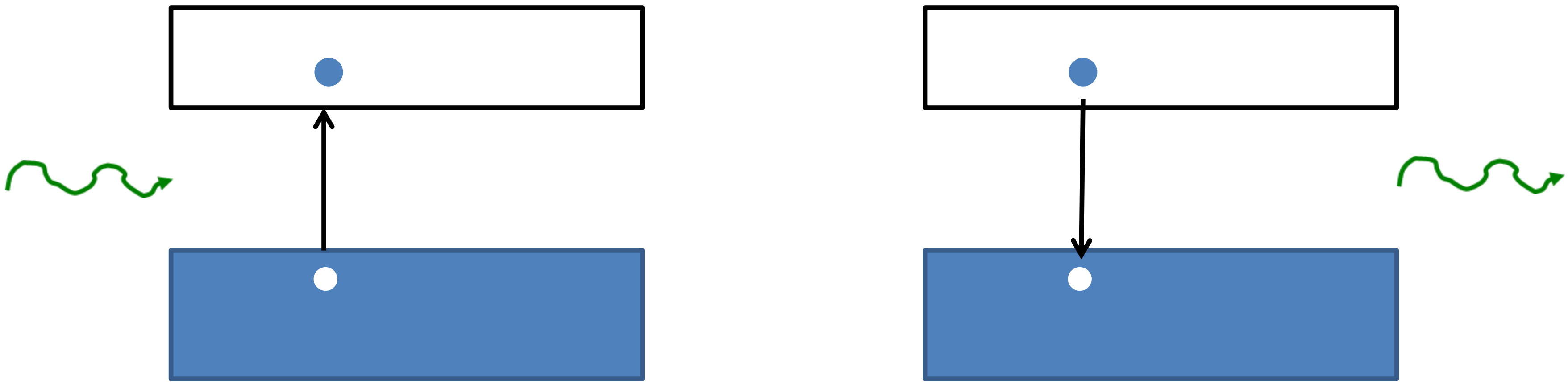
Entropy

- In addition to absorbing energy from the sun, a solar cell also absorbs entropy.
- Therefore, by the second law, the solar cell must emit entropy.
- The cell must emit energy to carry this entropy away.



Recombination

- The process by which the cell emits energy to carry away entropy is light emission
  - Light is emitted when electrons and holes recombine

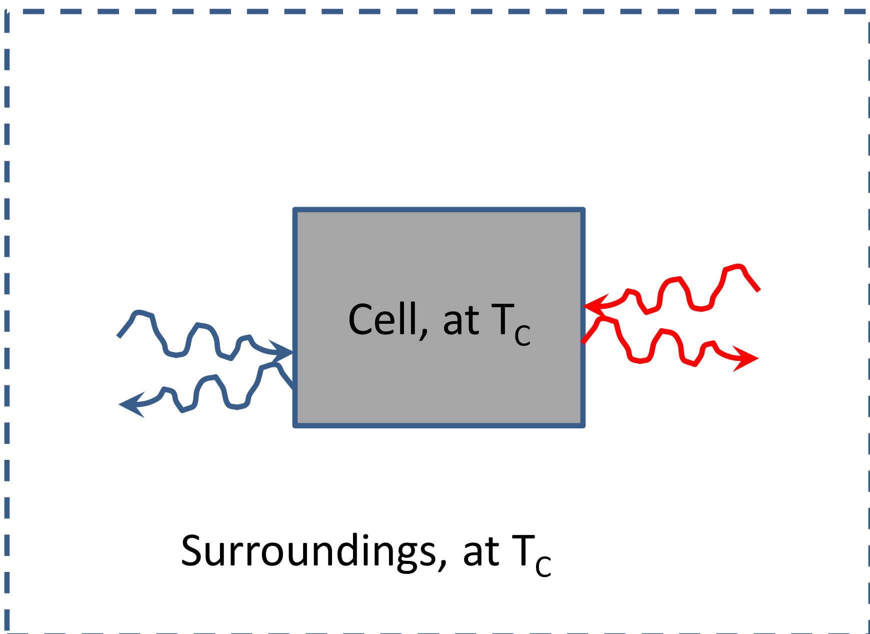


Photon absorbed

Photon emitted

Recombination

- Consider a cell in thermal equilibrium with its surroundings at temperature T_C.
- Assume the PV cell is a perfectly absorbing blackbody.
- Then the cell emits a blackbody spectrum at T_C since it's in thermal equilibrium.



