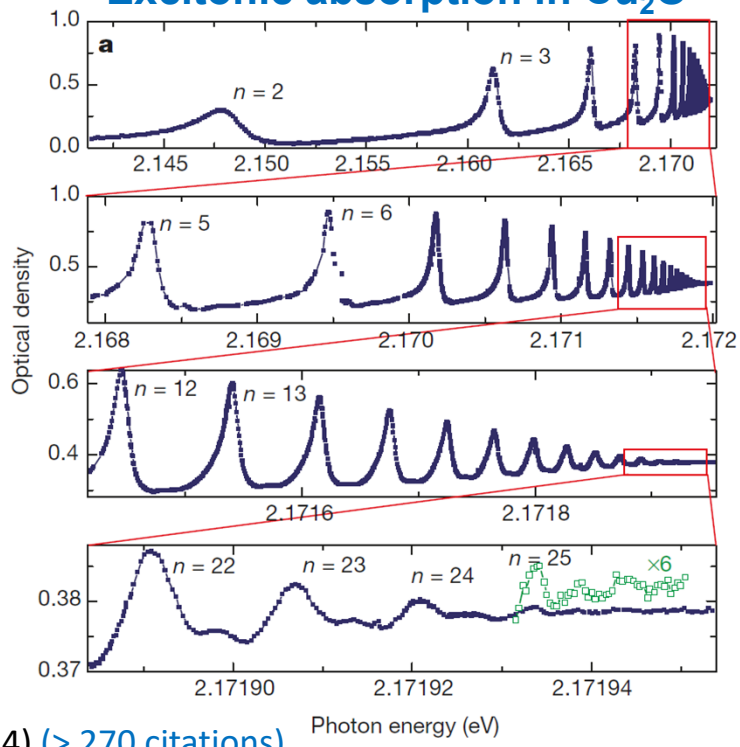
Lecture 13 – 11/12/2024

- Absorption
  - Refractive index
  - Absorption in doped semiconductors
  - Excitonic features in bulk semiconductors

Excitonic absorption in Cu_2O



T. Kazimierczuk *et al.*, Nature **514**, 343 (2014) (> 270 citations)

Summary Lecture 12 - Absorption

Idea: Want to describe absorption in semiconductors using the physical framework we know. Look at physics of transitions and electric field decay.

Transitions:

- Under interaction with an EM field, we can use $\widehat{W} = -q\,\vec{E}\cdot\hat{r}\cos(\vec{k}_{op}\cdot\vec{r}-\omega t)$ as the perturbative Hamiltonian (dipole approximation)
- Absorption is fundamentally a transition, so we use Fermi's golden rule $P \propto \left|\left\langle\psi_{n',\vec{k}'}\middle|\widehat{W}\middle|\psi_{n,\vec{k}}\right\rangle\right|^2 \delta(\Delta E-\hbar\omega)$
- Using Bloch waves, we calculate $\left\langle\psi_{n',\vec{k}'}\middle|\widehat{W}\middle|\psi_{n,\vec{k}}\right\rangle = -r_{vc} * qE\delta\left(\vec{k}'-\vec{k}_{op}-\vec{k}\right)$
- **In short, we have both conservation of momentum ($k' = k + k_{op}$) and energy** ($\hbar\omega = \Delta E$)
- **Typically,** $k_{op} \ll k$, so the transitions are very close to direct in *k*-space
- **There are multiple valence bands – The quantity x_{vc}^2 takes this into account**

$$r_{vc} = \frac{\hbar}{E_g}\sqrt{\frac{E_p}{2m_0}}$$

$$x_{vc}^2 = \frac{1}{3}\frac{\hbar^2}{E_g^2}\frac{E_p}{m_0}$$

Dissipation:

- **Solve Maxwell's equations in media for plane waves:**

$$\mathbf{E}(\mathbf{r},t) = \mathbf{E}_0\Re[e^{-i(\mathbf{kr}-\omega t)}] \qquad \mathbf{D} = \varepsilon(1+\varepsilon_0\chi(\omega)/\varepsilon)\mathbf{E} \qquad \mu_0\partial^2\mathbf{D}/\partial t^2 = \nabla^2\mathbf{E}$$

$$k = \frac{n_{op}\omega}{c}\left(1+\frac{\varepsilon_0}{2\varepsilon}\chi_\Re\right)+i\frac{\omega}{2n_{op}c}\chi_\Im = k_\Re + i\,k_\Im$$

$$\alpha(\omega) = -2k_\Im = -\frac{\omega}{cn_{op}}\chi_\Im \quad (\chi_\Im < 0)$$

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

Summary Lecture 12 - Absorption

Linking the susceptibility to band transitions:

$$\chi(\omega)=2\sum_{\mathbf{k}}\frac{q^2 x_{vc}(\mathbf{k})^2 T_2}{2\varepsilon_0\hbar}\frac{(\omega-\omega_{vc}(\mathbf{k}))T_2-i}{(\omega-\omega_{vc}(\mathbf{k}))^2T_2^2+1}(N_v(\mathbf{k})-N_c(\mathbf{k}))$$

spin

carrier relaxation time ≈ 100 fs

particle densities

To account for a single type of valence band
(factor overlooked by Rosencher & Vinter)

Results in (after some derivation, slide 14)

$$\chi_{\Im}(\omega)=-\frac{q^2x_{vc}^2\pi}{2\varepsilon_0\hbar}\rho_j(\omega)\left[f_v(E_v(\mathbf{k}))-f_c(E_c(\mathbf{k}))\right]$$

$$\rho_j(\omega)=\frac{1}{2\pi^2}\left(\frac{2m_r}{\hbar}\right)^{3/2}(\omega-E_g/\hbar)^{1/2}$$

$$\frac{1}{m_r}=\frac{1}{m_e}+\frac{1}{m_h}$$

Joint density of states: Number of possible transition pairs equal to the number of states available

Collecting everything and inserting the band structure:

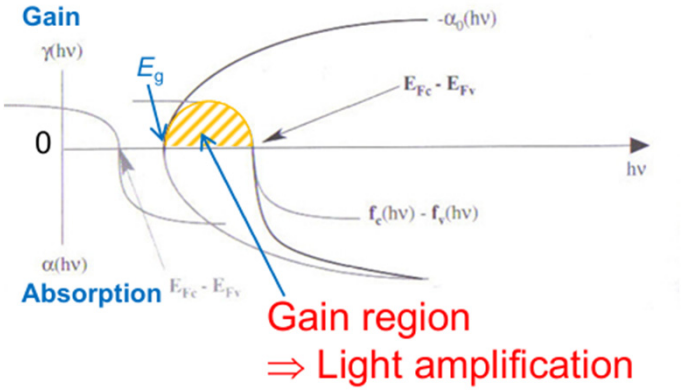
$$\alpha(\omega)=-\gamma(\omega)=\alpha_0(\omega)(f_v(\hbar\omega)-(f_c(\hbar\omega))$$

$$\alpha_0(\omega)=\frac{q^2x_{vc}^2\omega}{4\pi\epsilon_0\hbar n_{op}c}\left(\frac{2m_r}{\hbar}\right)^{\frac{3}{2}}\sqrt{\omega-\frac{E_g}{\hbar}}$$

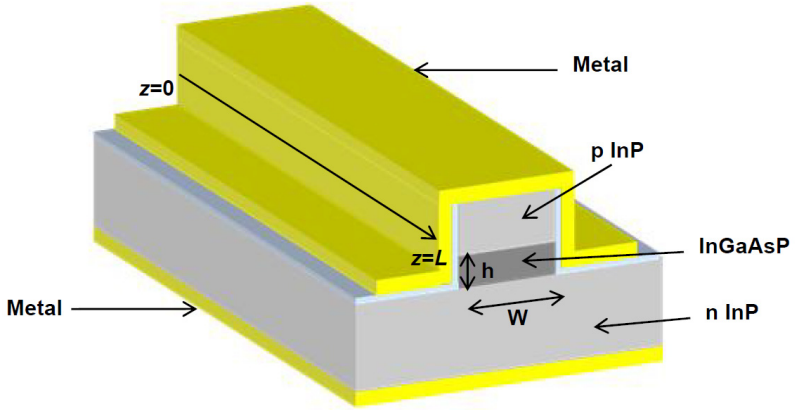
quasi-Fermi levels

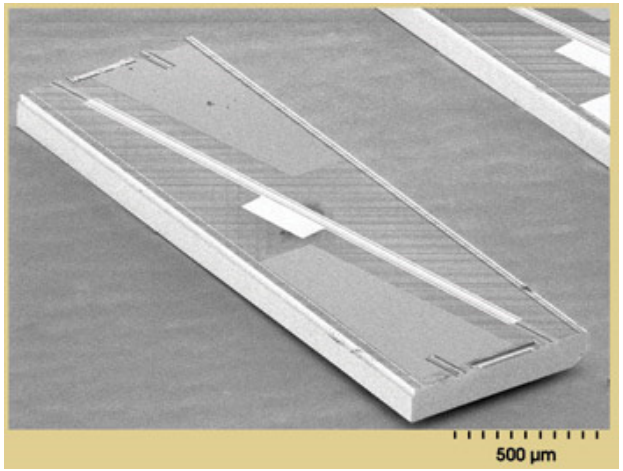
$$f_c(\hbar\omega)>f_v(\hbar\omega)\quad\Rightarrow\quad E_{Fc}-E_{Fv}>\hbar\omega>E_g$$

