

Modern PV-Technologies

3.1: Solar cell materials

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- Absorbers (semiconductor)
 - c-Si (best compromise btw. cost and efficiency)
 - CIGS, CdTe (high efficiency, potential bottleneck rare materials)
 - Organic, dye, perovskite (under research)
 - GaAs + III-V (highest efficiency, highest cost)
 - Thin film silicon (moderate efficiency, large area)
- Contacts (metals, TCOs)
 - Ag (reflectivity, conductivity)
 - Al (normally high reflectivity, but...)
 - $\text{In}_2\text{O}_3:\text{SnO}_2$ (ITO, rare element In)
 - ZnO (unstable with acids/bases)
 - $\text{SnO}_2:\text{F}$ (FTO, poor transparency)

Absorption in a medium

Wave vector in medium defined with refractive index $n + i\kappa$

$$k = \frac{2\pi}{\lambda_{eff}} = \frac{2\pi}{\lambda_0} (n + i\kappa) = \frac{2\pi}{\lambda_0} \sqrt{\epsilon}$$

Field amplitude and intensity:

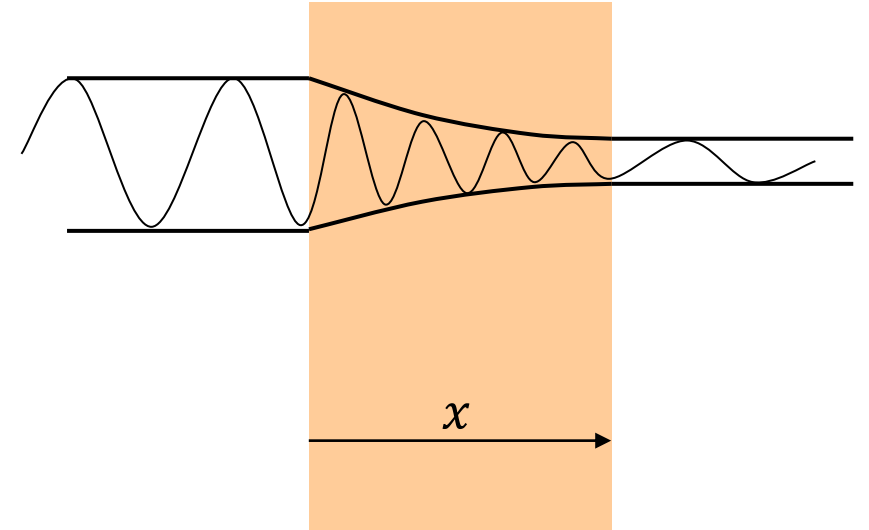
$$E(x, t) = E_0 \exp\{i((n + i\kappa)k_0x - \omega t)\}$$

$$\begin{aligned} |E(x, t)|^2 &= |E_0 \exp\{i((n + i\kappa)k_0x - \omega t)\}|^2 \\ &= |E_0|^2 \exp\{-\underbrace{(2\kappa \cdot 2\pi/\lambda)}_{\alpha} x\} \end{aligned}$$

Absorption coefficient: exponential decay of intensity

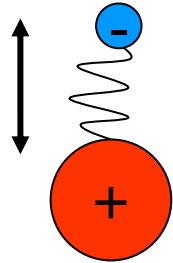
$$\alpha = 4\pi\kappa / \lambda$$

Issue: how to find n or ϵ



Dispersion (frequency dependence)

A (very) simple model for atoms in a solid: oscillator with damping
e.g. movement of electrons against cores



$$m\ddot{x} + 2\beta\dot{x} + \omega_0^2 x = eE_0 e^{-i\omega t}$$

inertia
damping
restoring force
harmonic driving force

Average amplitude of driven oscillator

$$x_0 = \frac{eE_0}{m} (-\omega^2 - 2i\beta\omega + \omega_0^2)$$

Dipole moment and macroscopic polarization (Clausius-Mosotti):

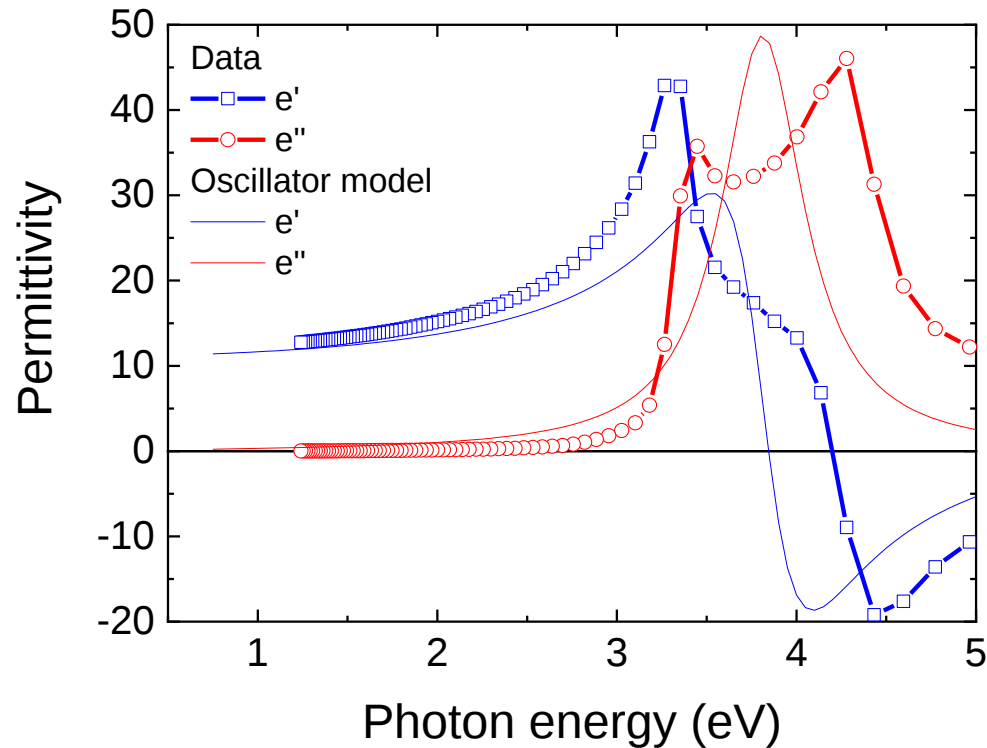
$$P = \frac{N}{V} p = \frac{N}{V} ex_0 = \epsilon_0(\epsilon - \epsilon_\infty)E$$

Find permittivity (dielectric function):

$$\epsilon(\omega) = (n + ik)^2 = \epsilon_\infty + \underbrace{\frac{e^2 N}{\epsilon_0 m V} \frac{1}{(\omega_0^2 - 2i\beta\omega - \omega^2)}}_{\chi \text{ (susceptibility)}}$$

empiric modification
(theoretically $\epsilon_\infty = 1$)

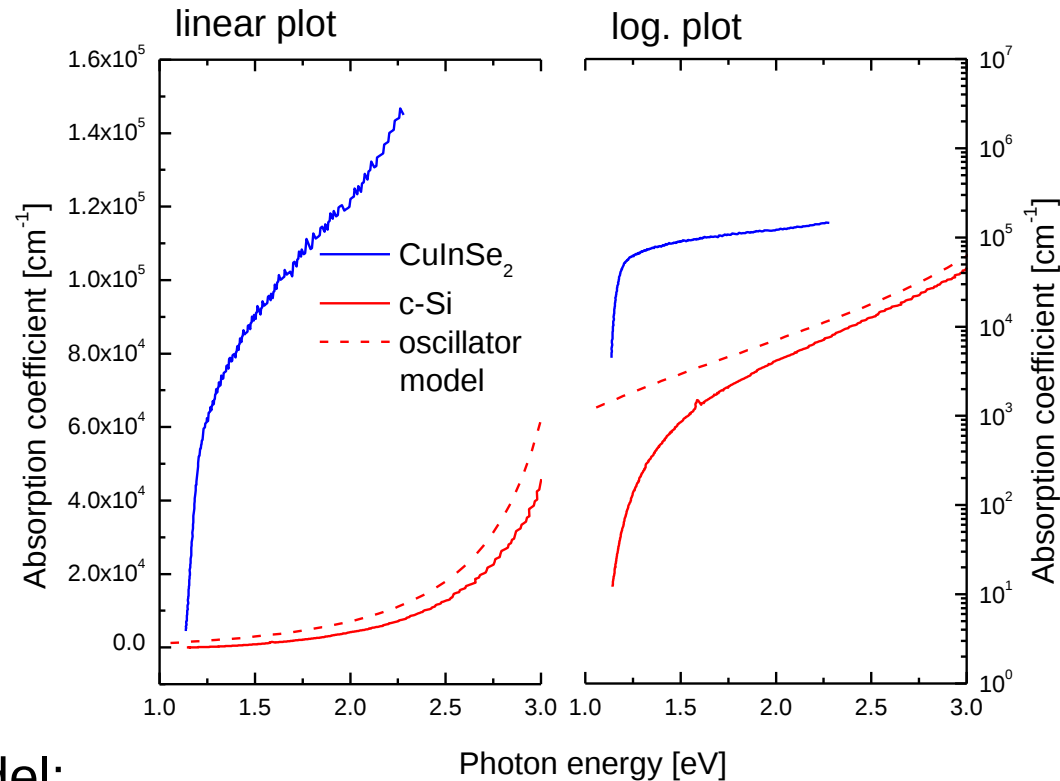
Comparison to measured dispersion (c-Si)



The primitive model with one oscillator yields dispersion effects
Two oscillators (or more) can yield better correspondence (χ is additive!)

