Modern PV-Technologies
3.1: Solar cell materials

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Materials

- 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

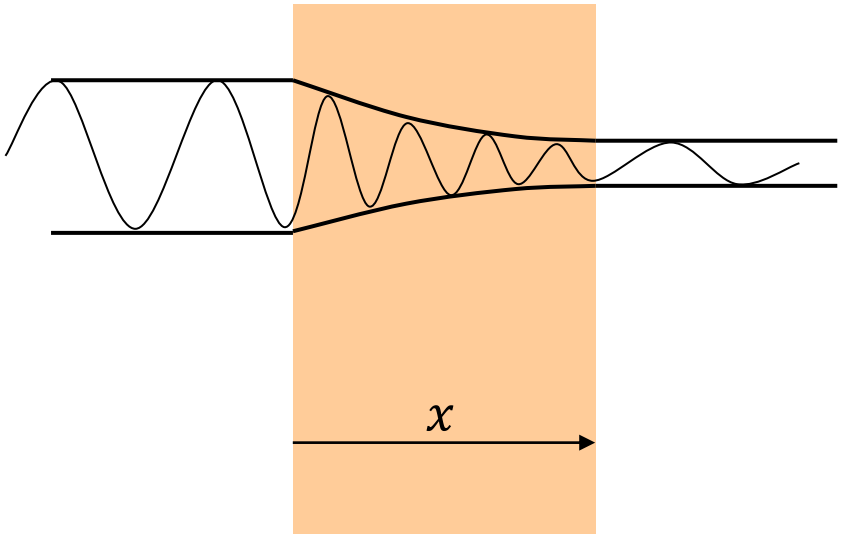
Wave vector in medium defined with refractive index $n + i\kappa$

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

Field amplitude and intensity:

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

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



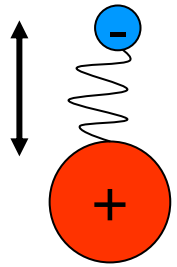
Absorption coefficient: exponential decay of intensity

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

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

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

Dipole moment and macroscopic polarization:

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

Find dielectric function:

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

Comparison to measured dispersion

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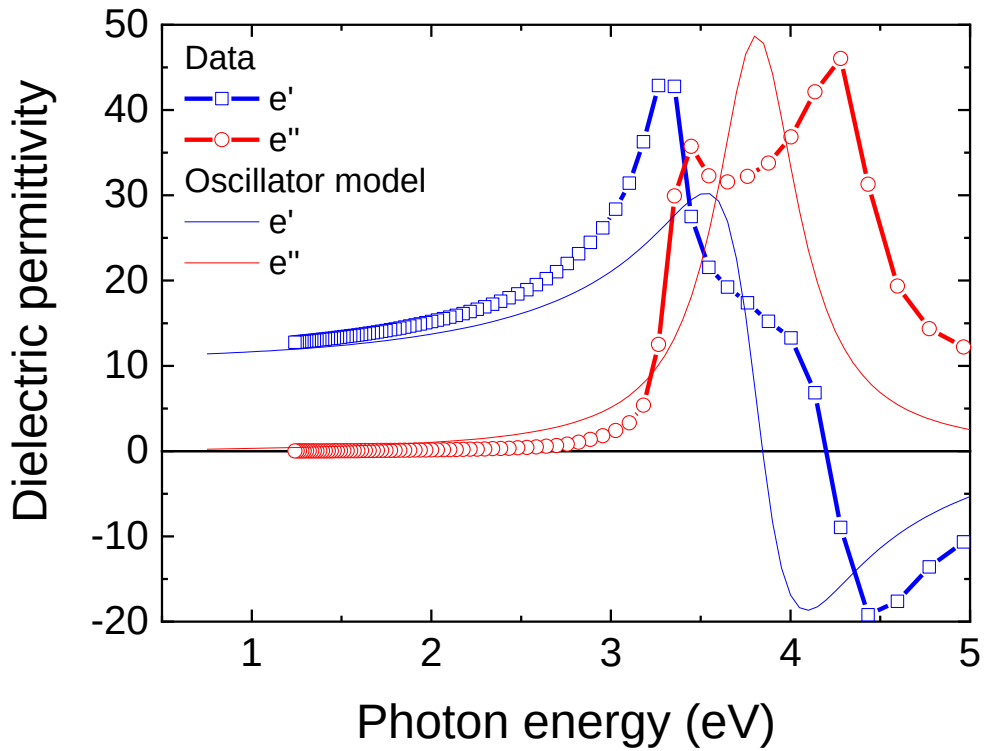
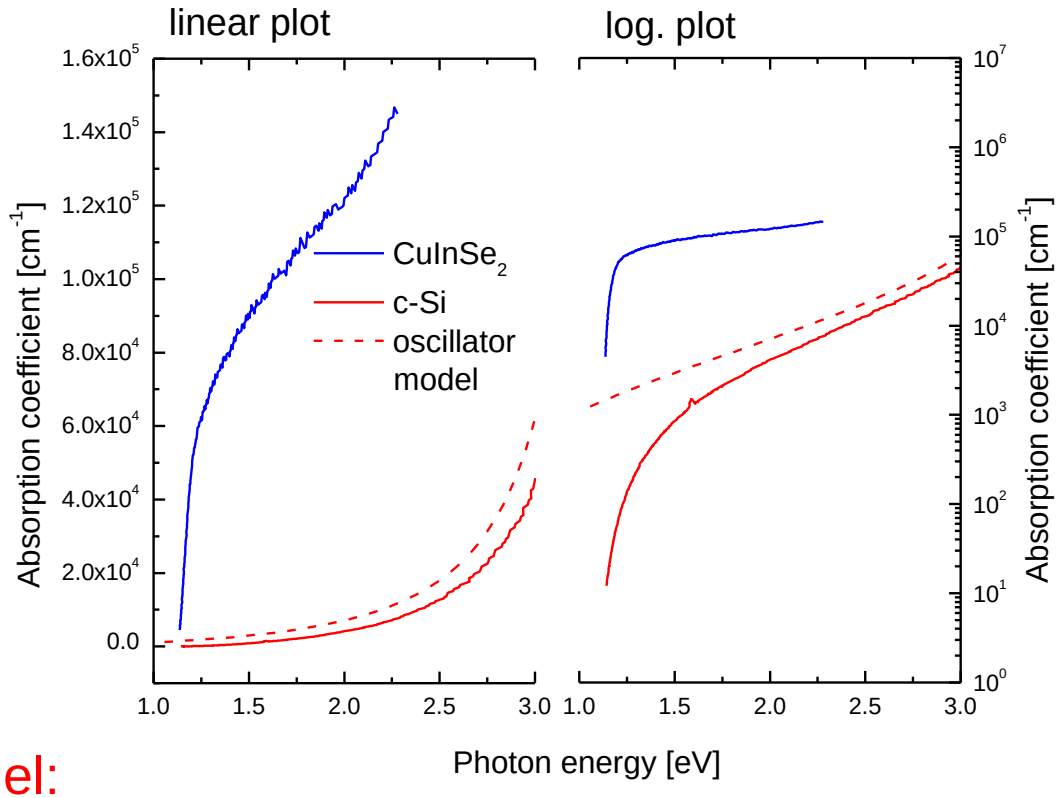


