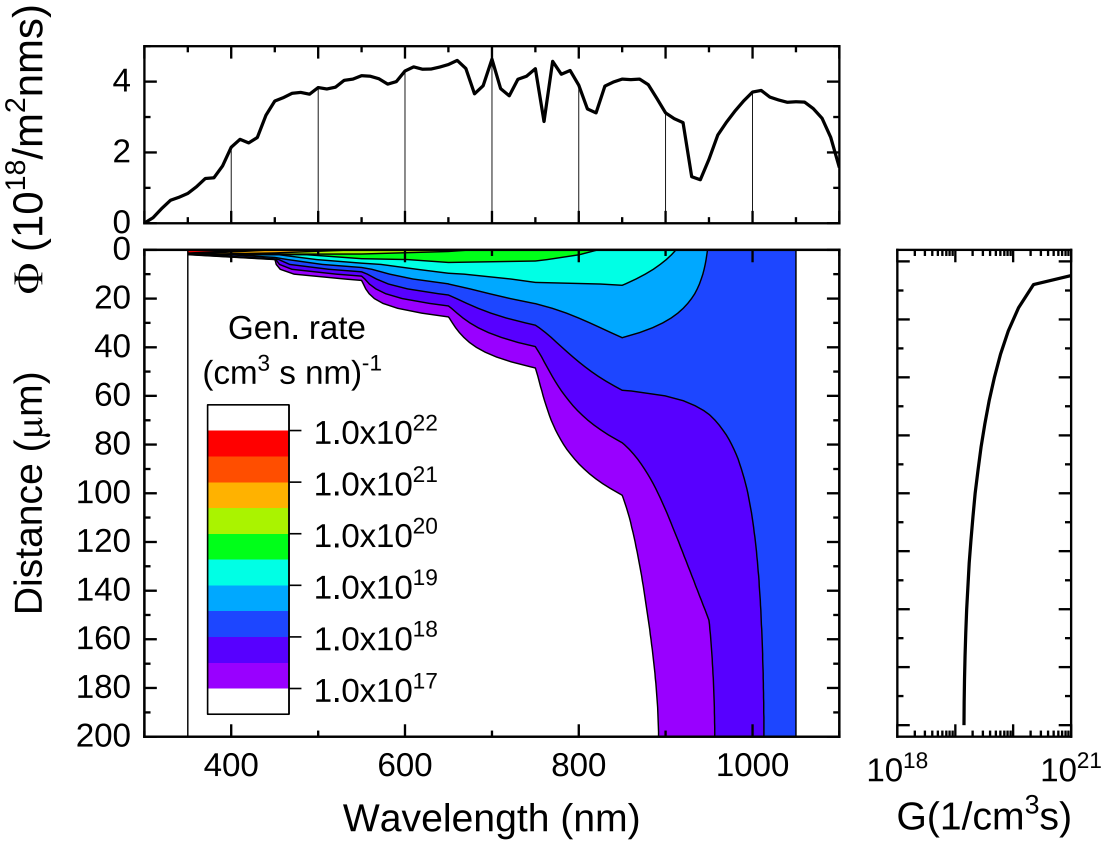
Fundamentals and processes for photovoltaic devices



Absorption and generation

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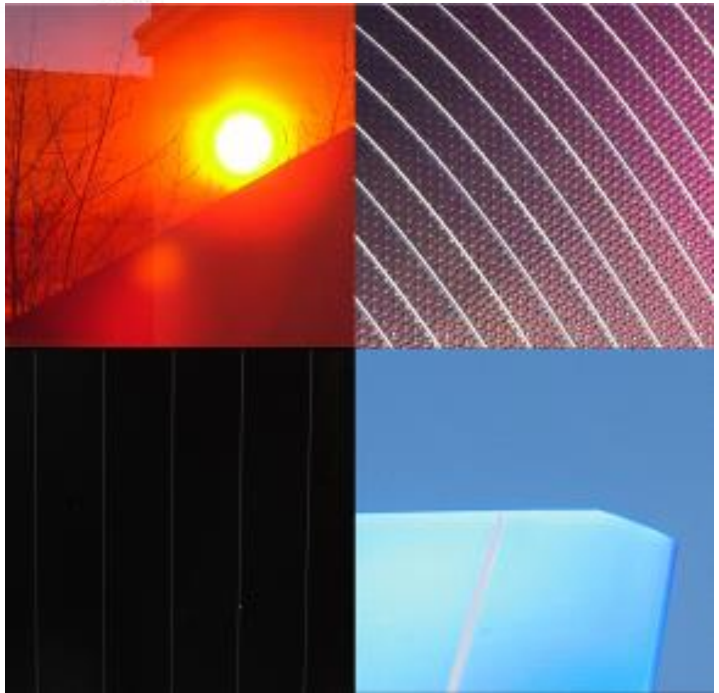


Lecture Outline

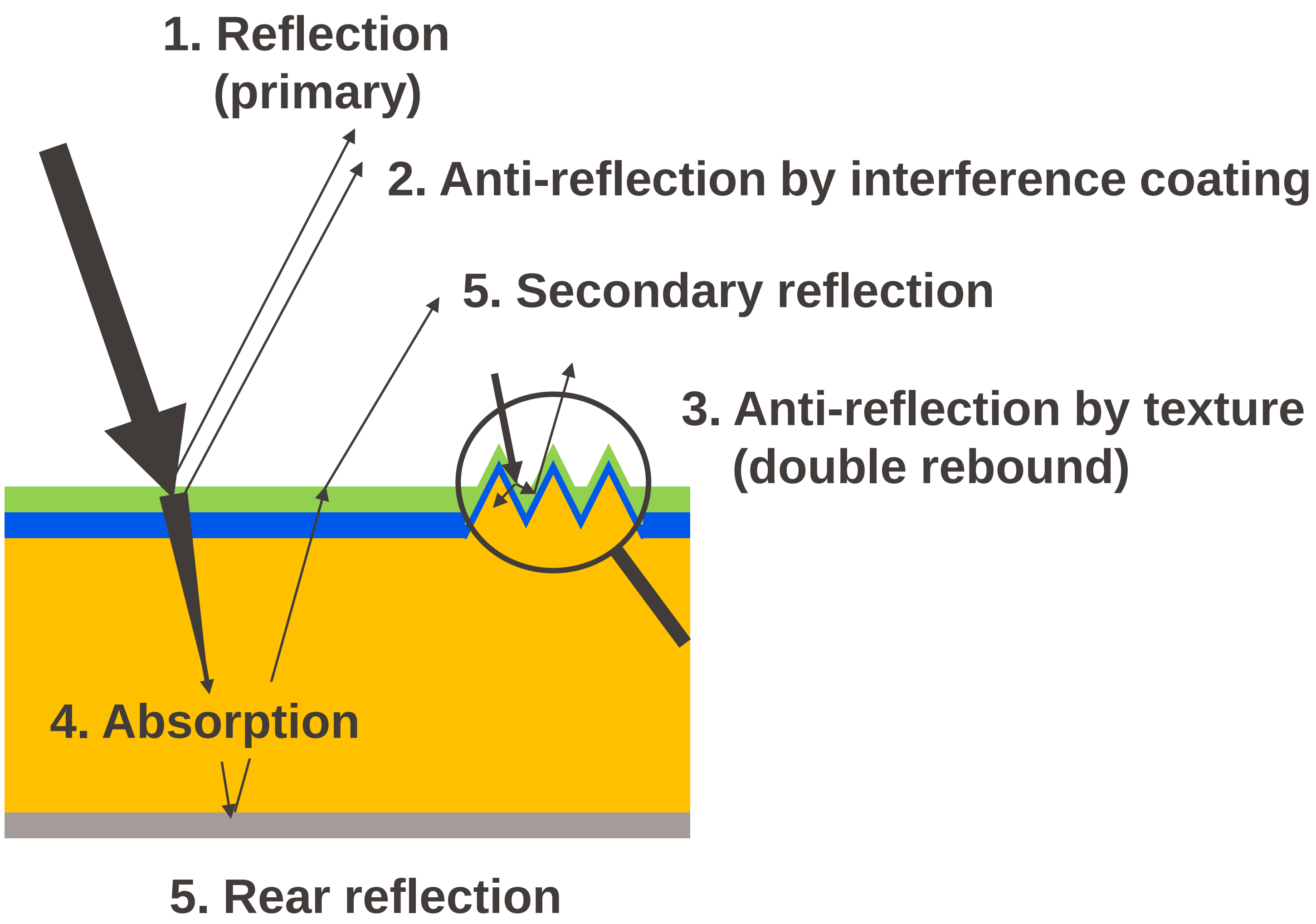
1. Optical properties of semiconductors & solar cells

2. Direct and indirect band gap

3. Generation profile

1. Optical properties of solar cells

Absorption



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1. Optical properties of solar cells

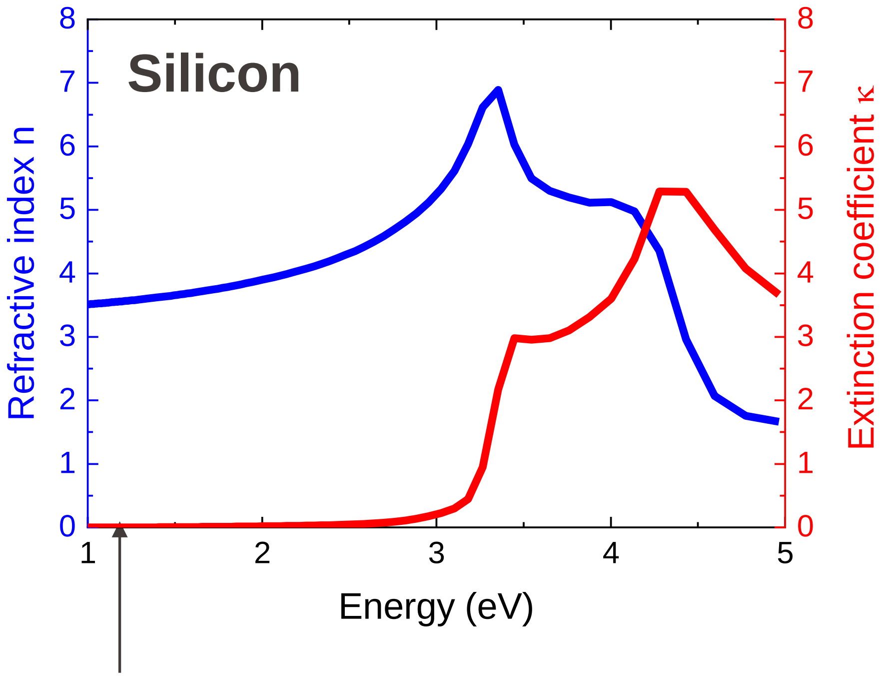
Refractive index

- The **refractive index** $\boldsymbol{n}$ governs properties at interfaces:
  - Reflection and transmission
  - Propagation angles (refraction)
  - Intensity and angular distribution of scattering

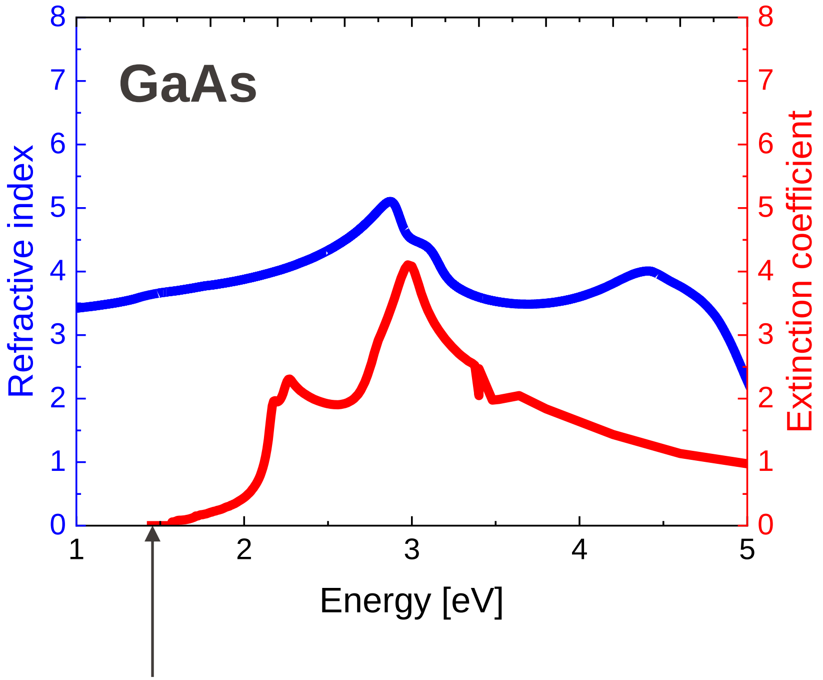
- The **extinction coefficient** $\boldsymbol{\kappa}$ (imaginary component of the refractive index)
  - Reflection and transmission (esp. metals for which $n \approx 0$)
  - Optical absorption (through its link to the absorption coefficient, α)