Data: c.f. Green, SEM (2008)

Absorption coefficient (measured)



Oscillator model:

- OK for c-Si on linear scale
- BUT no gap behaviour (c.f. logarithmic scale!)
- fails totally for CIS

Absorption coefficient of semiconductors

Needs quantum mechanics

Heuristic link between ϵ'' and absorption:

$$P_{abs} = \underbrace{\frac{1}{2} \omega \epsilon_0 \epsilon'' E_0 E_0^*}_{\text{Absorbed power from Poynting theorem}} = \underbrace{\hbar \omega \sum_{\vec{k}, \vec{k}'} w_{vc}}_{\text{Absorbed power by summing all allowed quantum-mechanical transitions}}$$

Absorbed power
from Poynting
theorem

Absorbed power by summing
all allowed quantum-mechanical
transitions

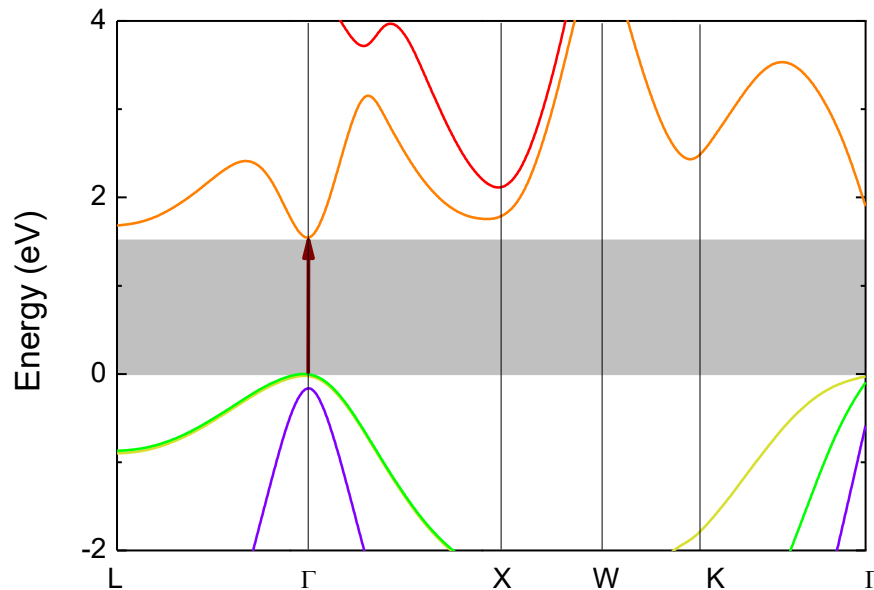
solve for ϵ'' , determine ϵ' via Kramers-Krönig relation

$$\epsilon'(\omega) = 1 + \frac{2}{\pi} \cdot \mathcal{P} \int_0^\infty \frac{\omega' \cdot \epsilon''(\omega')}{\omega'^2 - \omega^2} d\omega'$$

More precise derivation with density operator: Adler, Phys. Rev. (1962)

Direct absorption (e.g. GaAs)

Band diagram (pseudopotential method)



Interaction Hamiltonian:
electron-radiation

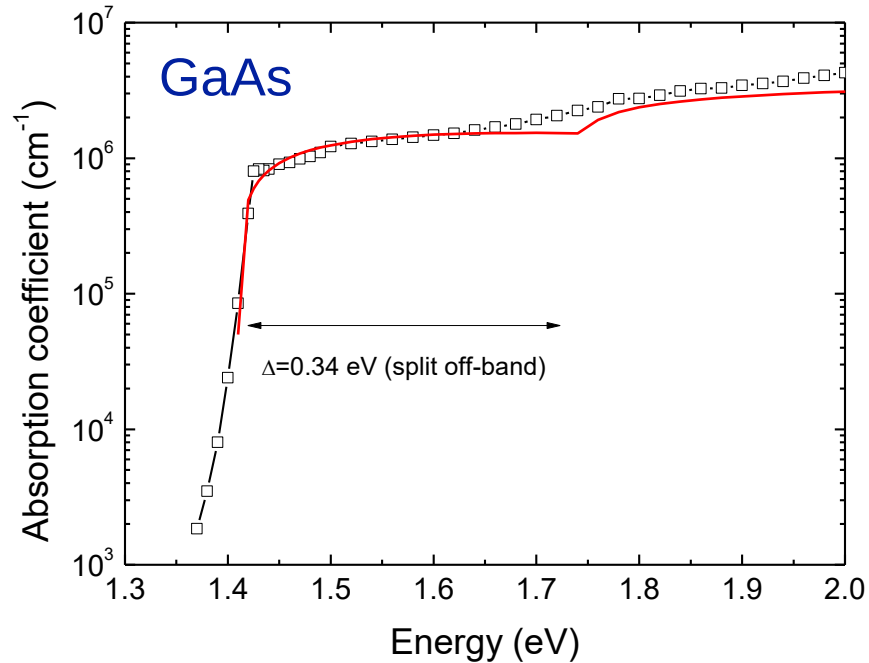
$$H' = H_{er} = -\frac{e}{m} \vec{A} \vec{p}$$

(neglect $|\vec{A}|^2$ term)

Transition probability:
Fermi's Golden rule

$$w_{vc} = \left| \left\langle c\vec{k}' \right| -\frac{e}{m} \vec{A} \vec{p} \left| v\vec{k} \right\rangle \right|^2 \cdot \frac{2\pi}{\hbar} \delta(E_c(\vec{k}) - (E_v(\vec{k}') + \hbar\omega))$$

details of derivation: see e.g. Hamaguchi, Basic Semiconductor Physics



$$\epsilon'' = \begin{cases} 0 & \text{for } \hbar\omega < E_g \\ \frac{e^2 p_{vc}^2}{2\pi\epsilon_0 m^{*2} \omega^2} \sqrt{\frac{8m^{*3}}{\hbar^6} (\hbar\omega - E_g)} & \text{for } \hbar\omega > E_g \end{cases}$$

+ term of split-off band for $\hbar\omega > E_g + \Delta E_{so}$

$$\epsilon'' = 2 \cdot n\kappa$$

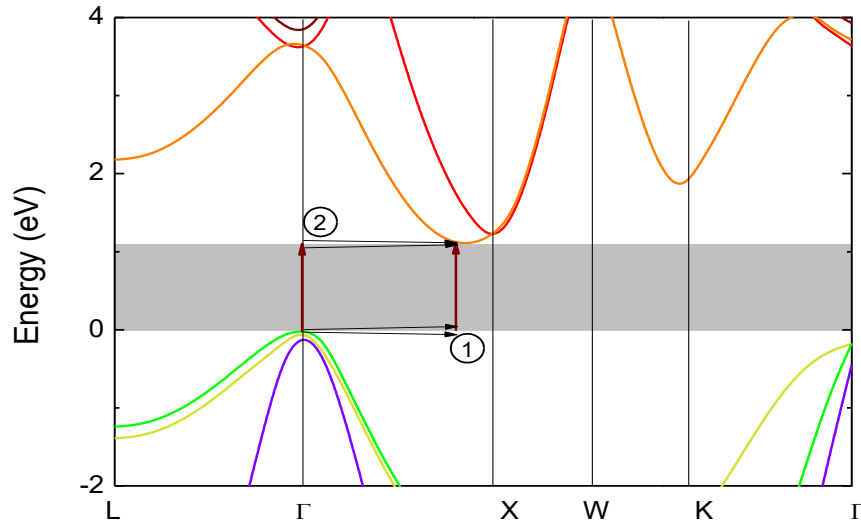
$$\alpha = 4\pi \cdot \kappa / \lambda \sim \frac{1}{\omega} \sqrt{\hbar\omega - E_g}$$

Thus, α proportional to square root!