The primitive model with one oscillator yields dispersion effects
Two oscillators (or more) can yield better correspondence (χ is additive!)

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

Absorption coefficient (measured)



Oscillator model:

- OK for c-Si on lin. scale
- BUT no gap behaviour (c.f. log scale!)
- fails totally for CIGS

Absorption coefficient of semiconductors

Needs quantum mechanics

Heuristic link between ϵ'' and absorption:

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

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)

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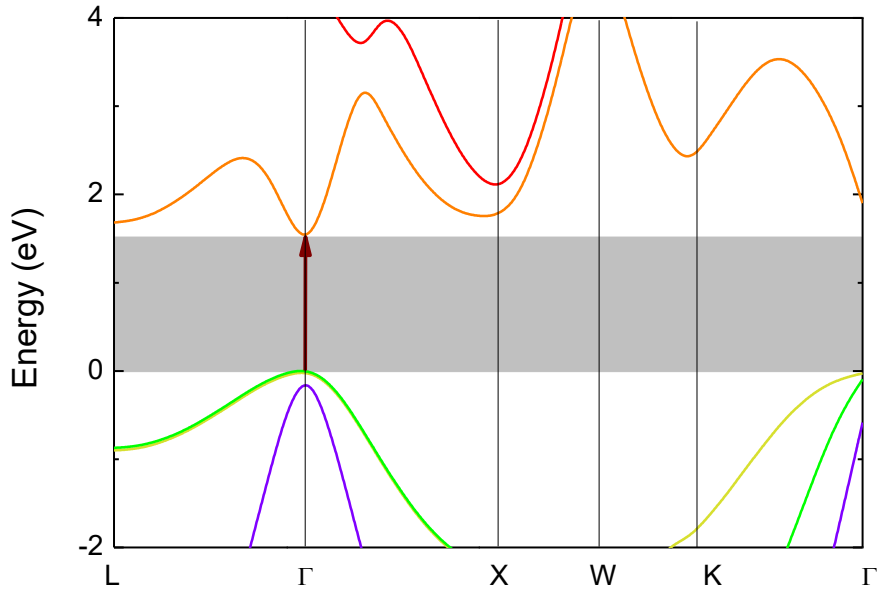
Direct absorption (e.g. GaAs)

Band diagram (pseudopotential method)



Interaction Hamiltonian: electron-radiation

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

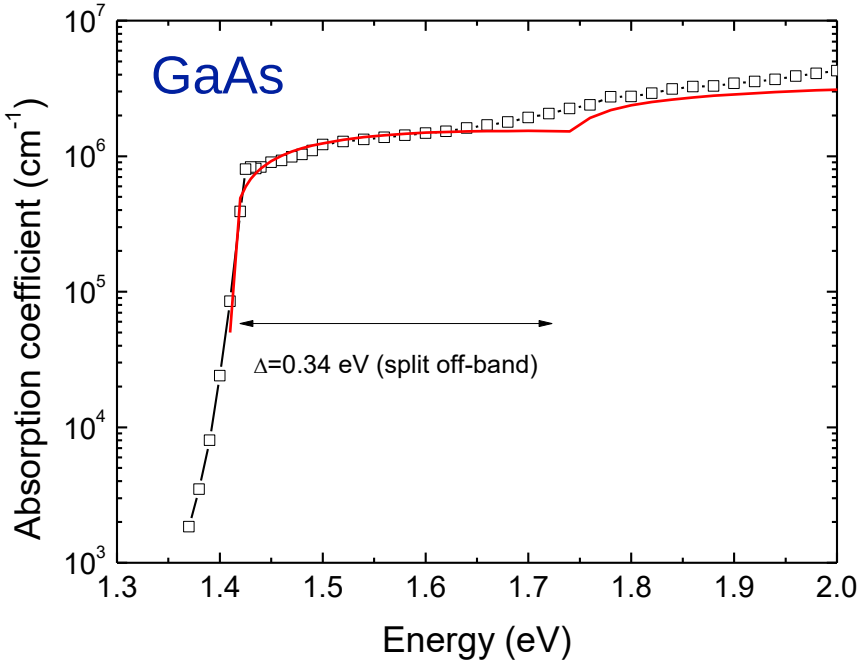
(neglect $\left|\vec{A}\right|^2$ term)

Transition probability: Fermi's Golden rule

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

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

Absorption coefficient



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

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

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

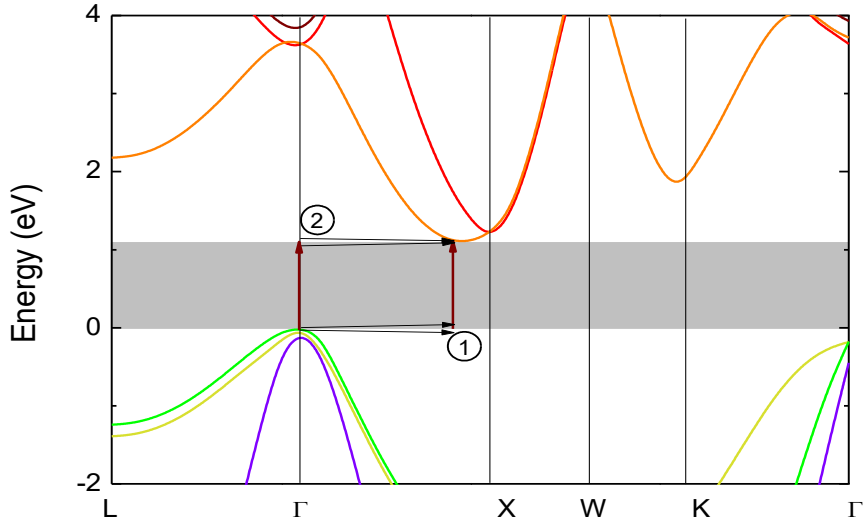
$$\alpha = 4\pi \cdot \kappa/\lambda \sim \frac{1}{\omega}\sqrt{\hbar\omega - E_g}$$

Proportional to square root!