Bernard-Duraffourg condition



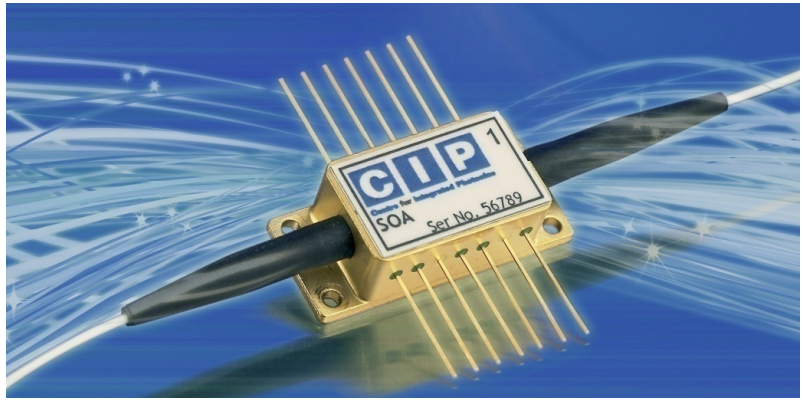
Semiconductor optical amplifier (SOA)





Light amplification via stimulated emission occurs while it propagates inside the waveguide

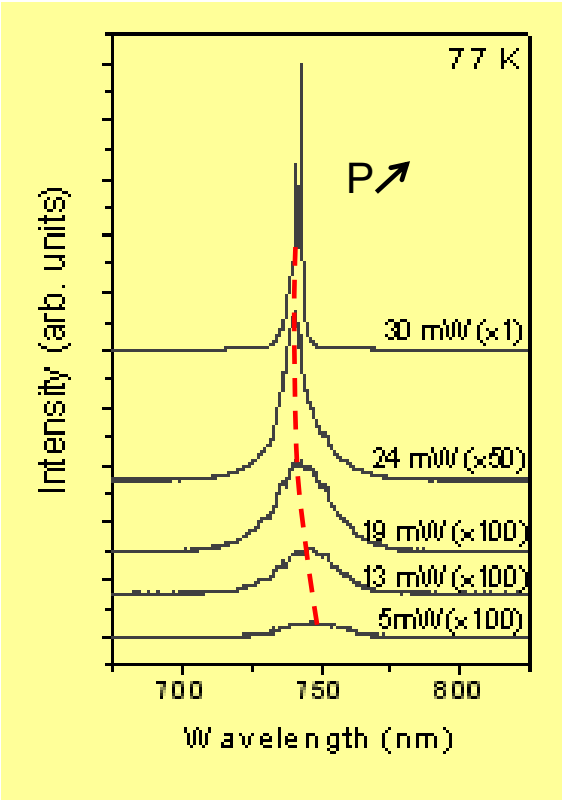
Single-pass device (i.e., no optical feedback)

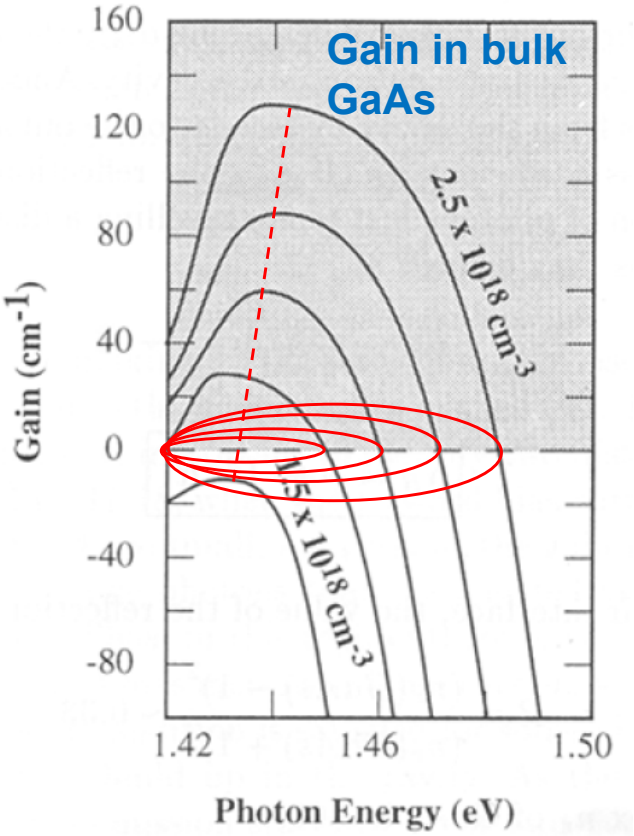


Gain up to 30 dB

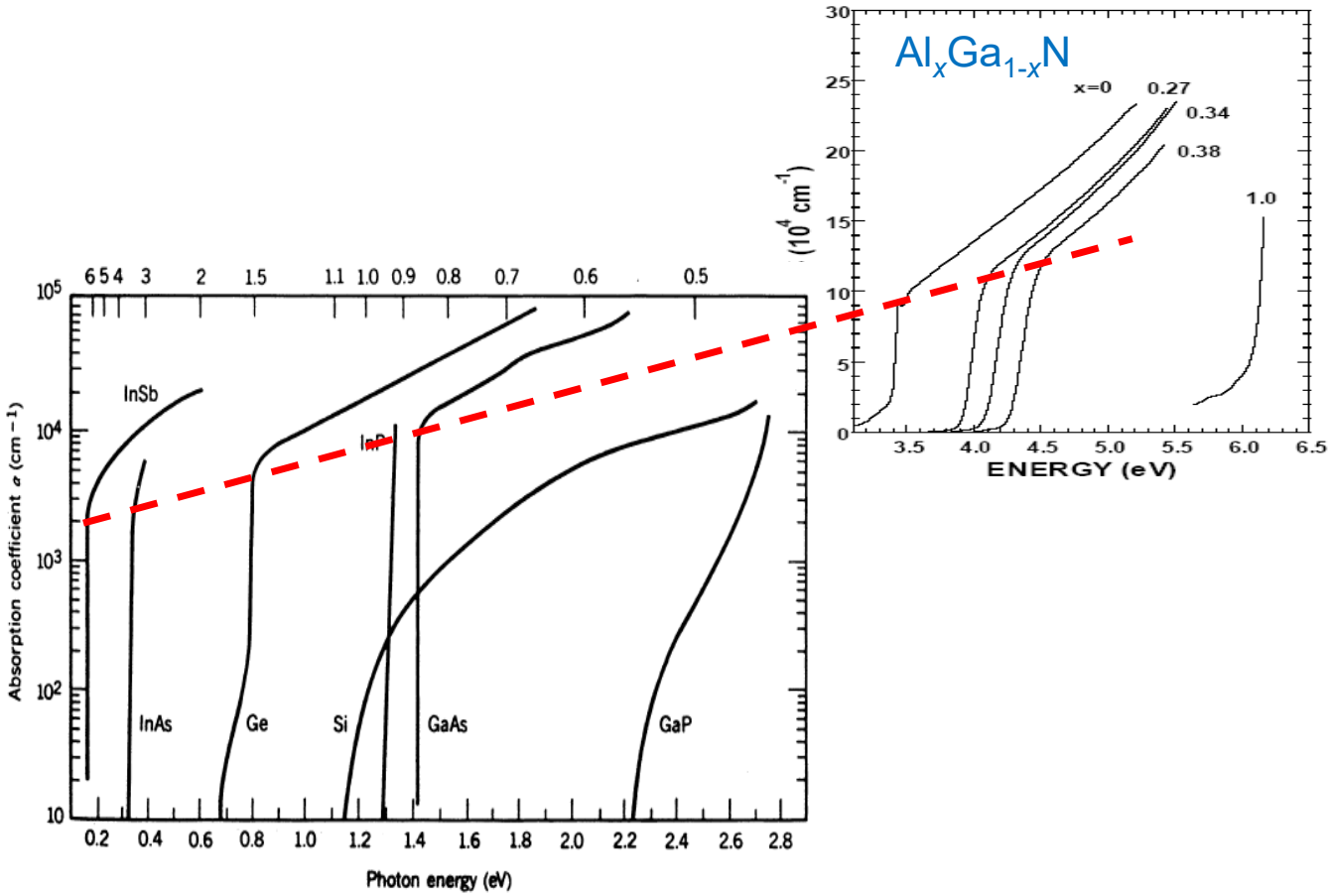
http://en.wikipedia.org/wiki/Wavelength-division_multiplexing

