Large Area Electronic Materials – Crystalline Silicon I

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 $n + i\kappa$

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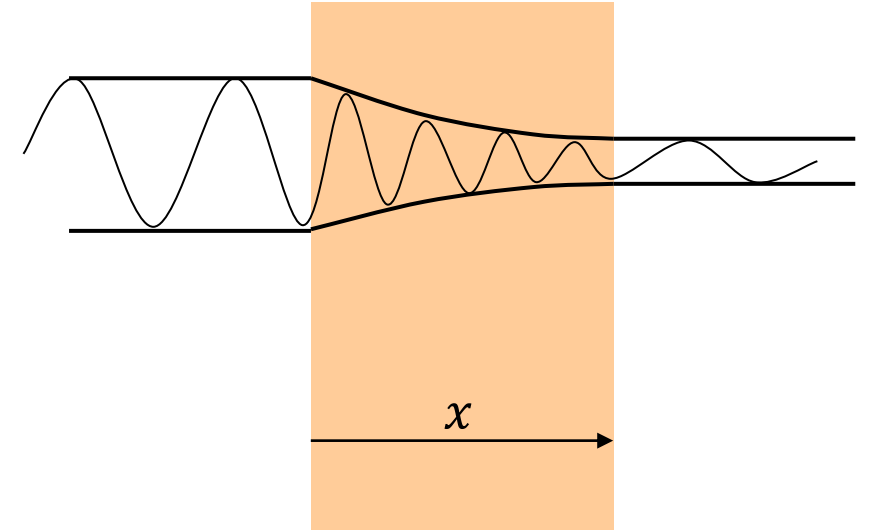
Field amplitude and intensity:

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

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

Absorption coefficient: exponential decay of intensity

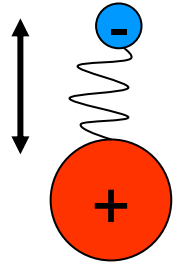$$\alpha = 4\pi\kappa / \lambda$$

Issue: how to find n or ε

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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

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

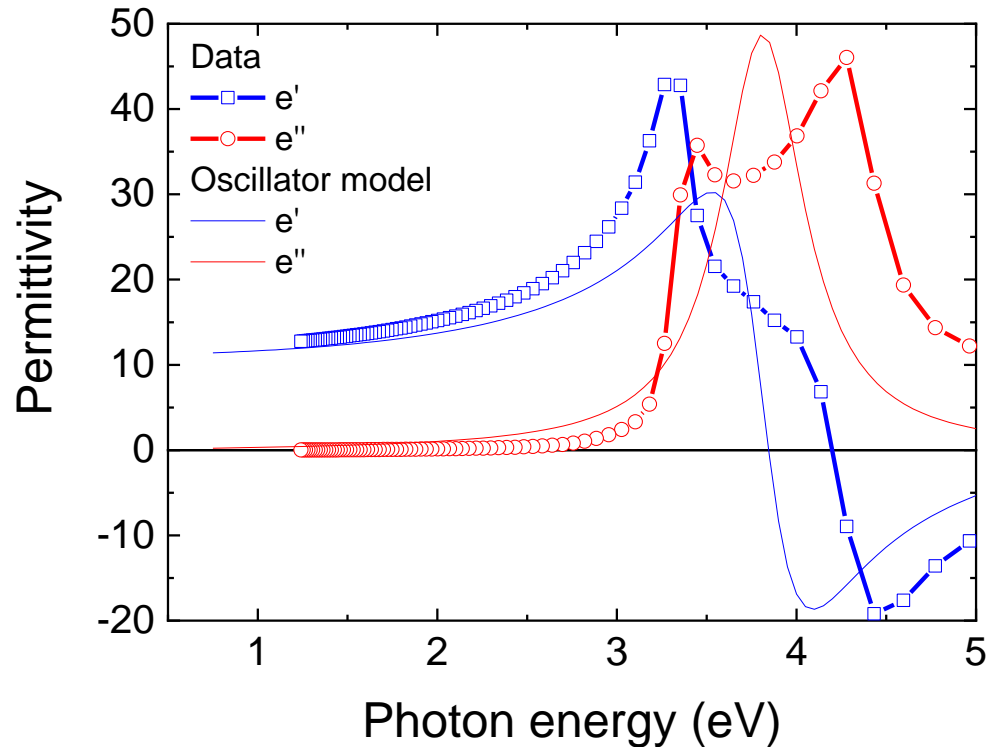Dipole moment and macroscopic polarization (Clausius-Mosotti):

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

Find permittivity (dielectric function):