Direct gaps: generally high absorption ~10^6 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

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

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

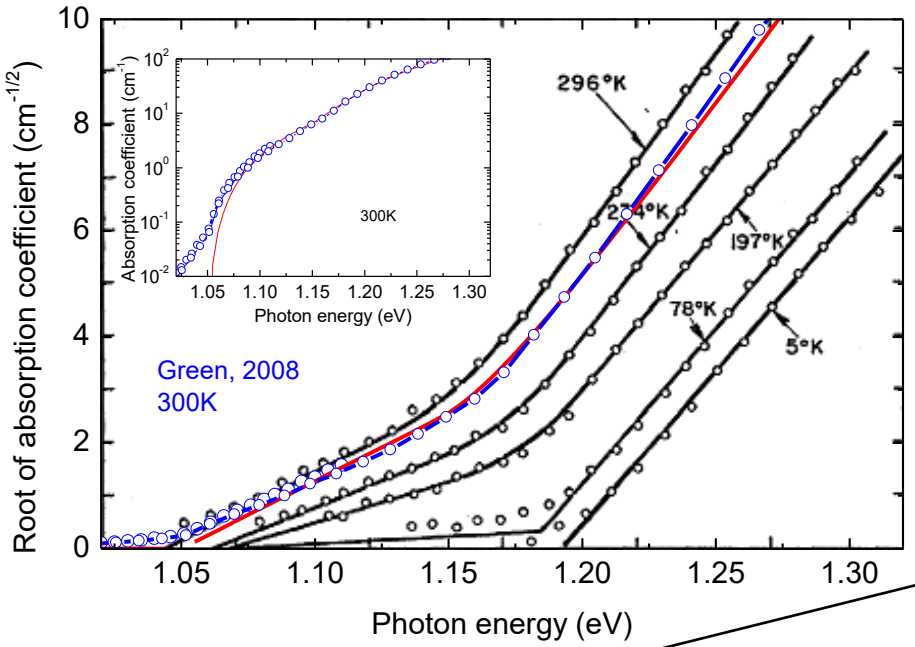
Fermi's Golden rule (second order)

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

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

$\hbar\omega_{\vec{q}} \approx 55\ \text{meV}$

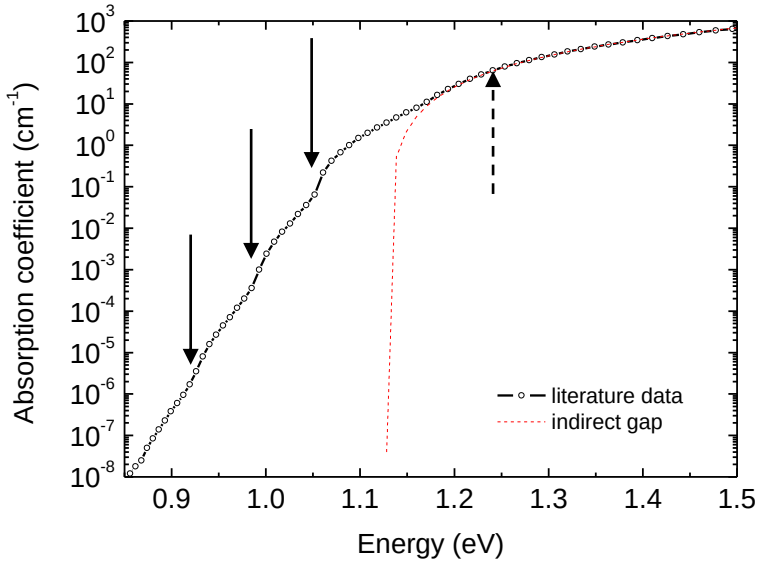
$$\alpha(h\nu) \sim \frac{1}{\omega}\left[\left(\frac{1}{e^{\frac{\hbar\omega_{\vec{q}}}{kT}}-1}\right)\left(\hbar\omega+\hbar\omega_{\vec{q}}-E_g\right)^2+\left(\frac{1}{e^{\frac{\hbar\omega_{\vec{q}}}{kT}}-1}+1\right)\left(\hbar\omega-\hbar\omega_{\vec{q}}-E_g\right)^2\right]$$

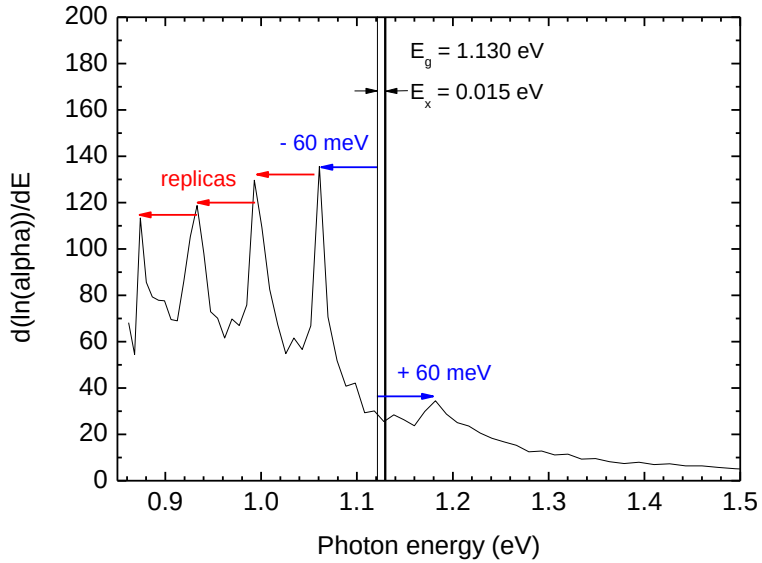
(lattice provides phonon) (lattice absorbs phonon)