Absorption and gain in semiconductors





Experimental account of absorption in semiconductors



Absorption in semiconductors

$$\alpha_0(\omega) \doteq \frac{q^2 x_{vc}^2 \omega}{4\pi\varepsilon_0 \hbar n_{op} c}\left(\frac{2m_r}{\hbar}\right)^{3/2}\sqrt{\omega - E_g/\hbar}$$

How does α_0 vary with the bandgap at $\omega \approx E_g/\hbar$?

$x_{vc}^2 \propto E_g^{-2}$

$m_r^{3/2} \propto E_g^{3/2}$ cf. nearly-free electron model and **k.p** method

$\omega \propto E_g$

n_{op} vs ω?

Refractive index in semiconductors

Refractive index:

A semiconductor is a dispersive medium $\Rightarrow$ the refractive index varies with ω

Refractive index modeling:

$$\mathbf{D} = \varepsilon_0\mathbf{E} + \mathbf{P} = \varepsilon\mathbf{E}$$

where $\varepsilon = \mathbf{D}/\mathbf{E} = \varepsilon_0 + \mathbf{P}/\mathbf{E}$ and $n_{op} = \sqrt{\frac{\varepsilon}{\varepsilon_0}}$

Determination of the polarization P of the medium when the latter experiences an electric field perturbation ($\Rightarrow$ modification of the charge distribution in the crystal)

Refractive index in semiconductors

Let us simplify the medium by considering a dipole experiencing an electric field perturbation

If one considers the analogy between a dipole and a spring then we get:

$F = -kx$ and the angular frequency is given by: $\omega_0^2 = k/m_0$

restoring force

This dipole undergoes an external force, which is given by: $F_{ext} = qE(t) = qE_0 \cos(\omega t)$
The equation of motion is given by:

$$qE_0 \cos(\omega t) - m_0 \omega_0^2 x = m_0 \frac{d^2 x}{dt^2}$$

of solution equal to:

$$x(t) = x_0 \cos(\omega t) = \frac{qE(t)}{\left[m_0\left(\omega_0^2 - \omega^2\right)\right]}$$

Refractive index in semiconductors

The polarization can be written as:

$P(t) = qx(t)N$

q	charge
x	displacement
N	electron density

The displacement $x(t)$ is equal to $\dfrac{qE(t)}{\left[m_0\left(\omega_0^2-\omega^2\right)\right]}$

Thus $P(t)=\dfrac{q^2NE(t)}{\left[m_0\left(\omega_0^2-\omega^2\right)\right]}$

One recalls that $\varepsilon = \mathbf{D}/\mathbf{E} = \varepsilon_0 + \mathbf{P}/\mathbf{E}$

$\varepsilon = \varepsilon_0 + q^2N/[m_0(\omega_0^2-\omega^2)]$

$$n_{op}^2(\omega)=1+\frac{q^2N}{\varepsilon_0 m_0\left(\omega_0^2-\omega^2\right)}$$

Refractive index in semiconductors

Note that in solids (e.g., in semiconductors), atomic interactions lead to a damping of the oscillations (losses). This effect is accounted for by introducing a friction force $m_0\gamma\,dx/dt$.

$$n_{op}^2(\omega) = 1 + \frac{q^2 N}{\varepsilon_0 m_0\left(\omega_0^2 - \omega^2 + i\gamma\omega\right)}$$

We must also consider multiple resonances, then it comes*:

$$n_{op}^2(\omega) = 1 + \frac{q^2 N}{\varepsilon_0 m_0}\sum_j \frac{f_{0_j}}{\omega_{0_j}^2 - \omega^2 + i\gamma_j\omega}$$

weight of resonance j
≡ ***oscillator strength***

$$f_{0_j} = 2\frac{\left|\langle f_j|\boldsymbol{\eta}\cdot\mathbf{p}|i\rangle\right|^2}{m_0\hbar\omega_{0_j}} = \frac{2m_0\omega_{0_j}}{\hbar}\left|\langle f_j|\boldsymbol{\eta}\cdot\mathbf{r}|i\rangle\right|^2$$

η is the unit polarization vector of the EM wave

$$\sum_j f_{0_j} = 1$$

Thomas-Reiche-Kuhn sum rule

Generalization necessary, e.g., to account for the degeneracy or the near degeneracy of optical transitions

Far from the resonance ($\omega << \omega_{0j}$), the refractive index slowly varies and depends on ω_{0j}. On the other hand, it rapidly increases close to the bandgap.

* The full expression is much more complicated due to long-distance interactions

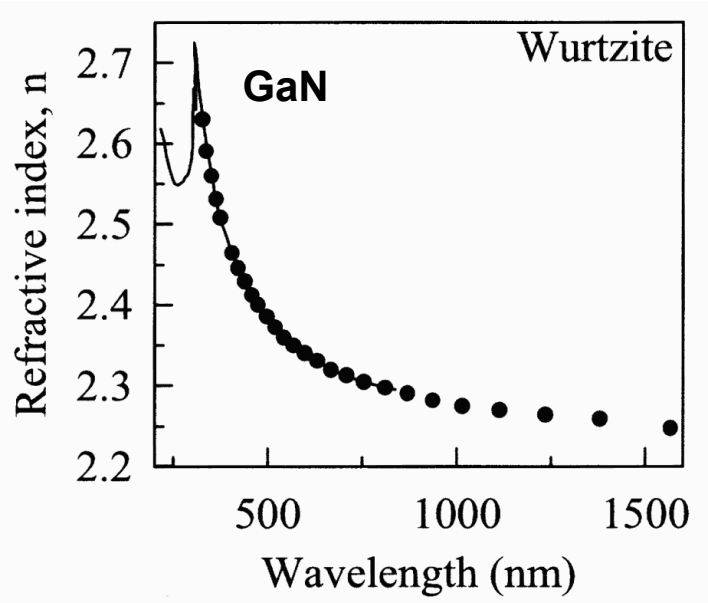
Examples:

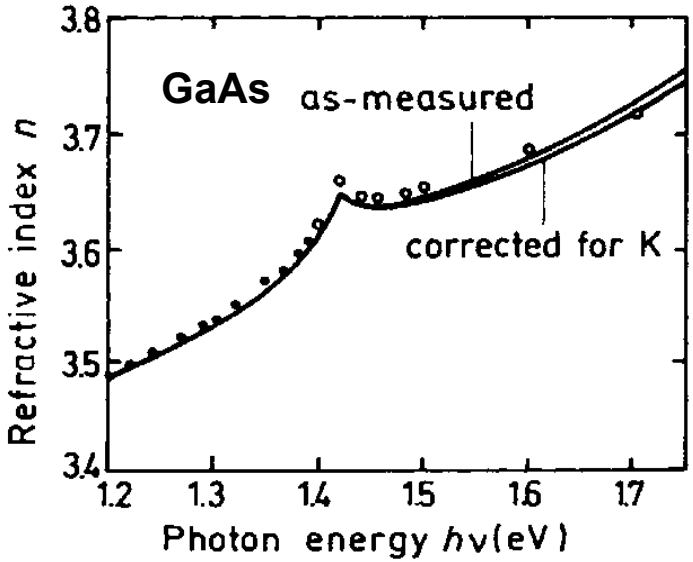
GaAs $n_{op} \approx 3.6$ with bandgap of 1.42 eV