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

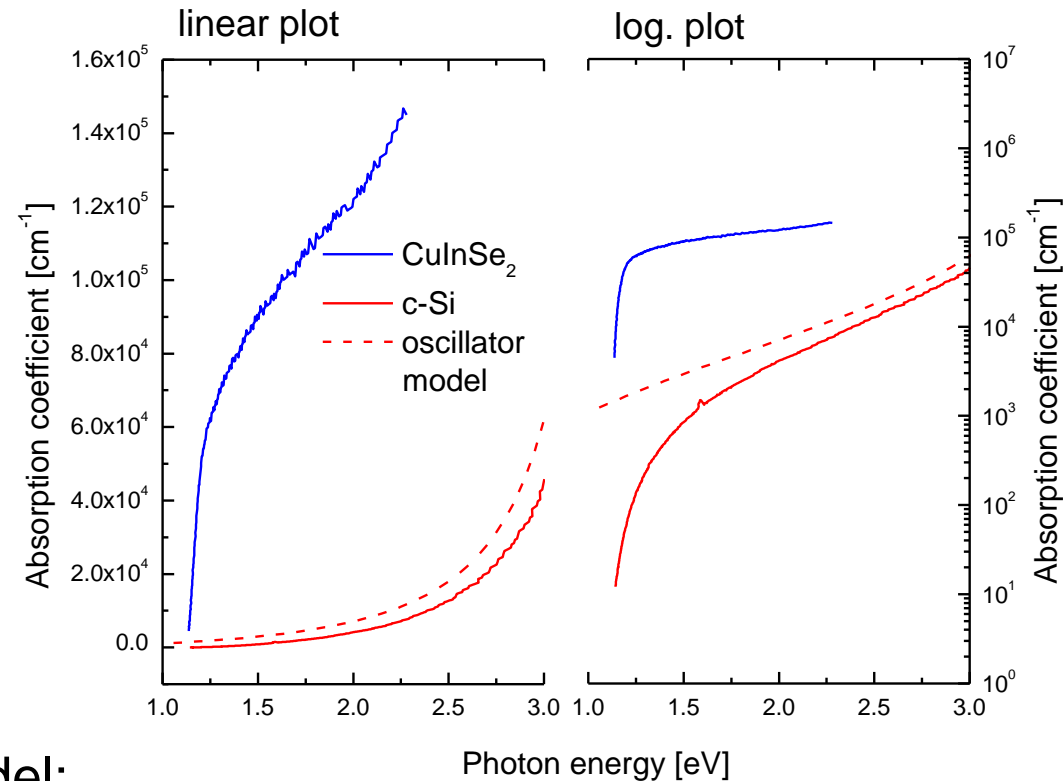empiric modification (theoretically $\epsilon_\infty = 1$)

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)

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Absorption coefficient (measured)

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

Absorption coefficient of semiconductors

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Needs quantum mechanics

Heuristic link between ϵ'' and absorption:

$$P_{abs} = \frac{1}{2}\omega\epsilon_0\epsilon''E_0E_o^* = \hbar\omega\sum_{\vec{k},\vec{k}'}w_{vc}$$

Absorbed power from Poynting theorem

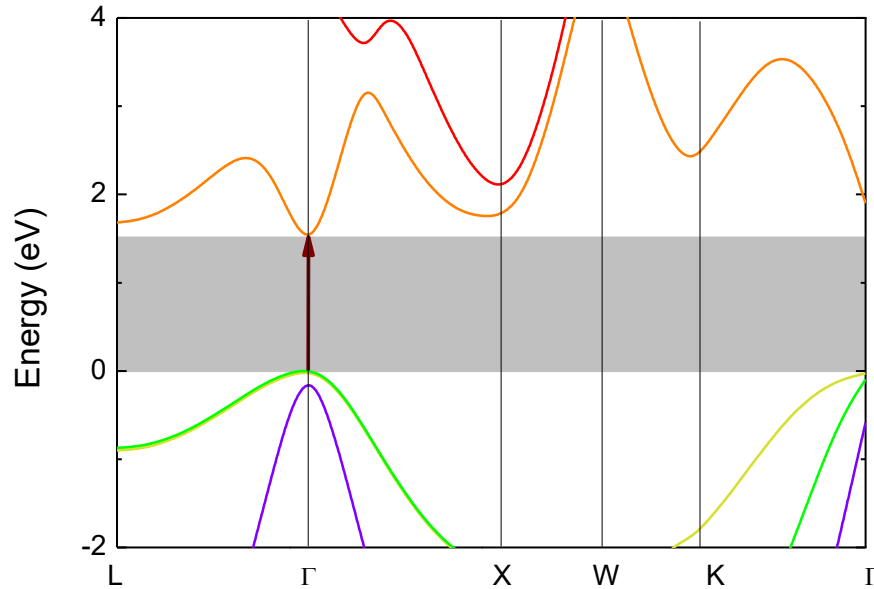Absorbed power by summing all allowed quantum-mechanical transitions

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)