Excellent correspondence to measured data

MacFarlane, PR 1955
Braunstein, PR 1959

Close-up of low absorption region





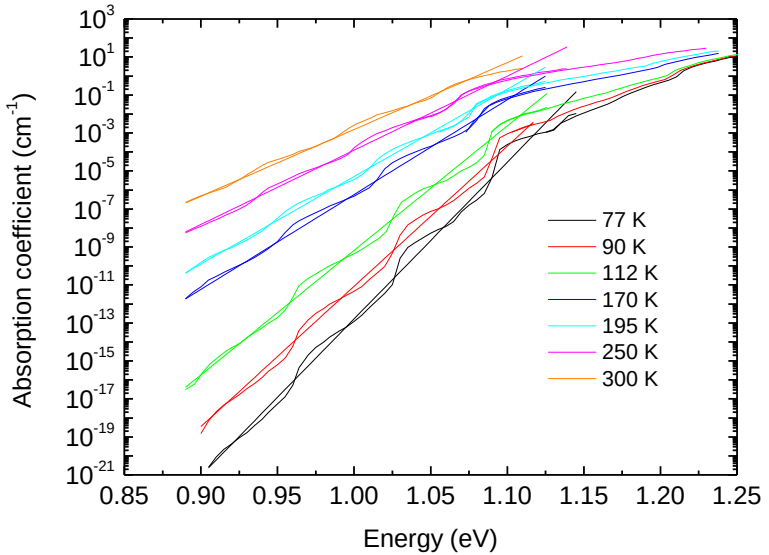
Weakly absorbing tail below gap
Fine structure:
- large signatures at ± 60 meV
- weak signatures at ± 20 meV

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)

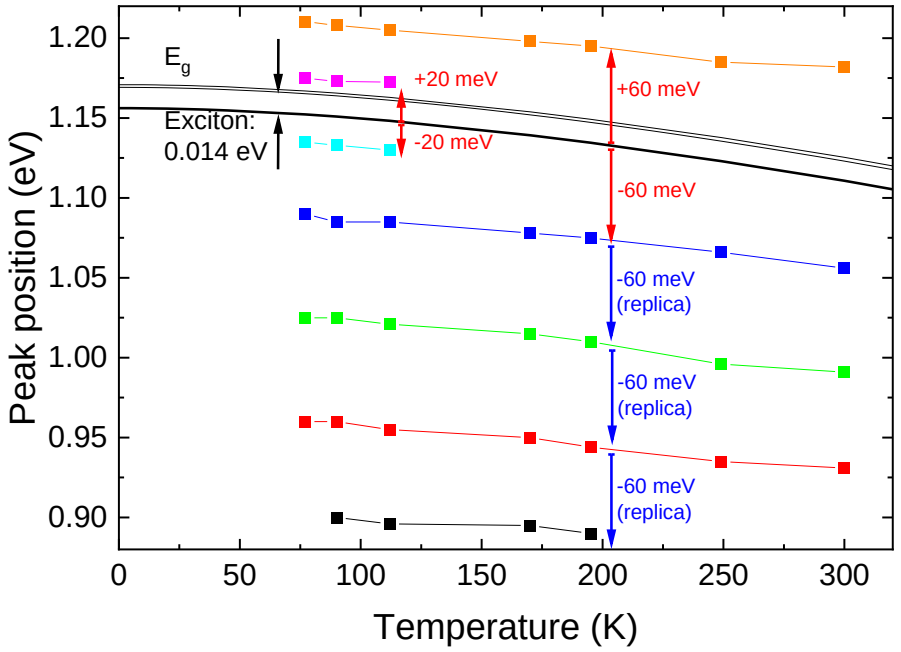


at low temperature:

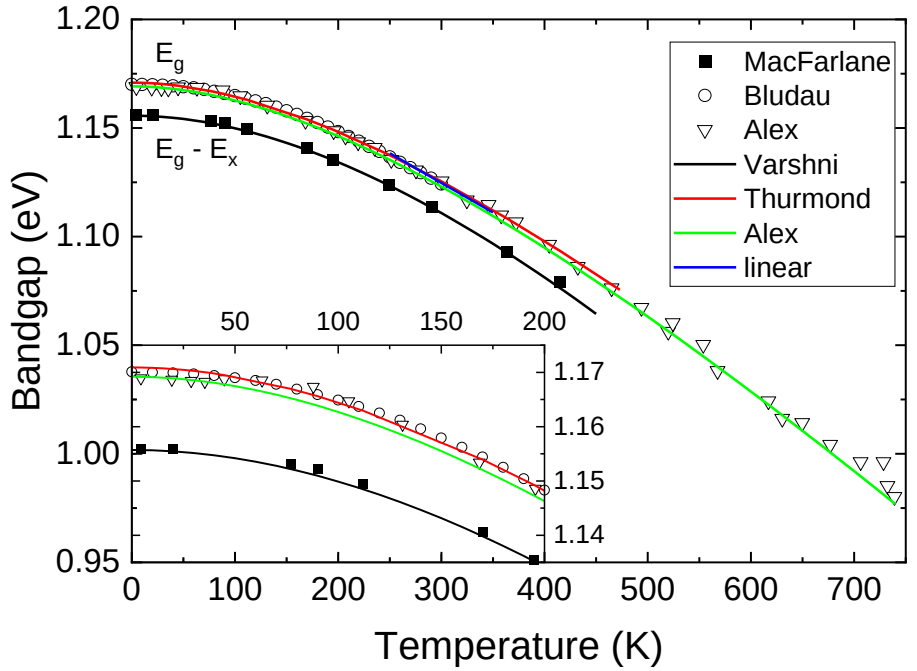
- Absorption drops massively (lattice must provide phonons)
- Steps become more prominent (less thermal broadening)
- Average slope changes (up to about 10 meV)

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

Temperature dependence of E_g (c-Si)



