Modern PV-Technologies
3.1: Solar cell materials

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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…)
  - In_2O_3:SnO_2 (ITO, rare element In)
  - ZnO (unstable with acids/bases)
  - SnO_2:F (FTO, poor transparency)

Absorption in a medium

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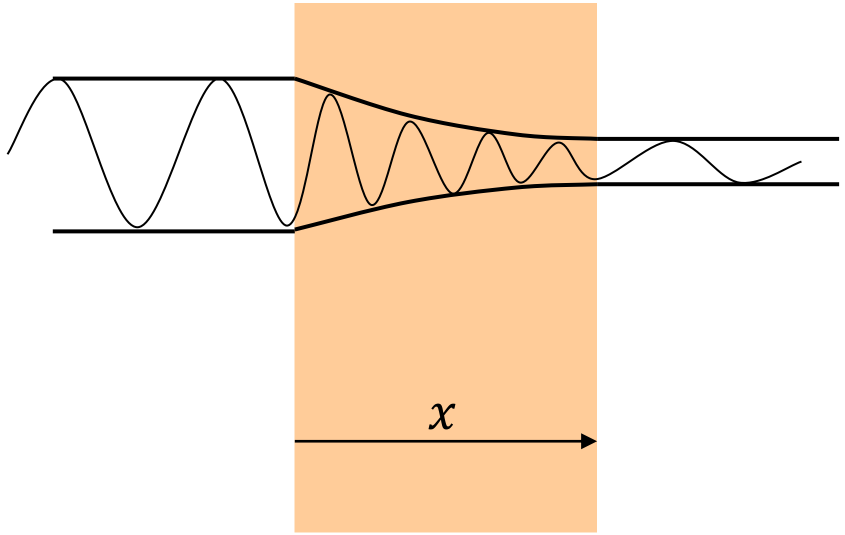
Wave vector in medium defined with refractive index $n + i\kappa$

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



Field amplitude and intensity:

$$E(x,t) = E_0 \exp\{i((n + i\kappa)k_0 x - \omega t)\}$$

$$|E(x,t)|^2 = |E_0 \exp\{i((n + i\kappa)k_0 x - \omega t)\}|^2$$
$$= |E_0|^2 \exp\{-\underbrace{(2\kappa \cdot 2\pi/\lambda)}_{\alpha}x\}$$

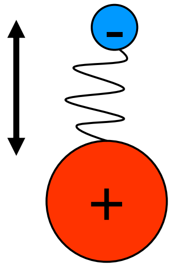
Absorption coefficient: exponential decay of intensity

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

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

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

Dipole moment and macroscopic polarization (Clausius-Mosotti):

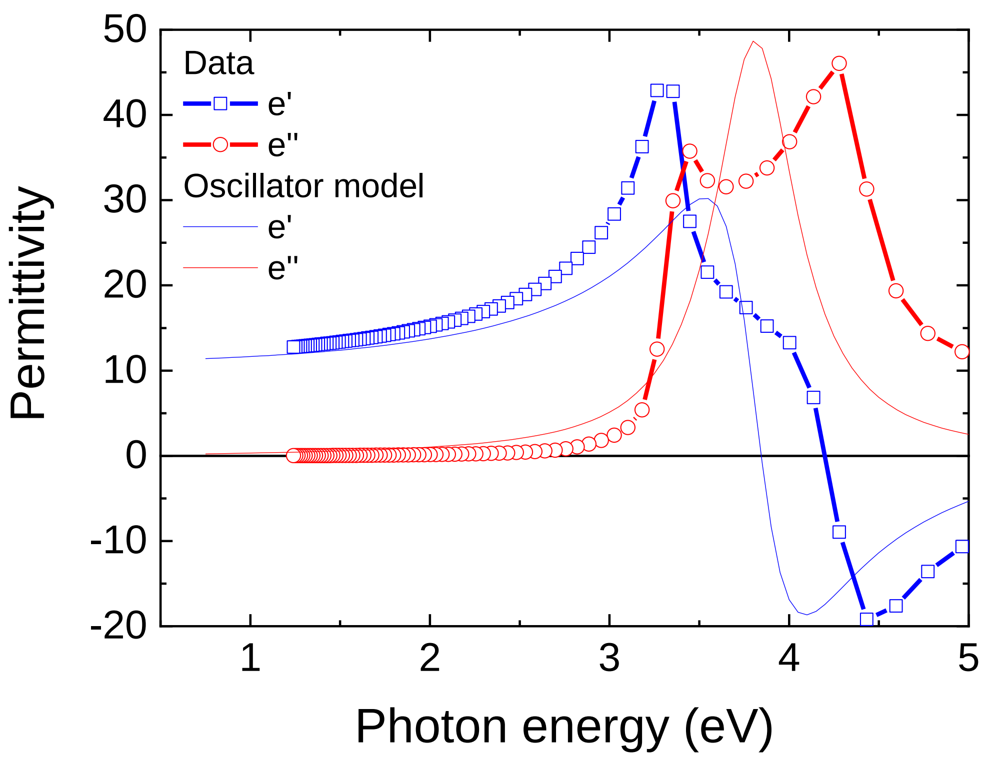
$$P = \frac{N}{V}p = \frac{N}{V}ex_0 = \epsilon_0(\epsilon - \epsilon_\infty)E$$

Find permittivity (dielectric function):

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

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

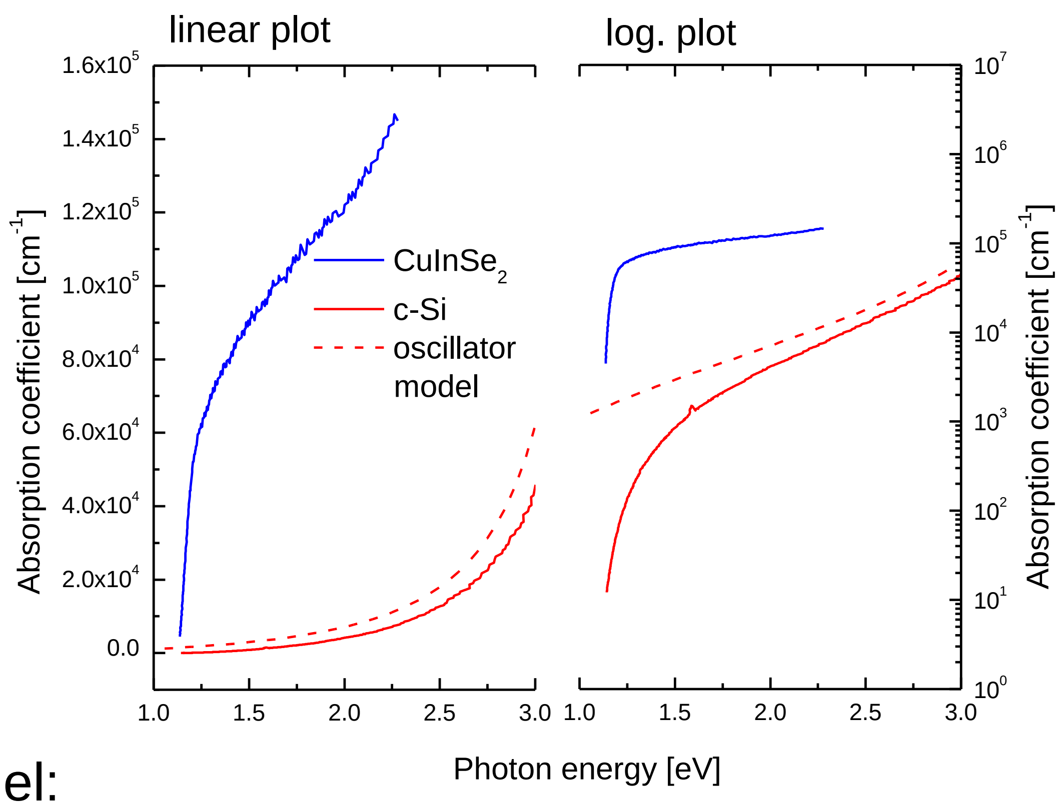
Comparison to measured dispersion (c-Si)