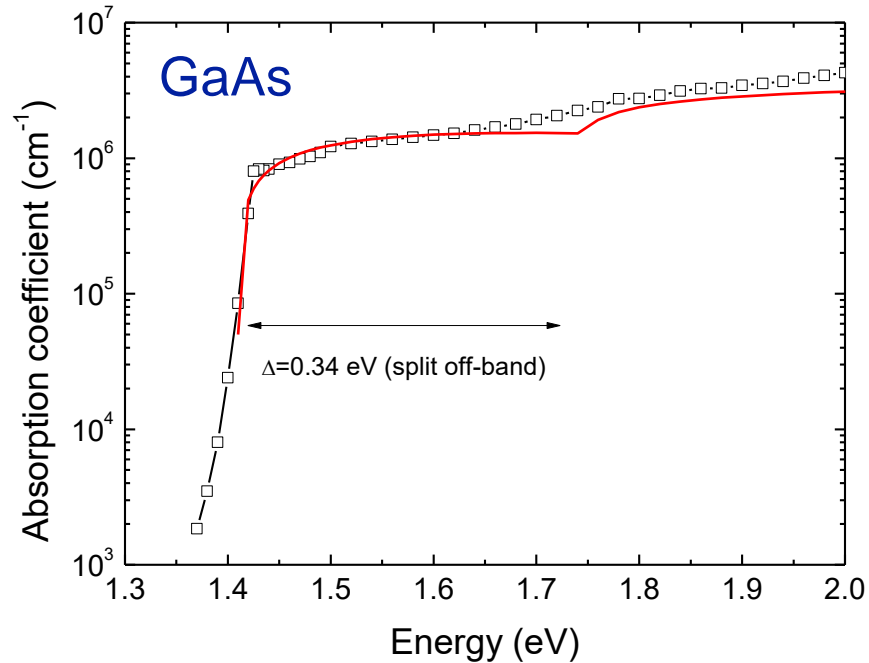Interaction Hamiltonian:
electron-radiation

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

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

Transition probability:
Fermi's Golden rule

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

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

Absorption coefficient

GaAs

Δ=0.34 eV (split off-band)

Absorption coefficient (cm^{-1})

Energy (eV)

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

+ 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

Indirect absorption (e.g. Silicon)

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Band diagram

Interaction Hamiltonian:
electron-radiation + electron-lattice

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

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

Deformation potential

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

$$= D_V \sqrt{\frac{\hbar}{2M\omega_q}} \cdot \left(i\vec{e}_{\vec{q}}\vec{q}\right)\left(a \cdot e^{i\vec{q}\vec{r}} - a^{\dagger} \cdot e^{-i\vec{q}\vec{r}}\right)$$
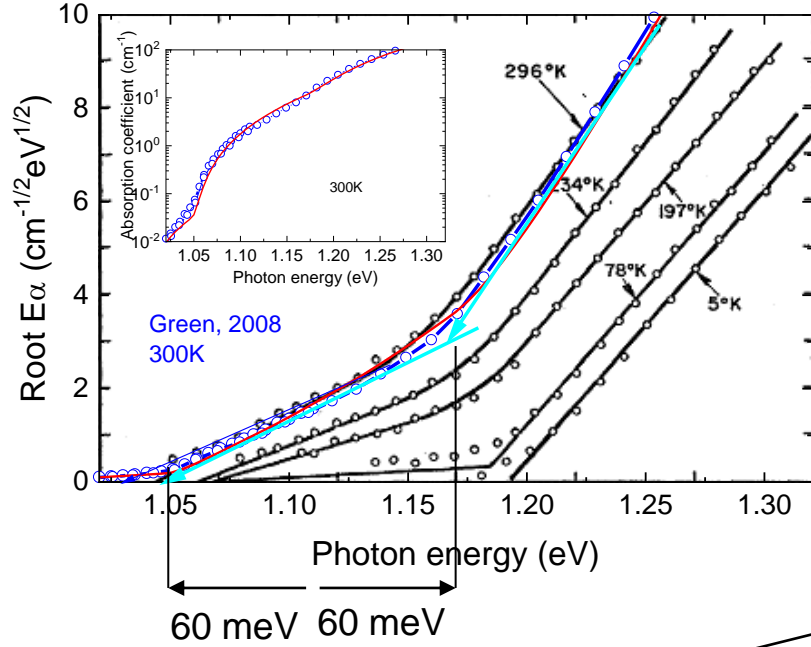
Fermi's Golden rule
(second order $i \rightarrow f$)

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

Integrated:

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

Absorption coefficient c-Si

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

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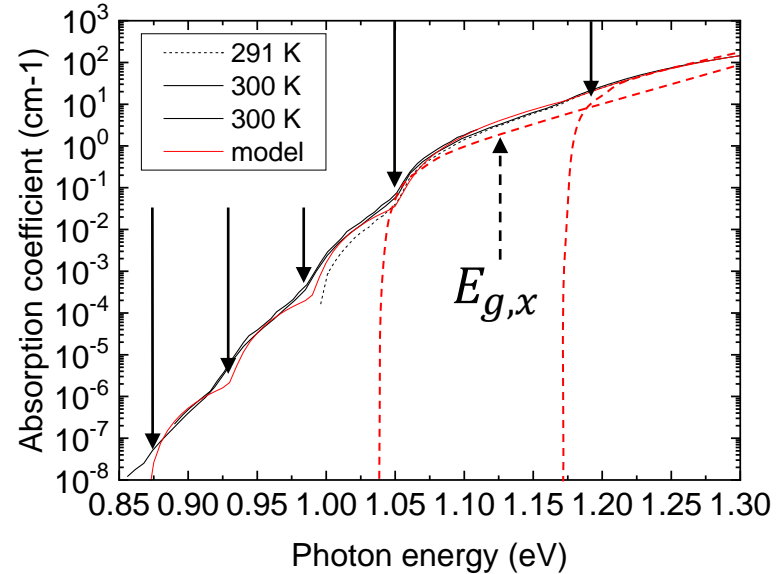
(lattice provides phonon, cooling)   (lattice absorbs phonon, heating)

Excellent correspondence to measured data

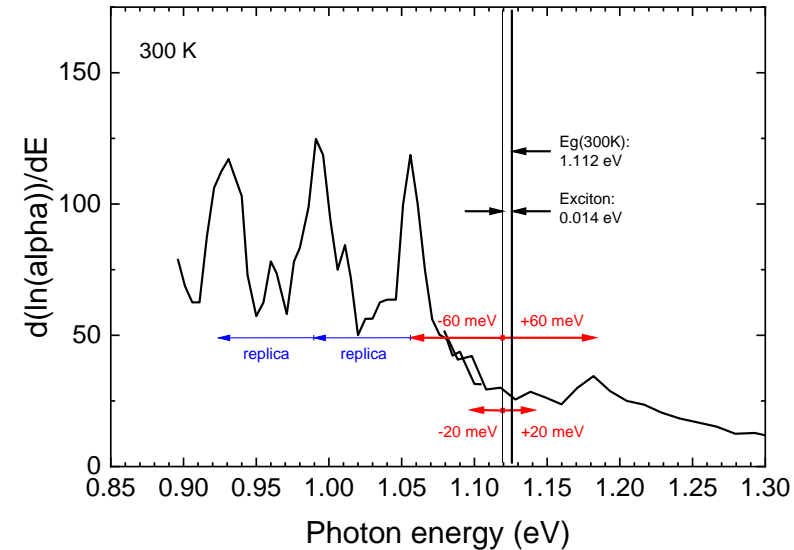MacFarlane, PR 1955
Braunstein, PR 1959

Close-up of low absorption region

Weakly absorbing tail below gap
Fine structure:
- large signatures at ± 60 meV
- weak signatures at ± 20 meV

Explanation: LO and TO phonons
mediate absorption
below gap: lattice must provide phonons (cooling)
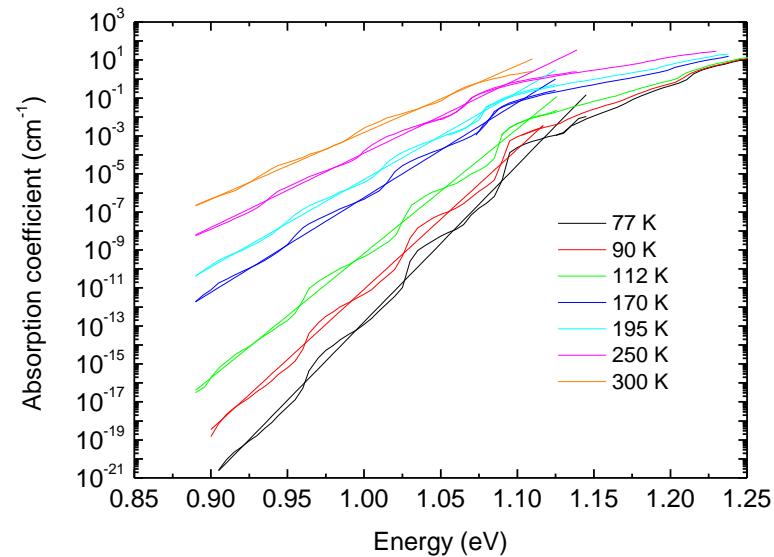above gap: phonons are emitted (heating)