Direct gaps: generally high absorption $\sim 10^6 \text{ cm}^{-1}$ close to gap

Indirect absorption (e.g. Silicon)

Band diagram



Interaction Hamiltonian:
electron-radiation + electron-lattice

$$H' = H_{er} + H_{el}$$

$$H_{er} = -\frac{e}{m} \vec{A} \vec{p}$$

Deformation
potential

$$H_{el} = D_V \cdot \nabla \vec{u} =$$

$$= D_V \sqrt{\frac{\hbar}{2M\omega_q}} \cdot (i\vec{e}_{\vec{q}} \vec{q}) (a \cdot e^{i\vec{q}\vec{r}} - a^\dagger \cdot e^{-i\vec{q}\vec{r}})$$

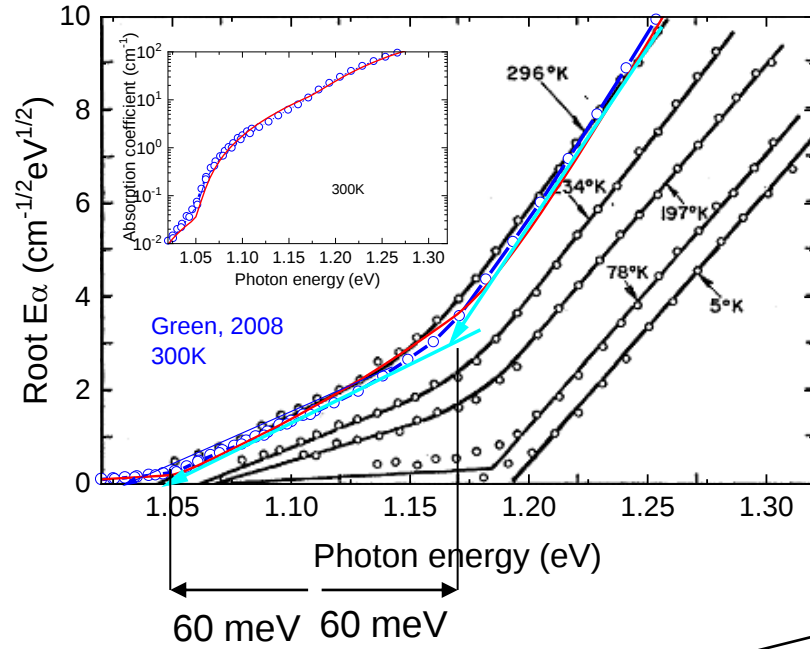
Fermi's Golden rule
(second order $i \rightarrow f$)

$$w_{if} = \left| \sum_m \frac{\langle f | H_{er} + H_{el} | m \rangle \langle m | H_{er} + H_{el} | i \rangle}{E_m - E_i} \right|^2 \cdot \frac{2\pi}{\hbar} \delta(E_f - E_i)$$

Integrated:

$$\epsilon'' \sim \frac{4\pi e^2}{\epsilon_0 \omega^2 m^2} \cdot \frac{2}{(2\pi)^4} \sqrt{\frac{64 m_e^{*3} m_h^{*3}}{\hbar^{12}}} \frac{\pi}{8} (\hbar\omega \pm \hbar\omega_{\vec{q}} - E_g)^2 \frac{\hbar}{2m\omega_q} \left(n \pm \frac{1}{2} + \frac{1}{2} \right)$$

Absorption coefficient c-Si



Phonon population
 $\hbar\omega_{\vec{q}} \approx 60 \text{ meV (LO)}$

$$\alpha(h\nu) \sim \frac{1}{\omega} \left[\left(\frac{1}{e^{\frac{\hbar\omega_{\vec{q}}}{kT}} - 1} \right) (\hbar\omega + \hbar\omega_{\vec{q}} - E_{g,x})^2 + \left(\frac{1}{e^{\frac{\hbar\omega_{\vec{q}}}{kT}} - 1} + 1 \right) (\hbar\omega - \hbar\omega_{\vec{q}} - E_{g,x})^2 \right]$$

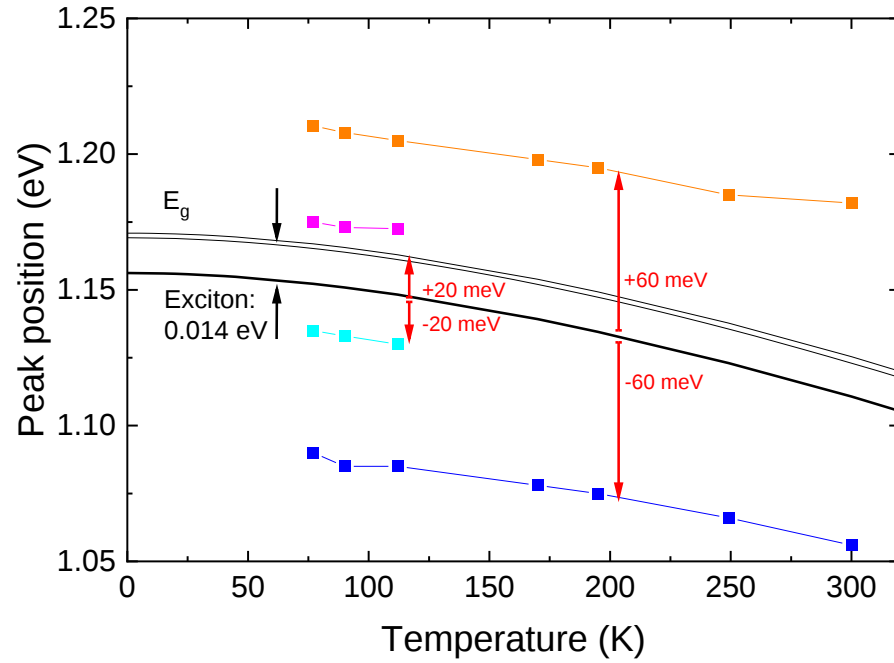
(lattice provides phonon, cooling)

(lattice absorbs phonon, heating)

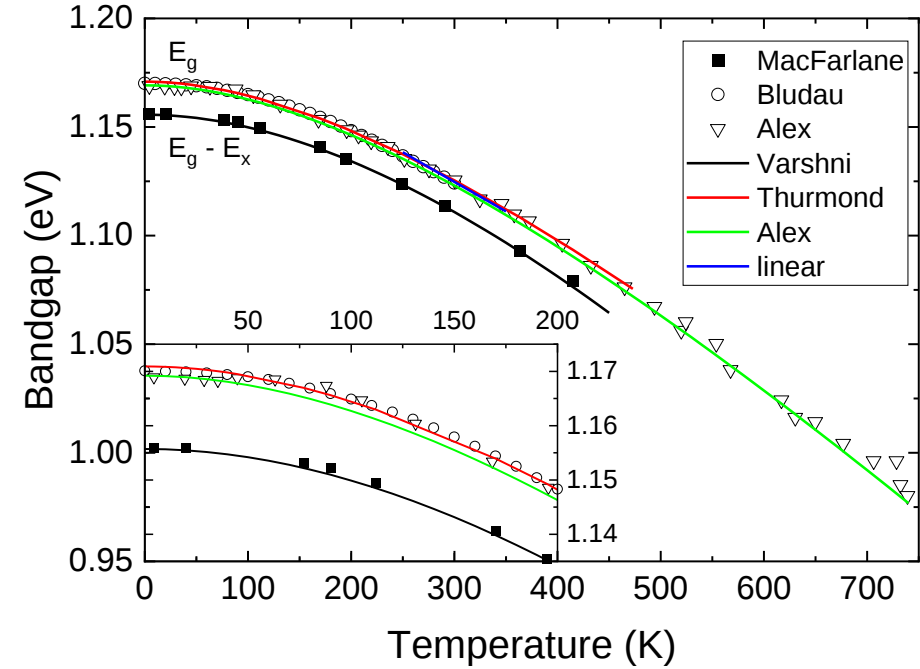
Excellent correspondence to measured data

