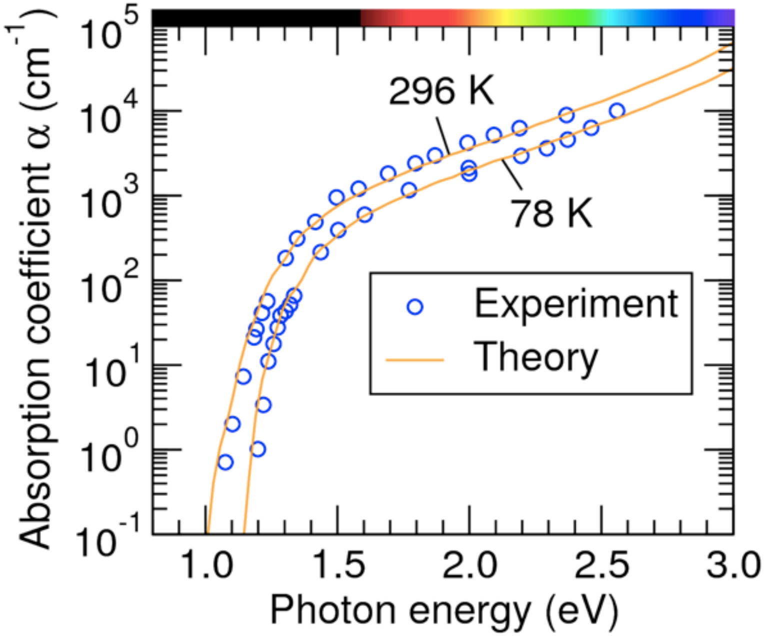

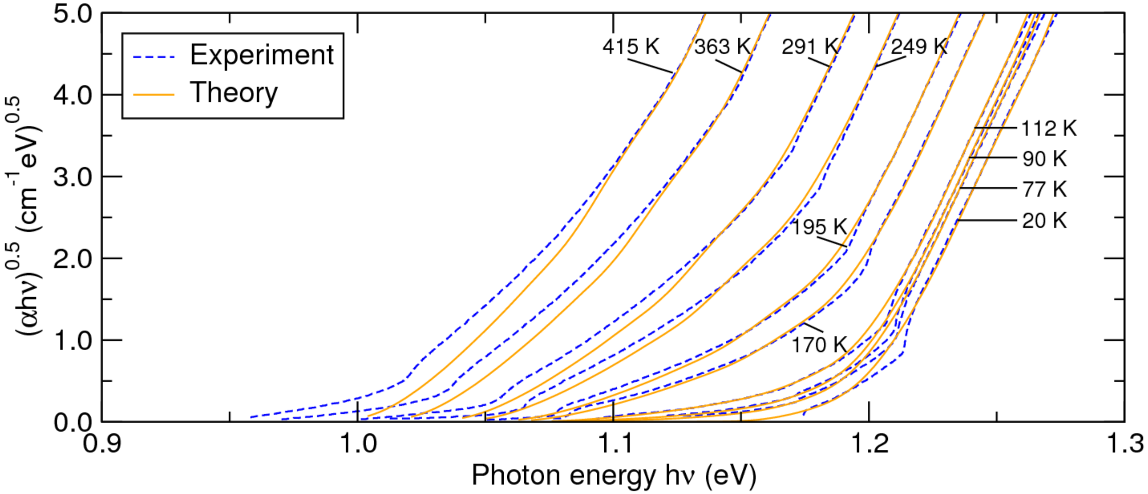

Phonon-assisted optical processes

Emmanouil (Manos) Kioupakis

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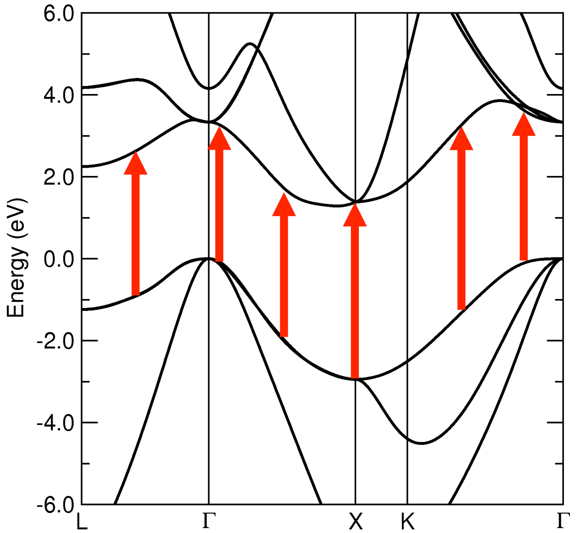
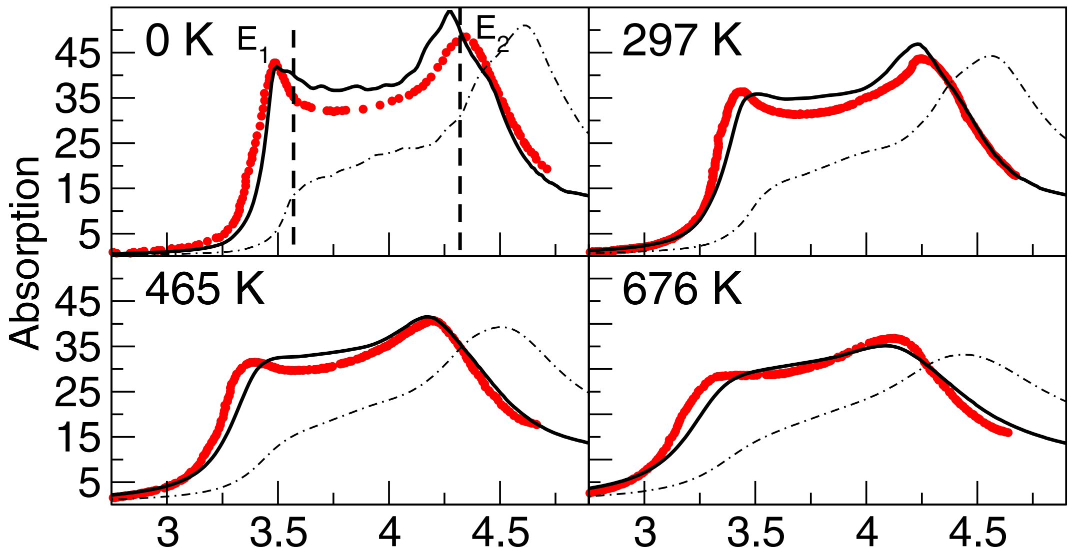
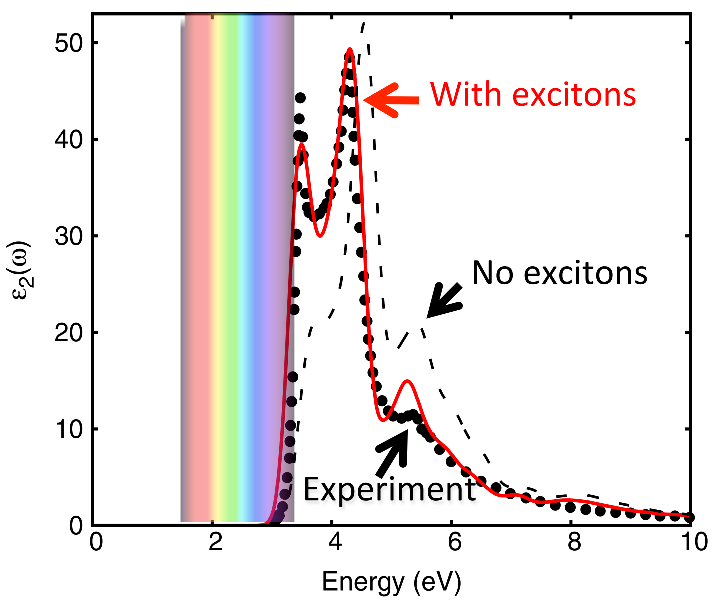
References

- Mark Fox, *Optical Properties of Solids*, Oxford Master Series in Condensed Matter Physics
- Bassani and Pastori Parravicini, *Electronic States and Optical Transitions in Solids*, Oxford, New York, Pergamon Press, Chapter 5.