GaN $n_{op} \approx 2.6$ with bandgap of 3.42 eV

Refractive index in semiconductors

Refractive index as a function of the wavelength/energy



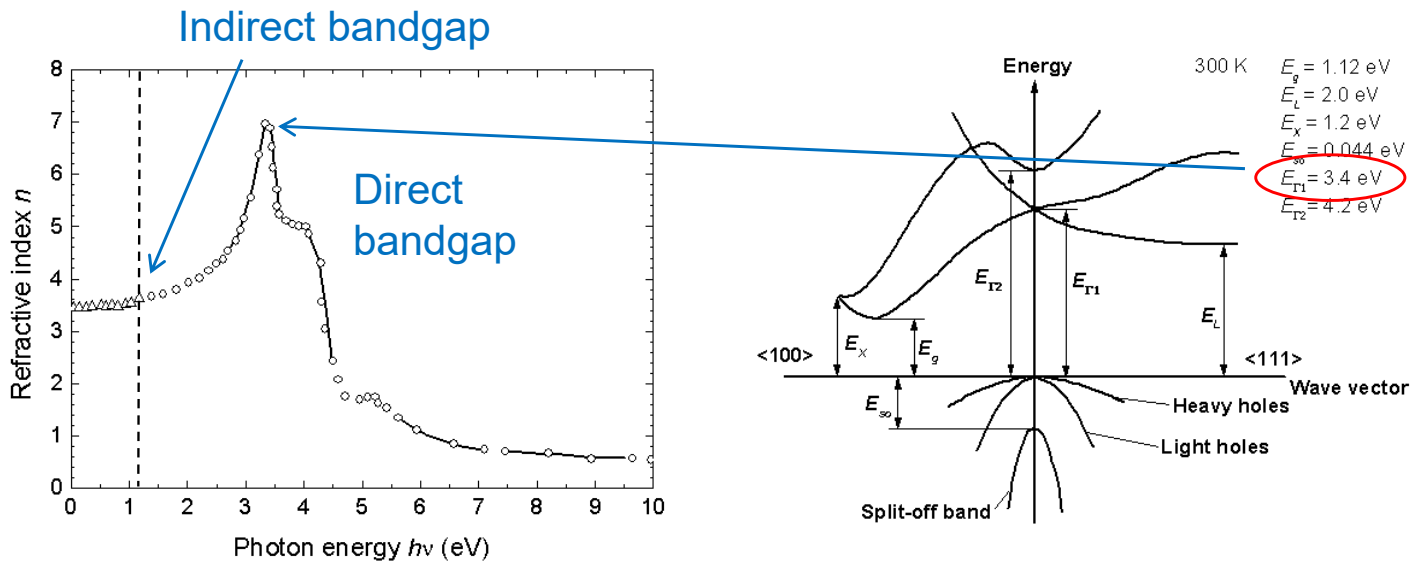


Empirical formula: $$n_{op}(\lambda) = \sqrt{a + \frac{b\lambda^2}{\lambda^2 - c^2}}$$ Sellmeier's law

a, *b* and *c* are material-dependent coefficients

Refractive index in semiconductors

Indirect bandgap semiconductor: the case of silicon



Absorption in semiconductors

$$\alpha_0(\omega) = \frac{q^2 x_{vc}^2 \omega}{4\pi\varepsilon_0 \hbar n_{op} c}\left(\frac{2m_r}{\hbar}\right)^{3/2}\sqrt{\omega - E_g/\hbar}$$

How does α_0 vary with the bandgap at $\omega \approx E_g/\hbar$?