Collect positions of phonon signatures



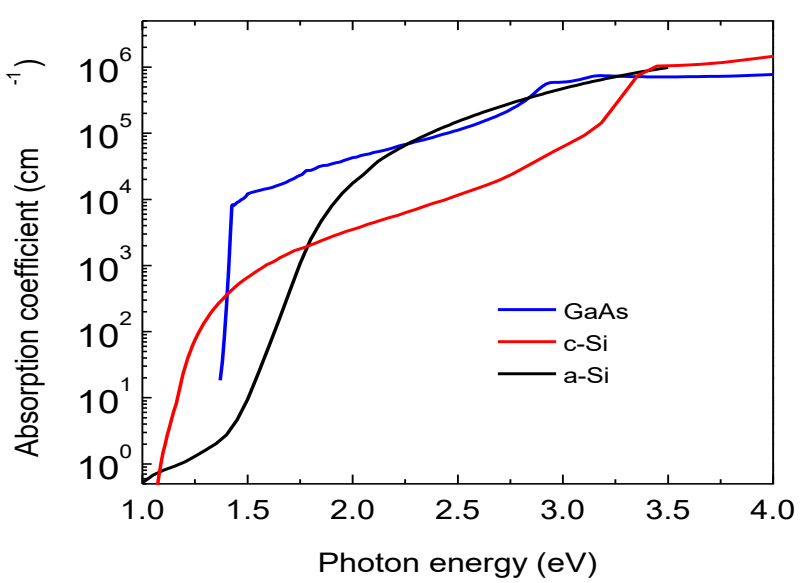
Empiric model:

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

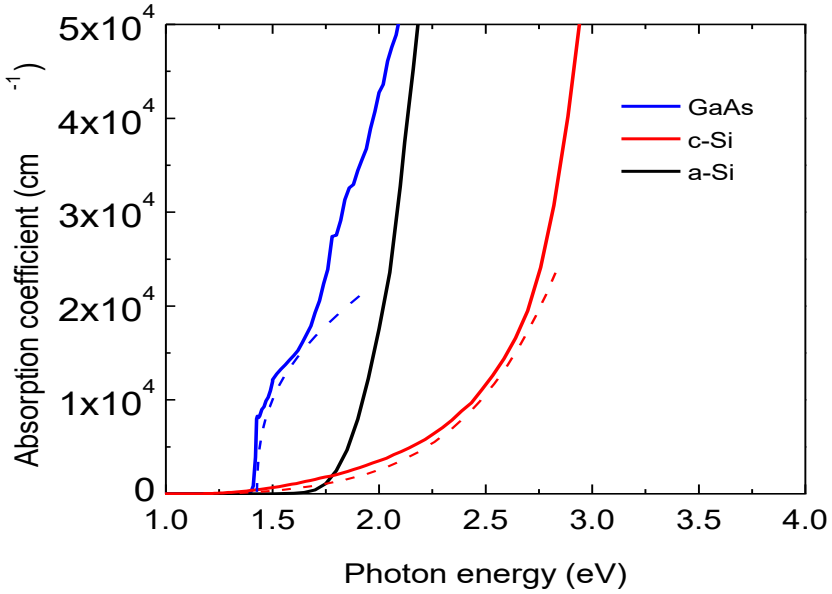
Varshni, physica (1967)

Absorption coefficient (summary)

logarithmic scale (usually shown)



linear scale (clearer proportionality)