MacFarlane, PR 1955
 Braunstein, PR 1959

Temperature dependence of E_g (c-Si)



Collect positions of phonon signatures



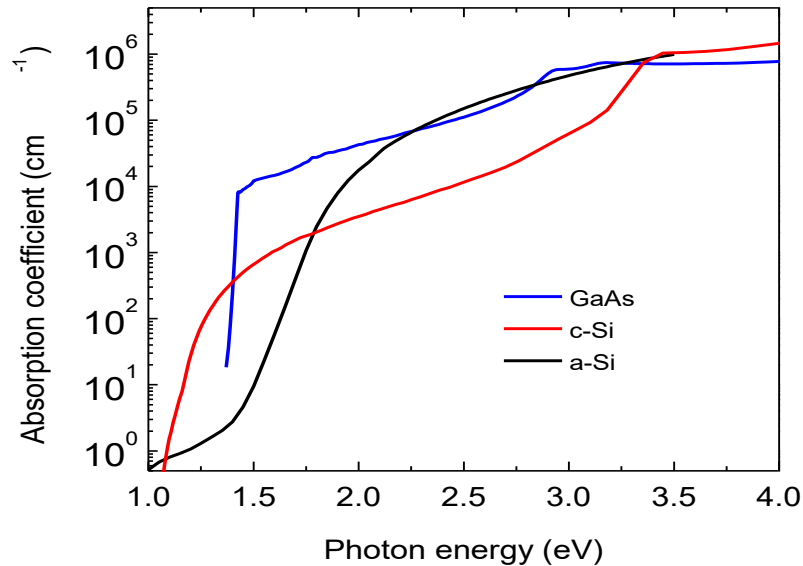
Empiric model:

$$E_g = 1.1557 - \frac{7.021 \times 10^{-4} \cdot T^2}{T + 1108} + E_{ex}$$

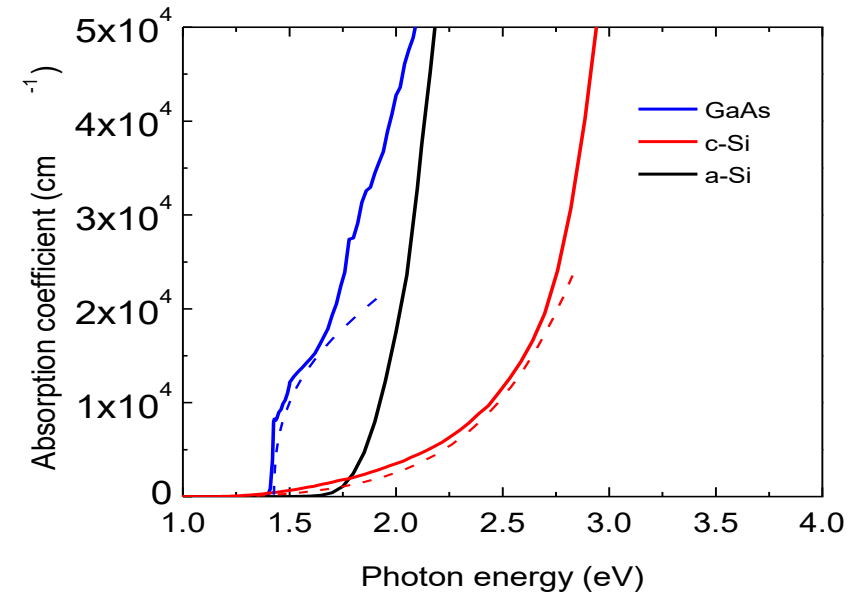
Varshni, physica (1967)

Absorption coefficient (summary)

logarithmic scale (usually shown)



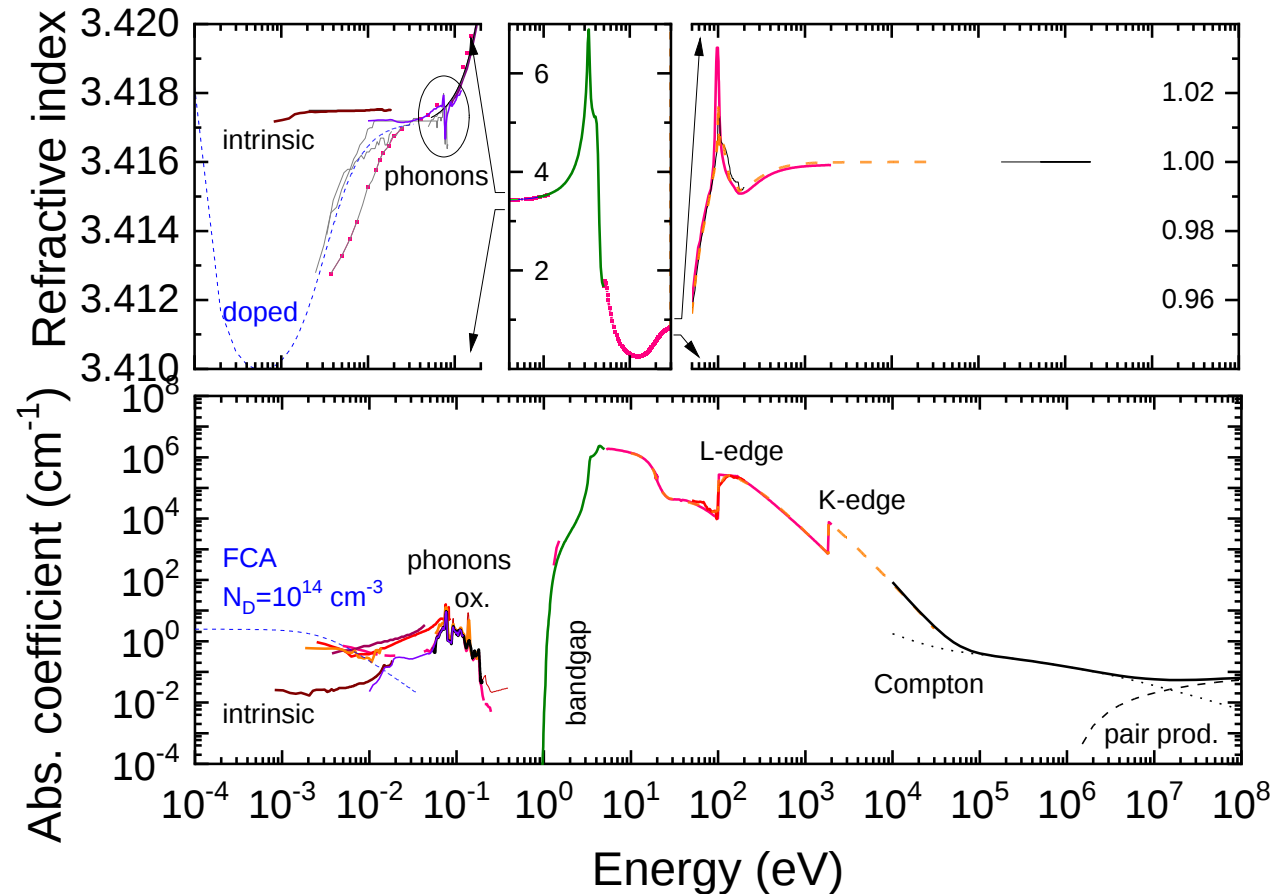
linear scale (clearer proportionality)



Direct: strong absorption close to gap $\alpha \sim (h\nu - E_g)^{\frac{1}{2}}$

Indirect gap: weak onset $\alpha \sim (h\nu - E_g)^2$, requires thick absorbers!

a-Si: essentially indirect



Contributions to polarizability

- free electron plasma
(depending on doping, can be up to vis)
- lattice vibrations (IR)
- displacement of valence electrons
(vis and UV)
- X-ray interactions with core electrons
- Compton scattering
- pair production