- Feliciano Giustino, *Rev. Mod. Phys*. **89**, 015003 (2017)
- Noffsinger, Kioupakis, Van de Walle, Louie, and Cohen, *Phys. Rev. Lett.* **108**, 167402 (2012)
- Peelaers, Kioupakis, and Van de Walle, *Phys. Rev. B* **92**, 235201 (2015)

Motivation: optical absorption in Si



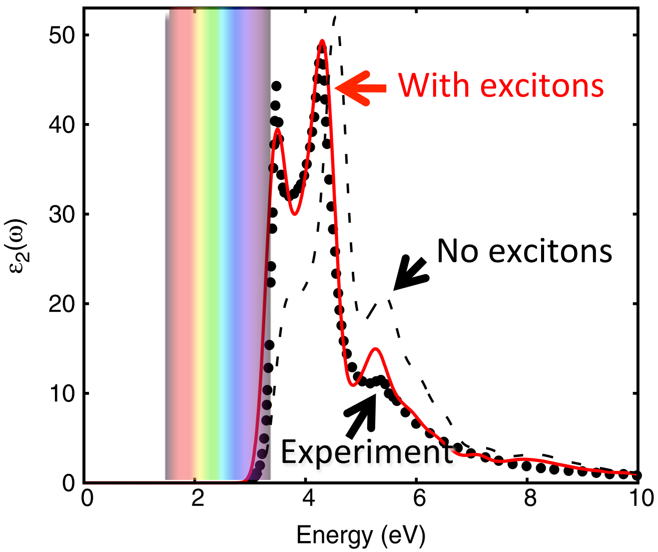




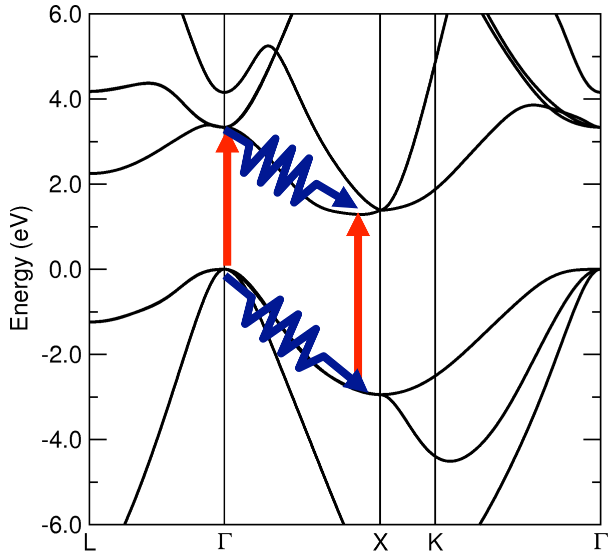
Direct absorption well understood, including excitons and temperature