Recombination

- Solar cell emission at thermal equilibrium at T_C.
- F_{C0} is the number of photons emitted per unit time at thermal equilibrium

$$F_{c0} = 2A_p Q_c$$

$$= 2A_p \times \int_{\epsilon_{gap}}^{\infty} \frac{\boldsymbol{2\pi}}{\boldsymbol{h^3 c^2}} \frac{\boldsymbol{\epsilon^2}}{\boldsymbol{e^{\epsilon/kT_c} - 1}} d\epsilon$$

- In fact, the solar cell is not in thermal equilibrium because there are carriers being generated by the sun.
- Therefore, there are more electron hole pairs than there were at equilibrium
- Recombination rate, F_C, is proportional to the number of electron hole pairs -> more recombination

$$F_c = \gamma \times np;$$

$$F_{c0} = \gamma \times {n_i}^2$$

$$\Rightarrow \; F_c = F_{c0} \frac{np}{{n_i}^2}$$

$$= \frac{F_{c0}}{n_i^2} N_c exp\left[-\frac{E_c - E_{Fn}}{kT_c}\right] N_v exp\left[-\frac{E_{Fp} - E_v}{kT_c}\right]$$

$$= F_{c0} exp\left(\frac{V}{V_c}\right); \qquad where\; V_c \equiv \frac{kT_c}{q}$$

Carrier continuity equation

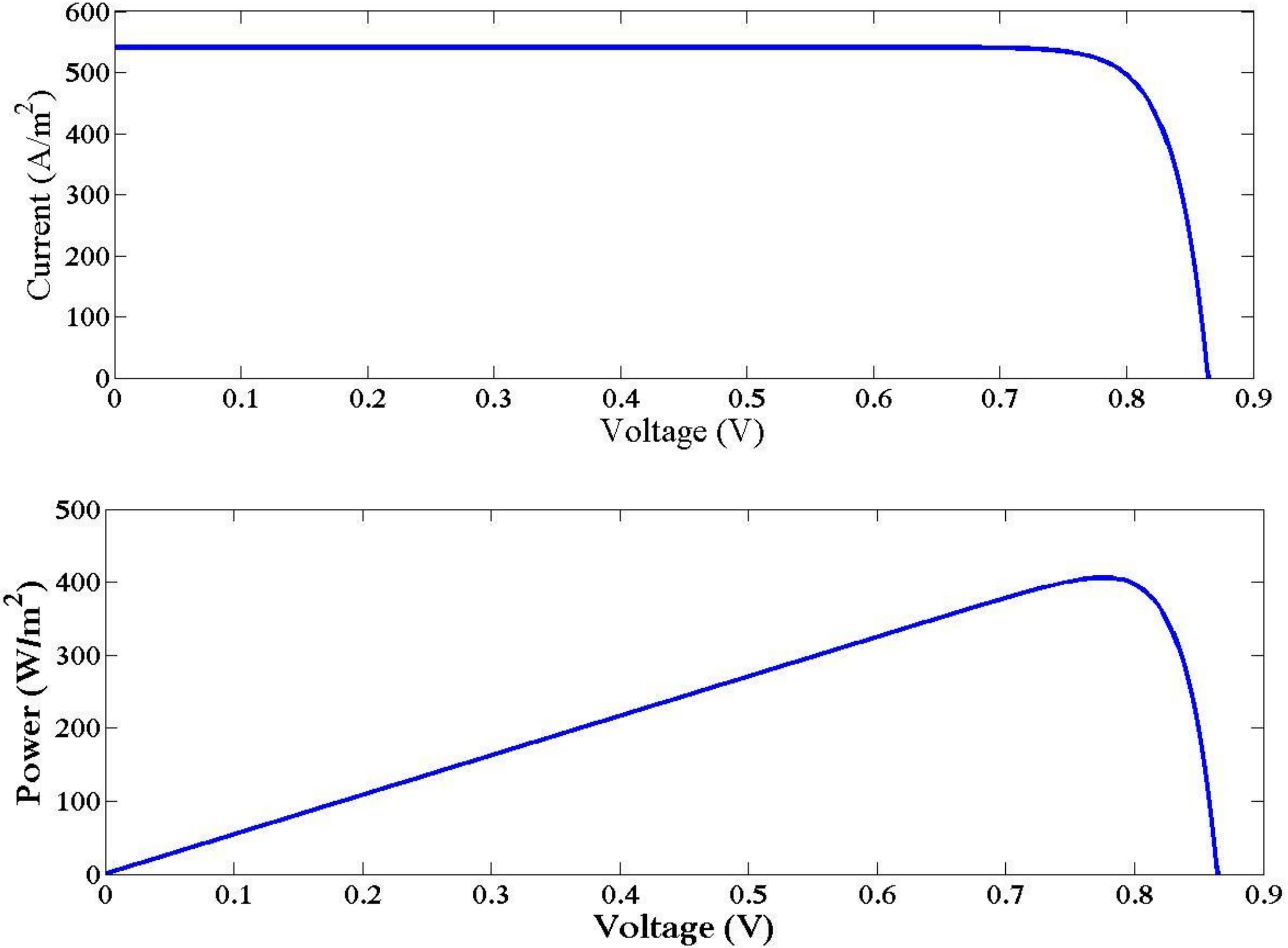
- We can infer a continuity equation for charge carriers since we know the processes by which they are gained and lost.

$$Generation = Recombination + Extraction$$

$$F_s = F_c(V) + \frac{I}{q}$$

$$I = I_{sc} + I_0\left[1 - exp\left(\frac{V}{V_c}\right)\right]$$

I-V curve



Current (A/m2)
600
500
400
300
200
100
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
Voltage (V)
Power (W/m2)
500
400
300
200
100
0
Voltage (V)