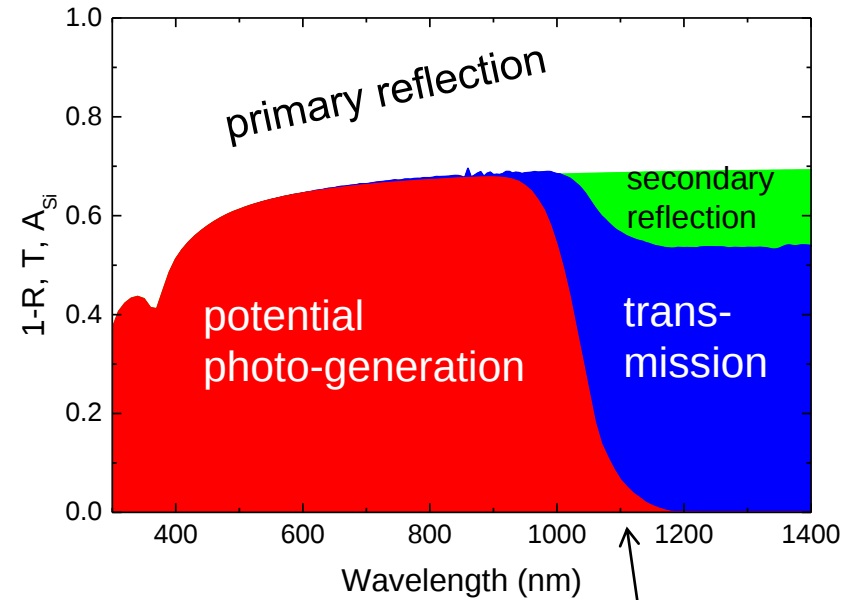
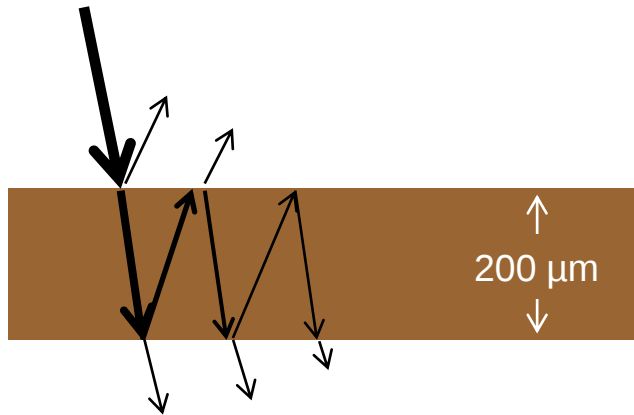
Chandler, JAP, (2005)

Green, Sol. En. Mat. (2008)

Palik, Handbook of Opt. Const.

Hubell, NIST (1969).

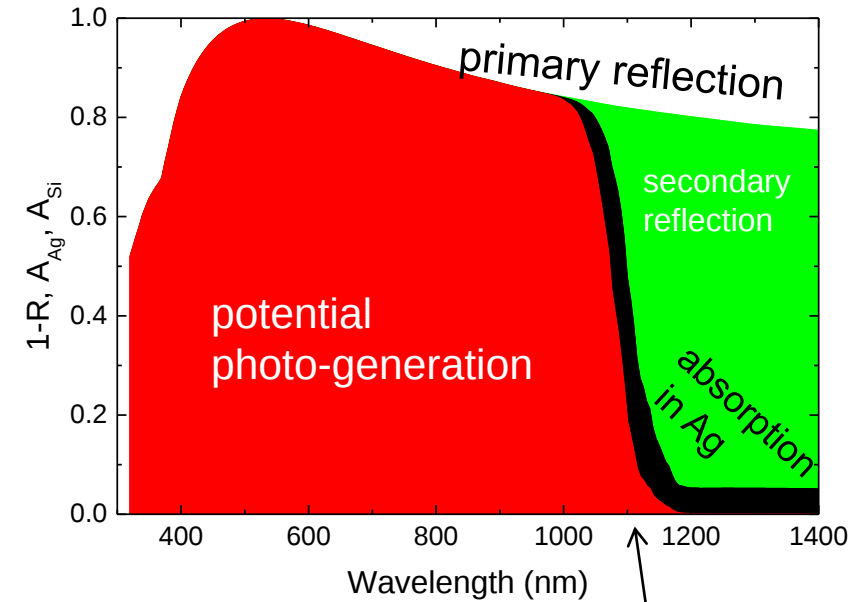
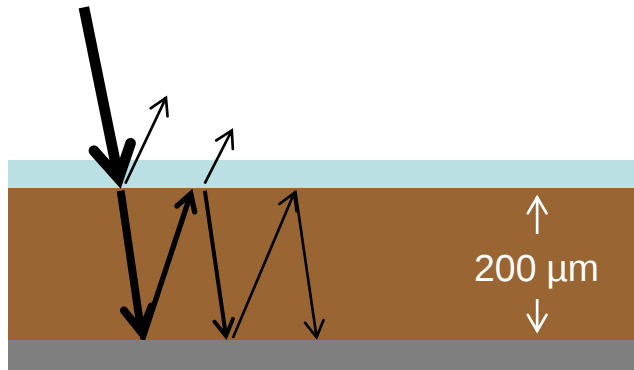
Absorption in a silicon slab



$$A = (1 - R) \left(\sum (1 - e^{-\alpha d}) + e^{-\alpha d} R (1 - e^{-\alpha d}) + e^{-2\alpha d} R^2 (1 - e^{-\alpha d}) + \dots \right)$$

$$= (1 - R) \frac{1 - e^{-\alpha d}}{1 - R e^{-\alpha d}}$$

- primary reflection (high refractive index) => needs AR functionality
- avoid transmission loss by rear reflector



Add AR coating (70 nm, $n \approx 2$ at front)
Add reflector, eg. silver (at rear)

still significant loss due to low absorption
 $\Rightarrow$ needs absorption enhancement

EPFL Enhancing absorption via prolonged light path

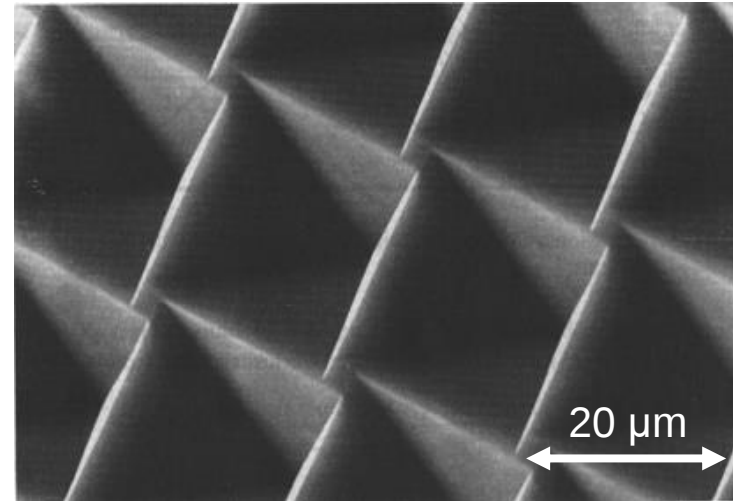
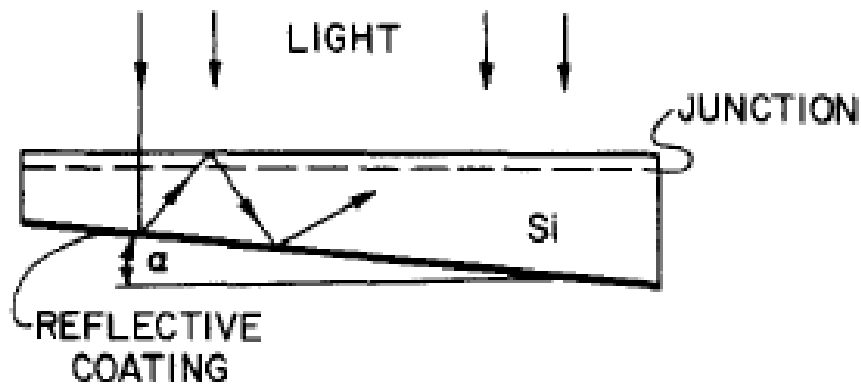
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Total internal reflection