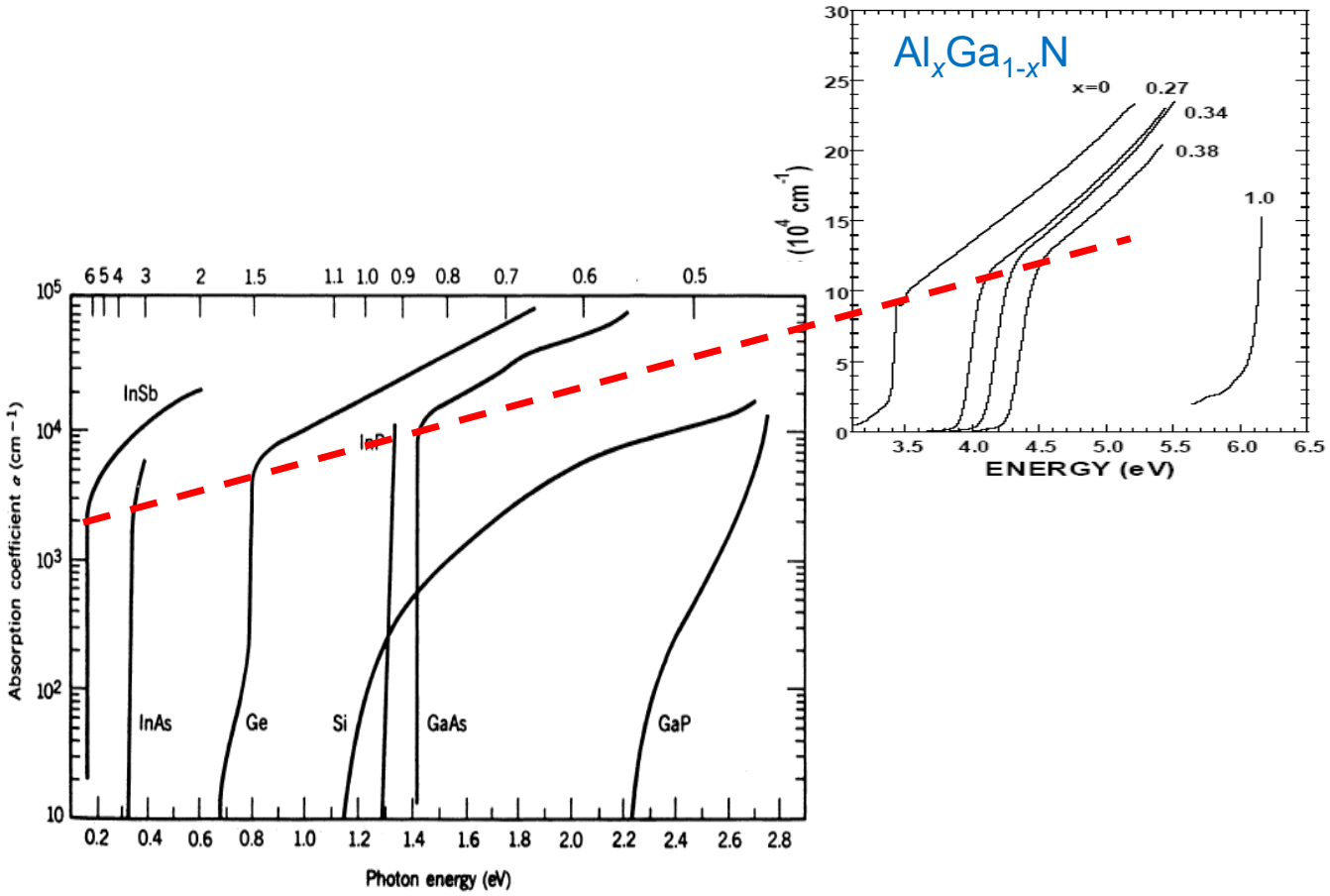
$$x_{vc}^2 \propto E_g^{-2}$$

$$m_r^{3/2} \propto E_g^{3/2}$$

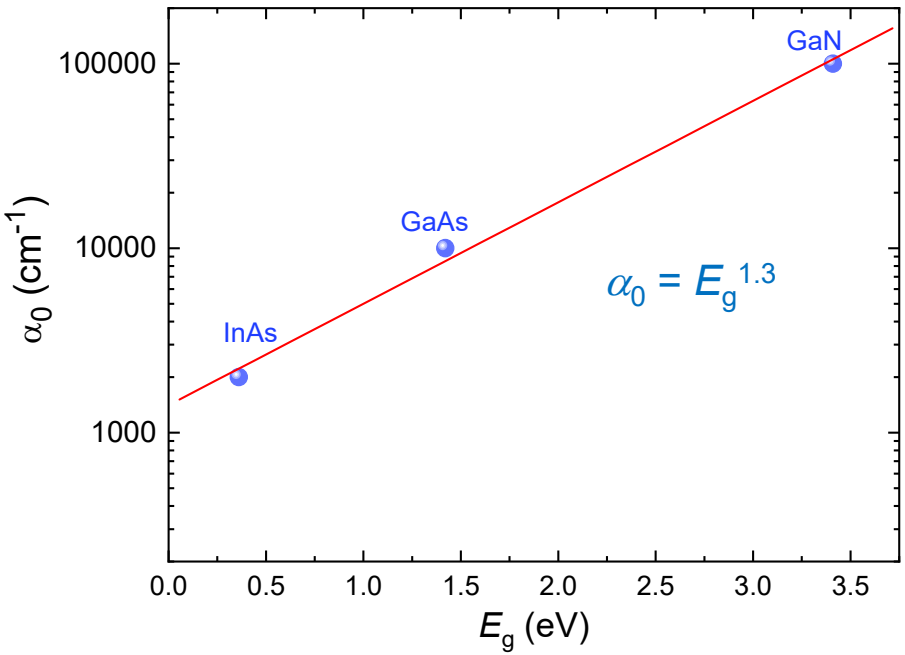
$$\omega \propto E_g$$

$$n_{op}^{-1} \propto E_g$$

Experimental observations



Absorption in semiconductors

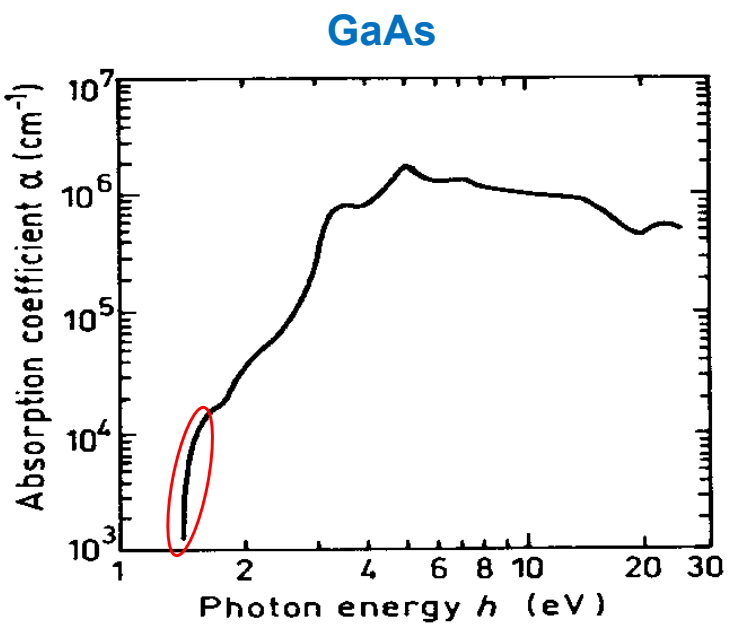


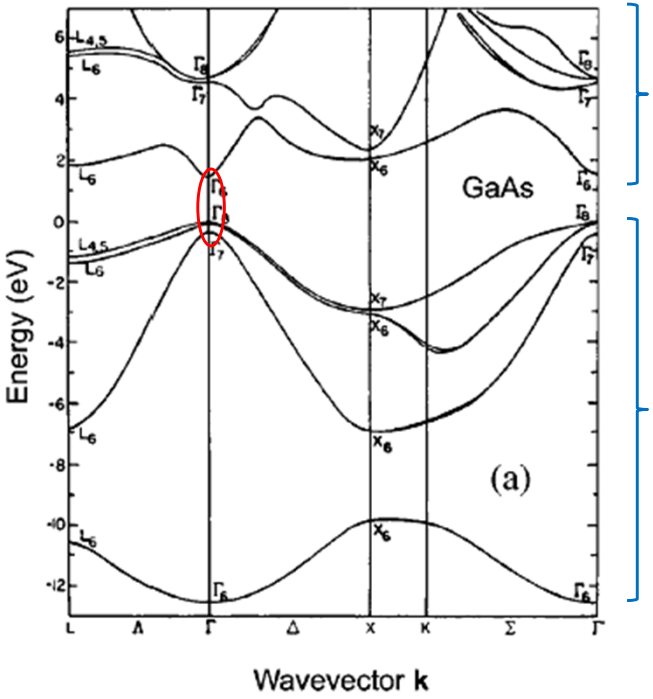
To be compared with theoretical prediction:

$\alpha_0 \propto E_g^{1.5}$

Absorption in semiconductors

Absorption far above the bandgap



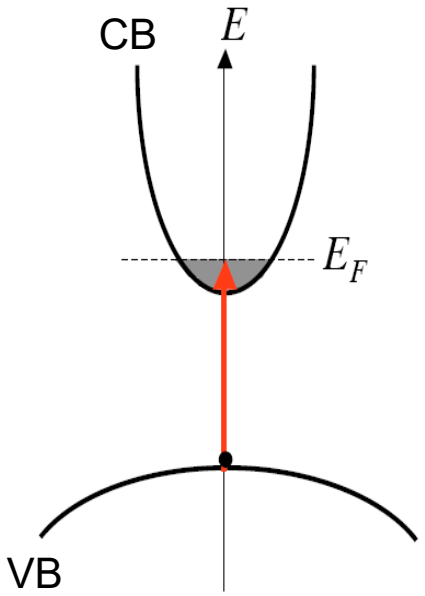


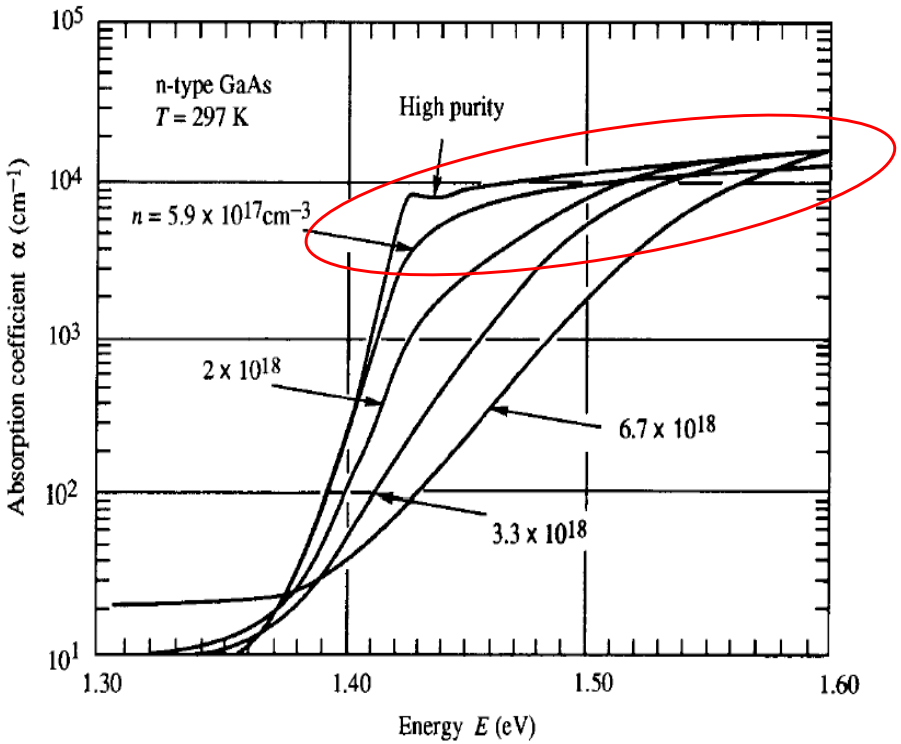
The joint-DOS is getting larger with increasing photon energy and hence $\alpha(\omega)$ until reaching a plateau-like region!