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 to describe electronic transitions

Heuristic link between ϵ'' and absorption:

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

Transform to integral to obtain ϵ''

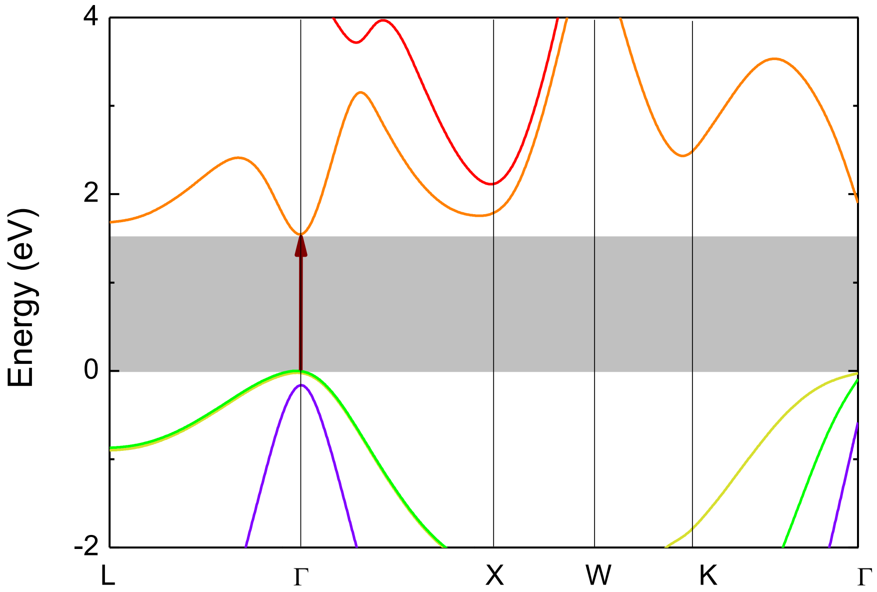
Determine ϵ' via Kramers-Krönig relation:

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

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

Direct absorption (example: GaAs)

Band diagram (pseudopotential method)



Interaction Hamiltonian: electron-radiation

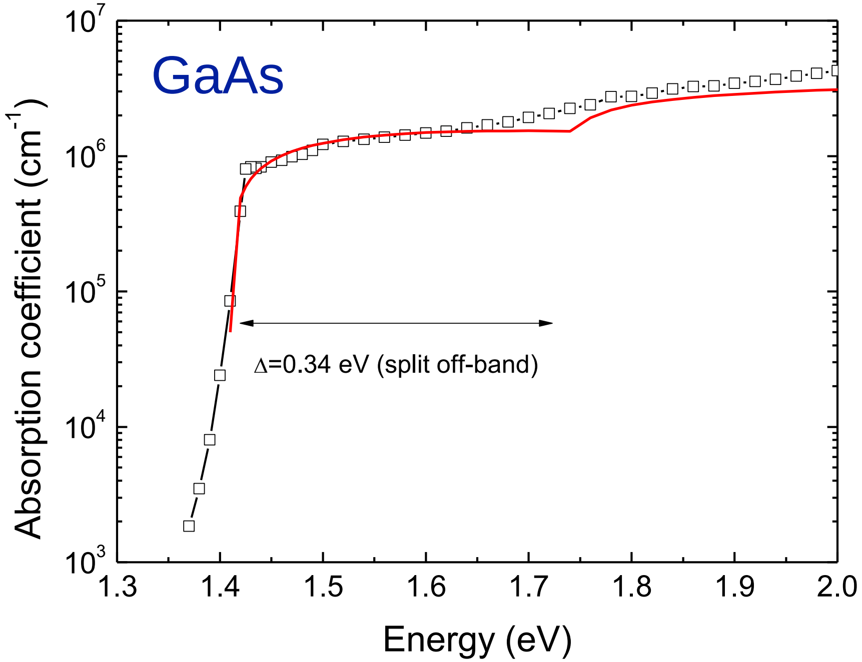
$$H' = H_{er} = -\frac{e}{m}\vec{A}\vec{p}$$

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

Transition probability from valence to conduction state: Fermi's Golden rule

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

Absorption coefficient



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

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

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

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

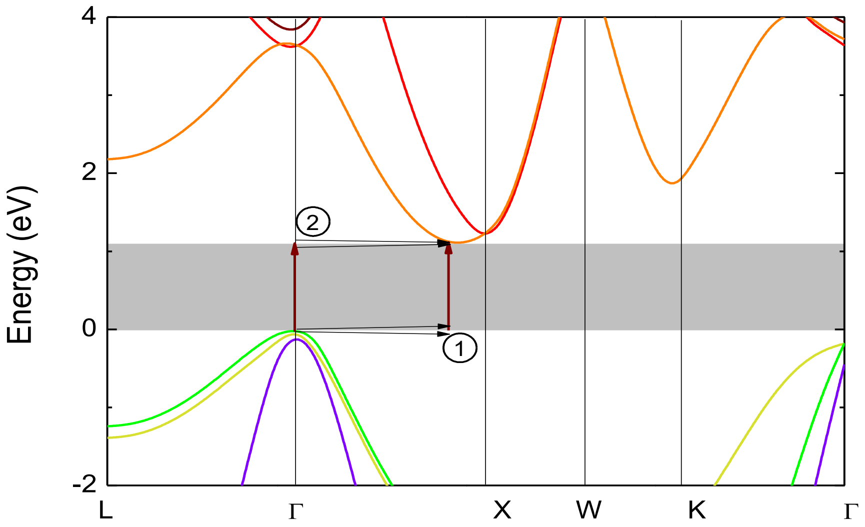
Thus, α proportional to square root!

Direct gaps: generally high absorption ~10^6 cm^{-1} close to gap

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

Indirect absorption (e.g. Silicon)

Band diagram



Interaction Hamiltonian:
electron-radiation + electron-lattice

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

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

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

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

Deformation potential

Fermi's Golden rule (second order $v \to c$)

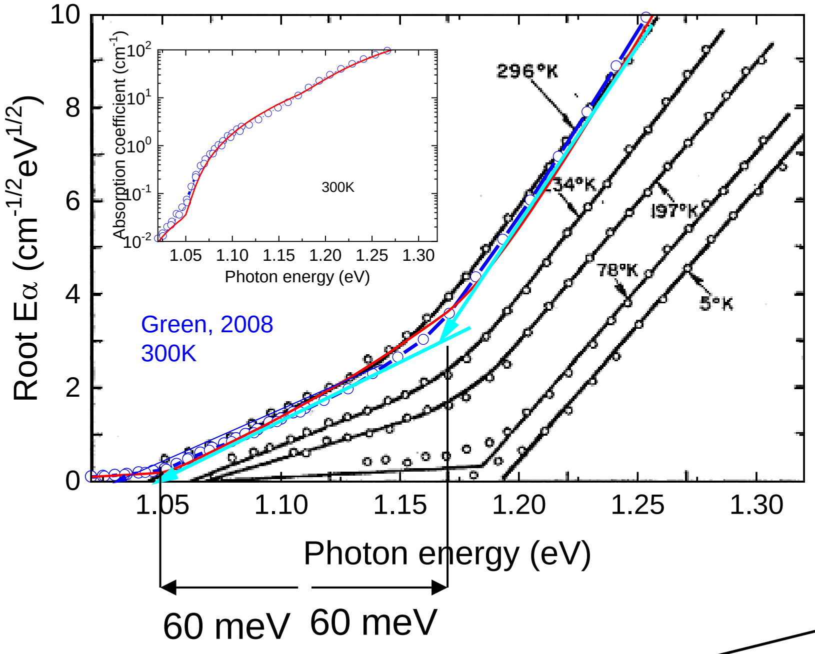
$$w_{vc} = \left|\sum_m \frac{\langle c|H_{er} + H_{el}|m\rangle\langle m|H_{er} + H_{el}|v\rangle}{E_m - E_v}\right|^2 \cdot \frac{2\pi}{\hbar}\delta(E_c - E_v)$$