Haynes, JPCS 1959
Vouk, JPC 1977
Cody, JNCS 1992

Close up: sub-gap absorption

Temperature dependence of ultra-low absorption:
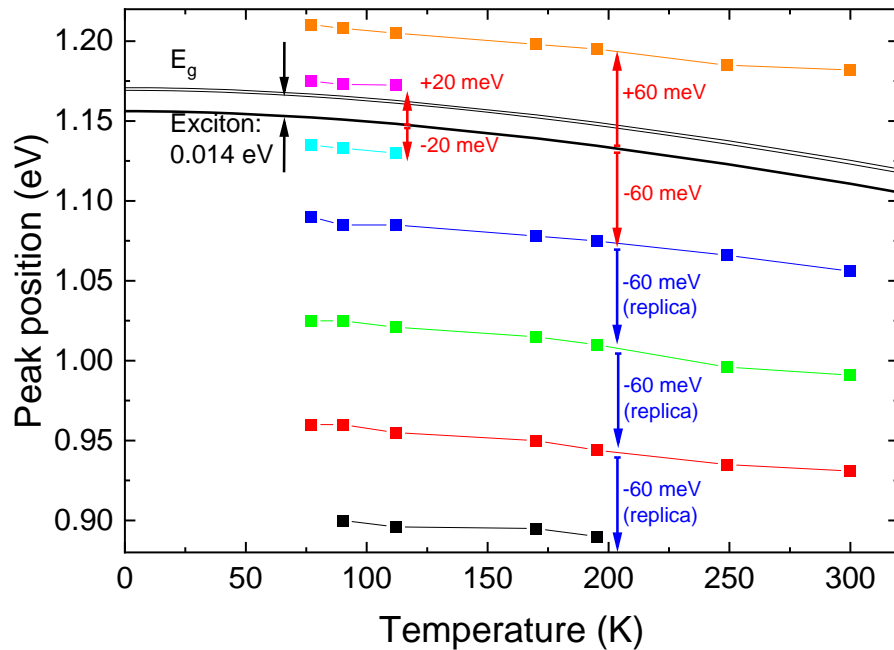(use generalized Planck radiation law to invert photoluminescence yield)
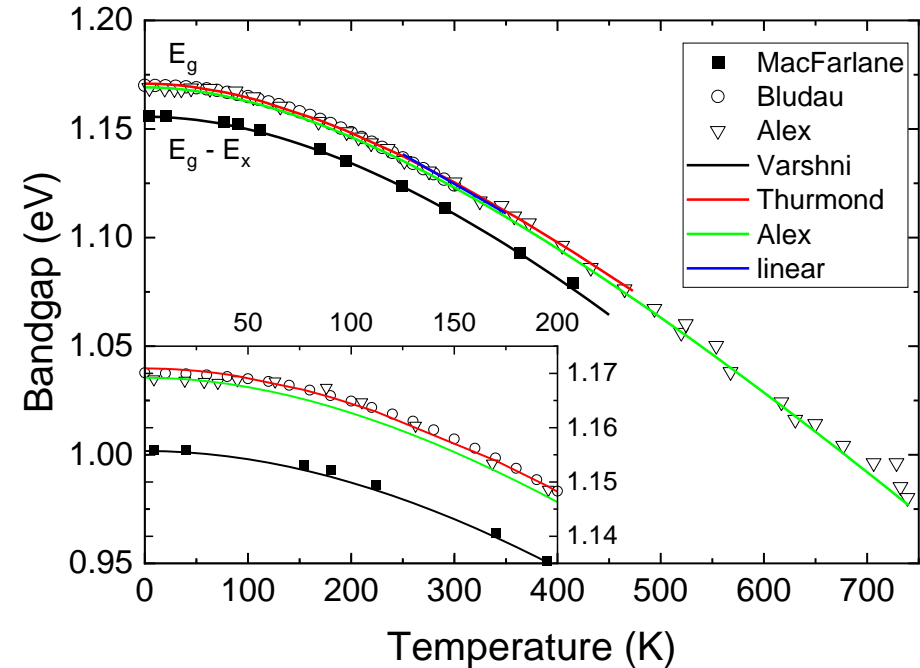
at low temperature:
- Absorption drops massively (lattice must provide phonons)
- Steps become more prominent (less thermal broadening)
- Average slope changes (up to about 10 meV)

McFarlane, PR 1958
Daub, PRL 1995
Trupke, JAP 2003

Temperature dependence of E_g (c-Si)

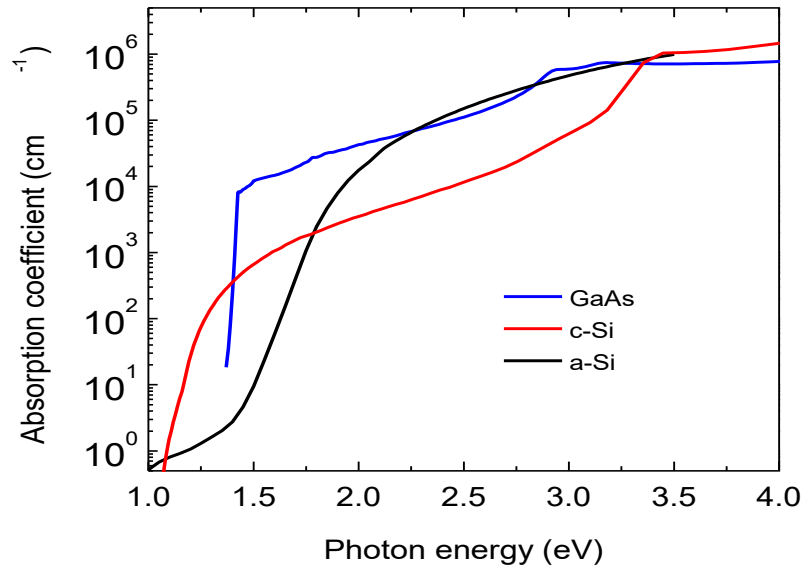Collect positions of phonon signatures

Empiric model:

$$E_g = 1.1557 - \frac{7.021 \times 10^{-4} \cdot T^2}{T + 1108} + E_{ex}$$
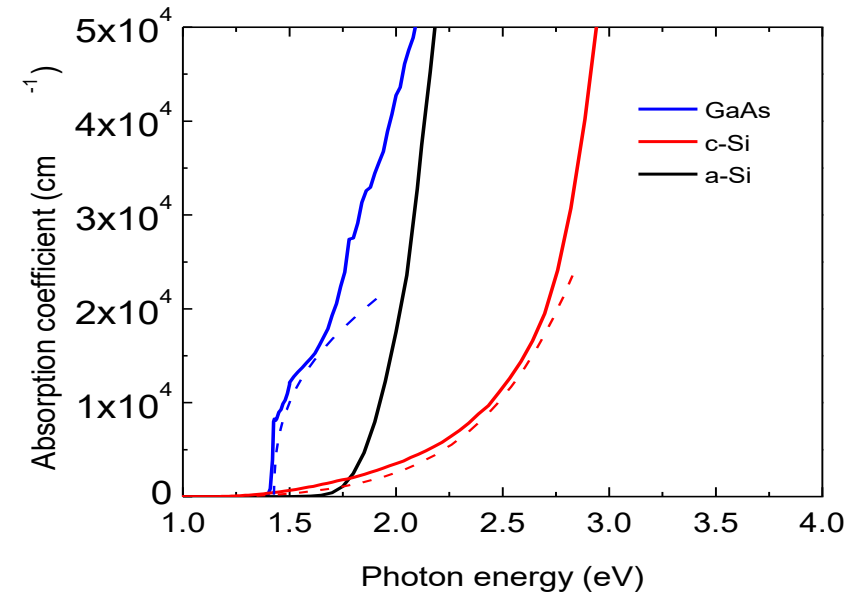
Varshni, physica (1967)

Absorption coefficient (summary)

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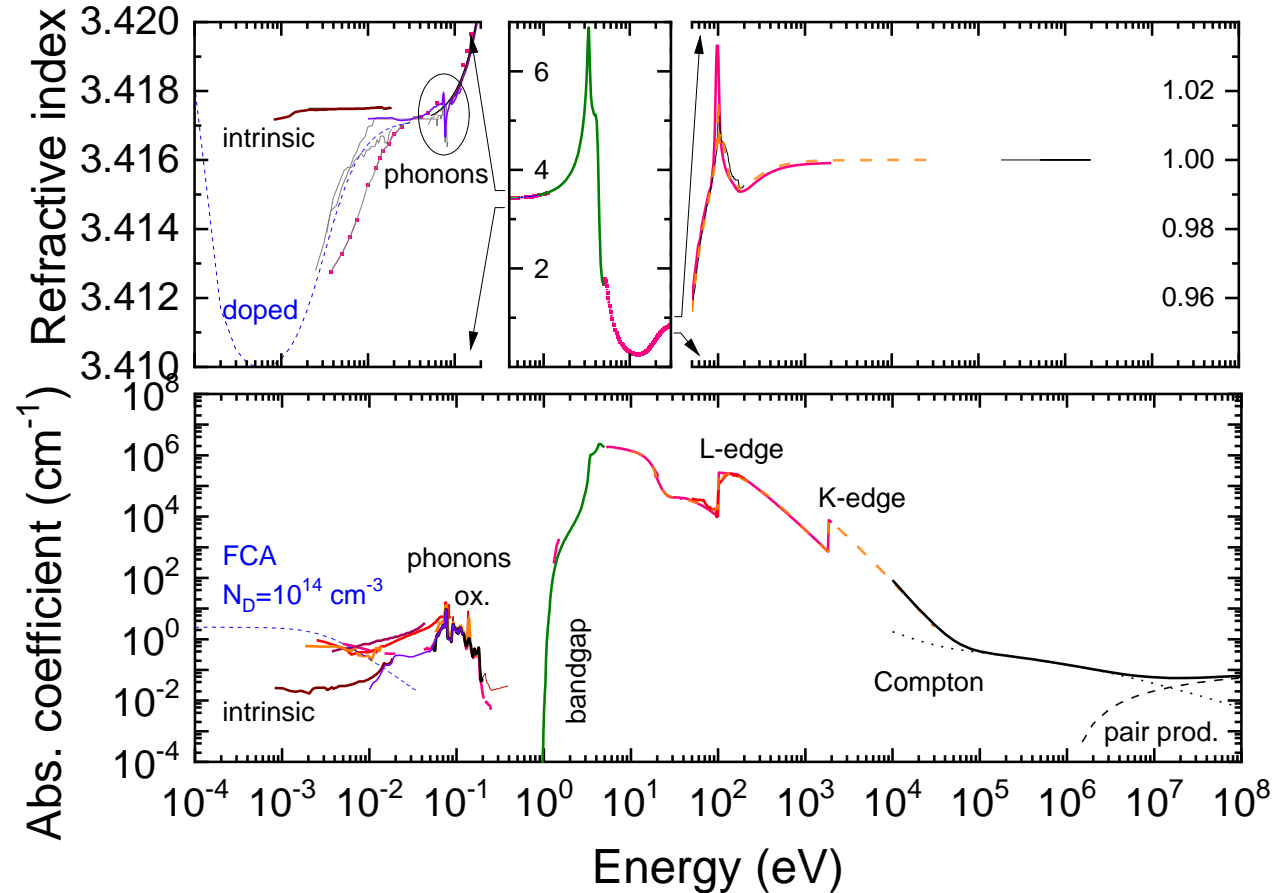logarithmic scale (usually shown)   linear scale (clearer proportionality)