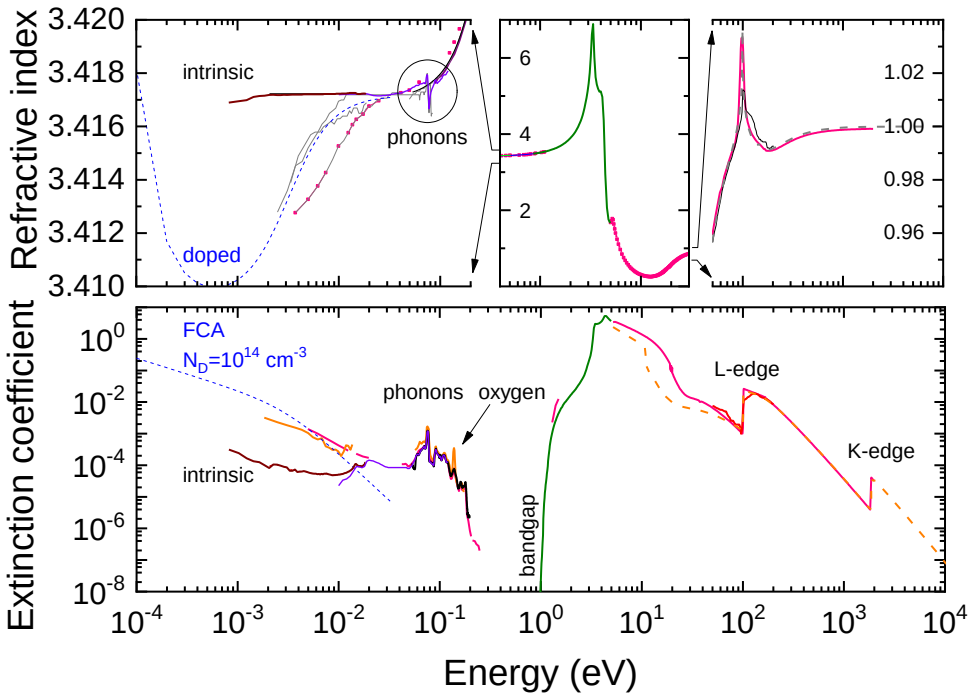


Direct: strong absorption close to gap $\alpha \sim (h\nu - E_g)^{\frac{1}{2}}$

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

a-Si: essentially indirect

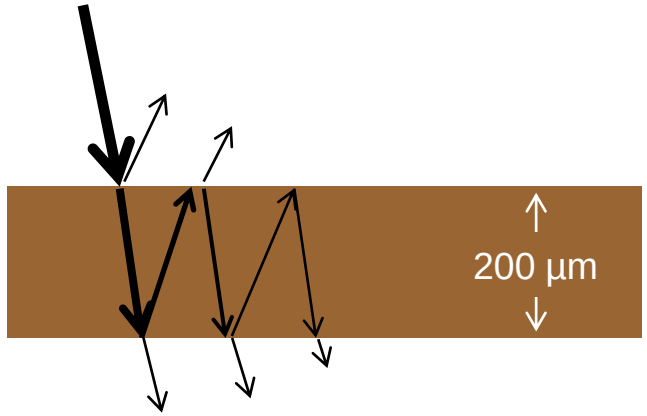
Other dispersion effects in c-Si

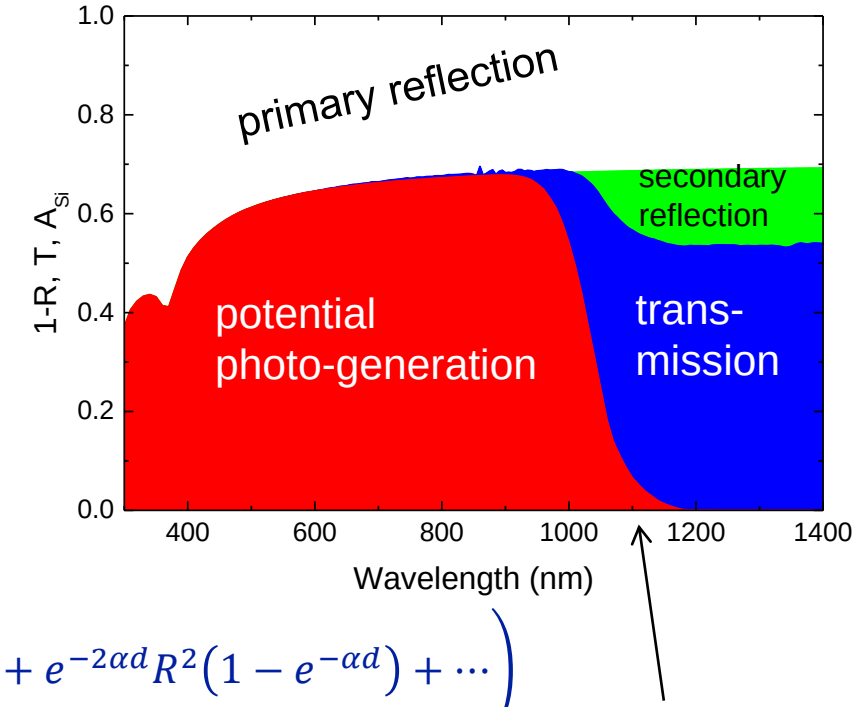


Frequency dependence of contributions to polarizability arising from
a) free electron plasma (depending on doping, can be up to vis)
b) lattice vibrations (IR)
c) displacement of electrons (vis and UV)
d) interactions with core electrons (X-ray regime)

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

Absorption in a silicon slab



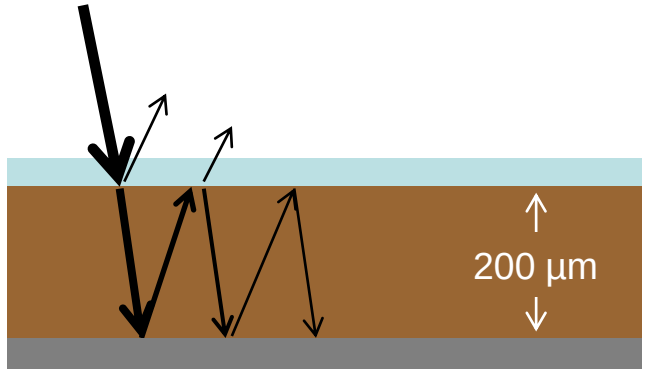


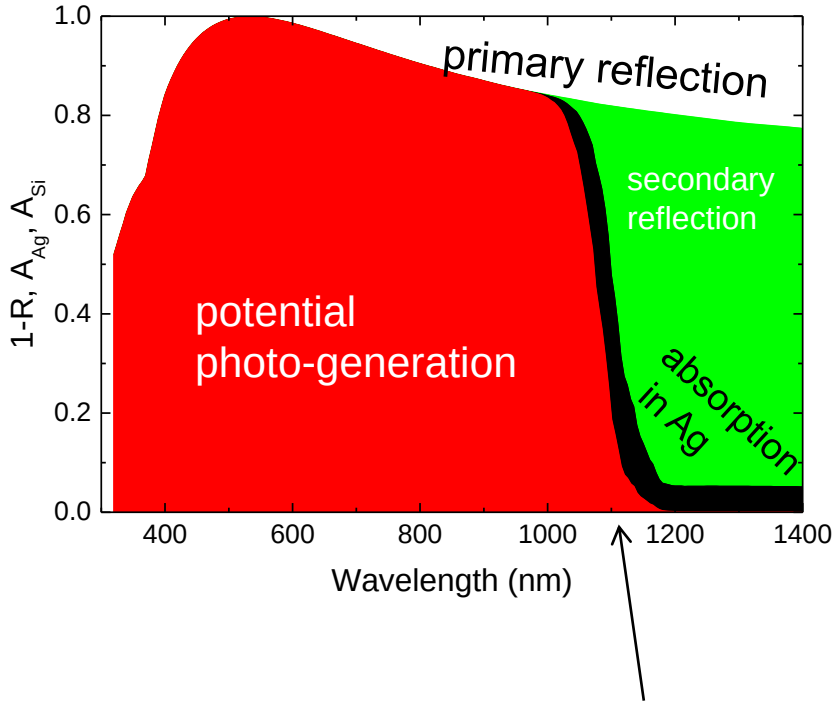
$$A = (1-R)\left(\sum\left(1-e^{-\alpha d}\right) + e^{-\alpha d}R\left(1-e^{-\alpha d}\right) + e^{-2\alpha d}R^2\left(1-e^{-\alpha d}\right) + \cdots\right)$$