Absorption in doped semiconductors

Doping effect: e.g., degenerate *n*-type semiconductor ($E_{Fn} \geq E_C$)

Burstein-Moss shift[1,2] → blueshift of the absorption edge due to band filling



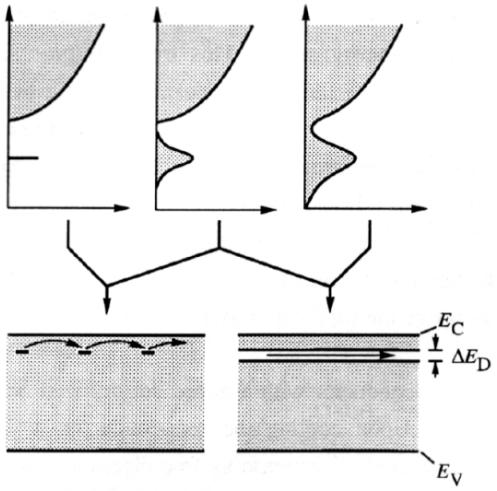


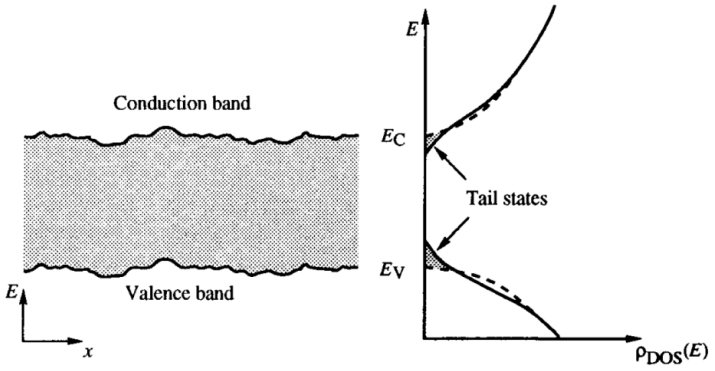
[1] E. Burstein, Phys. Rev. **93**, 632 (1954) (> 3600 citations)
[2] T. S. Moss, Proc. Phys. Soc. (London) **B76**, 775 (1954) (> 1800 citations)

Absorption in doped semiconductors

High doping level: tail states in the bandgap are observed and bandgap narrowing

"Band tailing" due to an impurity band and/or to bandgap potential fluctuations

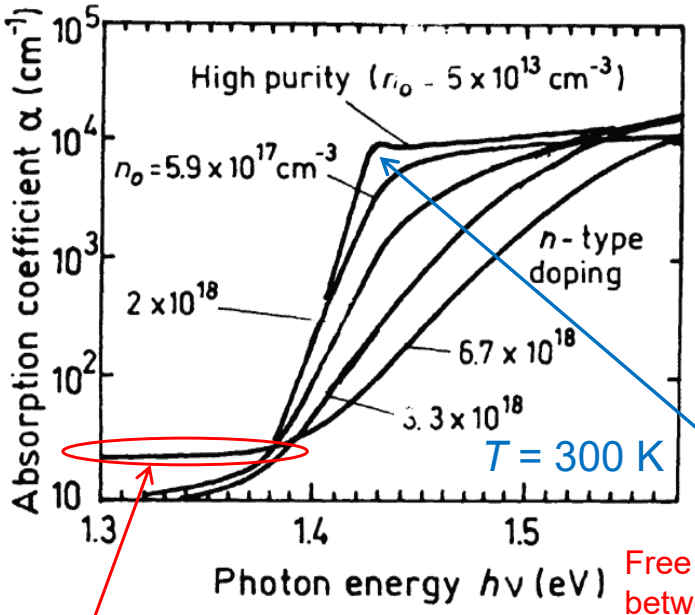




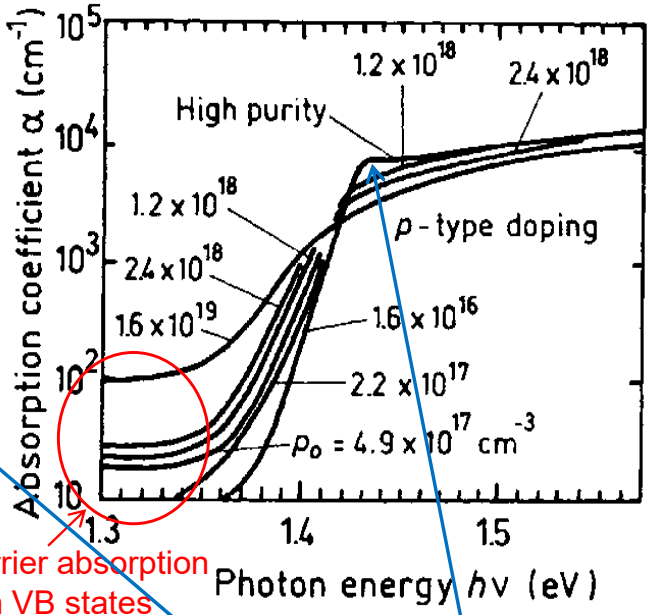
- Random distribution of impurities
- Ionized donors exert an attractive force on conduction electrons and a repulsive force on valence holes (reverse for acceptors)
- Local energy gap constant but DOS distribution is position dependent (number of states at each energy over whole volume) $\Rightarrow$ hence the presence of tail states

Absorption in doped semiconductors

_n_-doped GaAs



_p_-doped GaAs



Free carrier absorption between VB states

Free carrier absorption between CB state minima

Burstein-Moss shift

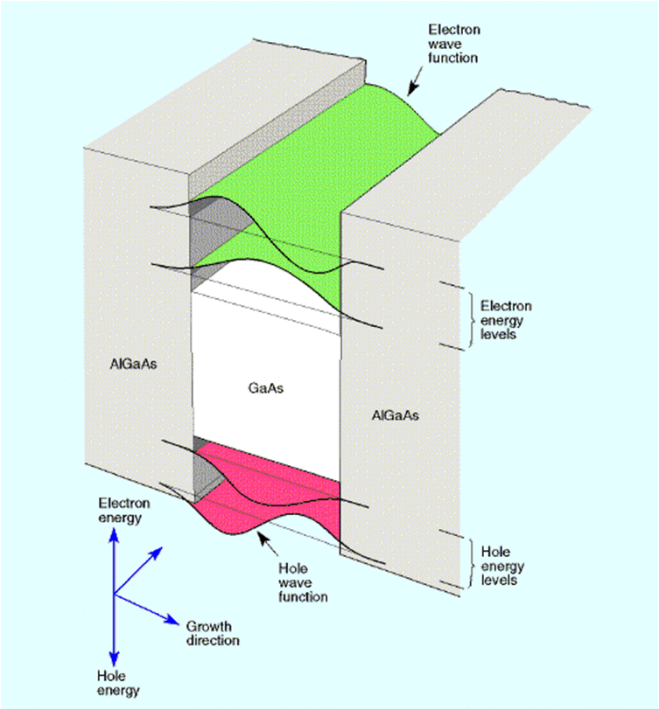
Band tailing

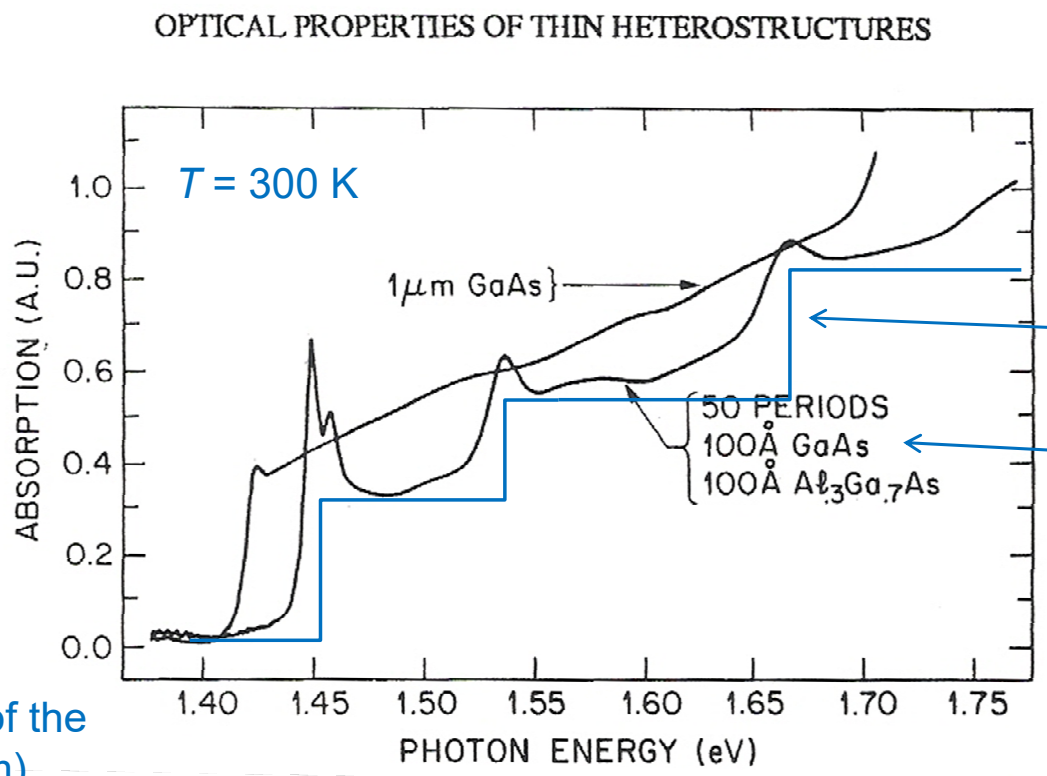
Absorption process promotes e^- from filled states near or above the parabolic VB edge to the CB tail ⇒ absorption edge shifts to lower E as band tails increase