Albrecht, Reining, Del Sole, Onida, *Phys. Rev. Lett.* **80**, 4510 (1998)
Rohlfing and Louie, *Phys. Rev. B* **62**, 4927(2000)
Marini, *Phys. Rev. Lett.* **101**, 106405 (2008)
Deslippe et al., *Comput. Phys. Commun*. **183**, 1269 (2012)

Motivation: silicon solar cells



Deslippe *et al. Comput. Phys. Commun*. **183**, 1269 (2012)

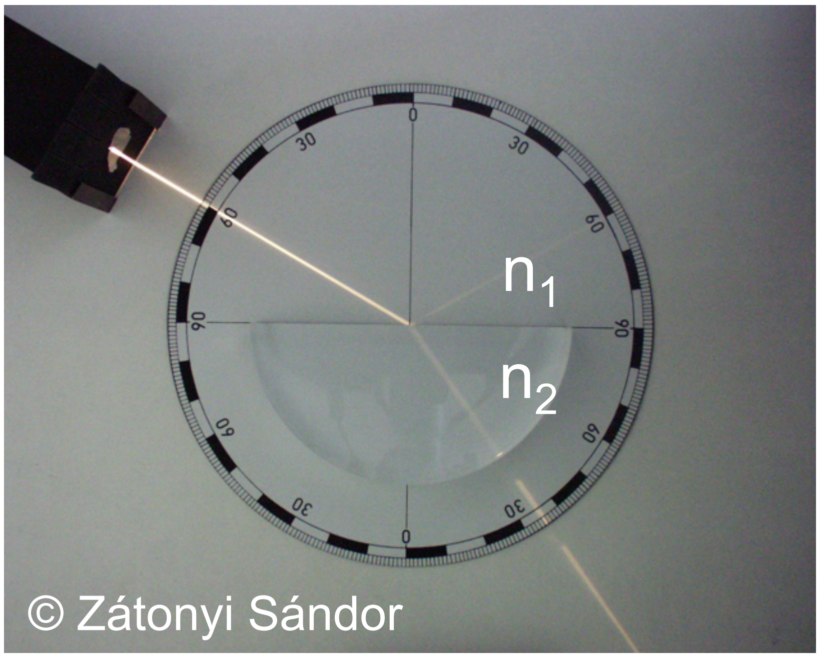


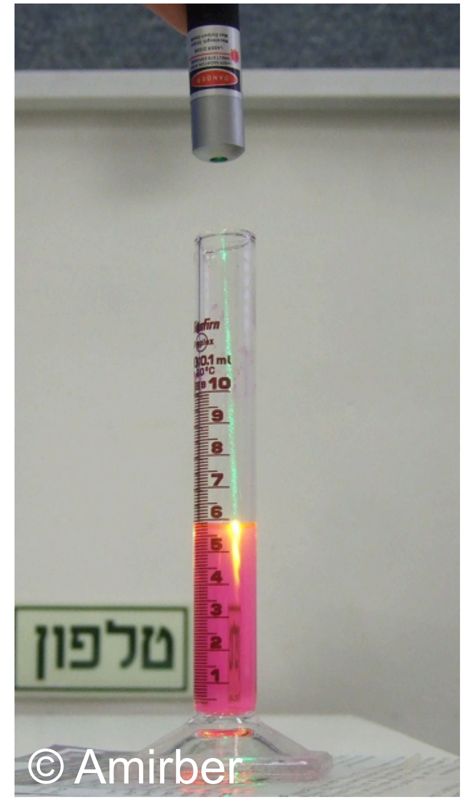
Gap of silicon is indirect (1.2 eV), minimum direct gap is 3.4 eV.
Direct optical absorption impossible in the visible.
Absorption in the visible is phonon-assisted, enables silicon solar cells.

Linear optics

Absorption: Beer-Lambert law

Refraction: Snell's law





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

α = absorption coefficient [cm^{-1}]

Strong absorbers: $\alpha \sim 10^5 - 10^6\ cm^{-1}$

Optical parameters of materials

Complex refractive index: $$\tilde{n} = n + i\kappa$$

Complex dielectric function: $$\tilde{\epsilon} = \epsilon_1 + i\epsilon_2$$

Their connection:

$$n = \frac{1}{\sqrt{2}} \left(\epsilon_1 + \left(\epsilon_1^2 + \epsilon_2^2 \right)^{\frac{1}{2}} \right)^{\frac{1}{2}}$$

$$\kappa = \frac{1}{\sqrt{2}} \left(-\epsilon_1 + \left(\epsilon_1^2 + \epsilon_2^2 \right)^{\frac{1}{2}} \right)^{\frac{1}{2}}$$