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

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

Optical improvement



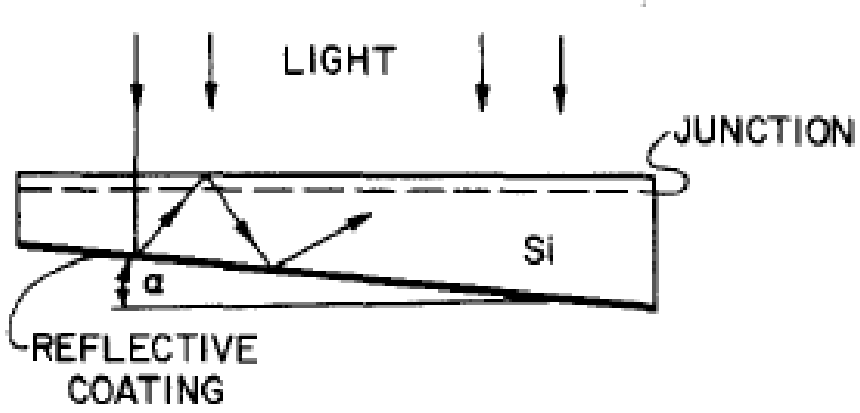


Add AR coating (70 nm, n ≈ 2 at front)
Add reflector, eg. silver (at rear)

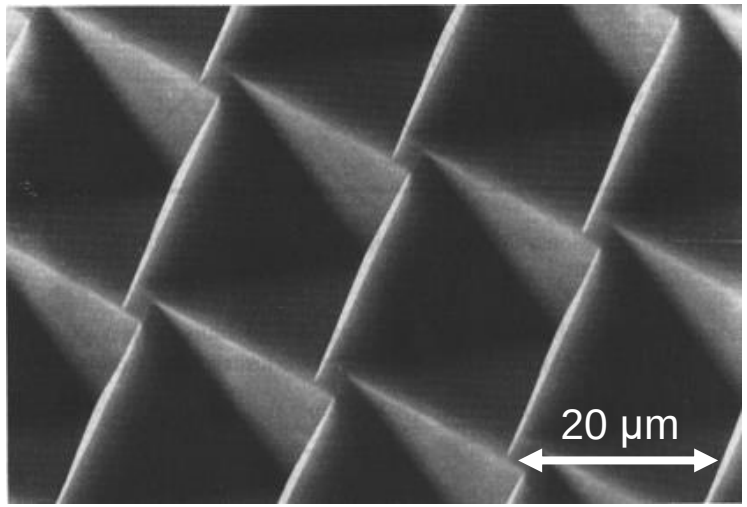
still significant loss due to low absorption
=> needs absorption enhancement

Enhancing absorption via prolonged light path

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



modern high eff. cells: inverted pyramids

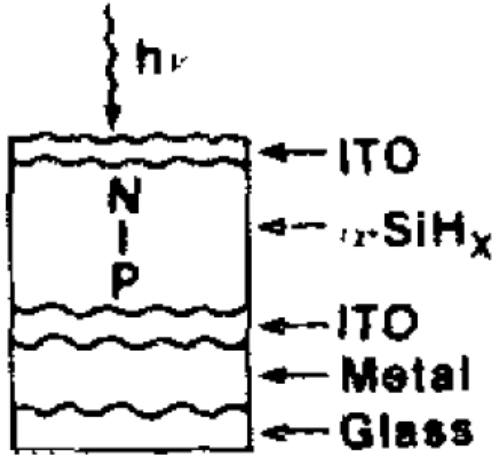


Apply geometric ray optics
for optimization

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

from Goetzberger, Sonnenenergie (1997)

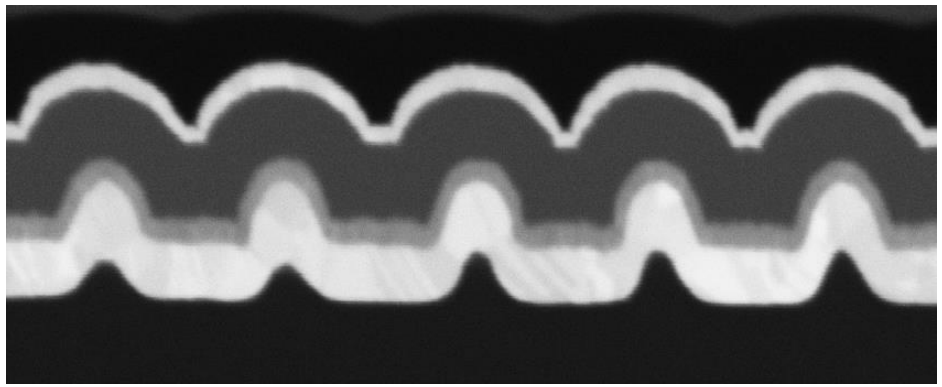
Thin cells: refraction → scattering

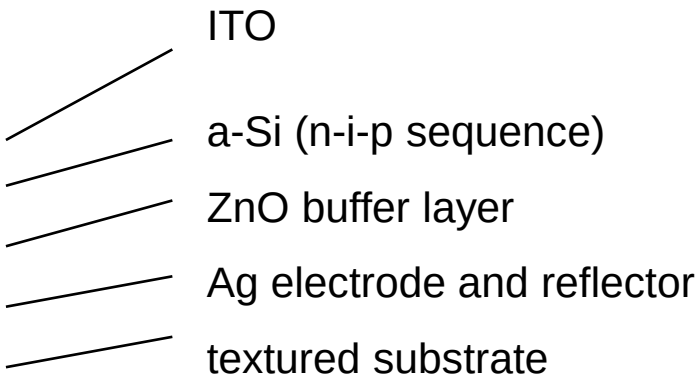


Reduce size of texture to film dimensions
Transport texture from interface to interface
(attention: texture gets modified by growth)

Deckman, JVST (1983)

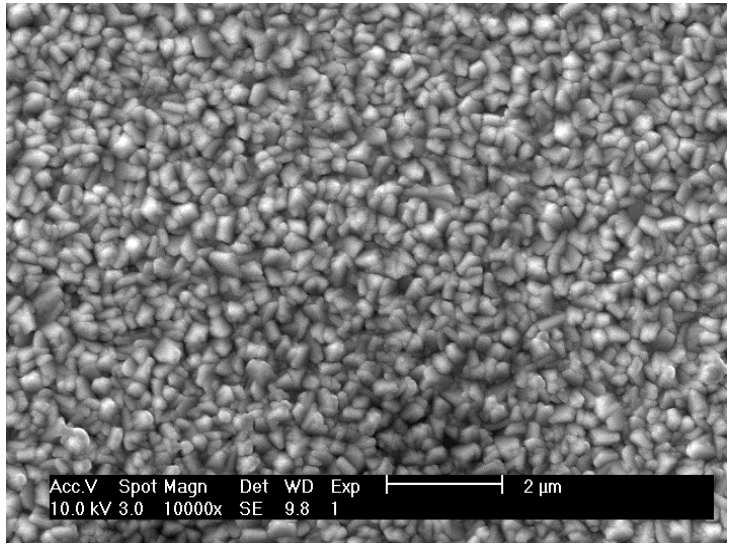
FIB cross-section through an n-i-p a-Si solar cell