1. Optical properties of solar cells

Dispersion of n and κ



E_g =1.12 eV at 300°K



E_g=1.42 eV at 300°K

Semiconductors are characterized by :

- refractive index $n(E)$, with typically $n = 3 \ldots 5$ in the visible region
- extinction coefficient $\kappa(E) = 0$ below E_g

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1. Optical properties of solar cells

Permittivity and refractive index

Permittivity ϵ (sometimes dielectric function)

$$\epsilon = \epsilon_1 + i\epsilon_2 = (n + i\kappa)^2$$

- appears in Maxwell equations, more fundamental property
- ϵ_1 and ϵ_2 are not independent, causality relates them through Kramers-Kroenig relations

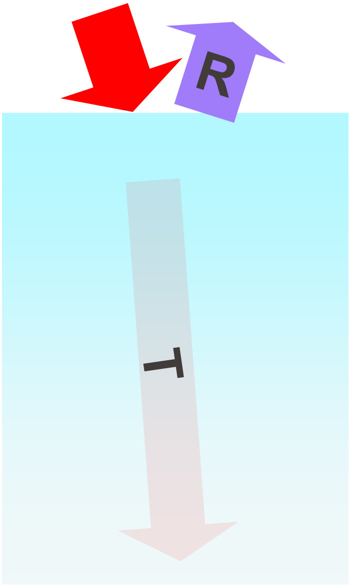
Inverse relations:

$$n = \sqrt{\frac{\epsilon_1 + \sqrt{\epsilon_1^2 + \epsilon_2^2}}{2}} \text{ and } \kappa = \sqrt{\frac{-\epsilon_1 + \sqrt{\epsilon_1^2 + \epsilon_2^2}}{2}}$$

1. Optical properties of solar cells

Fresnel reflection at an interface

$$R = \frac{(n_1 - n_2)^2 + \kappa_2^2}{(n_1 + n_2)^2 + \kappa_2^2}$$



Reflected beam **intensity**:

- for 0° incidence
- n_1 (transparent, e.g. air, glass, etc.)
- $n_2 + i\kappa_2$: absorbing film or metal

Example:

Air-Glass: $n_{air} = 1$, $n_{glass} = 1.5$, $\kappa = 0$ **=>** $R = 0.04 = 4\%$
Air-Silicon at 550 nm: $n_{Si} = 4.1$, $\kappa = 0.03$ **=>** $R = 0.37$
Encapsulation-Silicon at 550 nm: $n_{EVA} \approx 1.5$ **=>** $R = 0.21$

Note:

- For semiconductors κ is usually small, and plays mostly a role for absorption, but it hardly influences R.
- For metals κ is much higher ($\kappa \approx 3 \dots 5$) → high reflectivity.

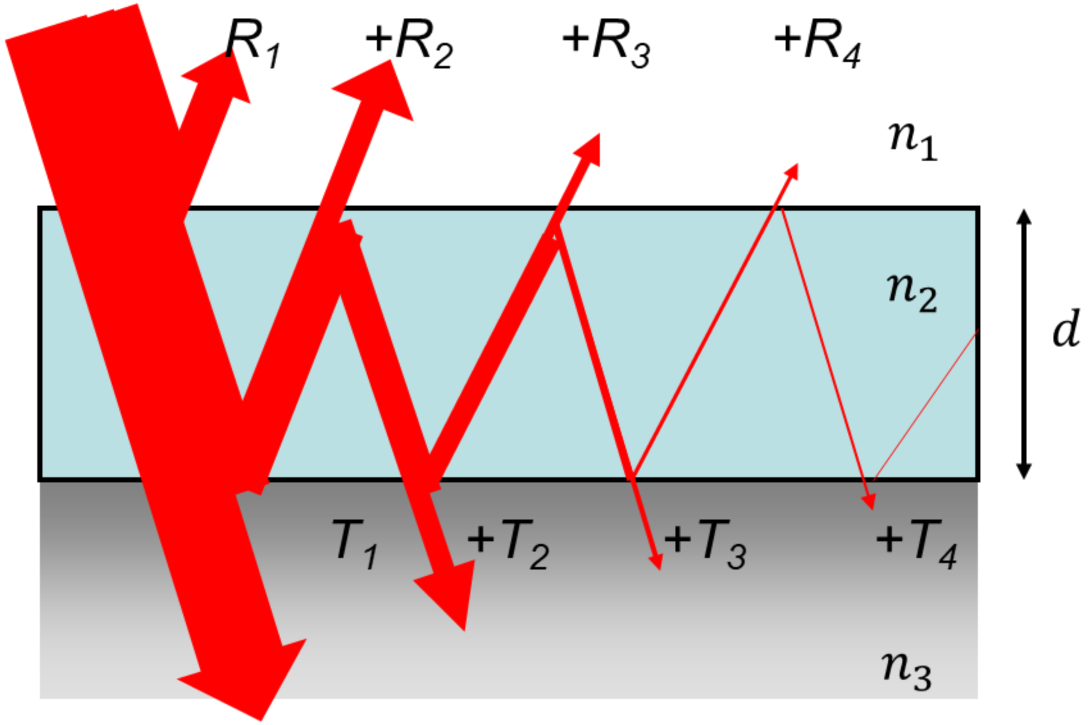
1. Optical properties of solar cells

illustration

Interference

For thin films: maintain coherency => wave optics

- At each interface the **wave** is partially reflected and transmitted
- Constructive or destructive interference yields maxima and minima in reflection and transmission



At each passage through the film, the wave changes its phase by a factor

$$\phi = kd = 2\pi/\lambda \cdot n_2 d$$

Note: the phase is shifted by an additional 180° if it transmits from a high to a low index material

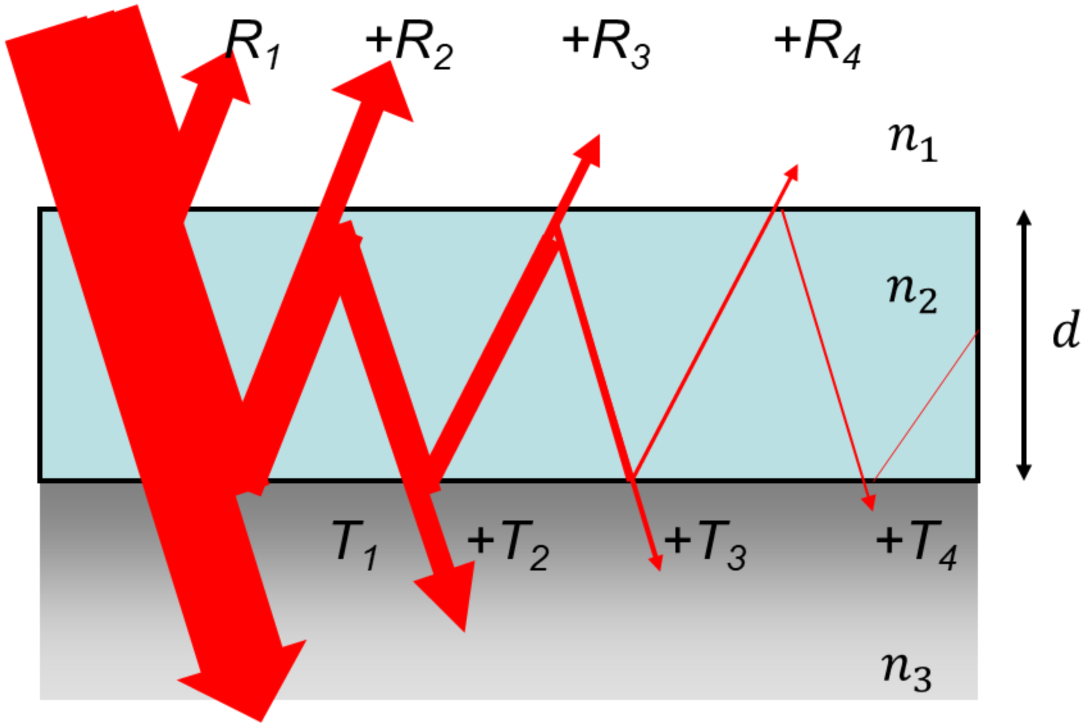
1. Optical properties of solar cells

Antireflection coatings

We request that all waves reflected from the second interface and escaping the sample are at 180° (π out of phase) with the primary reflection

$$\phi = 2 \times 2\pi n_2 d/\lambda \overset{!}{=} m \cdot \pi$$

m : odd number



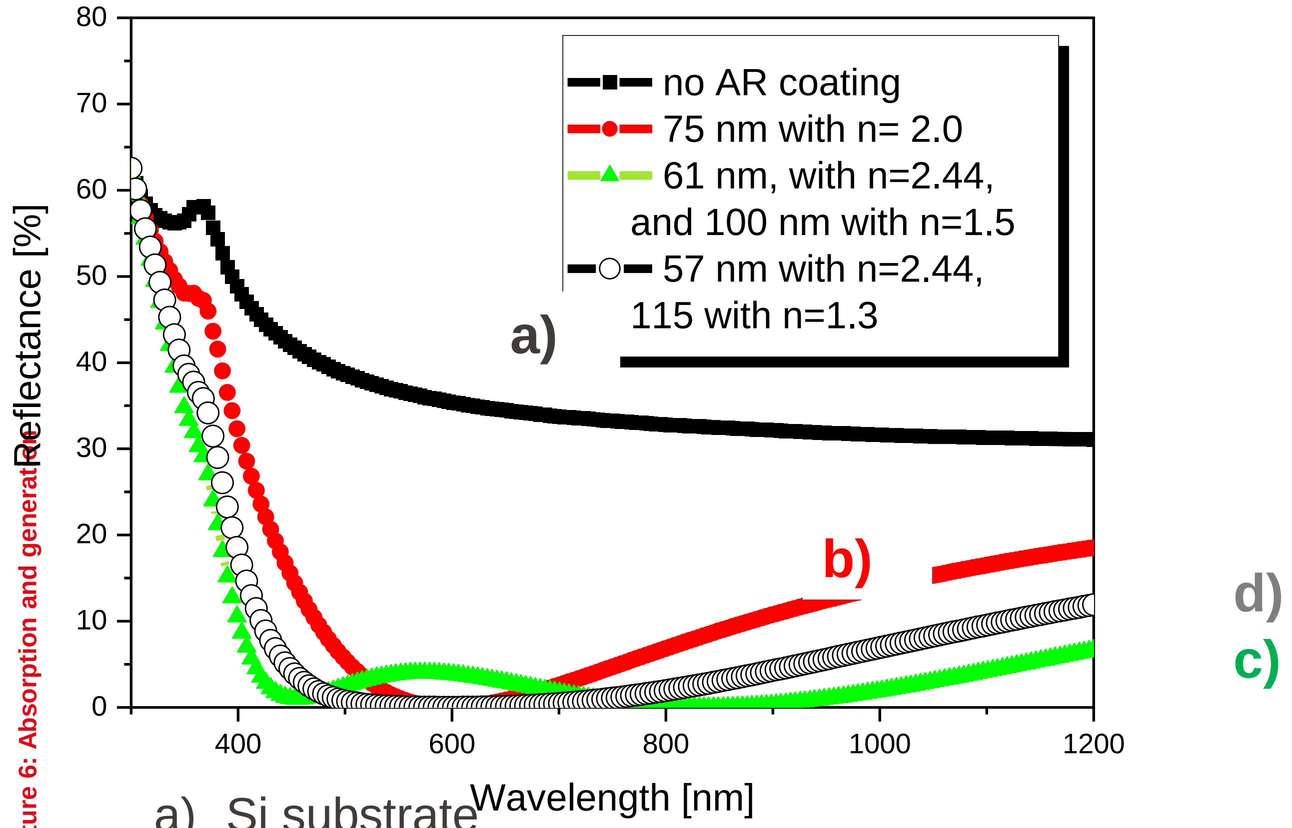
→ *first AR maximum for*

$$n_2 d = \lambda/4$$

(quarter wavelength layer)