Stronger weight for (1)

Integrated:

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

Absorption coefficient c-Si



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

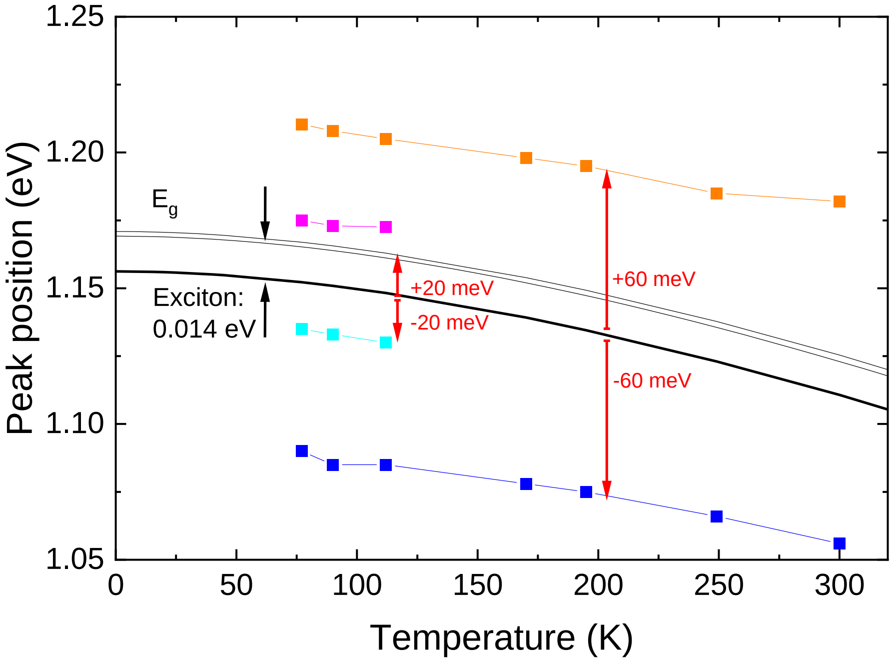
$$\alpha(h\nu) \sim \frac{1}{\omega}\left[\left(\frac{1}{e^{\frac{\hbar\omega_{\vec{q}}}{kT}}-1}\right)\left(\hbar\omega+\hbar\omega_{\vec{q}}-E_{g,x}\right)^2+\left(\frac{1}{e^{\frac{\hbar\omega_{\vec{q}}}{kT}}-1}+1\right)\left(\hbar\omega-\hbar\omega_{\vec{q}}-E_{g,x}\right)^2\right]$$

(lattice provides phonon, cooling) (lattice absorbs phonon, heating)

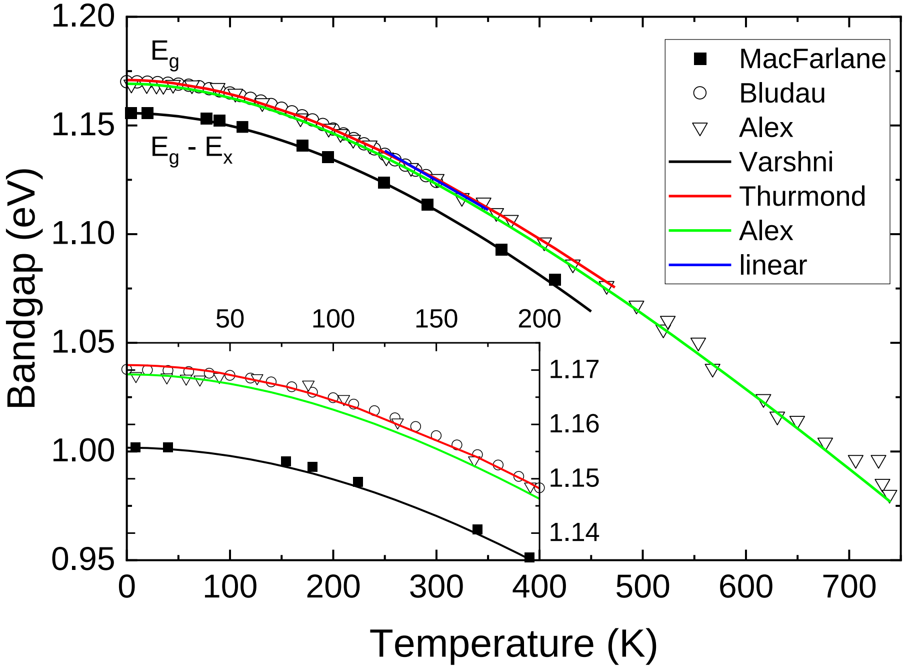
Excellent correspondence to measured data

MacFarlane, PR 1955
Braunstein, PR 1959

Temperature dependence of E_g (c-Si)



Collect positions of phonon signatures



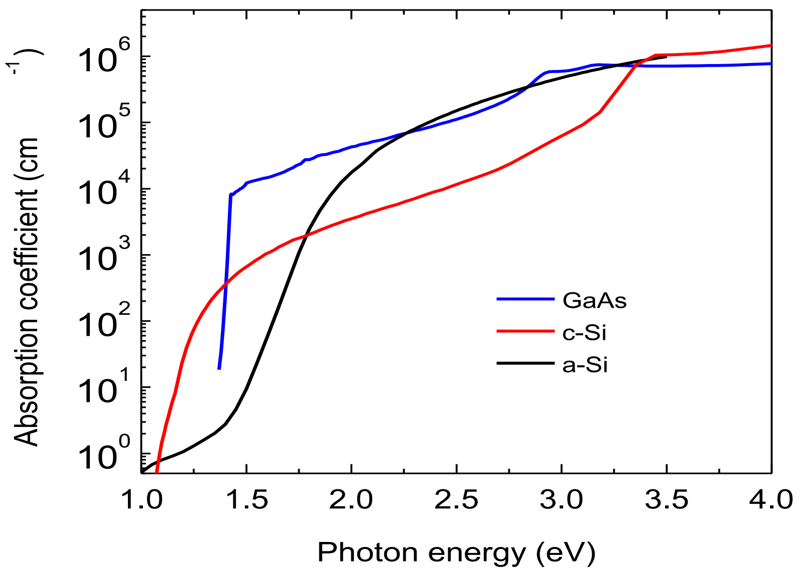
Empiric model:

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

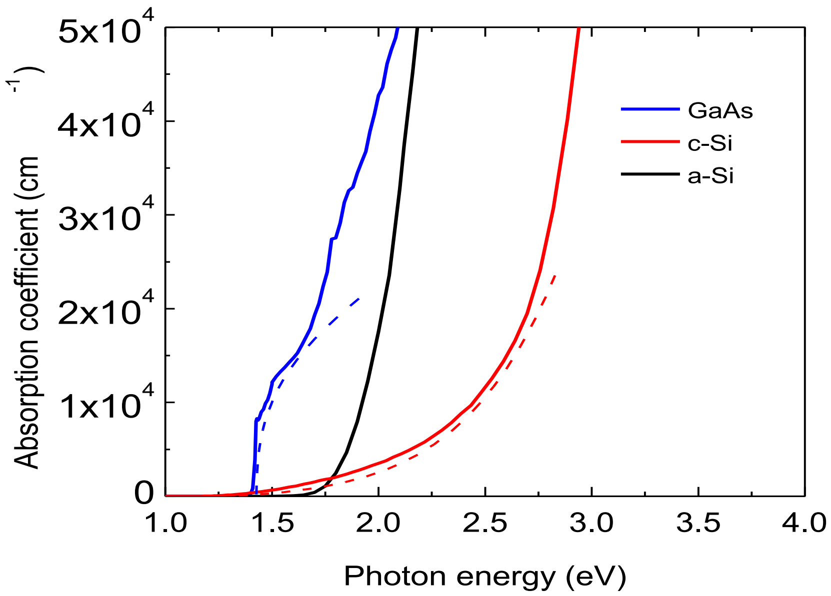
Varshni, physica (1967)