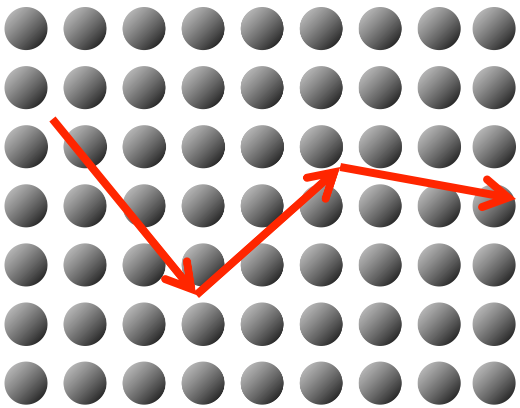
Absorption coefficient:

$$\alpha = \frac{2\kappa\omega}{c} = \frac{4\pi\kappa}{\lambda}$$

Classical theory of light absorption

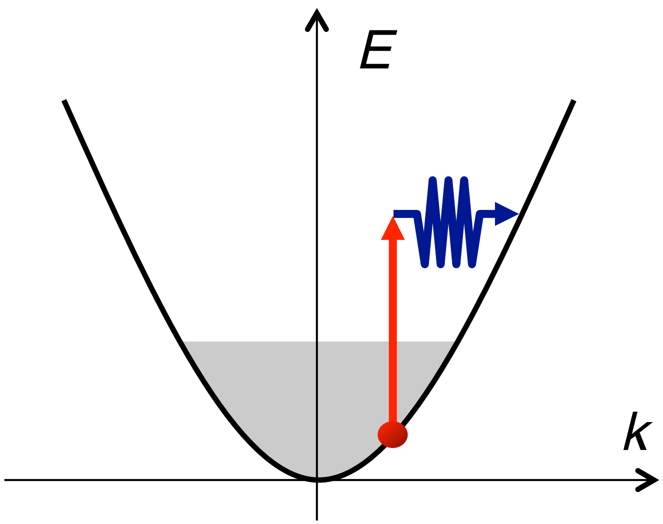
Semiclassical Drude model: $m^* \frac{d\vec{v}}{dt} = -e\vec{E} - \frac{m^*\vec{v}}{\tau}$

e.g., DC conductivity: $\sigma = \frac{ne^2\tau}{m^*}$



AC field: Absorption coefficient in metals

$$\alpha(\omega) = \frac{4\pi n e^2}{m^* n_r c \tau} \frac{1}{\omega^2}$$



But: τ : Phenomenological

Quantum theory of optical absorption

Treat with perturbation theory

Unperturbed state = DFT of GW wave functions and eigenvalues

Perturbation: electron-photon Hamiltonian

$$H_{\text{el-phot}} = \frac{e}{mc}\vec{A} \cdot \vec{p}$$

Recombination probability per unit time:

$$P_{i \to f} = \frac{2\pi}{\hbar} \left| \langle f | H_{\text{el-phot}} | i \rangle \right|^2 \delta(E_f - E_i)$$

Initial and final states: $E_i = \varepsilon_{n\boldsymbol{k}}, E_f = \varepsilon_{m\boldsymbol{k}} + \hbar\omega$

Absorbed power: $\hbar\omega \sum_{i,f} (f_i - f_f) P_{i \to f}$

Incident power: $\frac{n^2 A^2 \omega^2}{2\pi c^2}$

Quantum theory of optical absorption

Absorption coefficient:

$\boldsymbol{p}$ = optical matrix elements
$\boldsymbol{\lambda}$ = light polarization

$$\alpha = \frac{\hbar\omega \sum_{i,f}(f_i - f_f)P_{i\to f}}{\frac{n^2 A^2 \omega^2}{2\pi c^2}}$$

$$= 2\frac{4\pi^2 e^2}{n_r c m_e^2 \omega}\frac{1}{N_{\boldsymbol{k}}}\sum_{n,m,\boldsymbol{k}}(f_{n\boldsymbol{k}} - f_{m\boldsymbol{k}})\left|\boldsymbol{\lambda}\cdot\boldsymbol{p}_{nm}\right|^2 \delta(\varepsilon_{m\boldsymbol{k}} - \varepsilon_{n\boldsymbol{k}} - \hbar\omega)$$

Dielectric function:

Imaginary:

$$\epsilon_2 = \frac{n_r c}{\omega} = 2\frac{4\pi^2 e^2}{m_e^2 \omega^2}\frac{1}{N_{\boldsymbol{k}}}\sum_{n,m,\boldsymbol{k}}(f_{n\boldsymbol{k}} - f_{m\boldsymbol{k}})\left|\boldsymbol{\lambda}\cdot\boldsymbol{p}_{nm}\right|^2 \delta(\varepsilon_{m\boldsymbol{k}} - \varepsilon_{n\boldsymbol{k}} - \hbar\omega)$$

Real: from Kramers-Kronig relation:

$$\epsilon_1 = 1 + 2\frac{8\pi e^2}{m_e^2}\frac{1}{N_{\boldsymbol{k}}}\sum_{n,m,\boldsymbol{k}}(f_{n\boldsymbol{k}} - f_{m\boldsymbol{k}})\frac{\left|\boldsymbol{\lambda}\cdot\boldsymbol{p}_{nm}\right|^2}{(\varepsilon_{m\boldsymbol{k}} - \varepsilon_{n\boldsymbol{k}})/\hbar}\frac{1}{(\varepsilon_{m\boldsymbol{k}} - \varepsilon_{n\boldsymbol{k}})^2/\hbar^2 - \omega^2}$$