Decrease of α near the undoped E_g value due to the quenching of excitonic features

Absorption and excitons in semiconductors

Exciton: electron-hole pair bound via Coulomb interaction





Staircase profile

≡ 2D multiple quantum well system

- The shape of $\alpha(\omega)$ is a function of the joint-DOS (e.g., 3D vs 2D system)
- The stability of excitons is reinforced when decreasing the dimensionality of the system

Absorption in quantum wells

Absorption and excitons in semiconductors

Temperature effect

Bulk GaAs

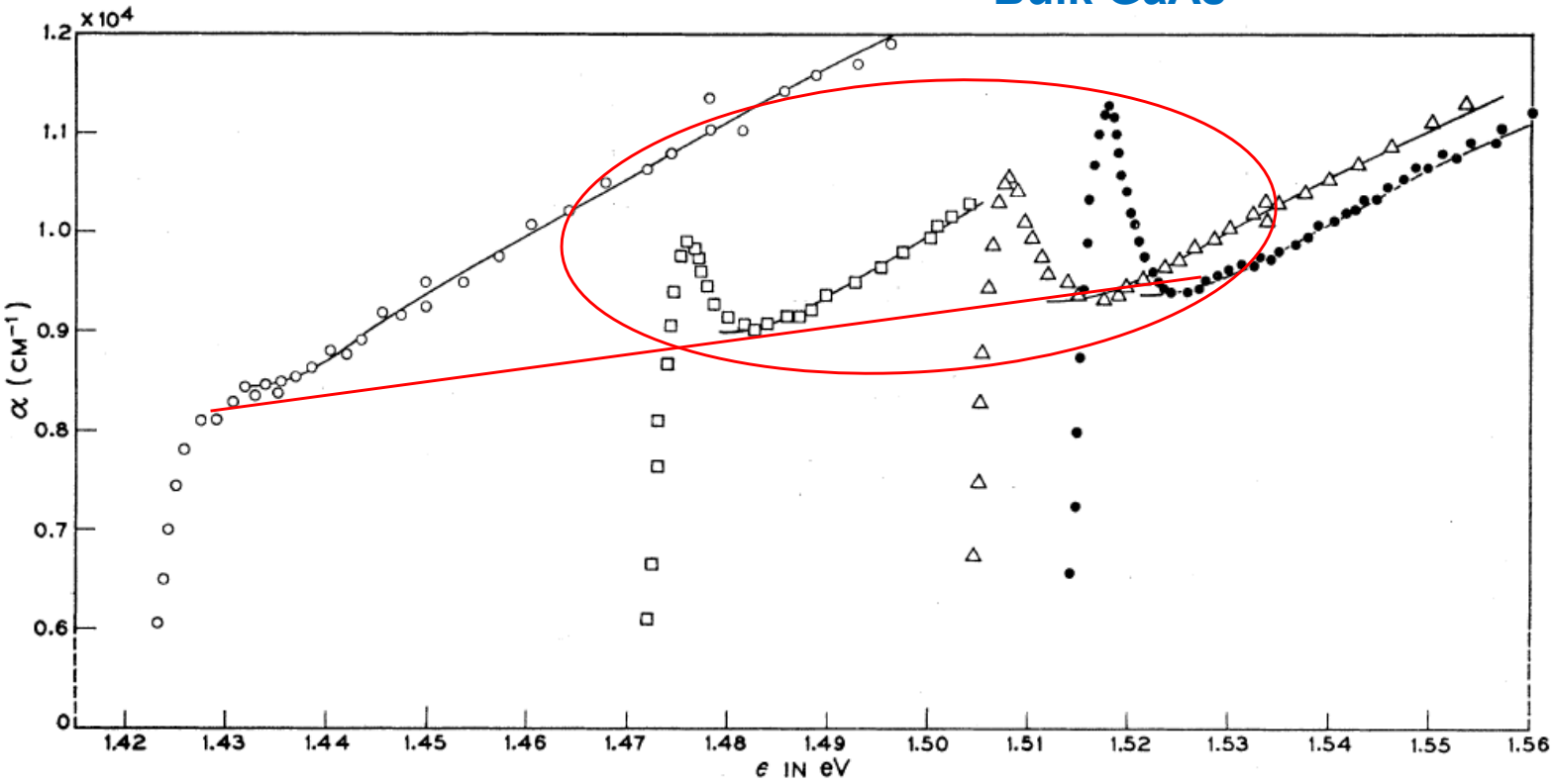
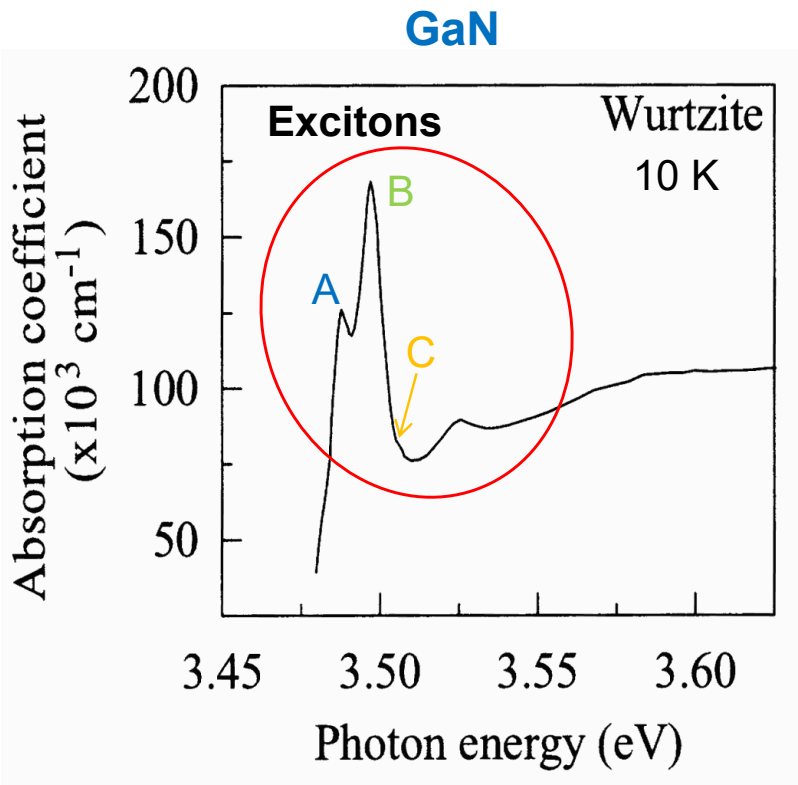


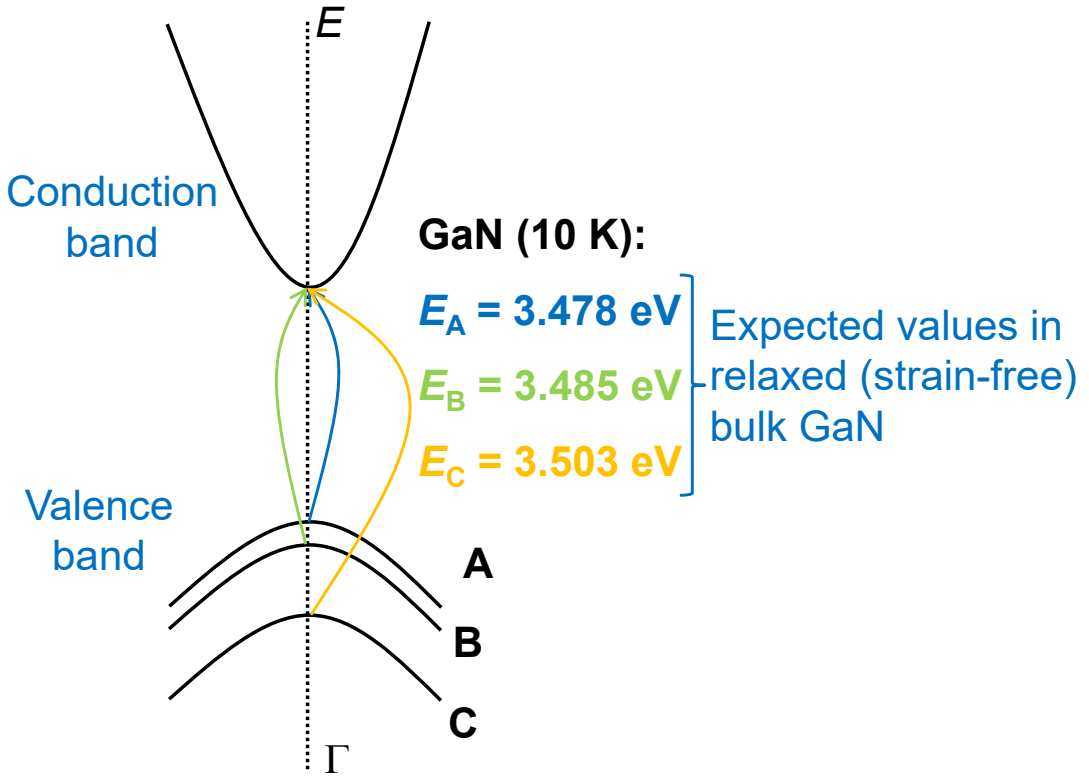
FIG 3 Exciton absorption in GaAs; ○ 294°K, □ 186°K, Δ90°K, ● 21°K.