Absorption coefficient (summary)

logarithmic scale (usually shown)



linear scale (clearer proportionality)

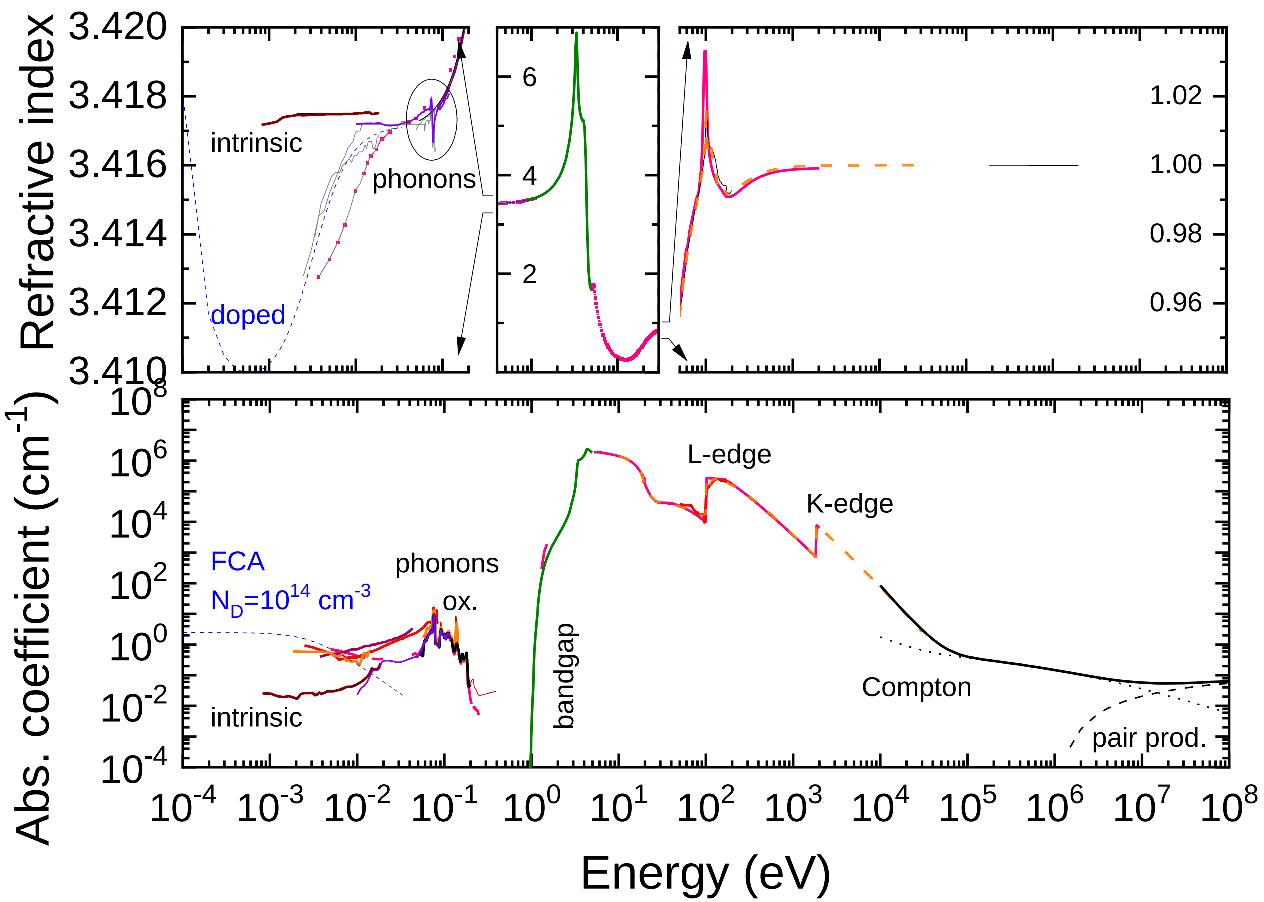


Direct: strong absorption close to gap $\alpha \sim (h\nu - E_g)^{\frac{1}{2}}$

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

a-Si: essentially indirect

Other dispersion effects in c-Si



Contributions to polarizability

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

Chandler, JAP, (2005)
Green, Sol. En. Mat. (2008)
Palik, Handbook of Opt. Const.
Hubell, NIST (1969).

Absorption in a silicon slab

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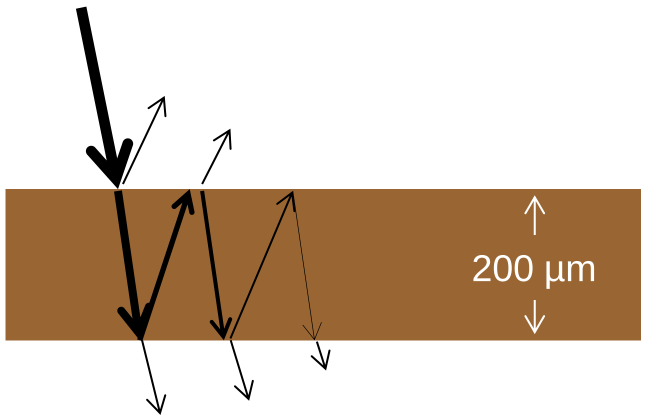
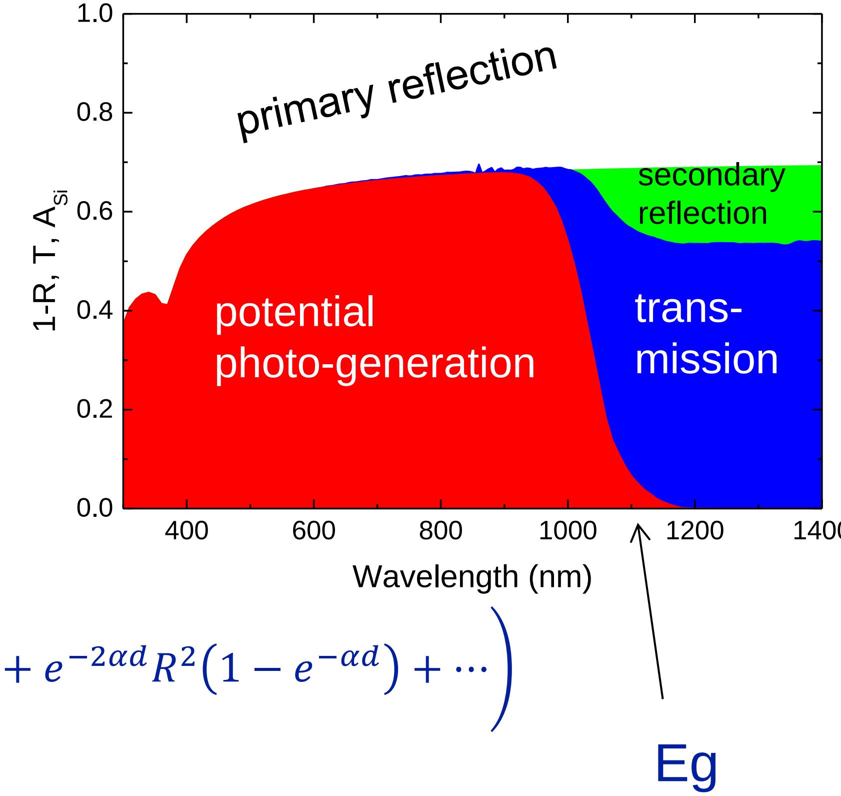