Phonon-assisted optical absorption

Second order perturbation theory

Perturbation: electron-photon + electron-phonon Hamiltonian

$$P_{i\to f} = \frac{2\pi}{\hbar}\left|\sum_m \frac{\langle f|H|m\rangle\langle m|H|i\rangle}{E_m - E_i}\right|^2 \delta(E_f - E_i)$$

Keeping cross terms only (other terms are two-photon and two-phonon absorption/emission:

$$P_{i\to f} = \frac{2\pi}{\hbar}\left|\sum_m \frac{\langle f|H_{\text{el-phot}}|m\rangle\langle m|H_{\text{el-phon}}|i\rangle}{E_m - E_i} + \sum_{m'} \frac{\langle f|H_{\text{el-phon}}|m'\rangle\langle m'|H_{\text{el-phot}}|i\rangle}{E_{m'} - E_i}\right|^2 \delta(E_f - E_i)$$

Phonon-assisted optical absorption

Absorption coefficient:

$$\alpha = 2\frac{4\pi^2 e^2}{n_r c m_e^2 \omega}\frac{1}{N_{\boldsymbol{k}} N_{\boldsymbol{q}}}\sum_{i,j,\boldsymbol{k},\boldsymbol{q}} P\left|\boldsymbol{\lambda}\cdot(\boldsymbol{S}_1+\boldsymbol{S}_2)\right|^2$$

$$\times\,\delta(\varepsilon_{j,\boldsymbol{k}+\boldsymbol{q}} - \varepsilon_{i\boldsymbol{k}} - \hbar\omega \pm \hbar\omega_{\nu\boldsymbol{q}})$$

p = optical matrix elements
g = electron-phonon coupling
λ = light polarization

Two paths:

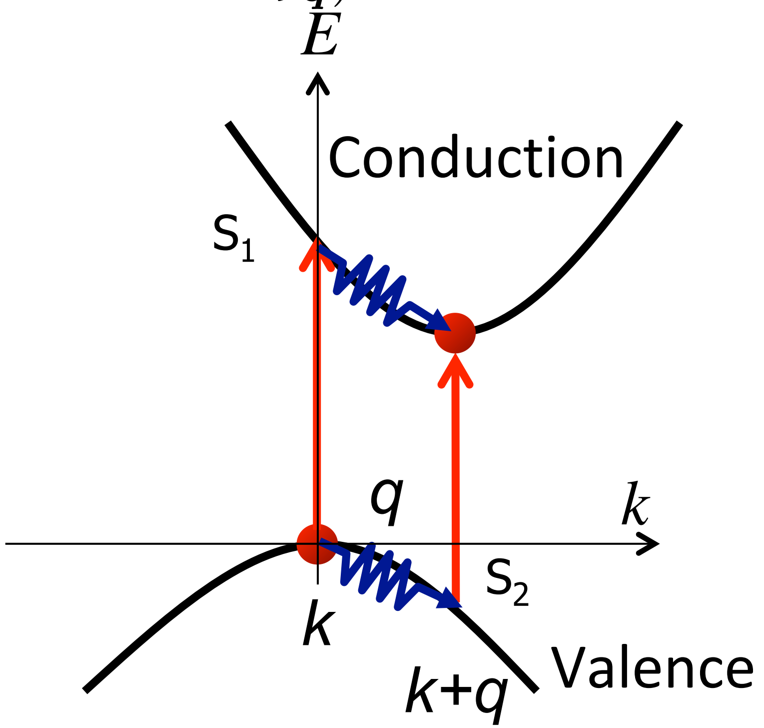
$$\boldsymbol{S}_1(\boldsymbol{k},\boldsymbol{q}) = \sum_m \frac{\boldsymbol{p}_{im}(\boldsymbol{k})\, g^{\text{el-ph}}_{mj,\nu}(\boldsymbol{k},\boldsymbol{q})}{\epsilon_{m\boldsymbol{k}} - \epsilon_{i\boldsymbol{k}} - \hbar\omega}$$

$$\boldsymbol{S}_2(\boldsymbol{k},\boldsymbol{q}) = \sum_m \frac{g^{\text{el-ph}}_{im,\nu}(\boldsymbol{k},\boldsymbol{q})\,\boldsymbol{p}_{mj}(\boldsymbol{k}+\boldsymbol{q})}{\epsilon_{m,\boldsymbol{k}+\boldsymbol{q}} - \epsilon_{i\boldsymbol{k}} \pm \hbar\omega_{\nu\boldsymbol{q}}}$$

Occupations:

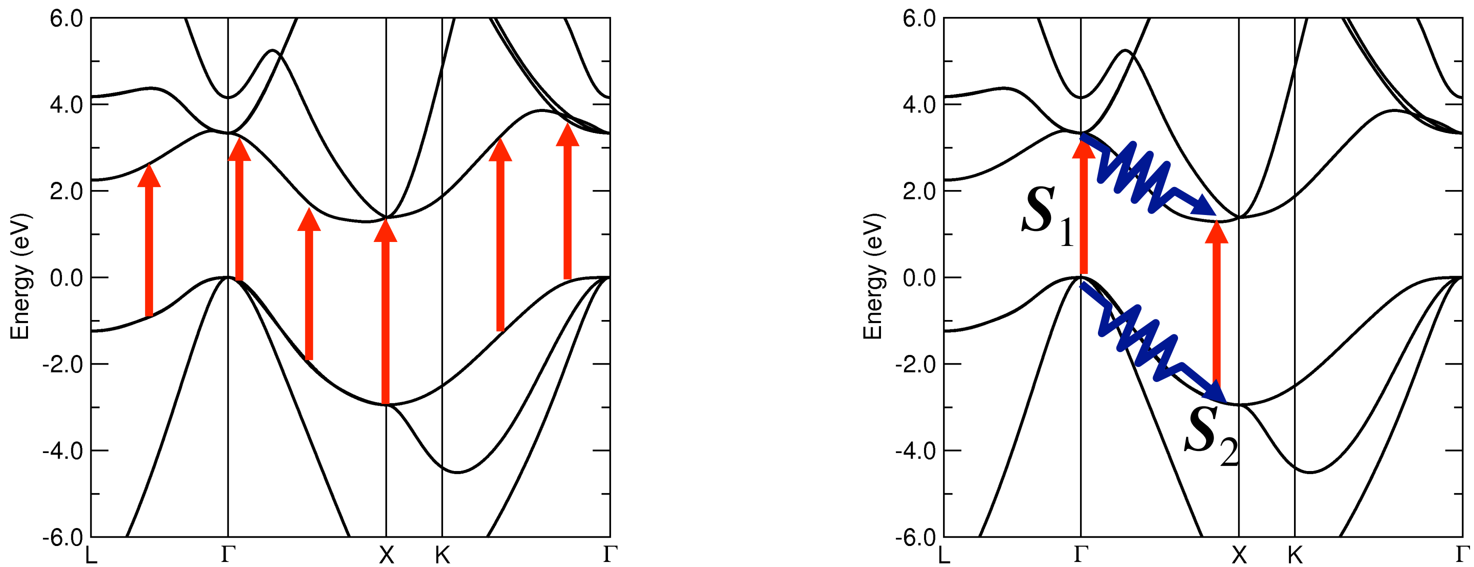
$$P = \left(n_{\nu\boldsymbol{q}} + \frac{1}{2} \pm \frac{1}{2}\right)(f_{i\boldsymbol{k}} - f_{j,\boldsymbol{k}+\boldsymbol{q}})$$

Upper sign: phonon emission
Lower sign: phonon absorption
Sum over *m*: both occupied + empty states



Computational challenge

Direct: **single** sum *vs.* Indirect: **double** sum

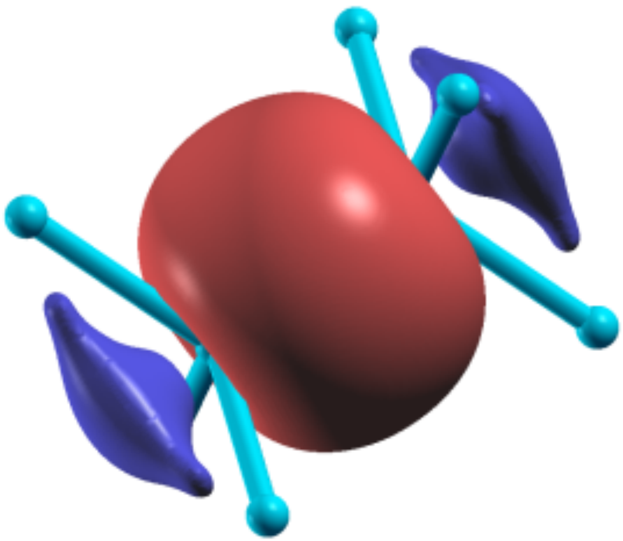


$$\alpha(\omega) \propto \sum_{i,j,\nu} P|\boldsymbol{S}_1 + \boldsymbol{S}_2|^2 \delta(\epsilon_j - \epsilon_i - \hbar\omega \pm \hbar\omega_\nu)$$

Double sum over all initial and final states is **expensive**:
For energy resolution of 0.03 eV → need 24×24×24 k-grid and q-grid, ~200M combinations of initial and final wave vectors

Solution: Wannier interpolation

Max. localized Wannier functions
From Bloch to Wannier basis

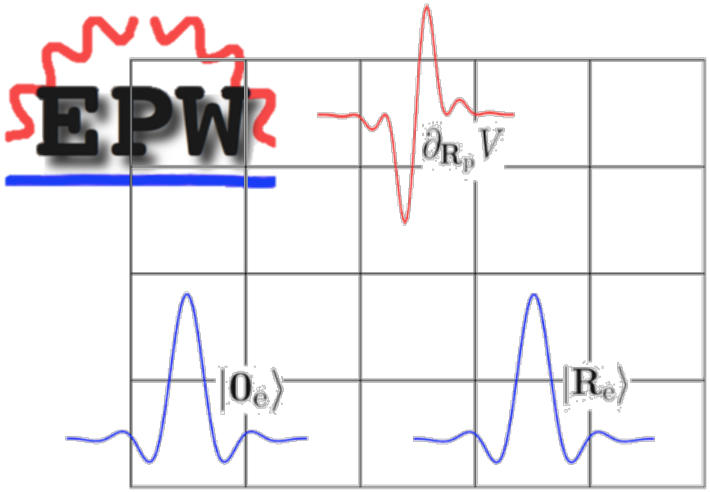


Interpolate *quasiparticle energies*, *optical matrix elements.*

Mostofi, Yates, Pizzi, Lee, Souza, Vanderbilt, Marzari, *Comput. Phys. Commun*. **185**, 2309 (2014). http://www.wannier.org/