With increasing T(K):

- Redshift of the absorption edge due to the anharmonic potential
- Decrease in the magnitude of excitonic absorption features
- Decrease in $\alpha_0(\omega)$

Absorption and excitons in semiconductors



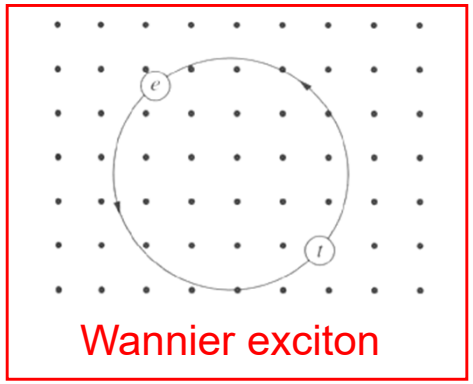


The magnitude of excitonic features in absorption spectra is a function of their oscillator strength!

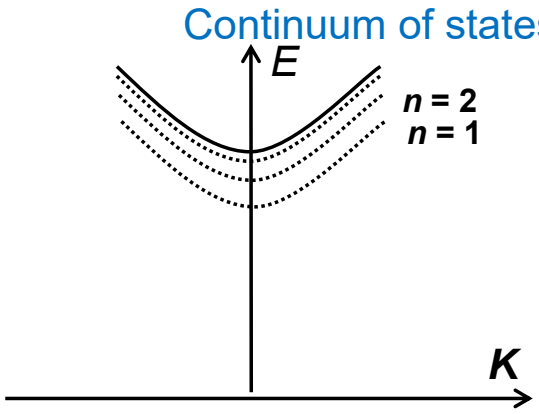
The exact transition energy of excitons is related to their binding energy!

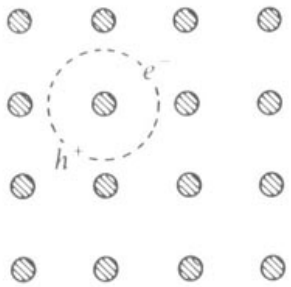
Excitons in semiconductors

Exciton: electron-hole pair bound via Coulomb interaction



⇒ III-V and II-VI semiconductors (but also TMDCs)





⇒ organic semiconductors

Hydrogenic model

$$E_X = E_g + \frac{\hbar^2 K^2}{2M} - \frac{Ry^*}{n^2}$$

$$Ry^* = \frac{m_r}{m_0 \varepsilon_r^2} E_{H_I} = \frac{m_r e^4}{2\hbar^2 (4\pi\varepsilon_0 \varepsilon_r)^2}$$

Same formula as that used for the binding energy of impurities (but $\neq m_r$)

Ry^* = 4 meV for GaAs

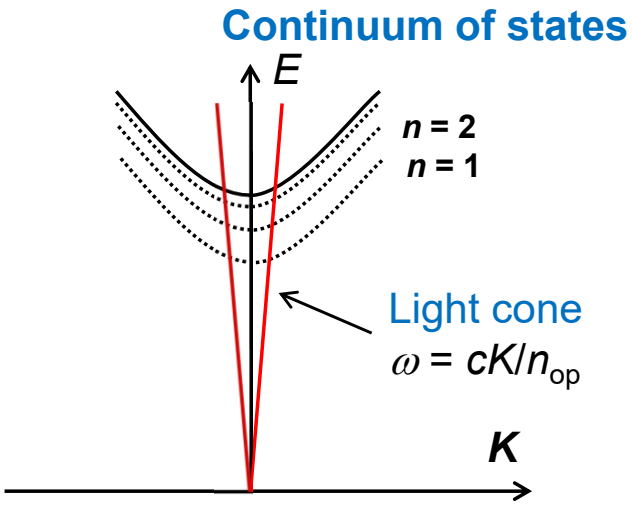
Ry^* = 26 meV for GaN

Ry^* = 60-70 meV for ZnO

$$a_B = \frac{m_0}{m_r} \varepsilon_r a_0 = \frac{\hbar^2 4\pi\varepsilon_0 \varepsilon_r}{m_r e^2}$$

Bohr radius

Excitons in semiconductors



Optical transitions imply energy and momentum conservation ⇒ radiative recombinations of excitons only allowed for excitons of wavevector K such that $E_{exc}(K)$ lies within the light cone!

[1]

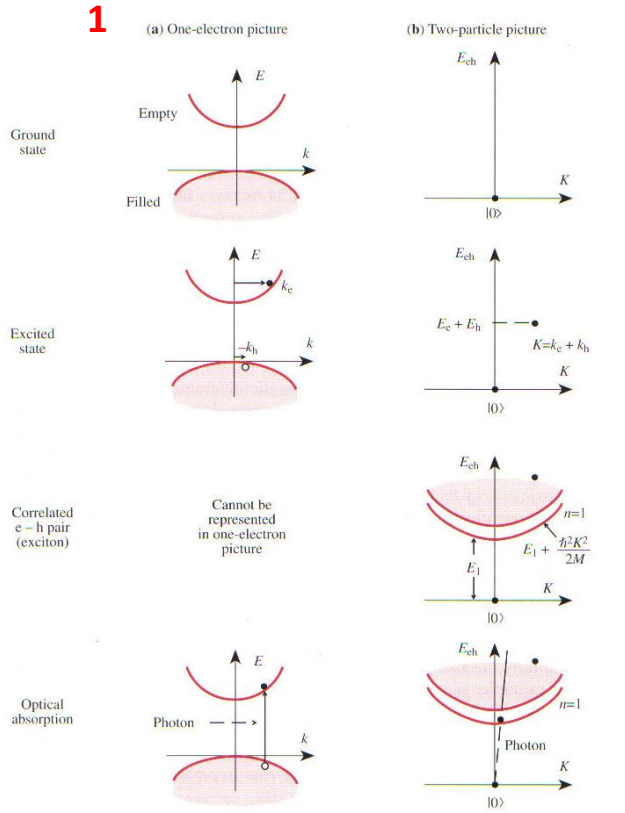


Fig. 6.20. Comparison between the energy levels of the ground state and excited states of a semiconductor in a one-electron band picture (**a**) and in a two-particle picture (**b**). Also, schematic diagrams showing processes in which a photon is absorbed while producing an electron-hole pair

[1] Yu & Cardona, Chapter 6

Some important features of excitons in bulk semiconductors

- Excitons are the fundamental electronic excitation in semiconductors, i.e., they form the lowest intrinsic energy state above the ground state (≡ no electron-hole pair).

- As a first approximation, their main features can be determined by solving Schrödinger's equation in the context of the hydrogenic model. The exciton center of mass behaves like a free particle of total mass $M = m_e + m_h$.

- The wavevectors $\mathbf{k_e}$ and $\mathbf{k_h}$ are not suitable quantum numbers anymore. One should consider the total wavevector $\mathbf{K}$ ($= \mathbf{k_e} + \mathbf{k_h}$) instead to depict the exciton that is a bosonic quasiparticle, i.e., a particle of integer spin inherited from the half-integer spin of its constituents.

- Excitons will remain stable until they get ionized. Hence, their stability is essentially governed by the magnitude of their binding energy vs. the thermal energy $k_B T$.