1. Optical properties of solar cells

Example of antireflection coatings



a) Si substrate
b) AR layer (λ/4)
c) Double layer AR, λ/4
d) Double layer AR, geometric mean

Si (n~3.5-4)

$R \approx 30 \dots 40\%$

$n_{AR} = \sqrt{n_{air} \cdot n_{Si}}$
minimum at
$\lambda = 4n_{AR} \cdot w_{AR}$ (w_{AR}: thickness)

In practice:
SiNx (70 nm), n=2…2.2
Glass cover n=1.5
(reflection diminished by the texture)

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1. Optical properties of solar cells

Antireflection coatings

In addition to the quarter wavelength conditions, zero reflection can be achieved at one wavelength if

$$n_2 = \sqrt{n_1 \cdot n_3}$$

geometric mean

Typical materials used as AR layers:

MgF_2, n=1.38
SiO_2, n=1.52
ZrO_2, n=2.1
TiO_2, n=2.2
CeF_3, n=1.63

Solar cells:
SiN_X, n=2-2.2
Al_2O_3 n=1.67

Derivation in exercise later today

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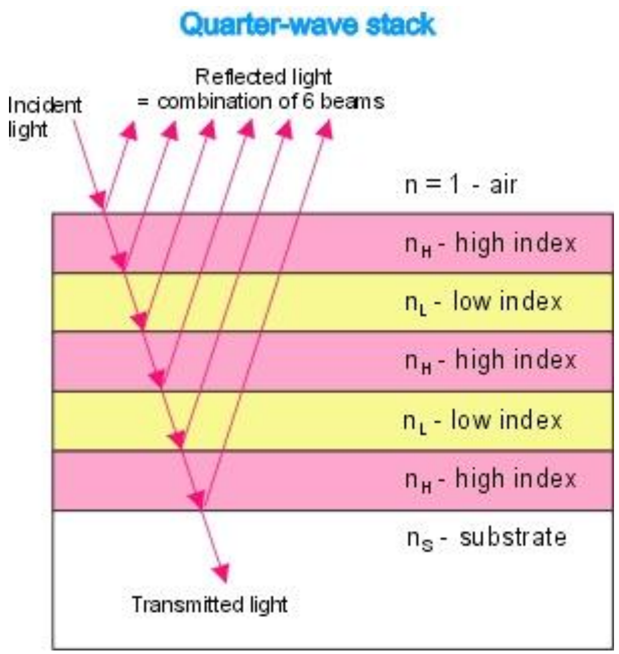
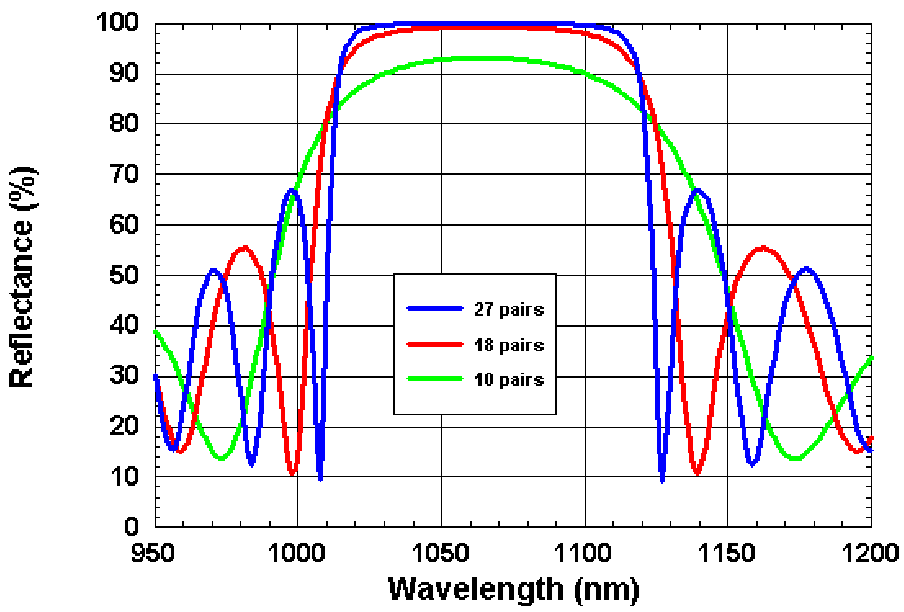
1. Discourse: “super-reflectors” = Bragg mirrors

Multi-layer stacks

→ broadband mirrors with high reflectance: alternating high and low index materials, with quarter layer stacks

→ additional phase shift of 180° → constructive interferences in reflection





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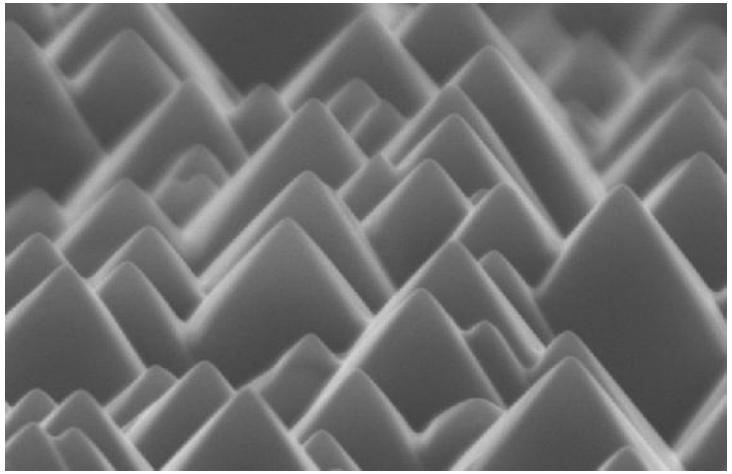
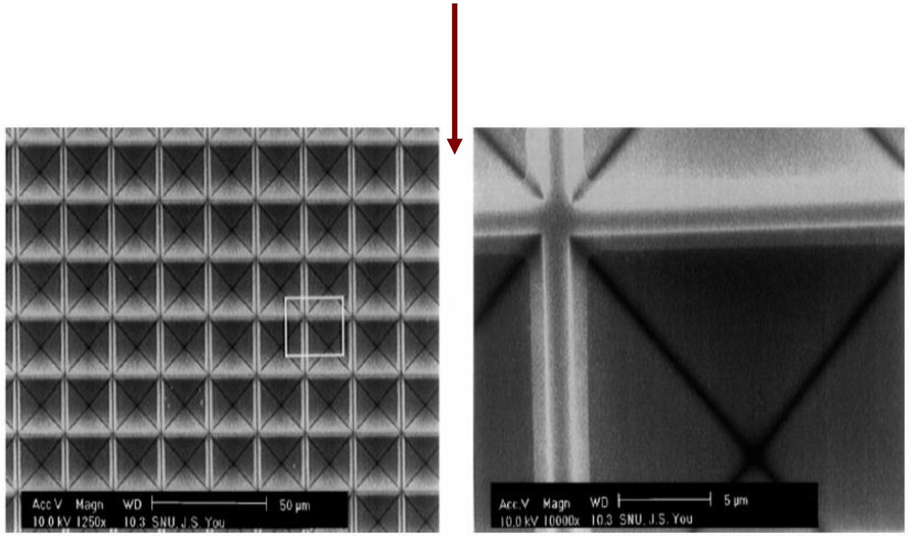
Reduction of reflection by texture

Surface texturing

Monocrystalline Si:

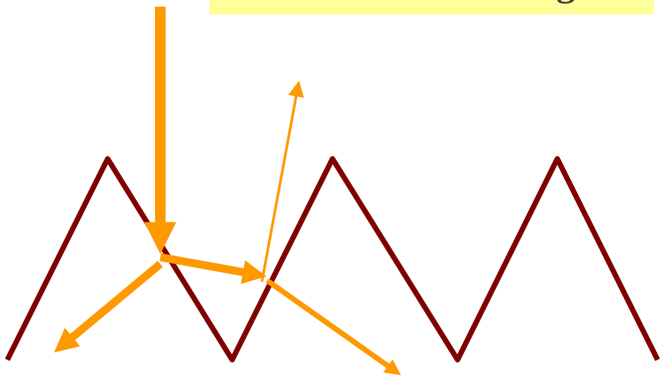
- “random pyramids” (111) (easy for mass production)
- inverted pyramids (requires masking)





Reflection:

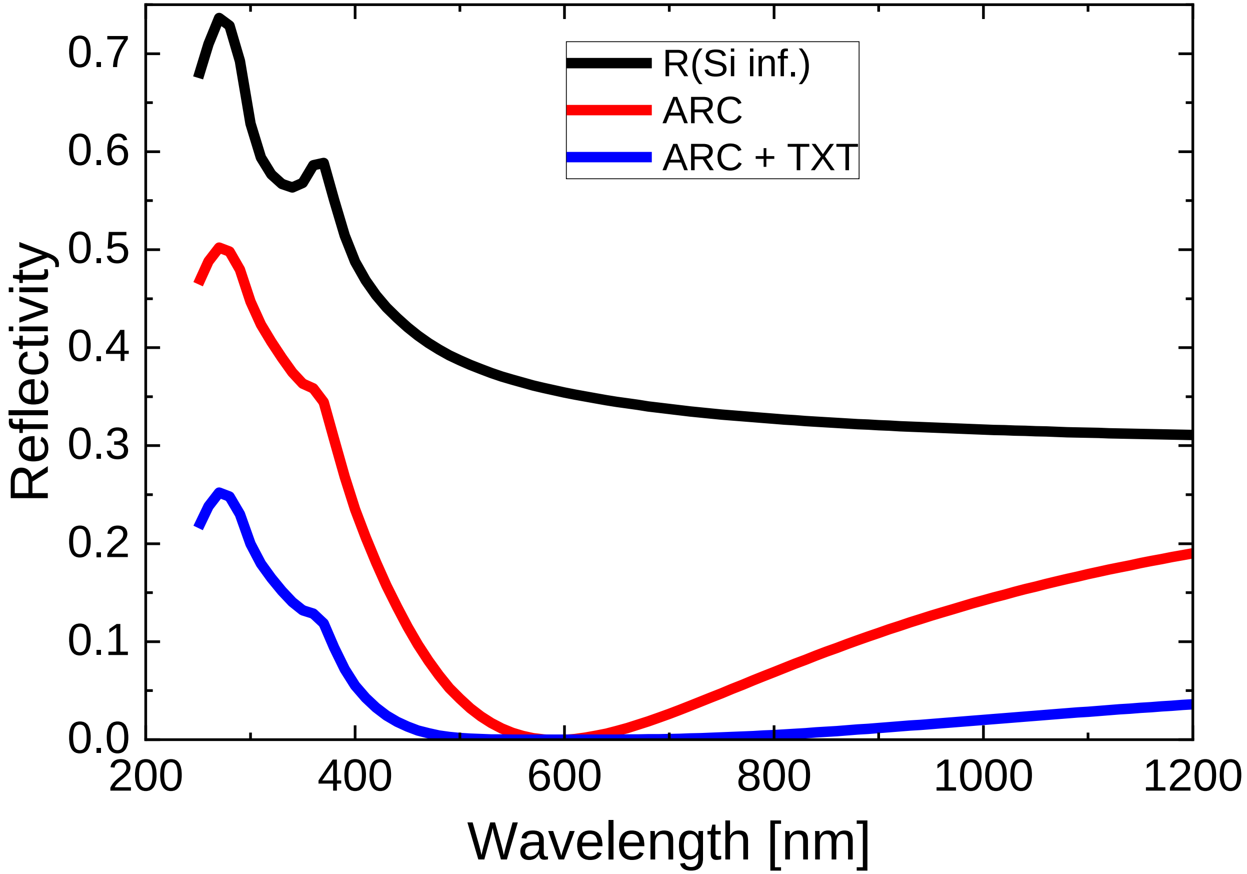
$R_{double} \approx R_{single}^2$



1. Optical properties of solar cells

Exercise

Reduction of reflection by texture



- Low reflection with «random pyramids»
- Blue and IR signals can decrease after embedding