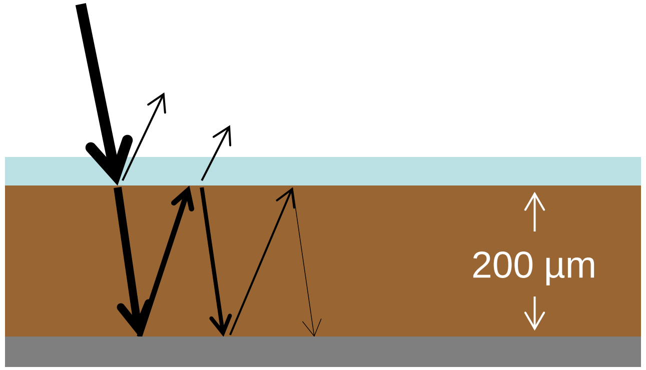


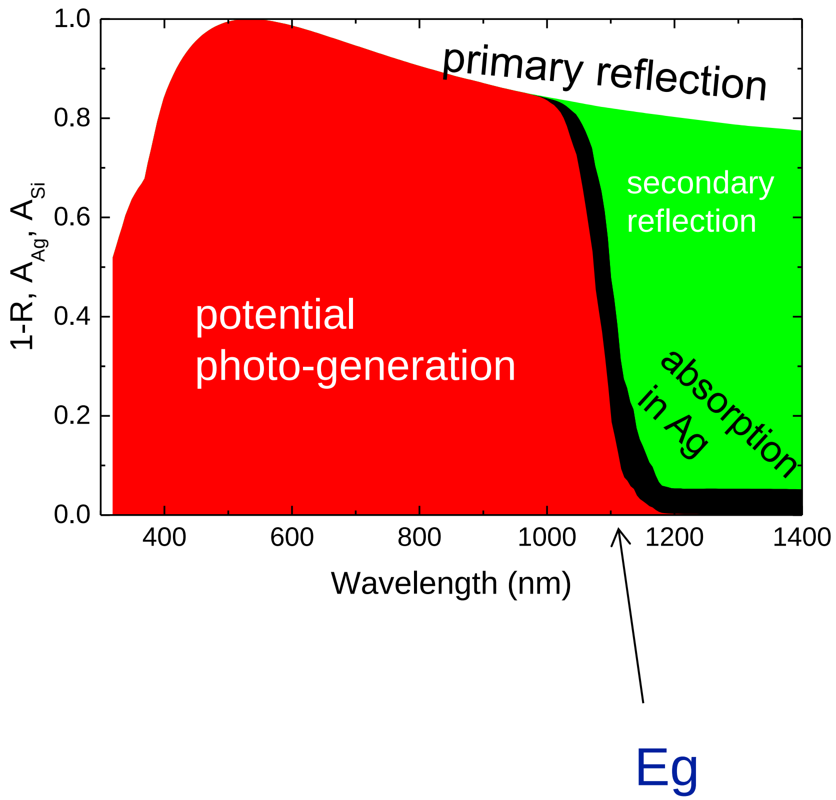
$$A = (1-R)\left(\sum(1-e^{-\alpha d}) + e^{-\alpha d}R(1-e^{-\alpha d}) + e^{-2\alpha d}R^2(1-e^{-\alpha d}) + \cdots\right)$$

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

- >30% primary reflection (high refractive index) => needs AR functionality
- avoid transmission loss by rear reflector

Optical improvement





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

still significant loss due to low absorption
=> needs absorption enhancement

Enhancing absorption via prolonged light path

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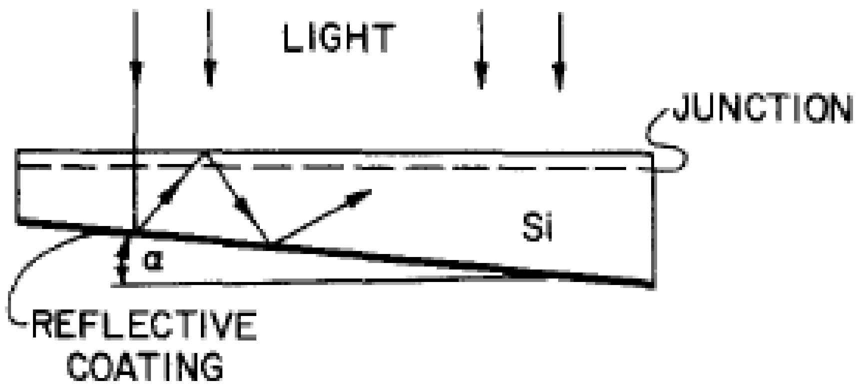
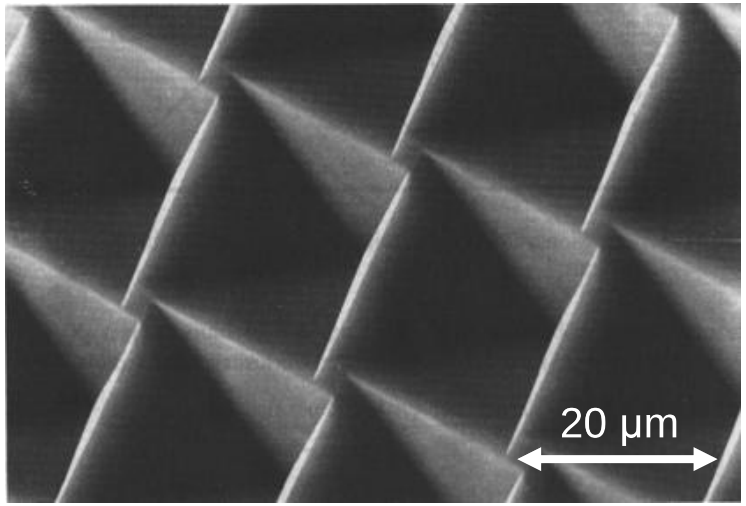
Total internal reflection
$\theta_{crit} \approx 17°$ (n ≈ 4)



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

modern high eff. cells: inverted pyramids



Apply geometric ray optics
for optimization

from Goetzberger, Sonnenenergie (1997)

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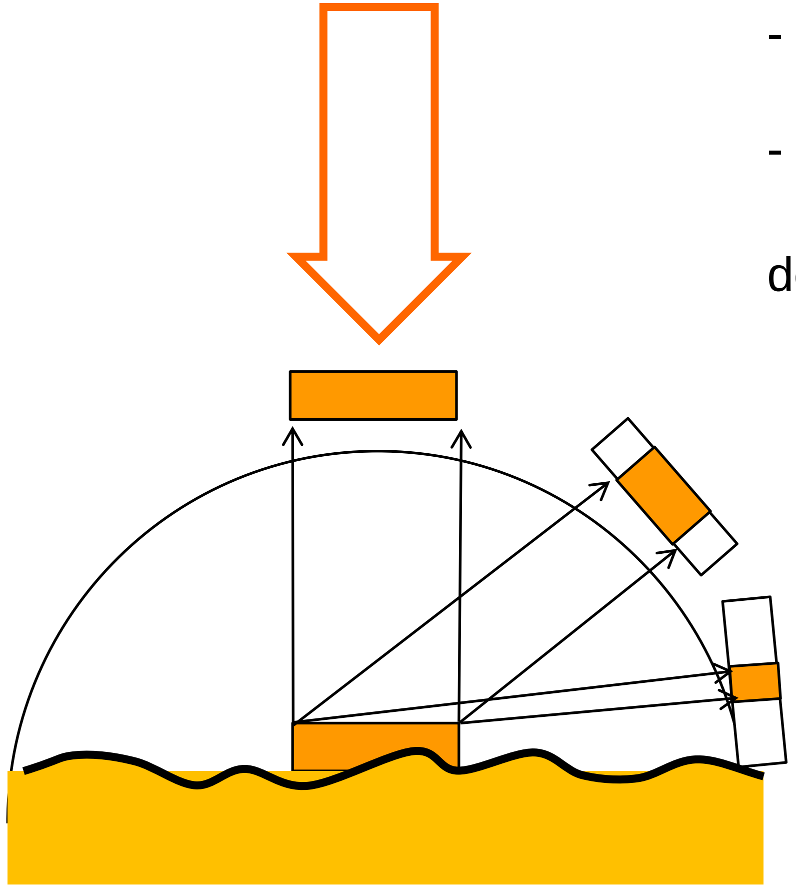
IEM NEUCHATEL