$$\theta_{\text{crit}} \approx 17^\circ \quad (n \approx 4)$$

modern high eff. cells: inverted pyramids



Apply geometric ray optics
for optimization

D. Redfield, Appl. Phys. Lett. (1974)

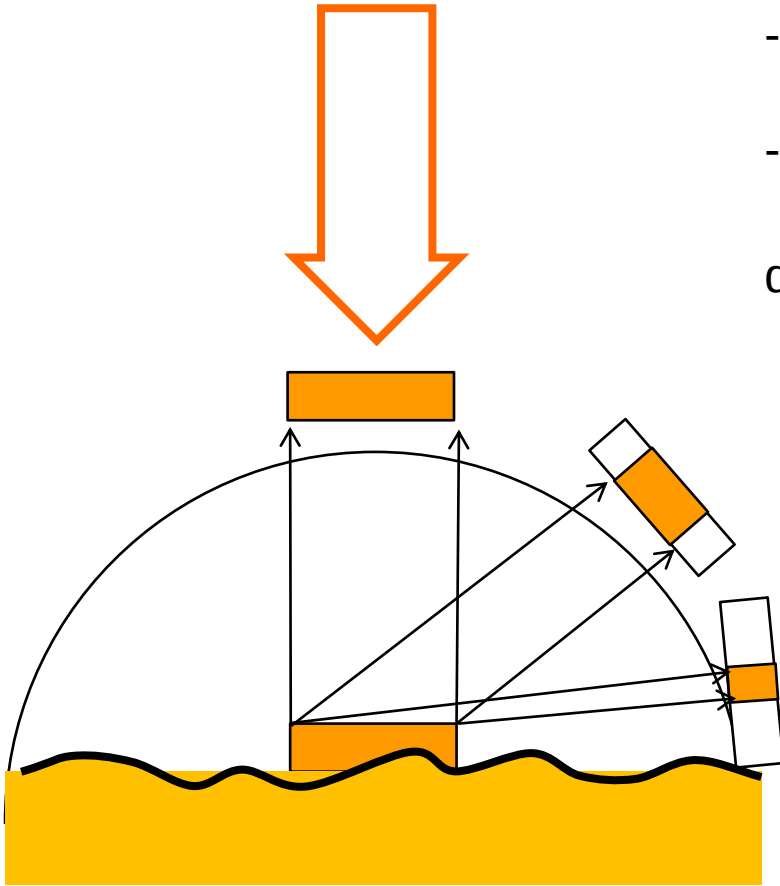
from Goetzberger, Sonnenenergie (1997)

Isotropic scattering (Lambertian)

Concept:

- surface scatters equally in all directions (e.g. white paper, projection screen, etc.)
- angular dependence because of projection

described by: $ARS_{Lambert} = \frac{1}{\pi} \cos \theta$



Lambert, Photometria (1760)

Prolongation of an oblique path

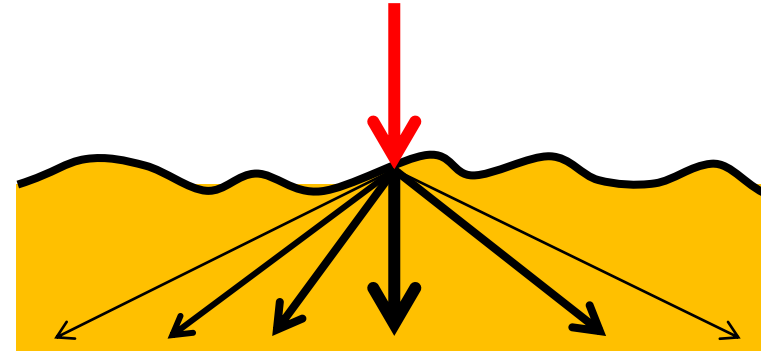
$$d' = d / \cos \theta$$

Average prolongation

$$d_{av} = \int d' \cdot ARS_{Lambert} d\Omega$$

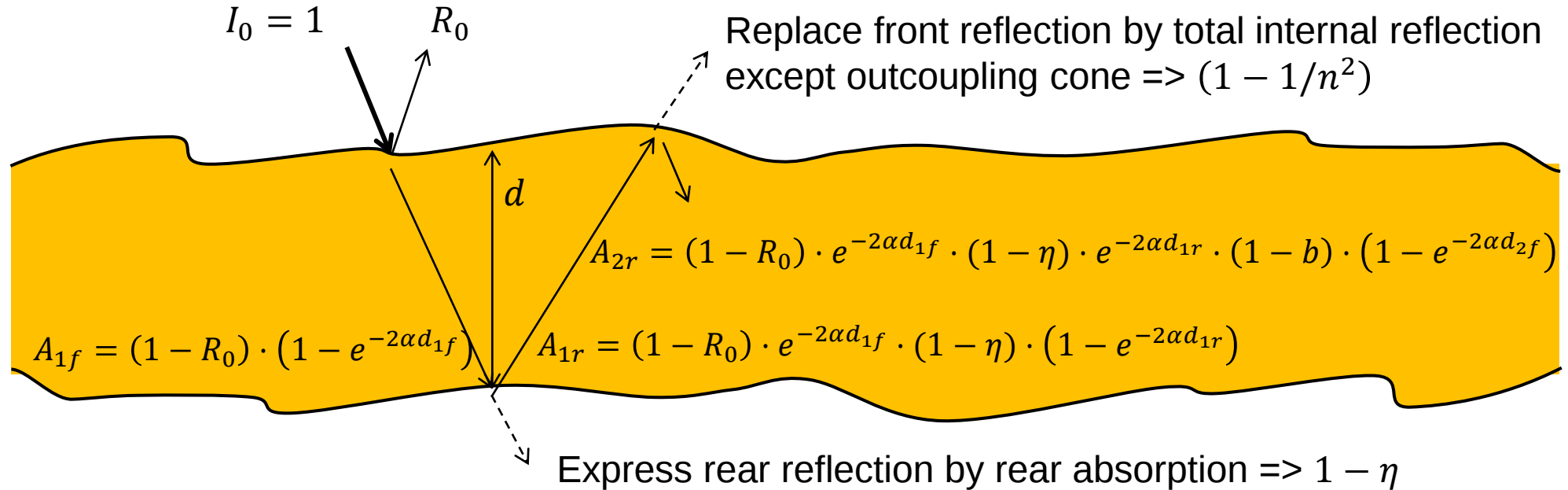
$$= 2\pi \cdot \int \frac{d}{\cos \theta} \cdot \underbrace{\frac{\cos \theta}{\pi} \cdot \sin \theta}_{\text{weighting factor, probability to find angle btw. } \theta \text{ and } \theta + d\theta} d\theta = 2 \cdot d$$

length of oblique path



Absorption with (ideal) light scattering

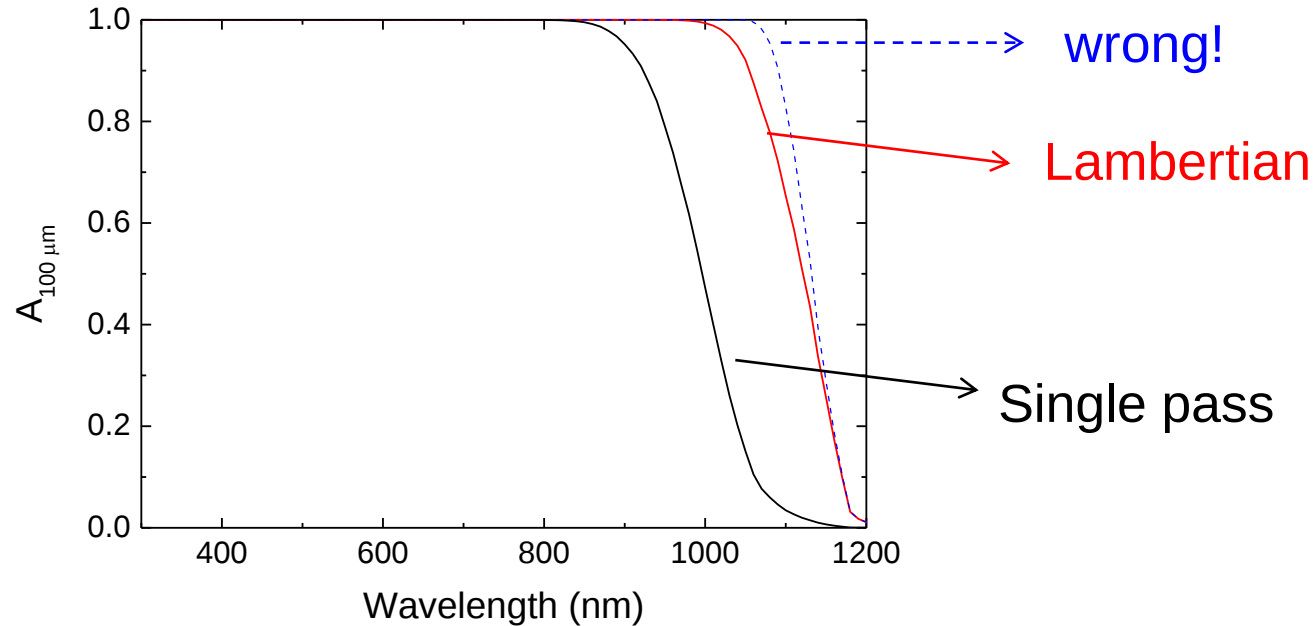
Sum up absorption upon bouncing forth and back