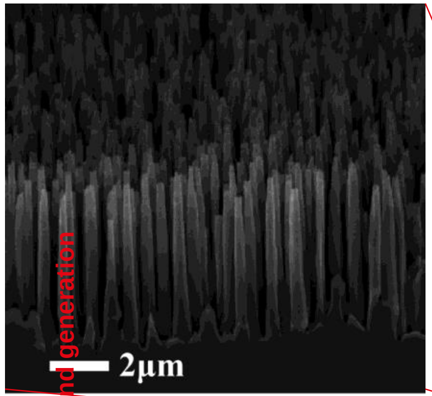
- Pyramids can be used in PC1D (texture)
- Texture influences J_0 (depending on size and shape) and optical path but not primary reflection

1. Optical properties of solar cells

Reduction of reflection by texture

Better surface texturing

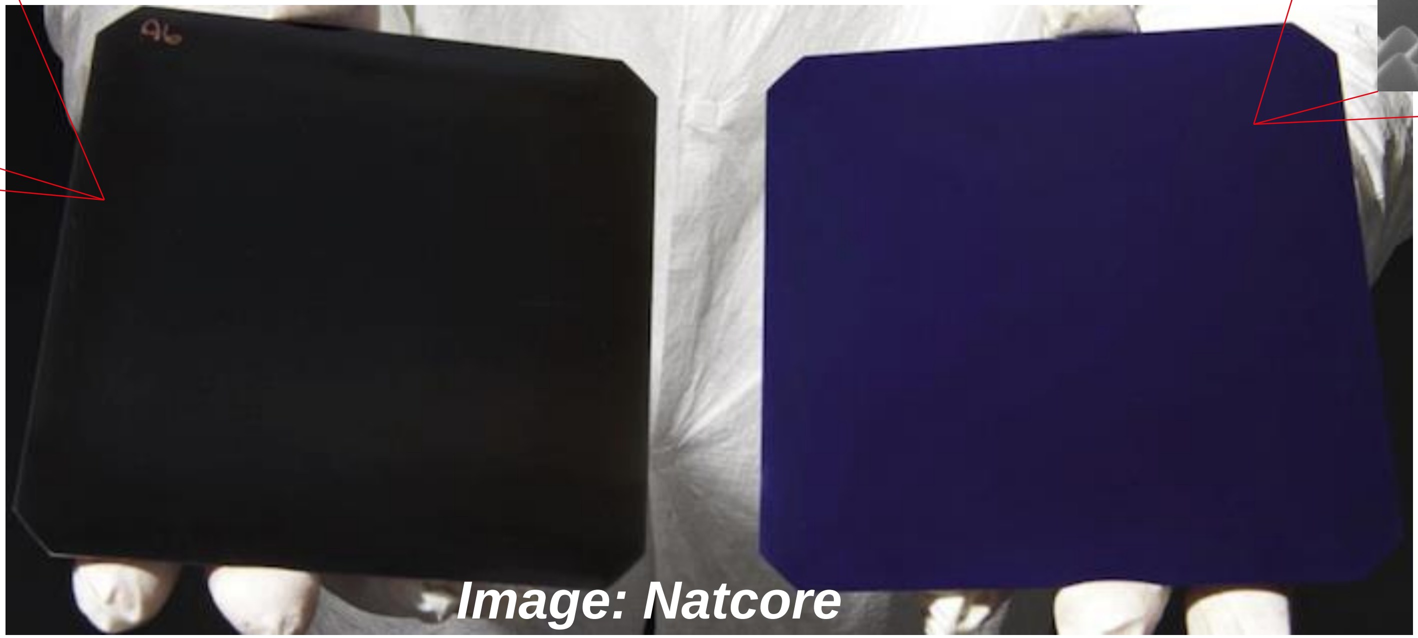
“double” bounce => multi-bounce

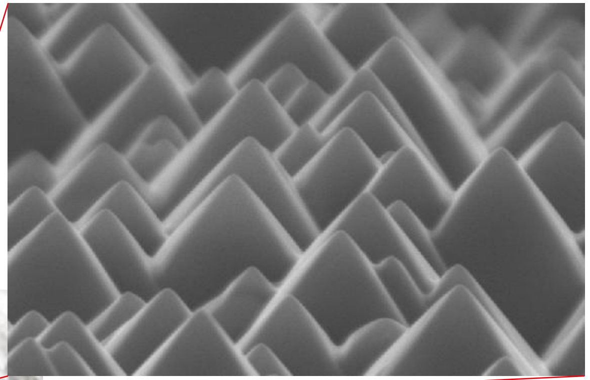


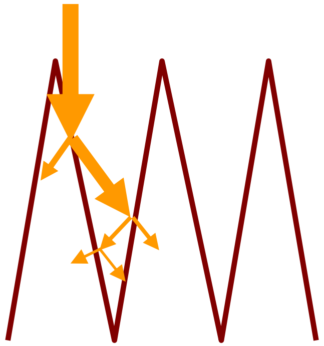
DOI: (10.1021/acsomega.1c06435)

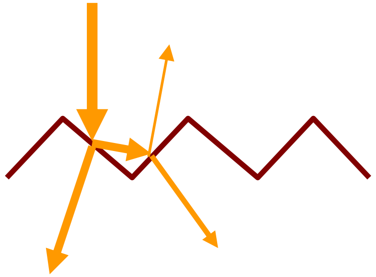
Reflection upon multiple bounces:

$R_{tot} \approx R^n \rightarrow 0$





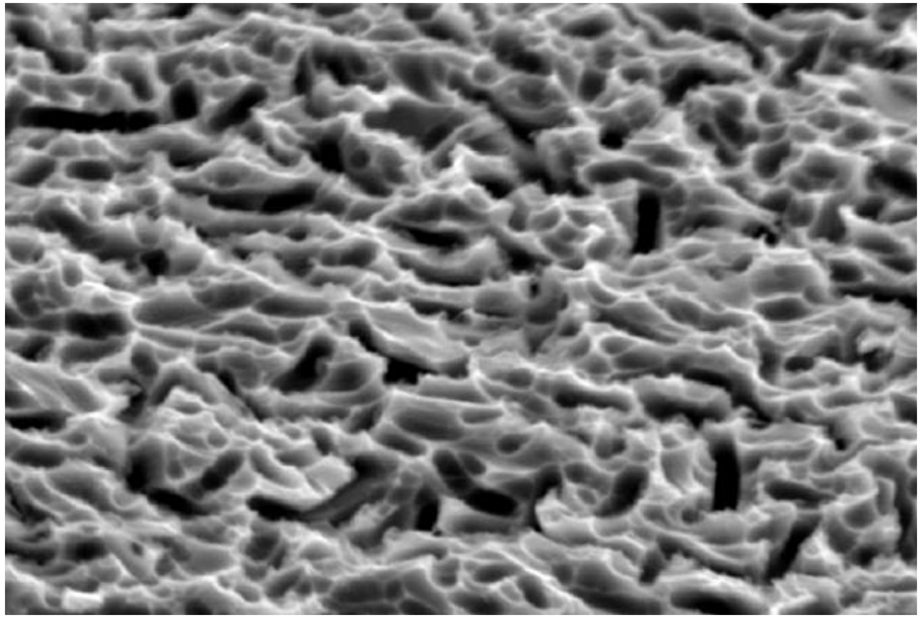


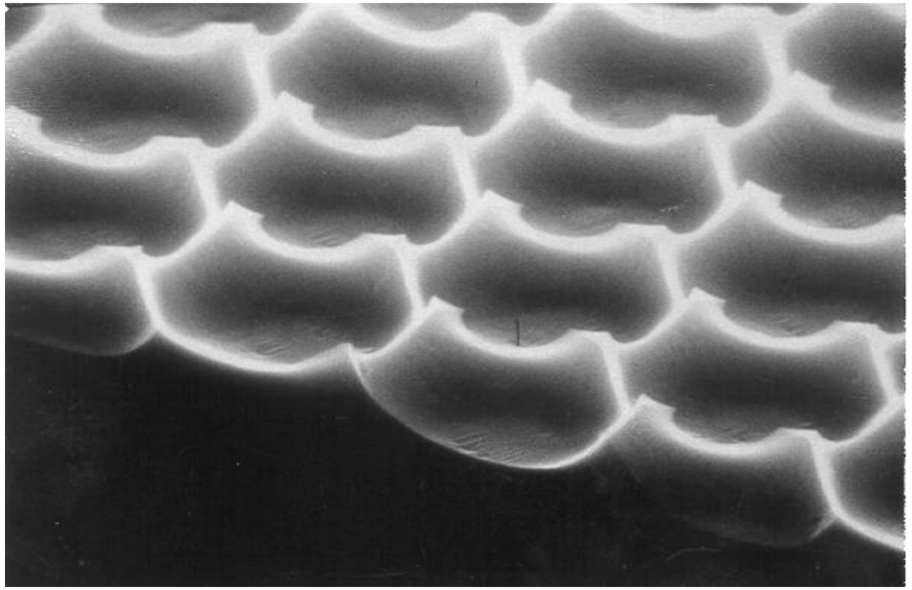


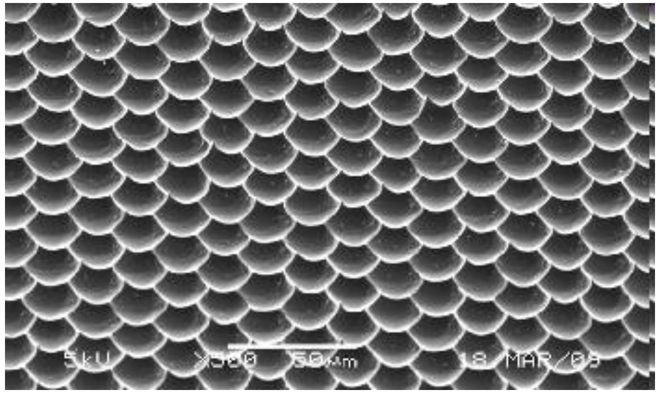
1. Optical properties of solar cells

Reduction of reflection by texture

Other neat structures



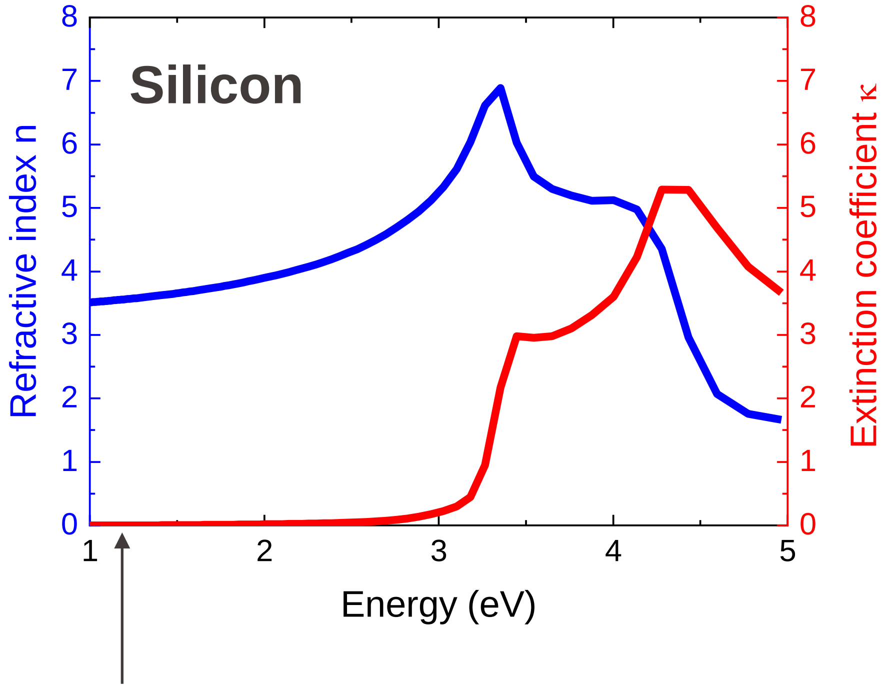


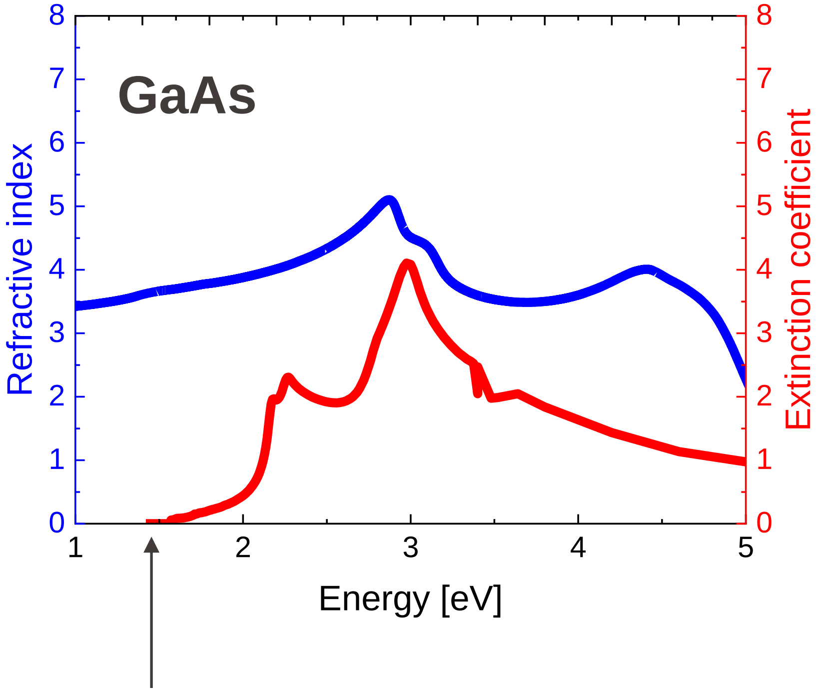


«honeycomb» structure for mc-Si (see e.g. www.1366tech.com)

1. Optical properties of solar cells

Dispersion of n and κ





E_g =1.12 eV at 300°K

E_g=1.42 eV at 300°K

Important for absorption:
Detailed behaviour close to bandgap ? ($\kappa = 0 \dots 1$)

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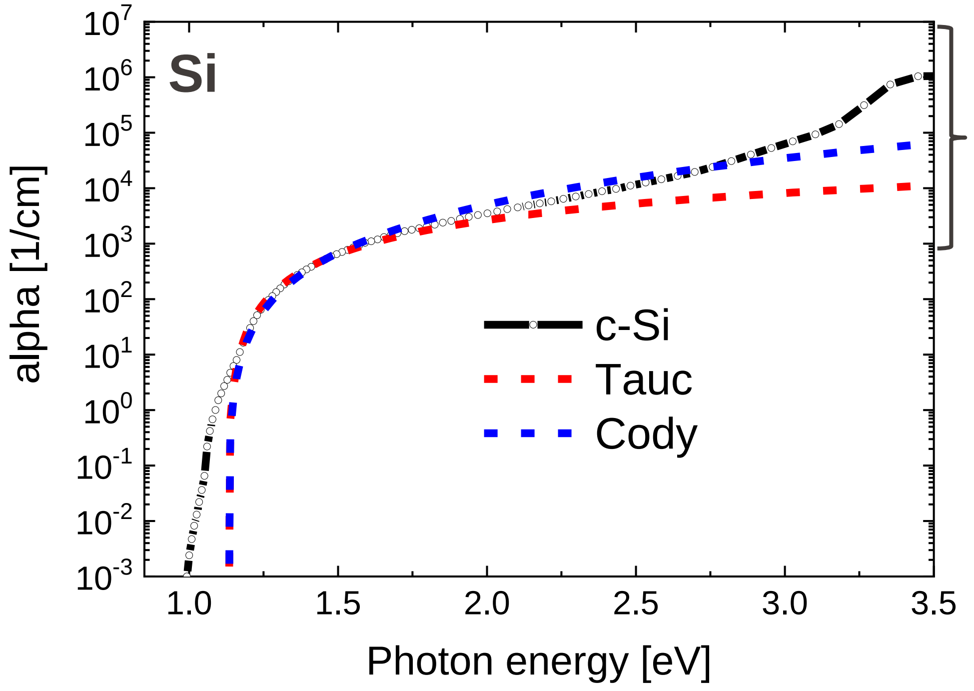
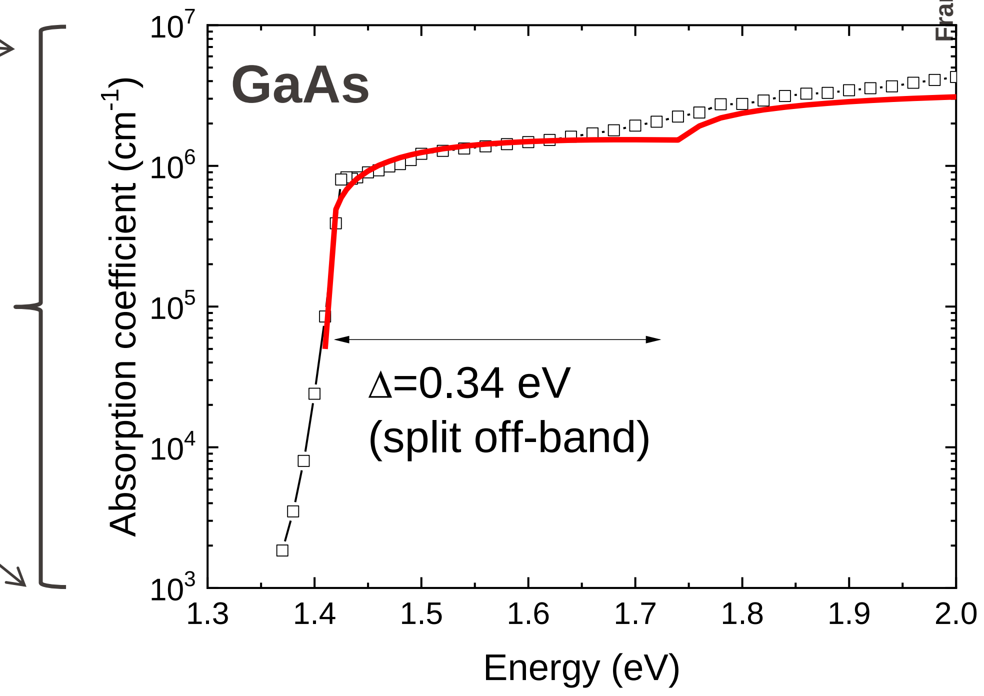
1. Optical properties of solar cells

Absorption coefficient





Note difference in scale:
GaAs $\approx 10^6\ \mathrm{cm}^{-1}$**, sharp edge**
Si $\approx 10^3 \ldots 10^4\ \mathrm{cm}^{-1}$**, round**

In c-Si some absorption still takes place below the bandgap

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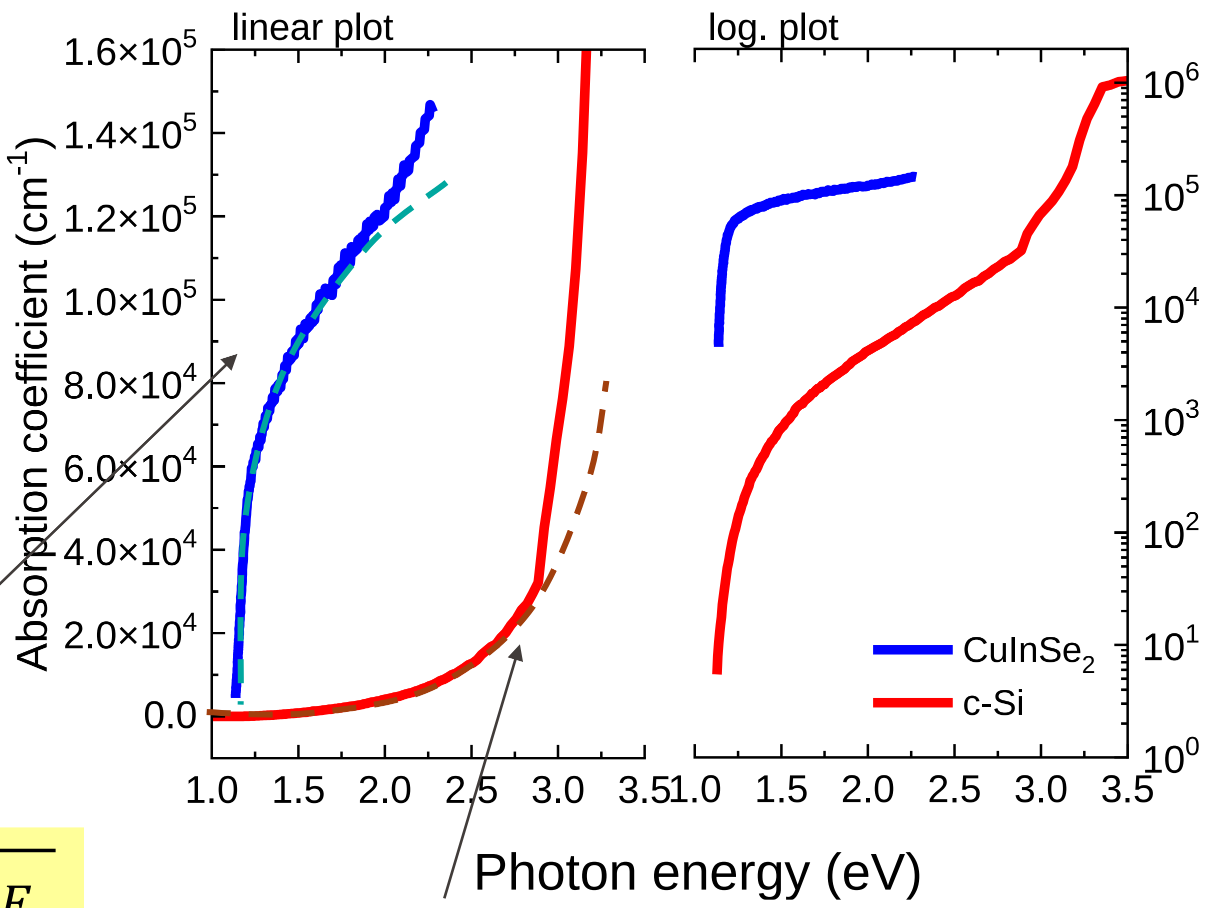
2. Direct and indirect bandgap

Summarized



$$\alpha_{dir} \sim \sqrt{h\nu - E_g}$$

$$\alpha_{ind} \sim \left(h\nu - E_g\right)^2$$

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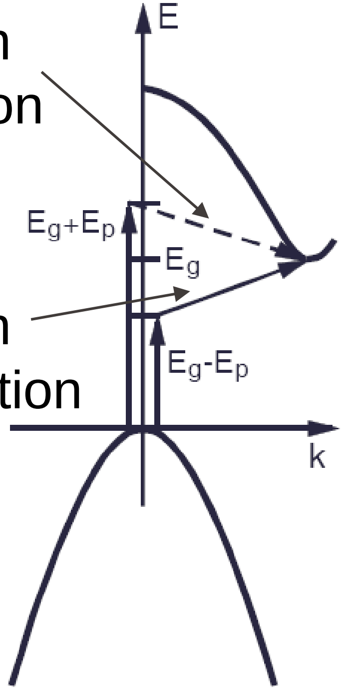
2. Reminder: Direct and indirect bandgap