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)

Lambertian path prolongation

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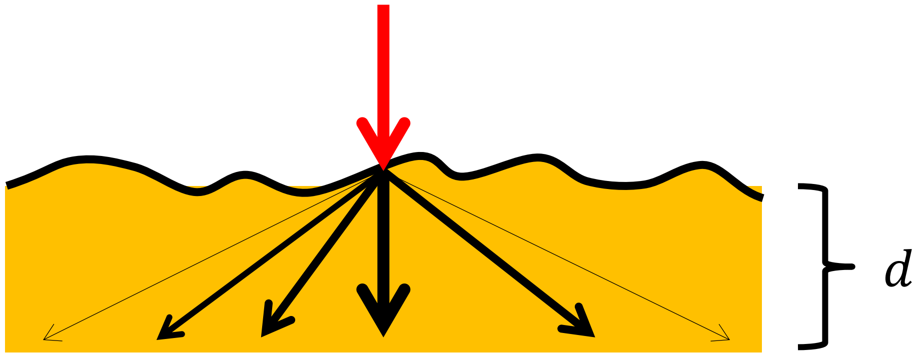
Prolongation of an oblique path

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



Average prolongation

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

$$= 2\pi \cdot \int \frac{d}{\cos\theta} \cdot \frac{\cos\theta}{\pi} \cdot \sin\theta \, d\theta = 2 \cdot d$$

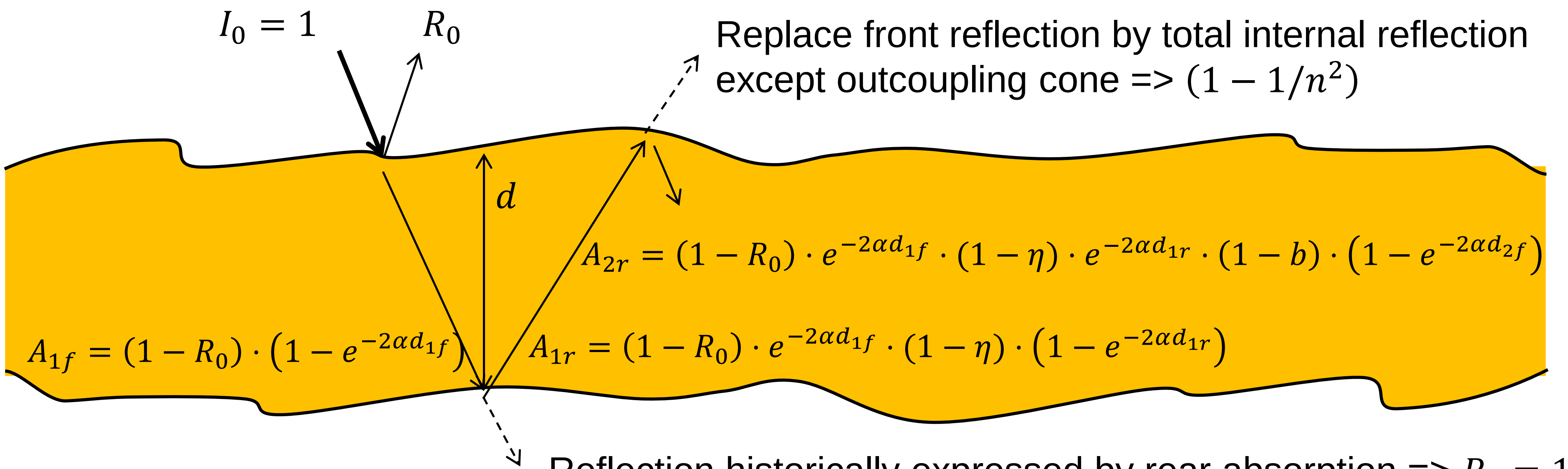
ARS (weighting factor, probability to find angle btw. θ and $\theta + d\theta$)

length of oblique path

Absorption with (ideal) light scattering

Sum up absorption upon bouncing forth and back

Replace front reflection by total internal reflection except outcoupling cone => $(1-1/n^2)$



Reflection historically expressed by rear absorption => $R_r = 1-\eta$

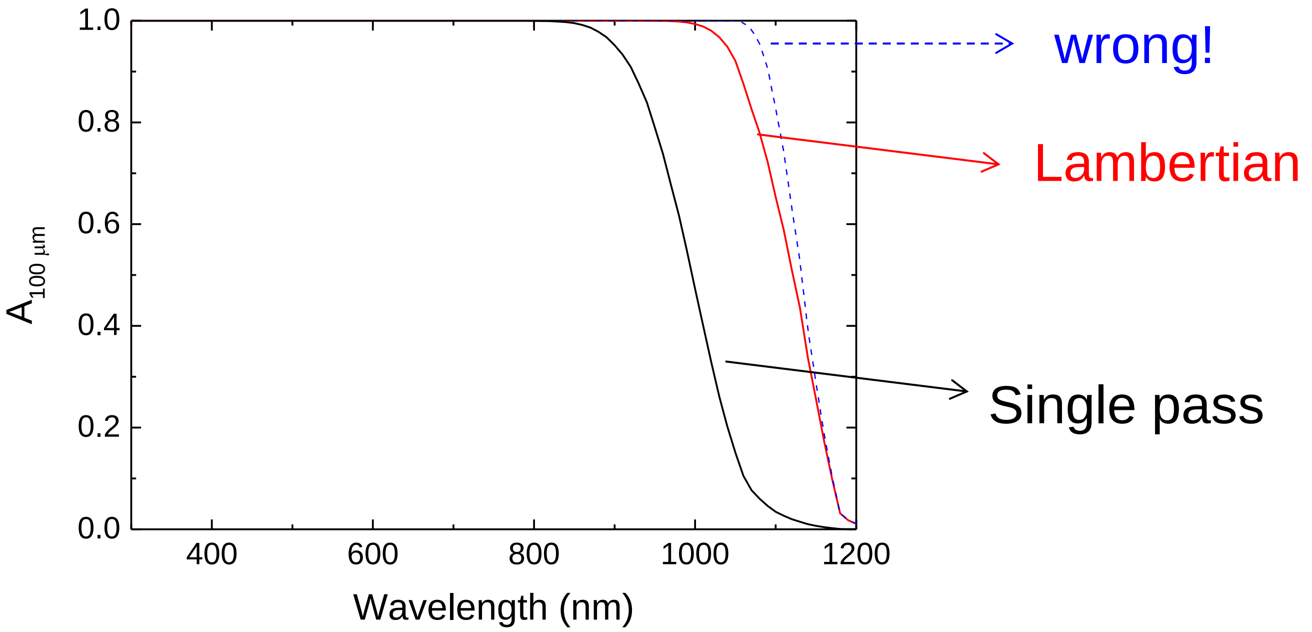
$$A = \sum_{k=0}^{\infty} \underbrace{\left[(1-e^{-2\alpha l}) + e^{-2\alpha l}(1-\eta)(1-e^{-2\alpha l})\right]}_{A_{\text{double pass}}} \cdot \underbrace{\left[e^{-4\alpha l}(1-\eta)(1-1/n^2)\right]^k}_{\text{Attenuation}}$$

$$= \frac{1-\eta e^{-2\alpha l} - (1-\eta)e^{-4\alpha l}}{1-(1-\eta)e^{-4\alpha l} + [(1-\eta)/n^2]e^{-4\alpha l}}.$$

$$\approx \quad 4n^2\alpha l \qquad \text{if: } \eta = 0, \alpha l \ll 1$$

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

Upper limit of light trapping (silicon)