Randomly textured TCOs as growth template

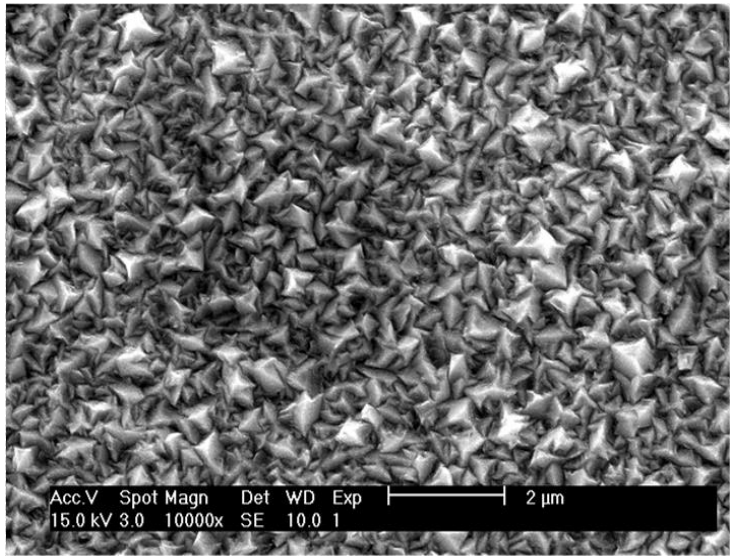
SnO_2:F (Asahi-U)



Atmospheric pressure CVD
(AP-CVD)
$SnCl_4 + HF + H_2O \rightarrow SnO_2$:F

Sato, Asahi Res. Rep. (1990)
Kambe, 3rd World PV Conf (2003)

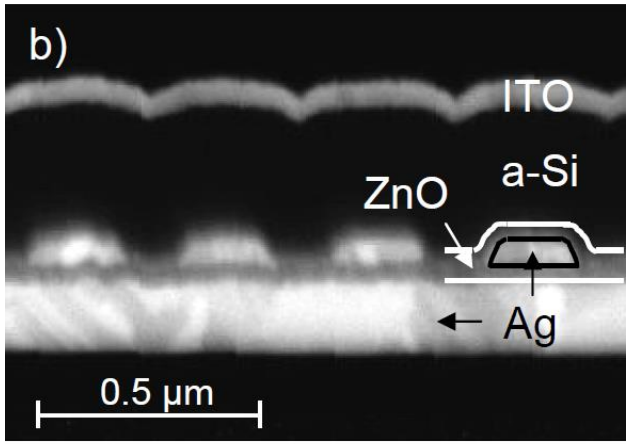
LP-CVD ZnO:B (Z2)

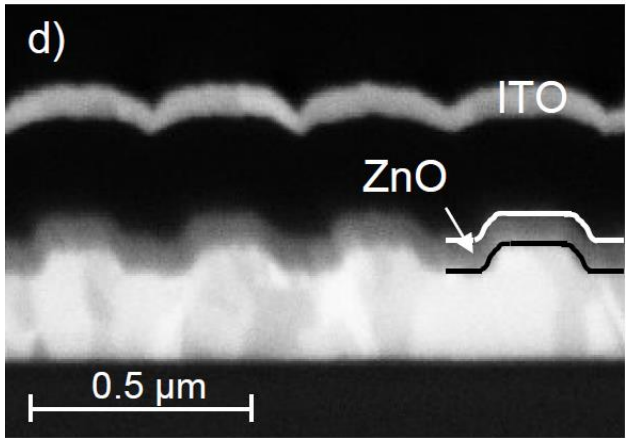


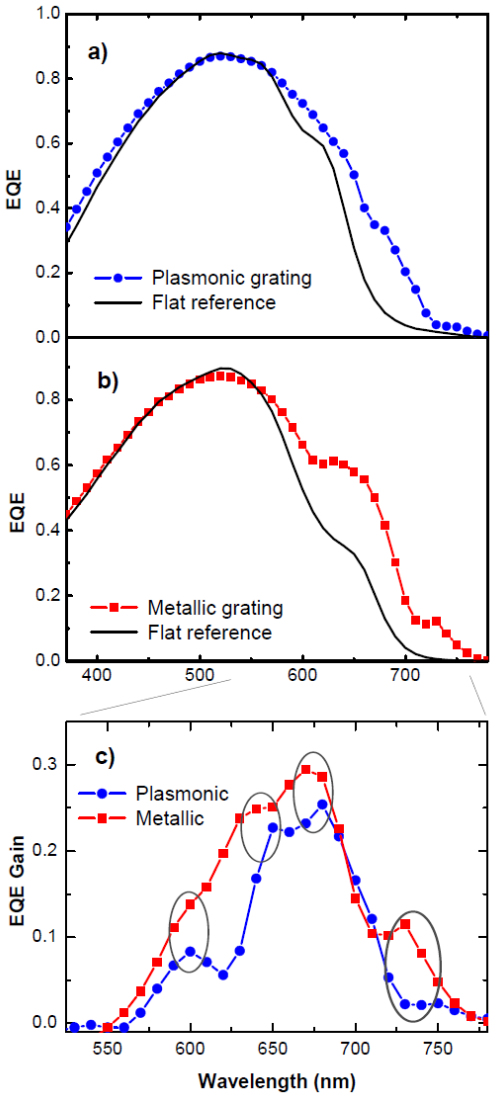
Low pressure CVD
(LP-CVD)
$Zn(C_2H_5)_2 + H_2O + B_2H_6 \rightarrow ZnO$:B

W. Wenas, Jap. J. Appl. Phys (1991)
S. Faÿ, EU PV Conf. (2000)

Scattering particles (here: in the back contact)







identical absorber geometry,
plasmonic performance not (yet?)
beyond “classic” structure

C. Pahud, IEEE JPV, (2012)

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)