Indirect band gap SC

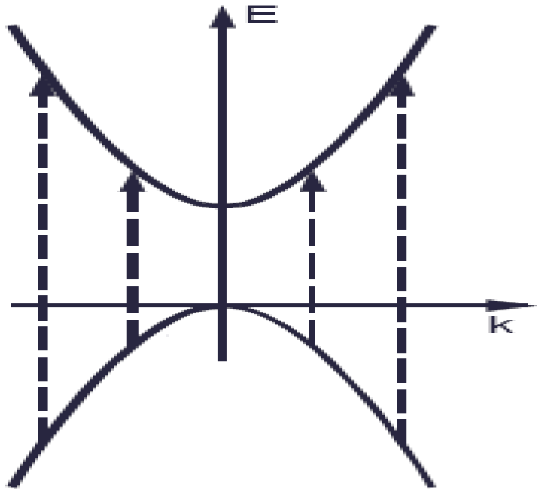


In addition to the absorption of a **photon**, a **phonon** with energy E_p must either be emitted or absorbed.

$$\alpha_{ind} \sim (h\nu - E_g)^2 \quad (5.7)$$

c-Si, Ge, μc-Si

Direct band gap SC



For an exactly parabolic band

$$\alpha_{dir} \sim \sqrt{h\nu - E_g} \quad (5.8)$$

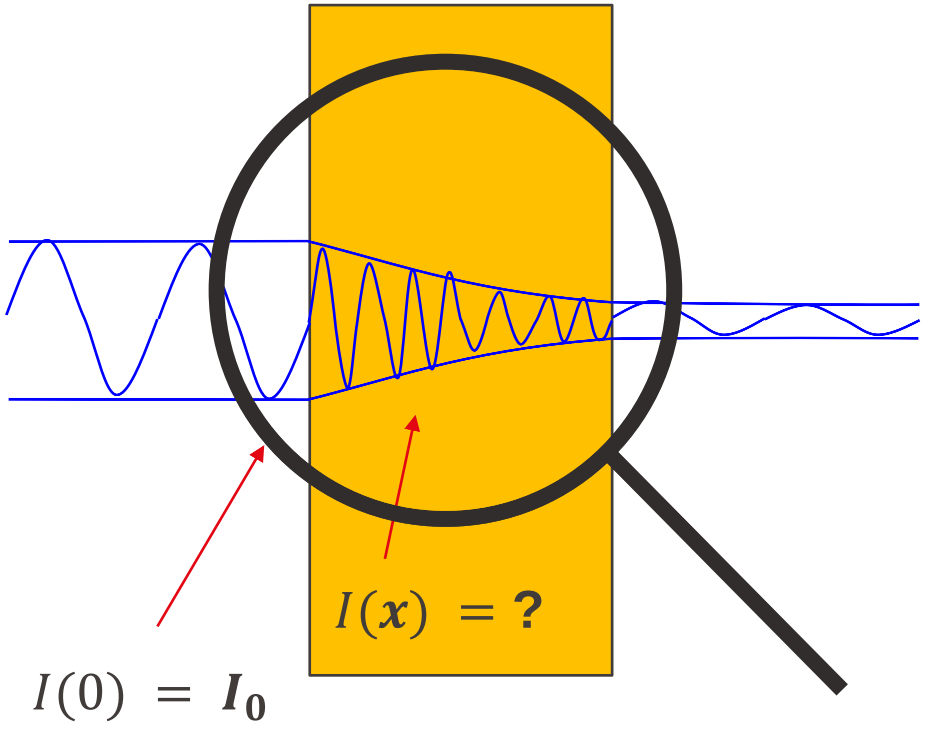
GaAs, CdTe, CIGS, InP

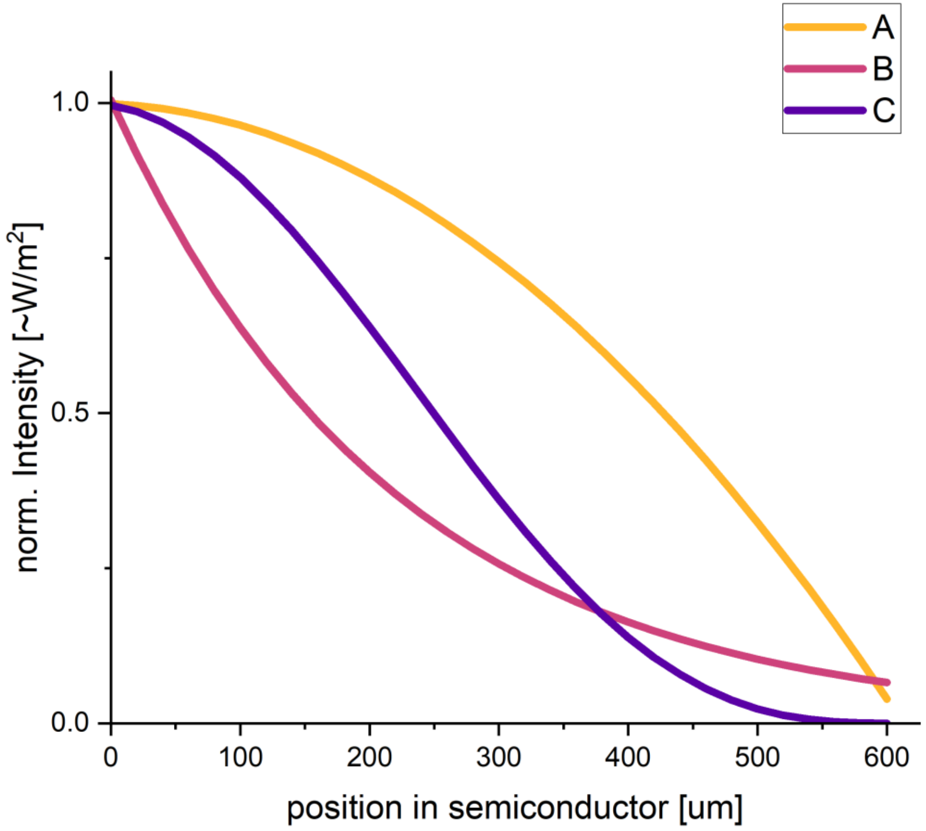
2. Optical properties of solar cells

Absorption

What is the absorption profile in a semiconductor for one wavelength?

Rephrase and ask: What is the light intensity profile ? Three examples, which represents reality?





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2. Optical properties of solar cells

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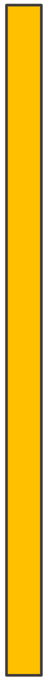

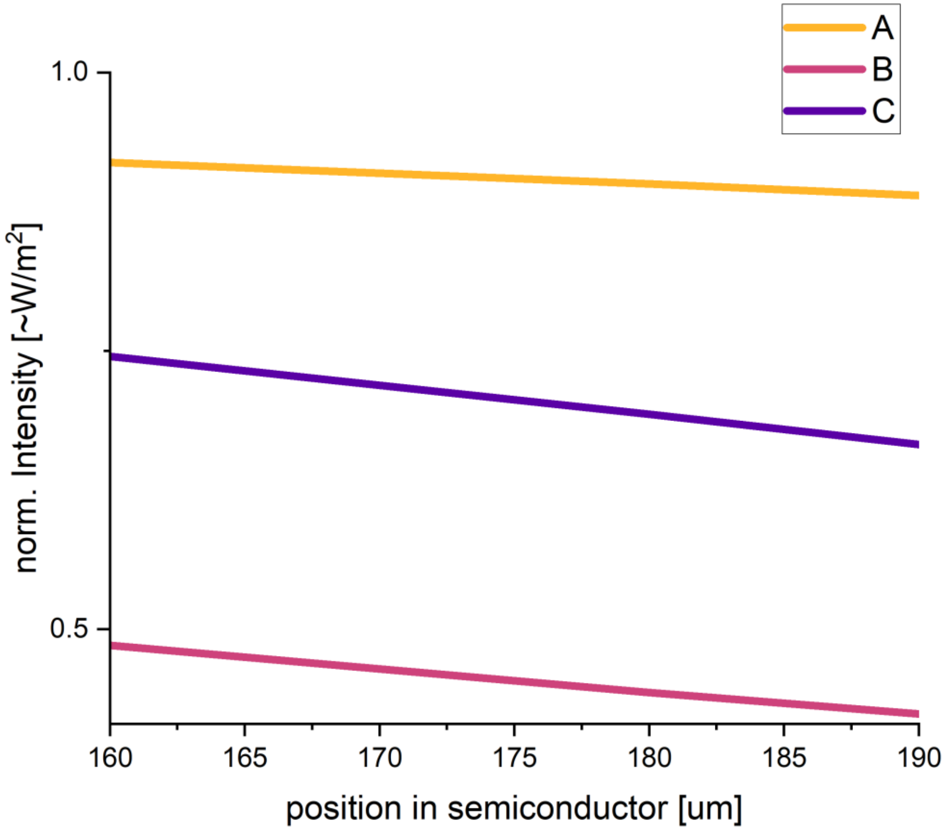

Within a narrow part the intensity decreases linearly, or at least that's a good local estimate.

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2. Optical properties of solar cells

Absorption

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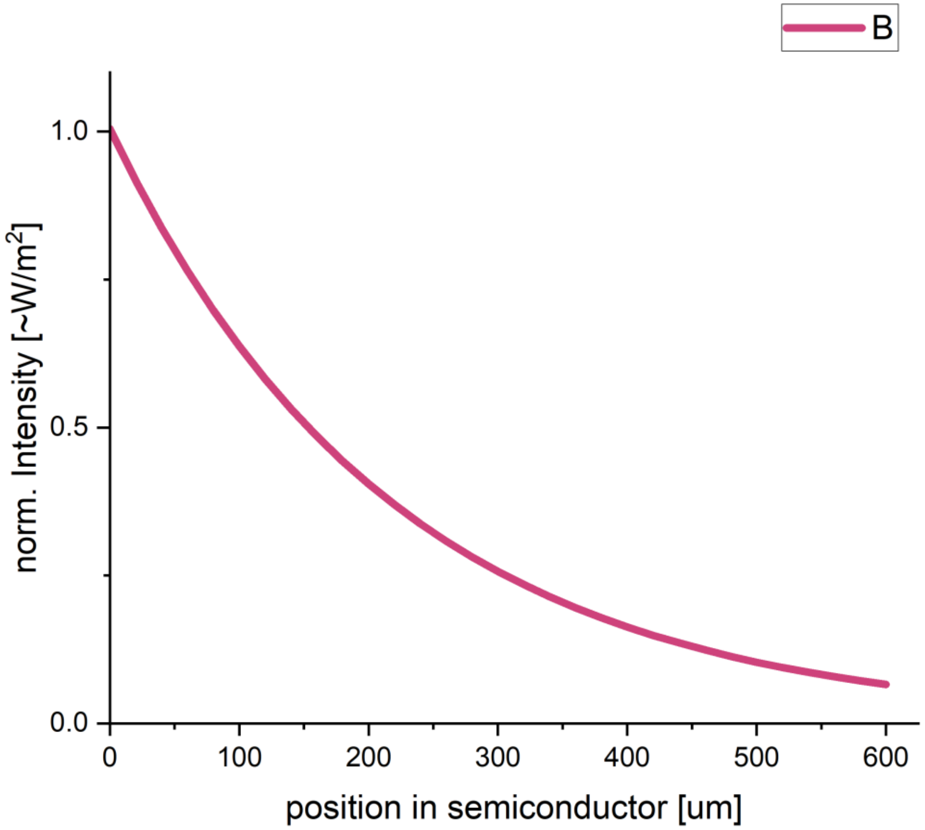