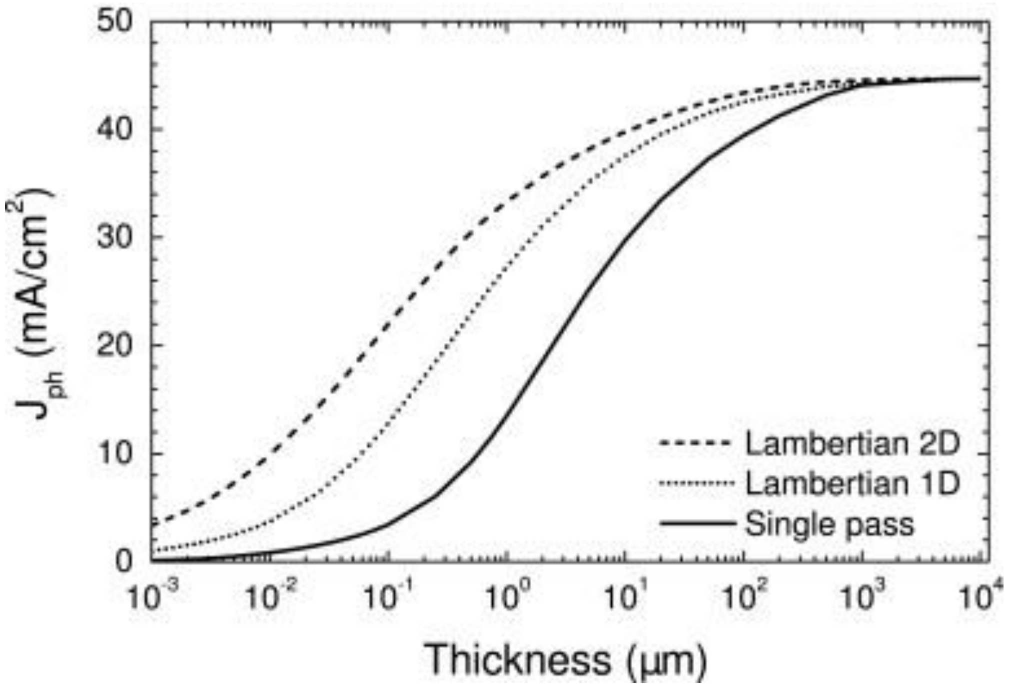
Single pass (100 µm): $A = 1 - e^{-\alpha l}$

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: $A = 1 - e^{-\alpha \cdot 4n^2 l}$

Maximum photocurrent (silicon)

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

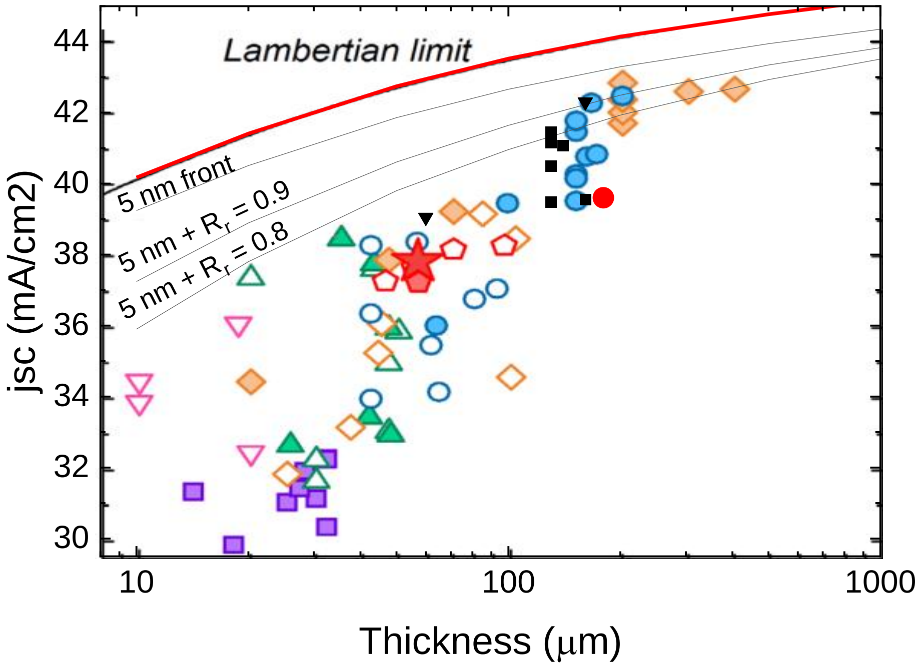


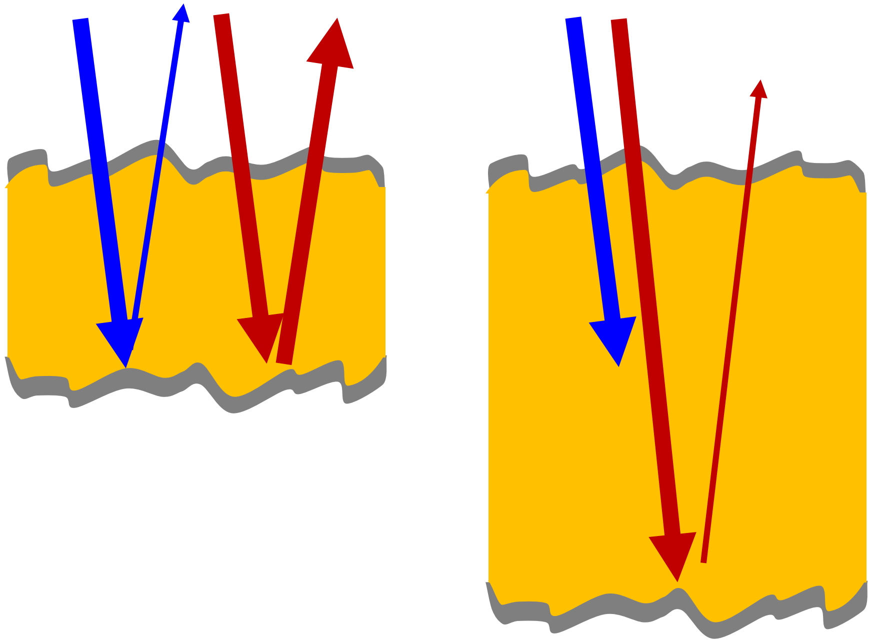
Saturation value: 46 mA/cm^2
With ideal light scattering: 70 to 100 μm sufficient

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

Andreani, SolMat (2015)