$$\begin{aligned}
 A &= \sum_{k=0}^{\infty} \underbrace{[(1 - e^{-2\alpha l}) + e^{-2\alpha l}(1 - \eta)(1 - e^{-2\alpha l})]}_{A_{\text{double pass}}} \underbrace{[e^{-4\alpha l}(1 - \eta)(1 - 1/n^2)]^k}_{\text{Attenuation}} \\
 &= \frac{1 - \eta e^{-2\alpha l} - (1 - \eta)e^{-4\alpha l}}{1 - (1 - \eta)e^{-4\alpha l} + [(1 - \eta)/n^2]e^{-4\alpha l}} \\
 &\approx 4n^2\alpha l \quad \text{if: } \eta = 0, \alpha l \ll 1
 \end{aligned}$$

Deckman, APL (1983)
 Boccard, APL (2012)
 Yablonovitch, TED (1982)

Upper limit of light trapping (silicon)



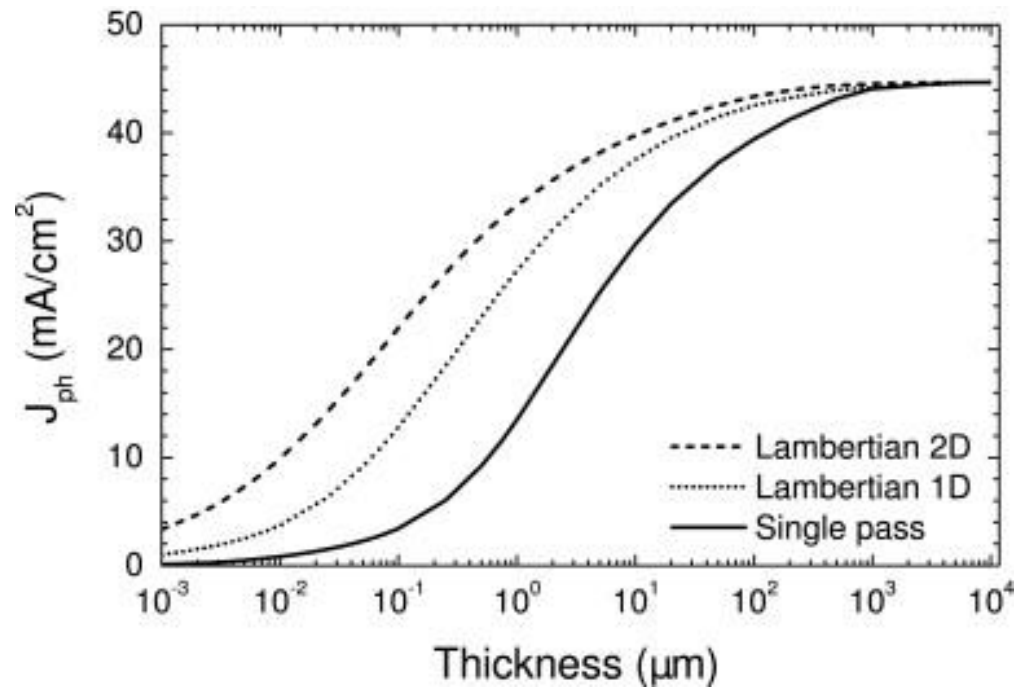
Single pass (100 μm): $A = 1 - e^{-\alpha l}$

Lambertian enhancement:
$$A = \frac{1 - e^{-4\alpha l}}{1 - e^{-4\alpha l} + 1/n^2 \cdot e^{-4\alpha l}}$$

Attention, Yablonovitch's $4n^2$ formula is often used wrongly: $A = 1 - e^{-\alpha \cdot 4n^2 l}$

EPFL Maximum photocurrent (silicon)

$$j_{sc} = q \int_{300}^{1200} \Phi_{sun} \cdot A \cdot d\lambda$$



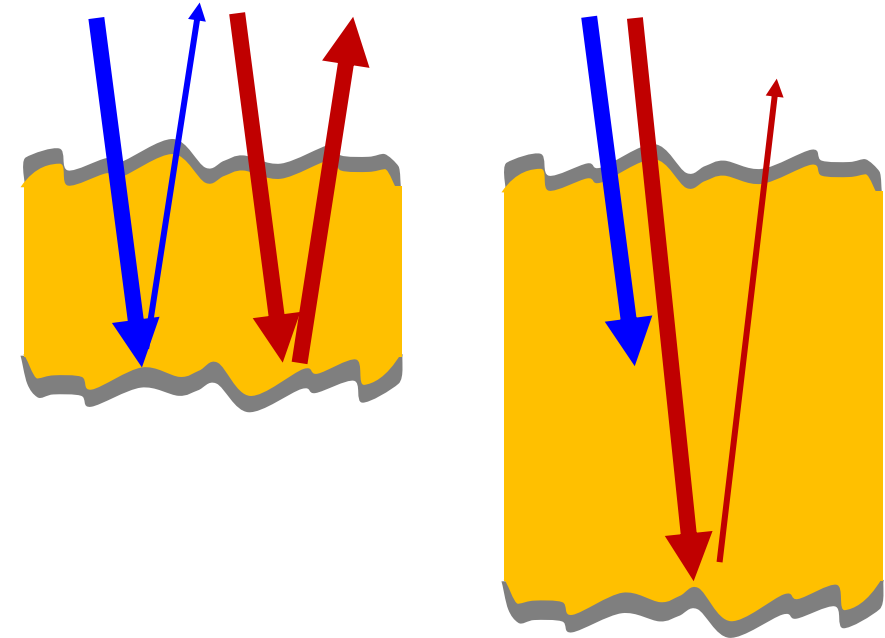
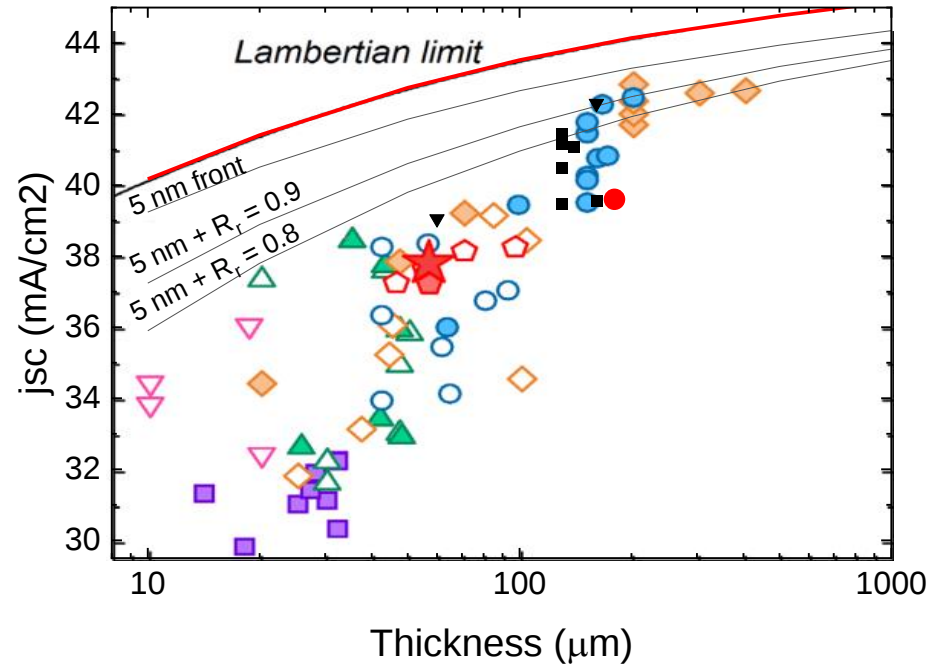
Saturation value: 46 mA/cm²

With ideal light scattering: 70 to 100 μm sufficient

Issue: most surfaces don't scatter Lambertian
maybe for some, but not for all wavelengths