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

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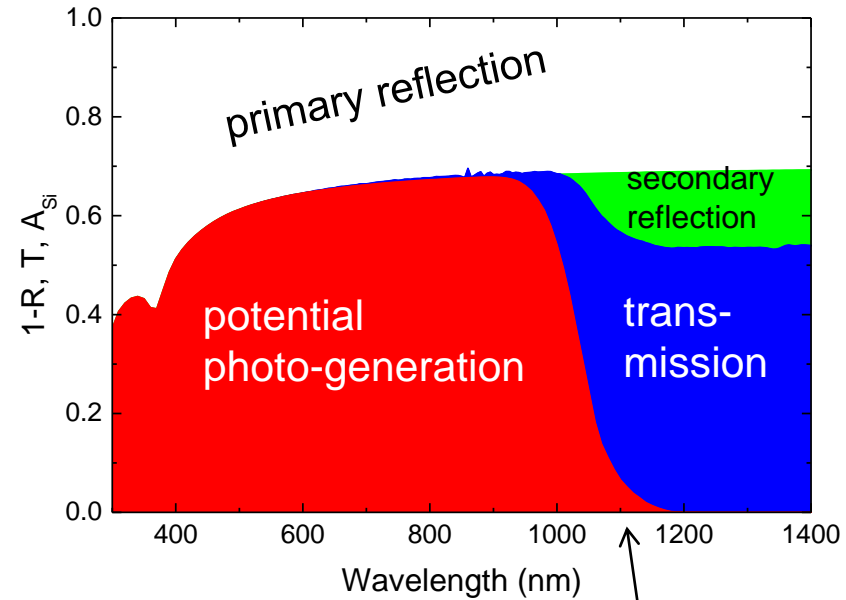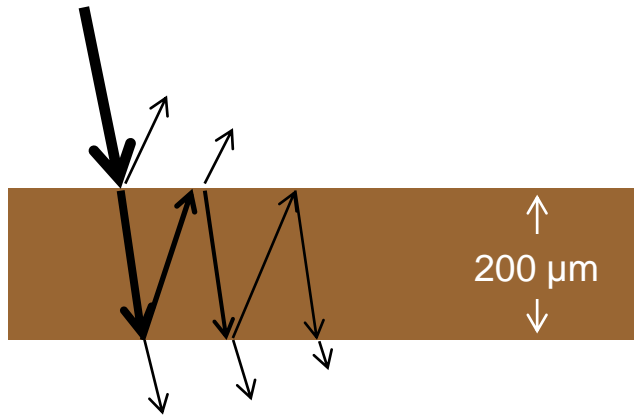Contributions to polarizability
a)   free electron plasma
     (depending on doping, can be up to vis)
b)   lattice vibrations (IR)
c)   displacement of valence electrons
     (vis and UV)
d)   X-ray interactions with core electrons
e)   Compton scattering
f)   pair production