Maximum photocurrent vs. thickness



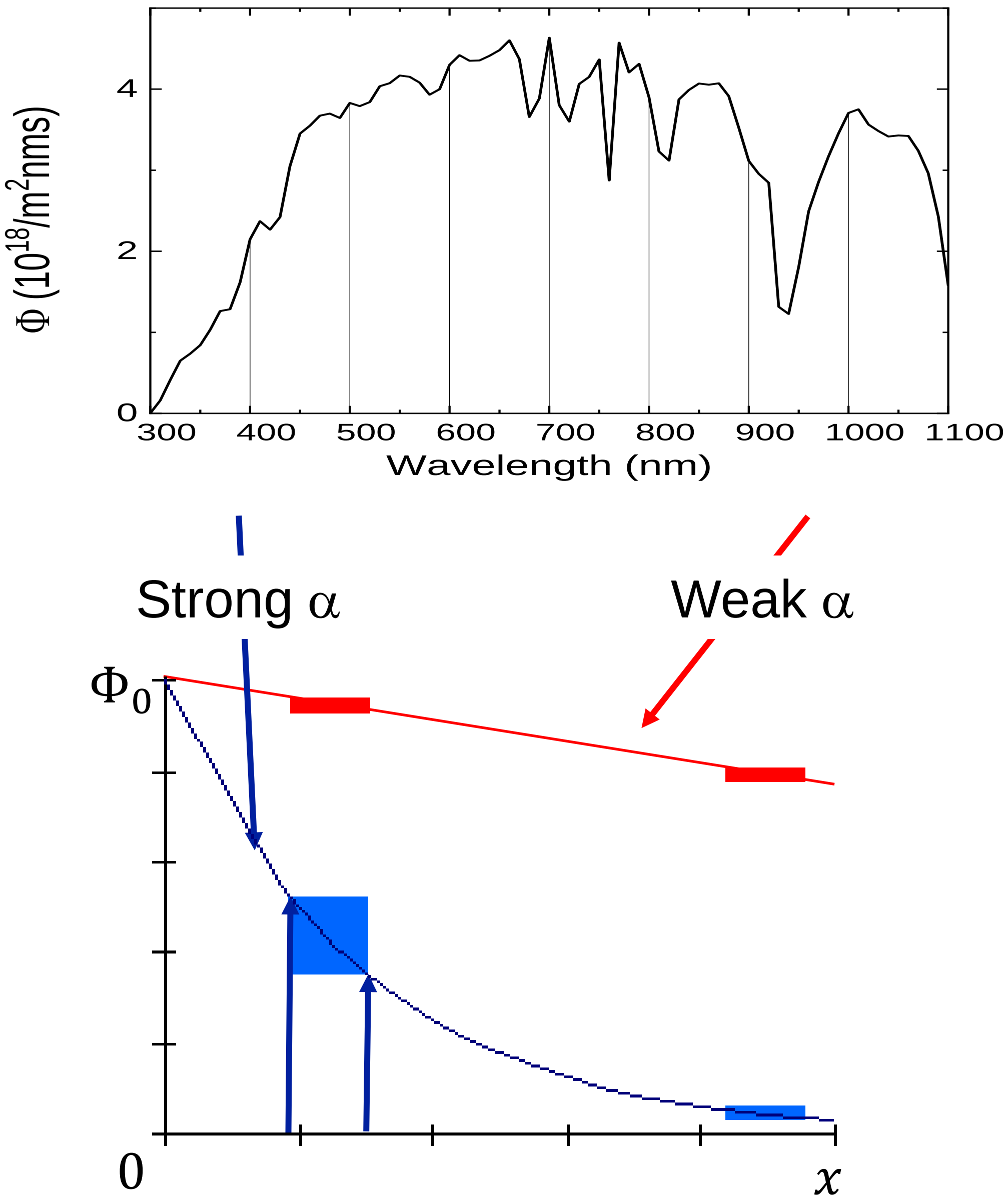


Real devices:

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

on jsc limit: Bozzola, EU-PVSEC (2011)
collection of data: Sai, RRL (2021)

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 $\alpha(\lambda)$

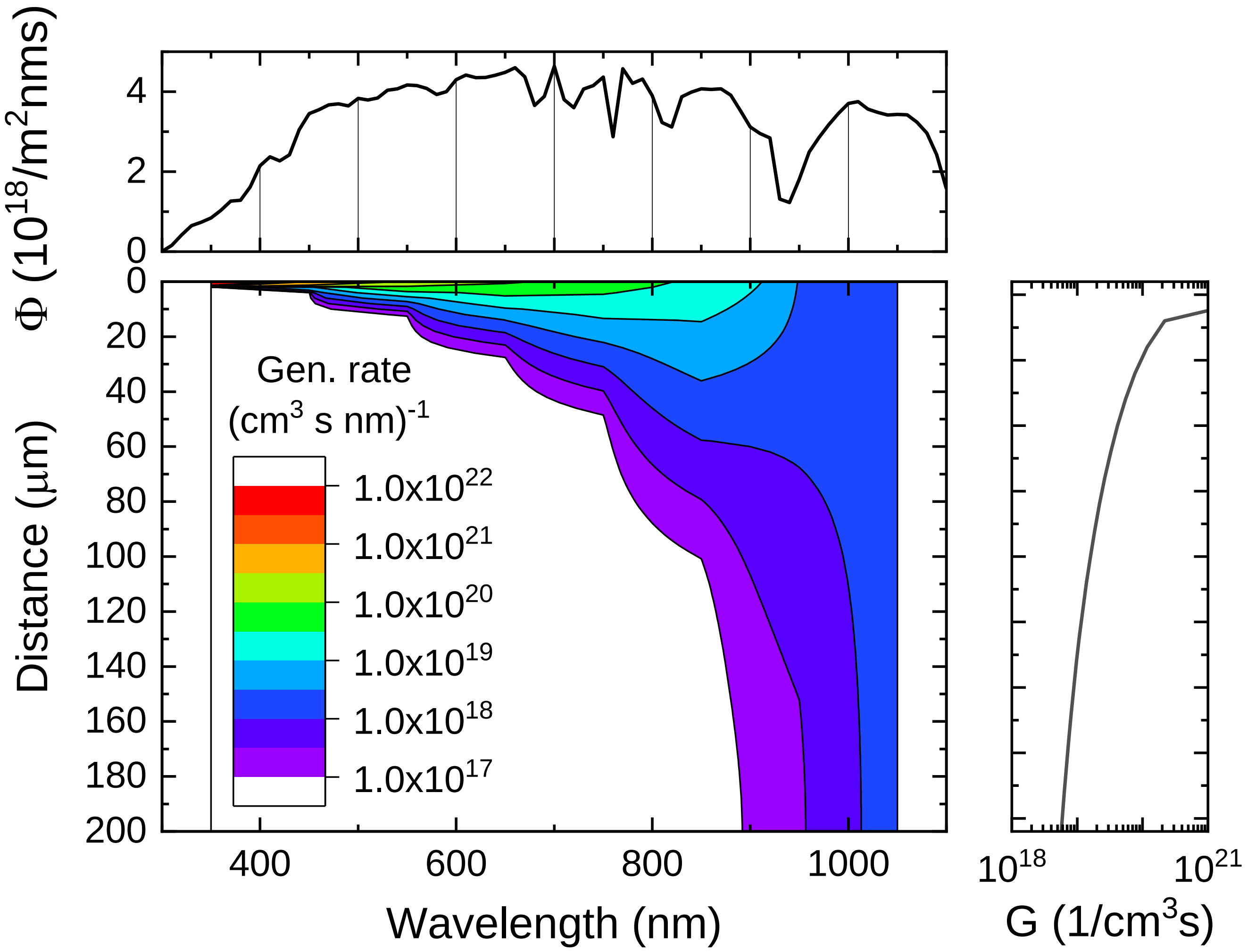
Light absorbed at depth x:
$\Phi(x) - \Phi(x + \Delta x) \equiv -d\Phi$

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

Generation rate



Short λ: strong absorption
=> Large $G(x)$ at front

Long λ: weak absorption
=> Almost uniform $G(x)$ in bulk

Summary

- 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)