Andreani, SolMat (2015)

Maximum photocurrent vs. thickness

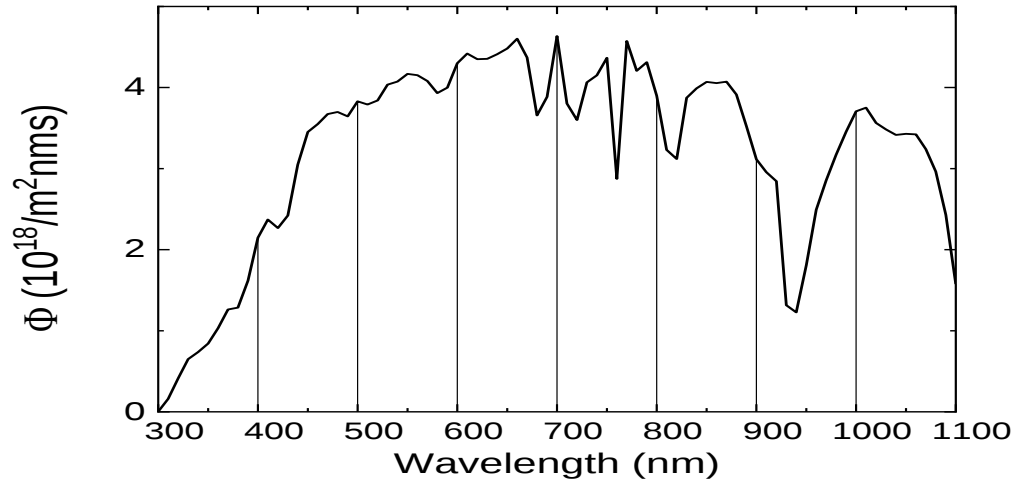


Real devices:

- loss at front (e.g. 5 nm of Si or grid shading)
- non-ideal rear reflectivity

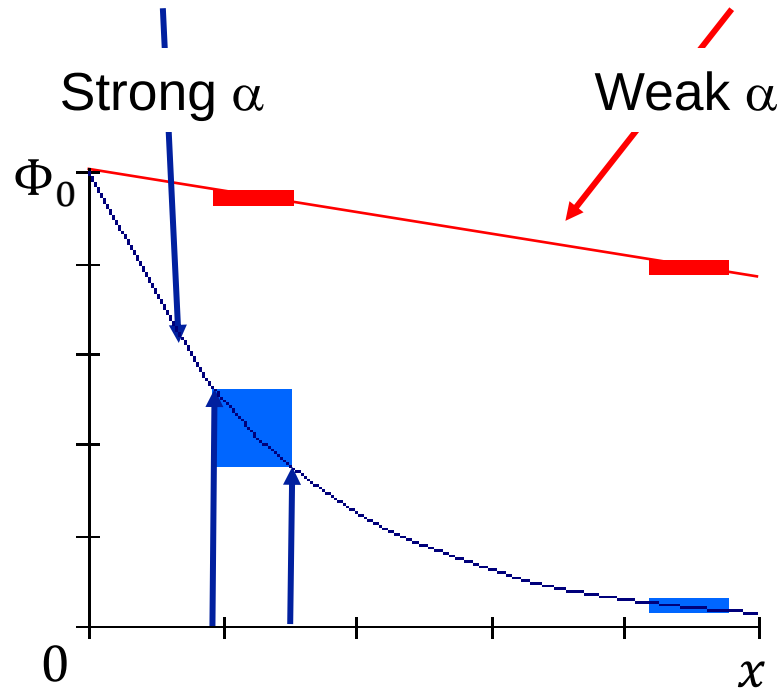
on j_{sc} limit: Bozzola, EU-PVSEC (2011)
collection of data: Sai, RRL (2021)

EPFL Generation rate



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

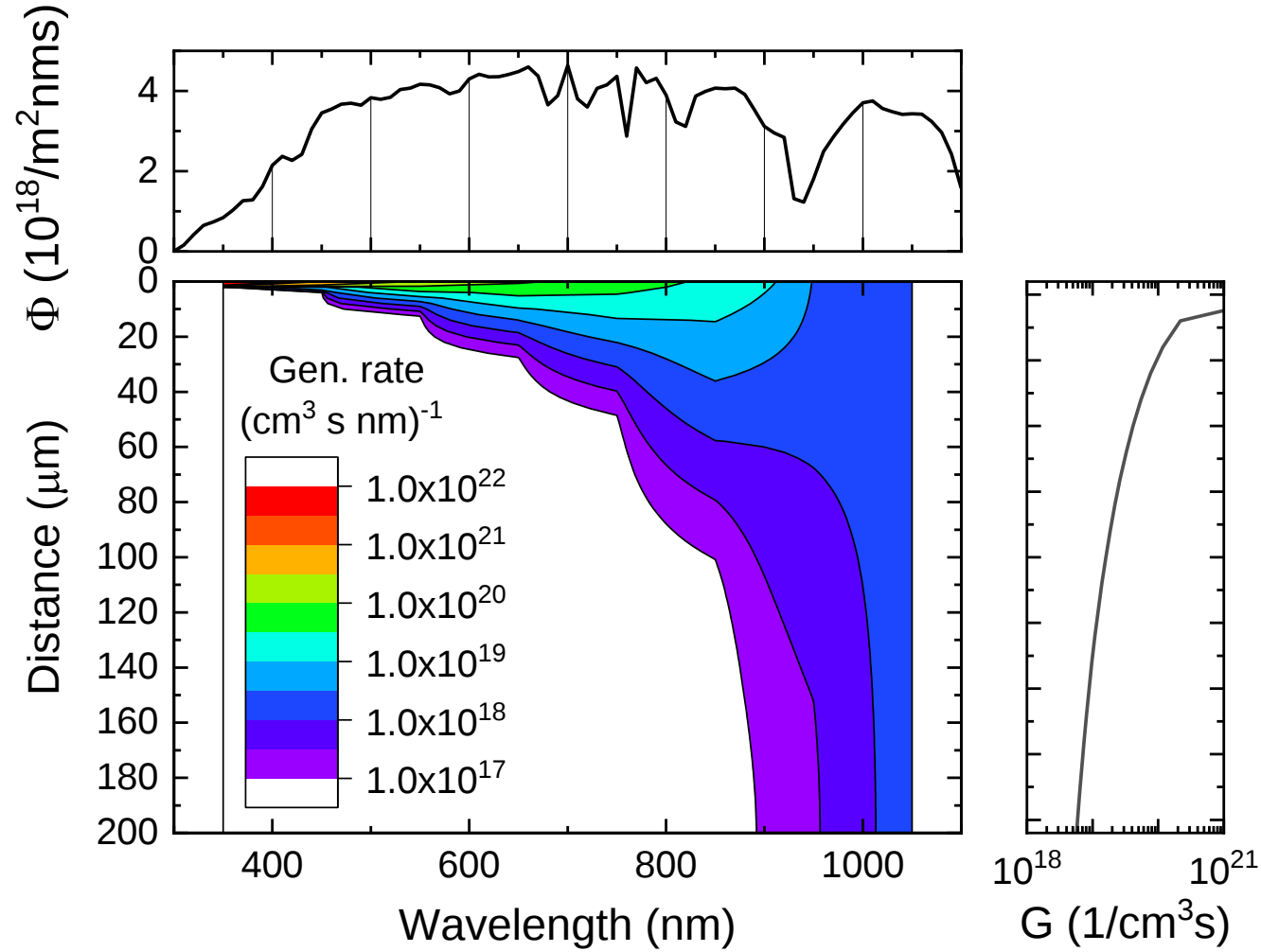
Light absorbed at depth x :
 $\Phi(x) - \Phi(x + \Delta x) \equiv -d\Phi$



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

blue: high G at front, strong decay

red: weak G , uniform through Si



Short λ : strong absorption
 $\Rightarrow$ Large $G(x)$ at front

Long λ : weak absorption
 $\Rightarrow$ Almost uniform $G(x)$ in bulk

- Enhanced optics (general)
 - AR coating (interference or by index grading)
 - reduce parasitic losses (contact layers with higher gaps)
- Enhanced absorption by scattering (needed for weakly absorbing cells, either indirect gap, or thin cells)
 - textures (proven for Si-based cells)
 - nanowires (so-so)
 - plasmonic scattering (theoretically interesting, but parasitic absorption)