Chandler, JAP, (2005)
Green, Sol. En. Mat. (2008)
Palik, Handbook of Opt. Const.
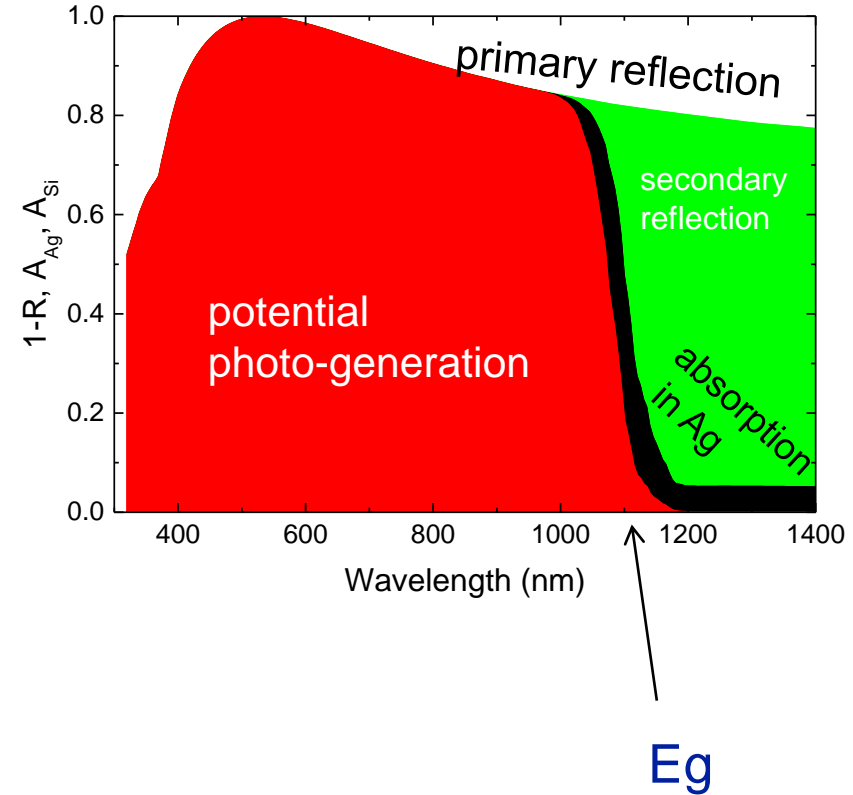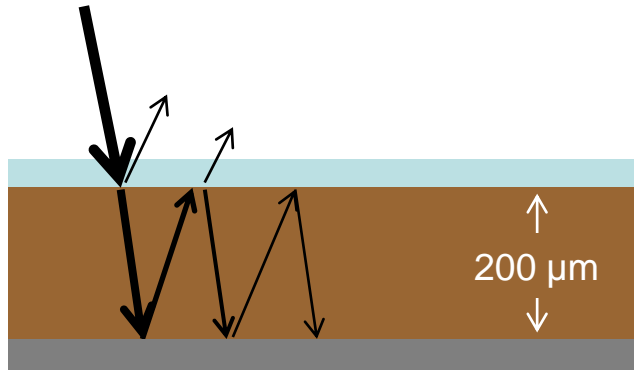
Absorption in a silicon slab

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

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

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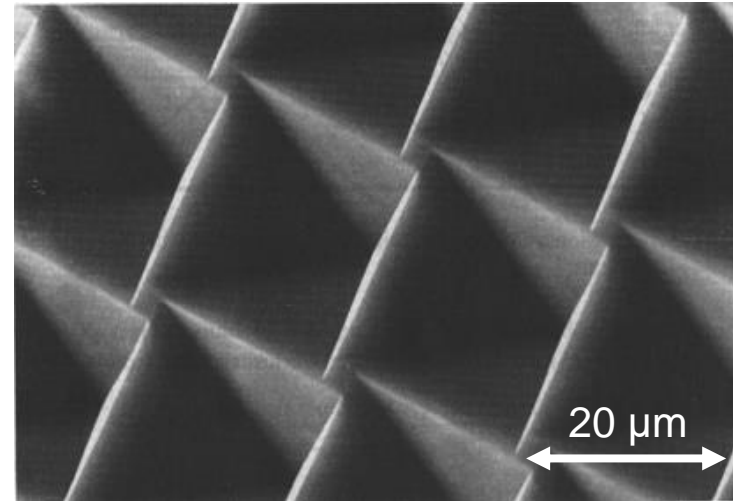- avoid transmission loss by rear reflector

Optical improvement

200 µm

1-R, A_{Ag}, A_{Si}

primary reflection

secondary reflection

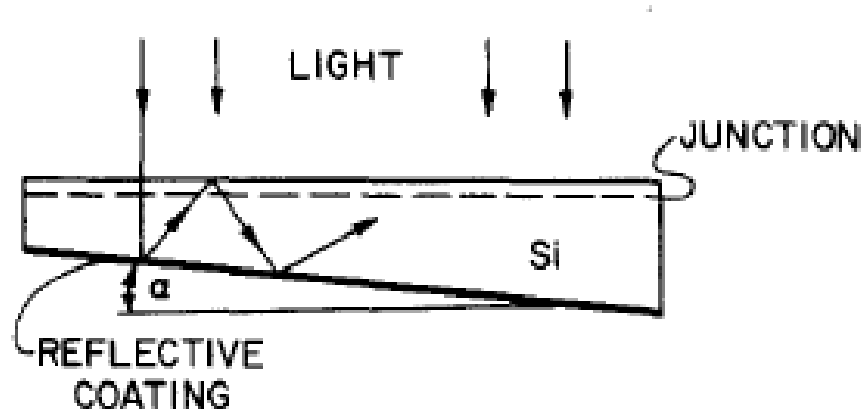potential photo-generation

absorption in Ag

Wavelength (nm)

Eg

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
$\theta_{crit} \approx 17°$ ($n \approx 4$)

modern high eff. cells: inverted pyramids

20 µm

Apply geometric ray optics
for optimization

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

from Goetzberger, Sonnenenergie (1997)

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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)

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