$$I(x+\Delta x) = I(x) - I(x) \cdot \alpha \cdot \Delta x$$

$$I(x+\Delta x) - I(x) = -I(x) \cdot \alpha \cdot \Delta x$$

$$\lim_{\Delta x \to 0} \frac{I(x+\Delta x) - I(x)}{\Delta x} = -\alpha \cdot I(x)$$

$$\frac{dI(x)}{dx} = -\alpha \cdot I(x)$$

$$I(x) = I_0 \cdot e^{-\alpha \cdot x}$$

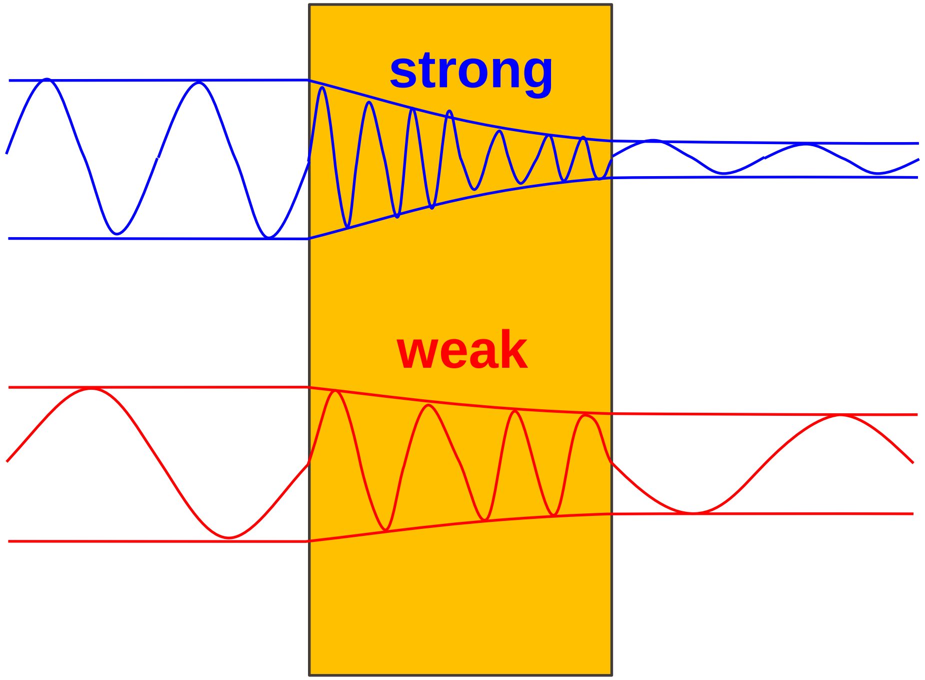
2. Optical properties of solar cells

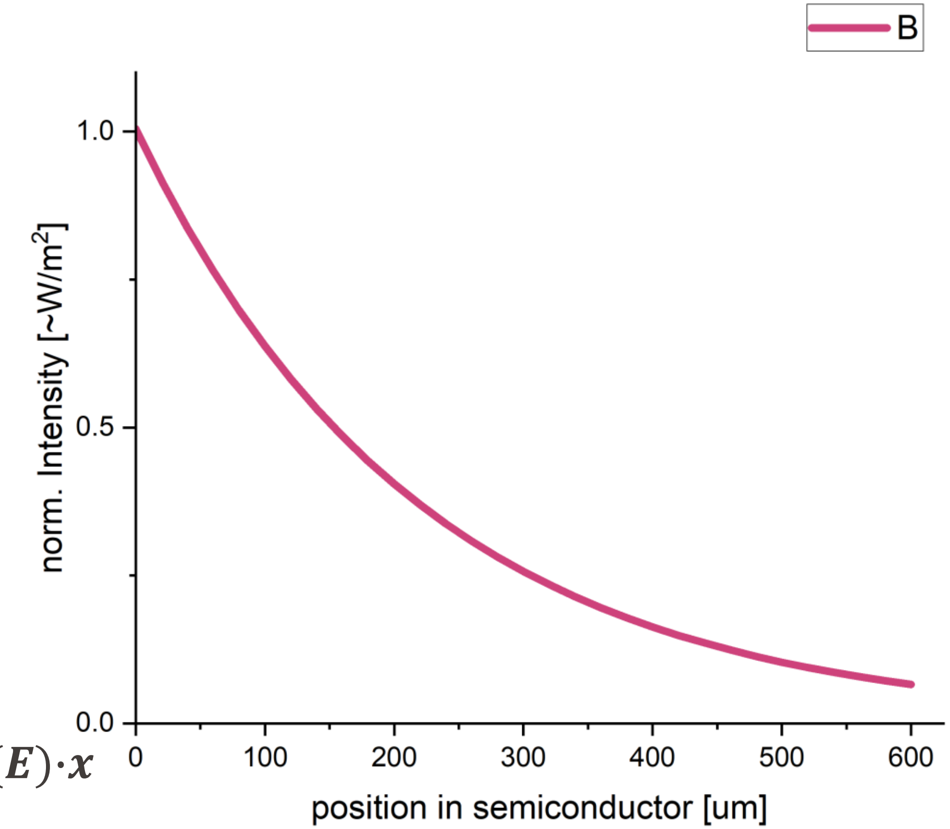
Exercise

Absorption

What is the absorption profile in a semiconductor for one wavelength?

Rephrase and ask: What is the light intensity profile ?





Beer-Lambert-Bouguer law: $I(E, x) = I_0(E) \cdot e^{-\alpha(E) \cdot x}$

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2. Optical properties of solar cells

Absorption and relation to $n + i\kappa$

The extinction coefficient κ => intensity decay of propagating waves

$$\vec{E}(x,t) = \vec{E}_0 \exp\{i(\underbrace{(n+i\kappa)k_0}_{\text{Reduced wavevector } k} x + \omega t)\} = \vec{E}_0 \exp\left\{-\frac{2\pi\kappa}{\lambda}\right\} \exp\{i(nk_0 x + \omega t)\}$$

=> Exponential decay of the «time averaged» intensity (law of Lamber-Beer-Bougouer)

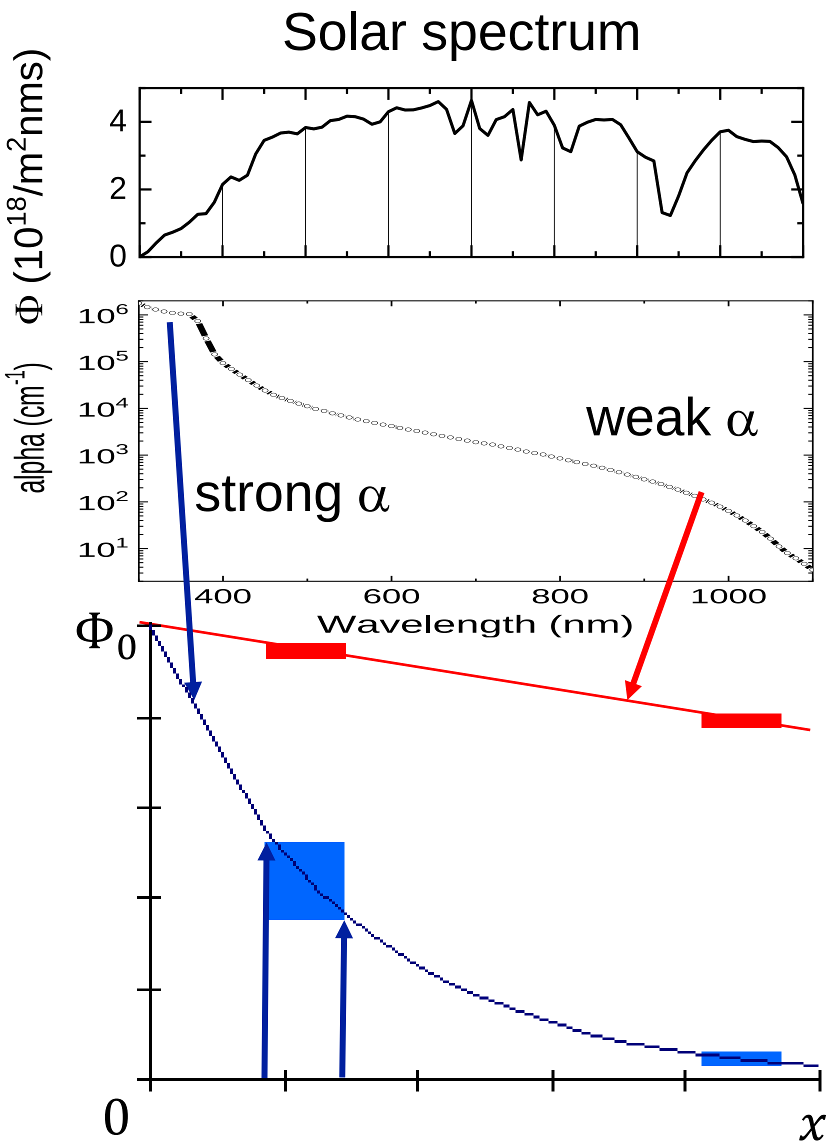
$$I(x) \sim \frac{\left|\vec{E}\right|^2}{2} = \left|\vec{E}_0\right|^2 \exp\left\{-\frac{4\pi\kappa}{\lambda} x\right\}$$

Relation between the absorption coefficient α [cm^{-1}] and κ

$$\alpha = 4\pi \cdot \kappa / \lambda$$

3. Generation profile

Generation rate



$\Phi_0(\lambda)$: photon flux density entering at surface $[\mathrm{cm}^{-2}\mathrm{nm}^{-1}\mathrm{s}^{-1}]$
exp. decay into wafer with $\alpha(\lambda)$

Define spectral generation rate

$$G(\lambda, x) = -\frac{d\Phi}{dx} = \alpha\Phi_0(\lambda)e^{-\alpha(\lambda)x}$$

blue: strong decay
- high G at front
- low G at front

red: weak decay
=> low but uniform G throughout Si

3. Generation profile

Exercise

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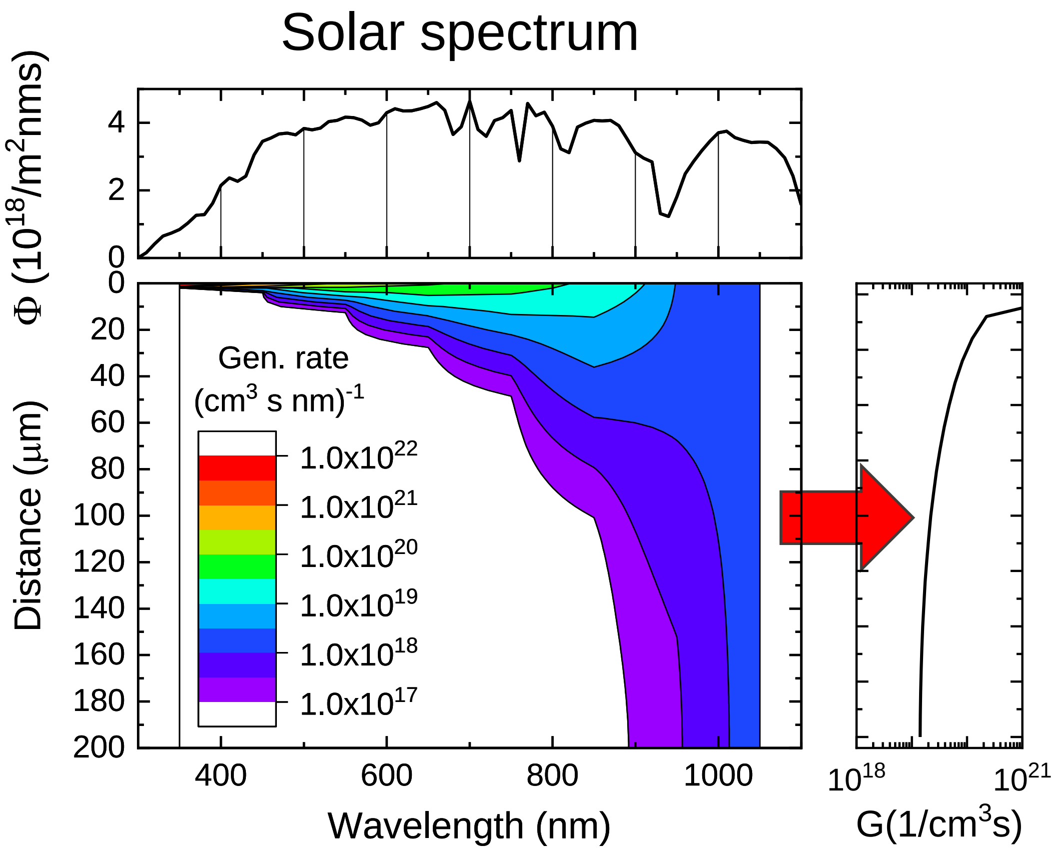
Generation rate