Overall efficiency

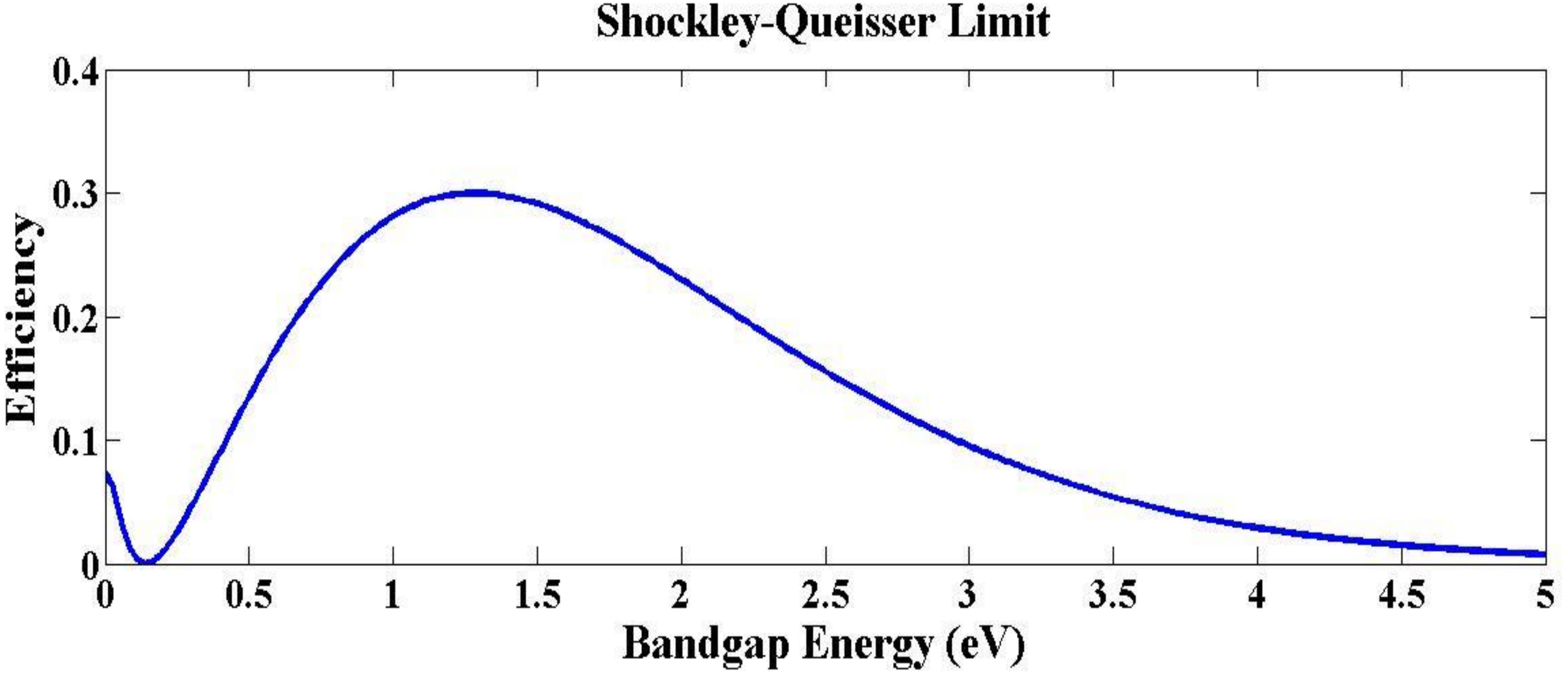
- To get the overall efficiency of the cell, we simply divide the maximum power by the incident power.

$$\eta = \frac{P_{max,\,electric}}{P_{inc,\,sun}}$$

$$\eta = \frac{P_{max}}{\frac{2\pi(kT_s)^4}{h^3c^2} f_\omega \int_0^\infty \frac{x^3}{e^x - 1}\,dx}$$

Optimum bandgap

- The efficiency we found above is a function of bandgap.
- Find the optimum bandgap graphically.



Summary of losses

1. Bandgap losses
   a) Low energy photons can't be absorbed
   b) High energy photons still only excite one electron which ends up at the bottom of the conduction band
2. Geometric factor
   a) By the time it gets to earth, the sun's radiation is spread over a shell of radius L=150 million km
   b) Therefore, only a fraction of the sun's radiation is incident on the cell
3. Recombination
   a) The second law implies that the cell must emit entropy (and therefore energy)
   b) The mechanism for this emission is recombination

References

1. B. Liao, W. Hsu. http://web.mit.edu/bolin/www/Shockley-Quisser-limit.pdf
2. J. Munday, J. Appl. Phys., vol. 112, 064501 (2012)
3. W. Shockley and H. J. Queisser, J. Appl. Phys., vol 32, 510 (1961).