Spectral generation rate

$$G(\lambda, x) = -\frac{d\Phi}{dx} = \alpha\Phi_0(\lambda)e^{-\alpha(\lambda)x}$$

For generation rate of electron-hole pairs:

- drop photon energy
- integrate only their number

$$G(x) = \int_{300}^{1200} G(\lambda, x)\, d\lambda$$

Examples for solar irradiation on earth ("one sun"):

c-Si, $d_{wafer} = 200$ µm, $R_{front} = 0$, $R_{rear} = 0.9$: $\langle G \rangle \approx 10^{19}\ \mathrm{cm}^{-3}\mathrm{s}^{-1}$ for most of bulk

Perovskite, $d_{thin-film} = 500\ nm$, $R_{front} = 0$, $R_{rear} = 0.9$: $\langle G \rangle \approx 2 * 10^{21}\ \mathrm{cm}^{-3}\mathrm{s}^{-1}$ for most of bulk

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Takeaways

- Materials have a real and an imaginary part of dielectric constant $\boldsymbol{\epsilon(h\nu) = \epsilon_1(h\nu) + i\epsilon_2(h\nu)}$ and corresponding refractive index $\boldsymbol{n}$ and extinction coefficient $\boldsymbol{\kappa}$ (typical values: air, glass, semiconductor, metal)

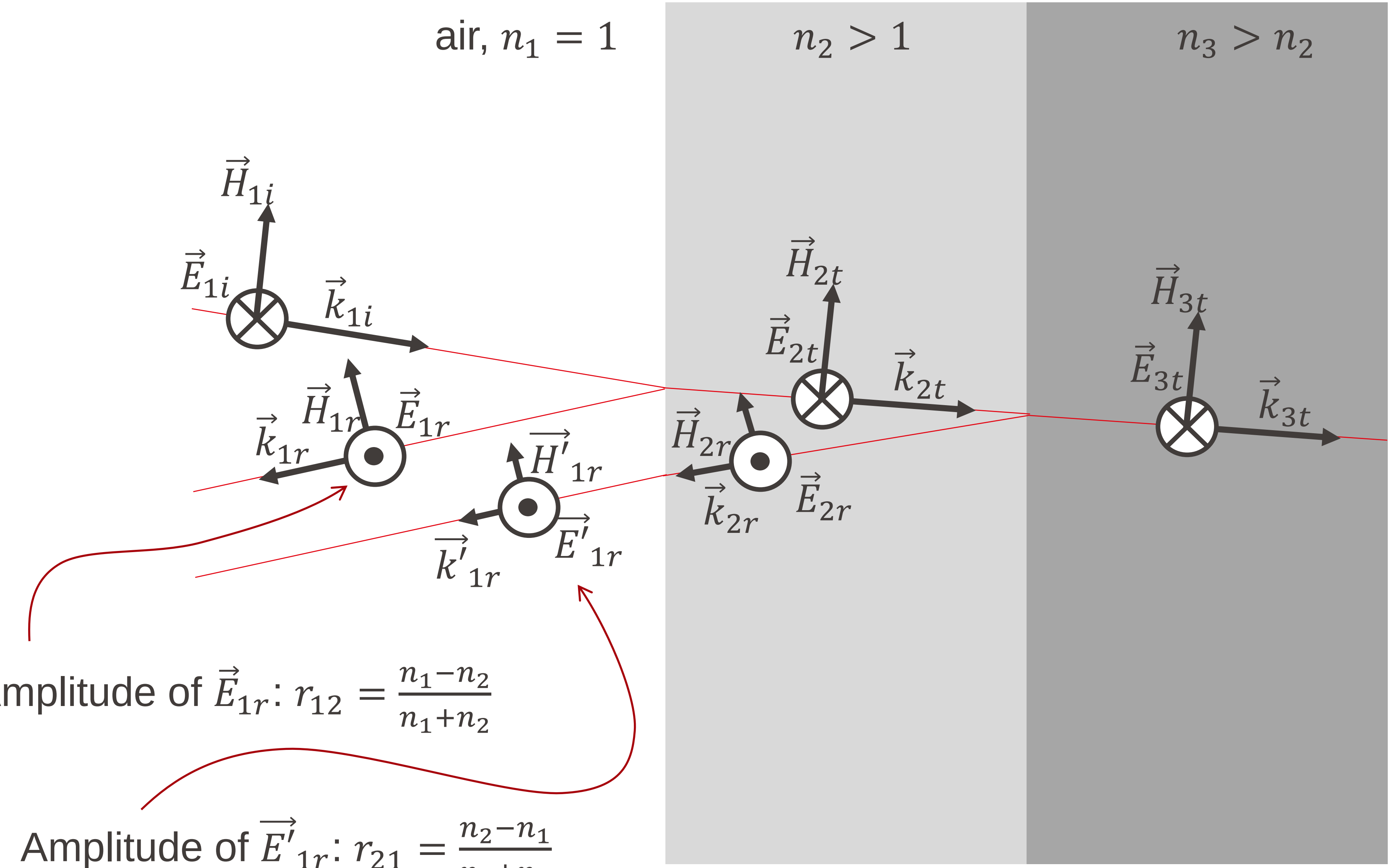
- Reflection at interfaces is determined primarily by the difference $||\boldsymbol{n_1} - \boldsymbol{n_2}||$ between two materials, but with texturization and/or anti-reflection layers with tailored thickness we can minimize reflection ($\lambda/4$ rule, geometric mean)

- direct and indirect bandgap semiconductors have different absorption onsets (what's the energetic line shape? – square vs. quadratic!)

- Absorption of light is effectively dictated by $\boldsymbol{\kappa} = \alpha \cdot \frac{\lambda}{4\,\pi}$ (rembember orders of magnitude for α for direct / indirect bandgap, including units!)

- Beer-Lambert-Bouguer law and intensity-profile (=> implications for generation profile and typically obtained **average** order of magnitude $10^{19}\ \mathrm{cm}^{-3}\mathrm{s}^{-1}$ - $10^{21}\ \mathrm{cm}^{-3}\mathrm{s}^{-1}$, for indirect / direct semiconductors, resp.)

Illustration of phase shift



Amplitude of $\vec{E}_{1r}$: $r_{12} = \frac{n_1 - n_2}{n_1 + n_2}$

Amplitude of $\vec{E'}_{1r}$: $r_{21} = \frac{n_2 - n_1}{n_2 + n_1}$

Lecture Exercise 1

How many bounces are enough?

For a material that has a reflection of 20%, how many bounces do you need to ensure >99% absorption?

$$P_{abs} > 99\%$$

$$1 - (P_{ref.})^n > 99\%$$

$$\mathrm{n} > 3$$

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Lecture Exercise 2

Absorption in first few µm

A light source delivers $I_0 = 1200\ \frac{W}{m^2}$ at $\lambda = 496nm$ (E=2.5eV) to a slab of material. Its absorption coefficient is $\alpha(496nm) = 10^4\ cm^{-1}$. How much energy is absorbed in the first 5 µm; ignore reflection?

$$\text{Abs. energy-dens.} = I_0 - I(x) = 1200\ \frac{W}{m^2}\left(1 - e^{-\frac{1}{\mu m}5\mu m}\right) \approx 1200\ \frac{W}{m^2}$$

So practically all light (99%≈100%) at this wavelength is absorbed within the first few µm.
Now: how much energy is absorbed on average within the first 5 µm? express this in units of $\frac{W}{cm^3}$

$\frac{\left(1200\frac{W}{m^2}\right)}{5\mu m} = 240\ \frac{W}{cm^3}$. how many photons have been absorbed per second on average?

Tip: $\mathrm{E_{photon}} = \frac{hc}{\lambda} = 4 \cdot 10^{-19}\ J$

$$\langle G \rangle_{5\ \mu m,\ \lambda = 496\ nm} = \frac{240\frac{W}{cm^3}}{\frac{hc}{\lambda}} \approx 6 \cdot 10^{20}\ \frac{1}{cm^3\ s}$$

average generation rate of blue light in first 5 µm

EPFL PV-lab IEM NEUCHATEL

Lecture Exercise 3

Franz-Josef Haug

What's the generated current?

Examples for solar irradiation on earth ("one sun"):

c-Si, $d_{wafer} = 200\ \mu m$, $R_{front} = 0$, $R_{rear} = 0.9$: $\langle G \rangle \approx 10^{19}\ cm^{-3}s^{-1}$ for most of bulk
Perovskite, $d_{thin-film} = 500\ nm$, $R_{front} = 0$, $R_{rear} = 0.9$: $\langle G \rangle \approx 2\ x\ 10^{21}\ cm^{-3}s^{-1}$ for most of bulk

$\langle G \rangle * d_{wafer} * e$

$$\langle G \rangle * d_{wafer} * e = 10^{19}\ cm^{-3}s^{-1} * 200um * 1.6e-19\ C = 32 \frac{mA}{cm^2}$$

: in reality ~40 mA/cm2

$$\langle G \rangle * d_{perovskite} * e = 2 * 10^{21}\ cm^{-3}s^{-1} * 500nm * 1.6e-19\ C = 16 \frac{mA}{cm^2} :$$

in reality ~22 mA/cm2

2. Optical properties of solar cells

Franz-Josef Haug

MATLAB

```
close
clear

no_of_samples =1e6;
x = linspace(0,100,no_of_samples);
p = 0.01;
jj = 2;
jjj=0;
P=zeros(no_of_samples,1);

for i = 1:no_of_samples
    j = 0;
    alive = 1;
    while alive
        if rand(1) < p
            alive = 0;
        else
            j = j+1;
        end
    end
    P(i) = j;
    if mod(i,4.^jj) == 0 | i == no_of_samples
        jj = jj+1
        jjj = jjj+1;
        figure(1)
        histogram(P(1:i),'BinWidth', 1,'Normalization','probability')
        xlim([-10 500])
        ylim([0 0.011])
        xlabel('position [um]')
        ylabel('probability of photon being absorbed [um^{-1}]')
        title(strcat('photons: ',num2str(i)))
        if jjj ==1
            gif('MCMC_Beer_Lambert_Bouguer.gif','DelayTime', 1);
        else
            gif
        end
        pause(2)
    end
end
```

Python

```python
import numpy as np
import matplotlib.pyplot as plt
from matplotlib.animation import FuncAnimation

np.random.seed(0)

no_of_samples = int(1e6)
x = np.linspace(0, 100, no_of_samples)
p = 0.01
jj = 2
jjj = 0
P = np.zeros(no_of_samples)

fig, ax = plt.subplots()
def update(i):
    global jj, jjj
    j = 0
    alive = True
    while alive:
        if np.random.rand() < p:
            alive = False
        else:
            j += 1
    P[i] = j
    update_condition = i % (4 ** jj) == 0 or i == no_of_samples - 1
    if update_condition:
        jj += 1
        jjj += 1
        ax.clear()
        ax.hist(P[:i+1], bins=np.arange(-0.5, 500.5, 1), density=True)
        ax.set_xlim([-10, 500])
        ax.set_ylim([0, 0.011])
        ax.set_xlabel('position [um]')
        ax.set_ylabel('probability of photons absorbed [um^{-1}]')
        ax.set_title(f'photons: {i+1}')
        plt.pause(0.01)

    return ax

for i in range(no_of_samples):
    update(i)

plt.show()
```