Fourier

$$\langle \boldsymbol{k} | \partial_{\boldsymbol{q}} V | \boldsymbol{k} + \boldsymbol{q} \rangle \rightarrow \langle \mathbf{0}_e | \partial_{\boldsymbol{R}_p} | \boldsymbol{R}_e \rangle$$

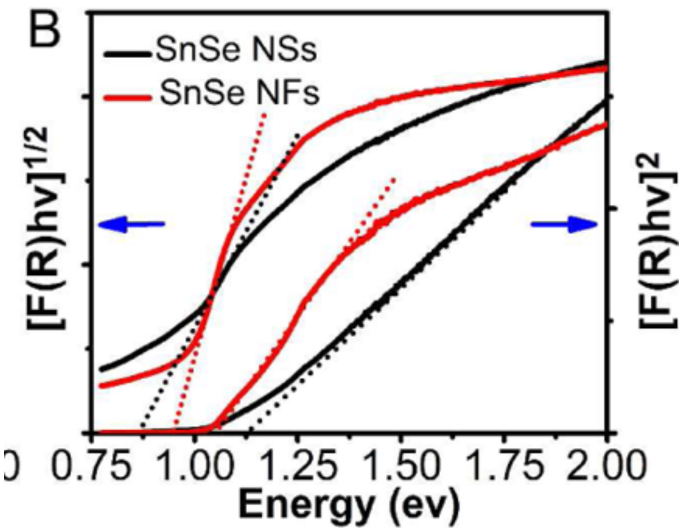


Interpolate *electron-phonon matrix elements.*
Current version: optical matrix elements = momentum operator.

S. Poncé et al, *Comput. Phys. Comm.* **209**, 116 (2016)
http://epw.org.uk/

Measuring direct and indirect band gaps

How does experiment determine whether a measured gap in optical absorption is direct or indirect?
A: Tauc plot



J. Am. Chem. Soc. 2013, 135, 1213–1216

For direct absorption:

$$\alpha \propto \frac{(\hbar\omega - E_g^d)^{1/2}}{\omega} \Rightarrow (\alpha\omega)^2 \propto \hbar\omega - E_g^d$$

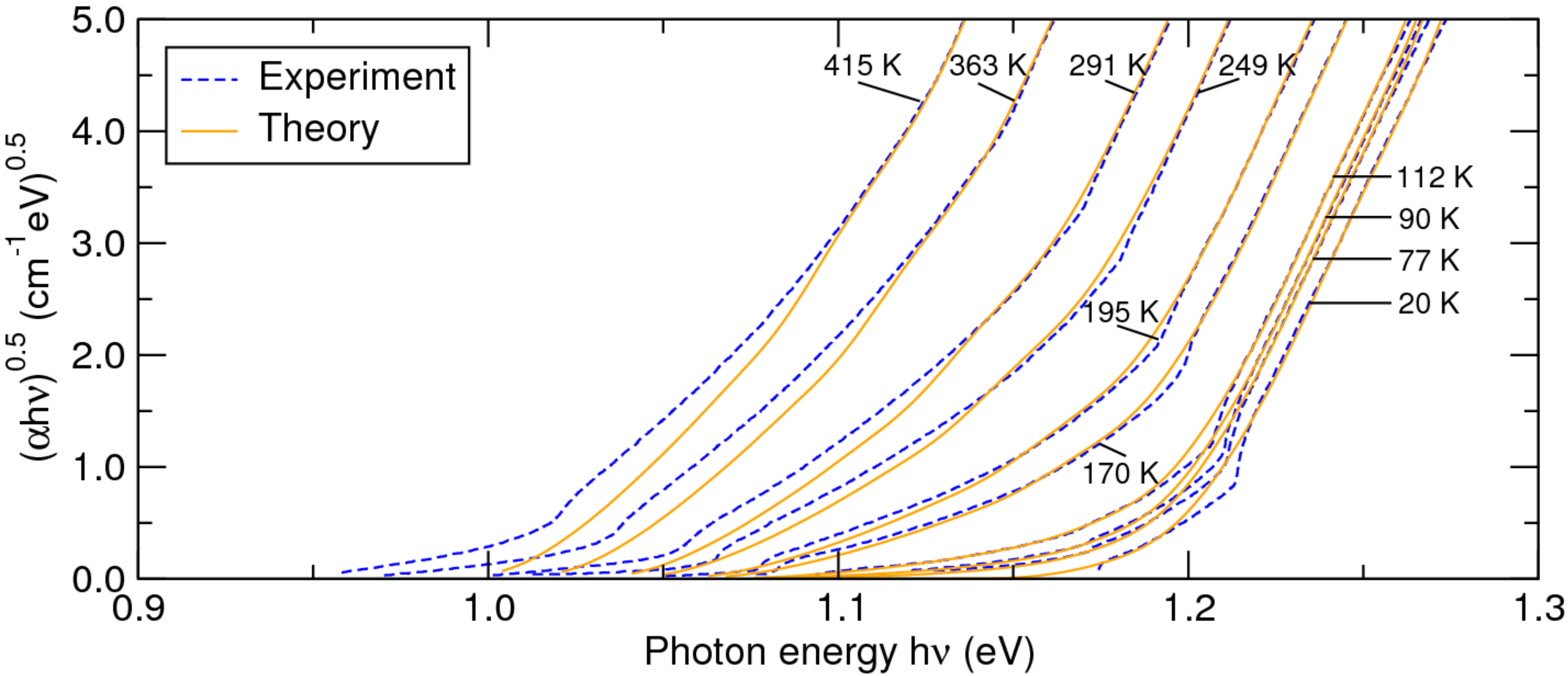
For indirect absorption:

$$\alpha \propto \frac{(\hbar\omega - E_g^i \pm \hbar\omega_{\text{phonon}})^2}{\omega} \Rightarrow$$

$$\Rightarrow (\alpha\omega)^{1/2} \propto \hbar\omega - E_g^i \pm \hbar\omega_{\text{phonon}}$$

Exponent determines type and value of gap.
Two indirect terms for emission/absorption.

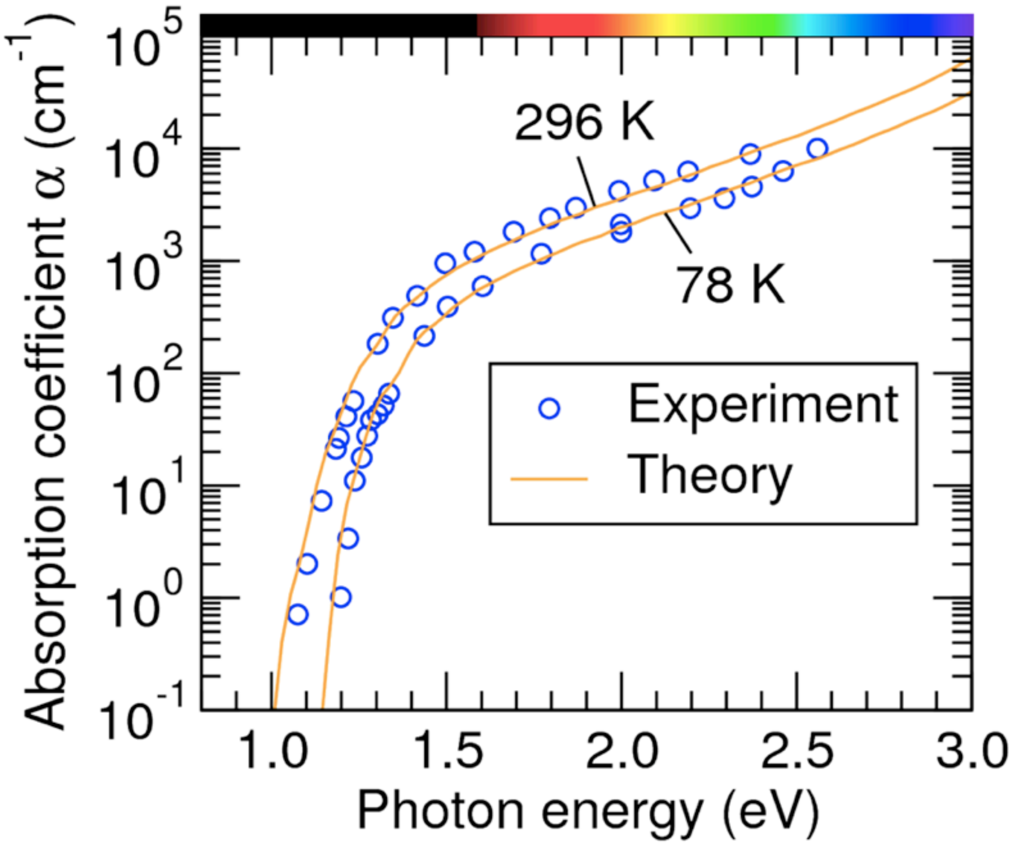
Indirect absorption edge for silicon



Noffsinger, Kioupakis, Van de Walle, Louie, and Cohen,
Phys. Rev. Lett. **108**, 167402 (2012)

* Shifted the energy of onset by 0.15-0.23 eV to match experimental linear region

Si absorption in the visible



Noffsinger, Kioupakis, Van de Walle, Louie, and Cohen, *Phys. Rev. Lett*. **108**, 167402 (2012)

* Shifted the energy of onset to match experimental trend

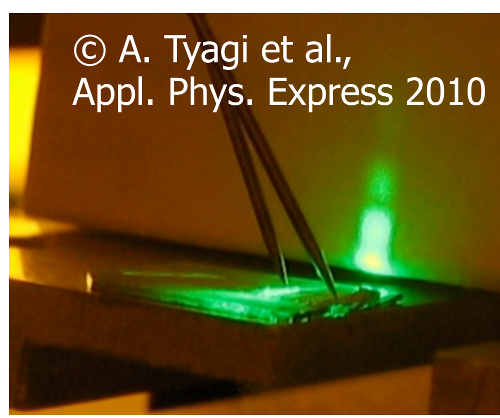
Laser diodes

Blu-ray laser diodes (405 nm , violet) based on GaN

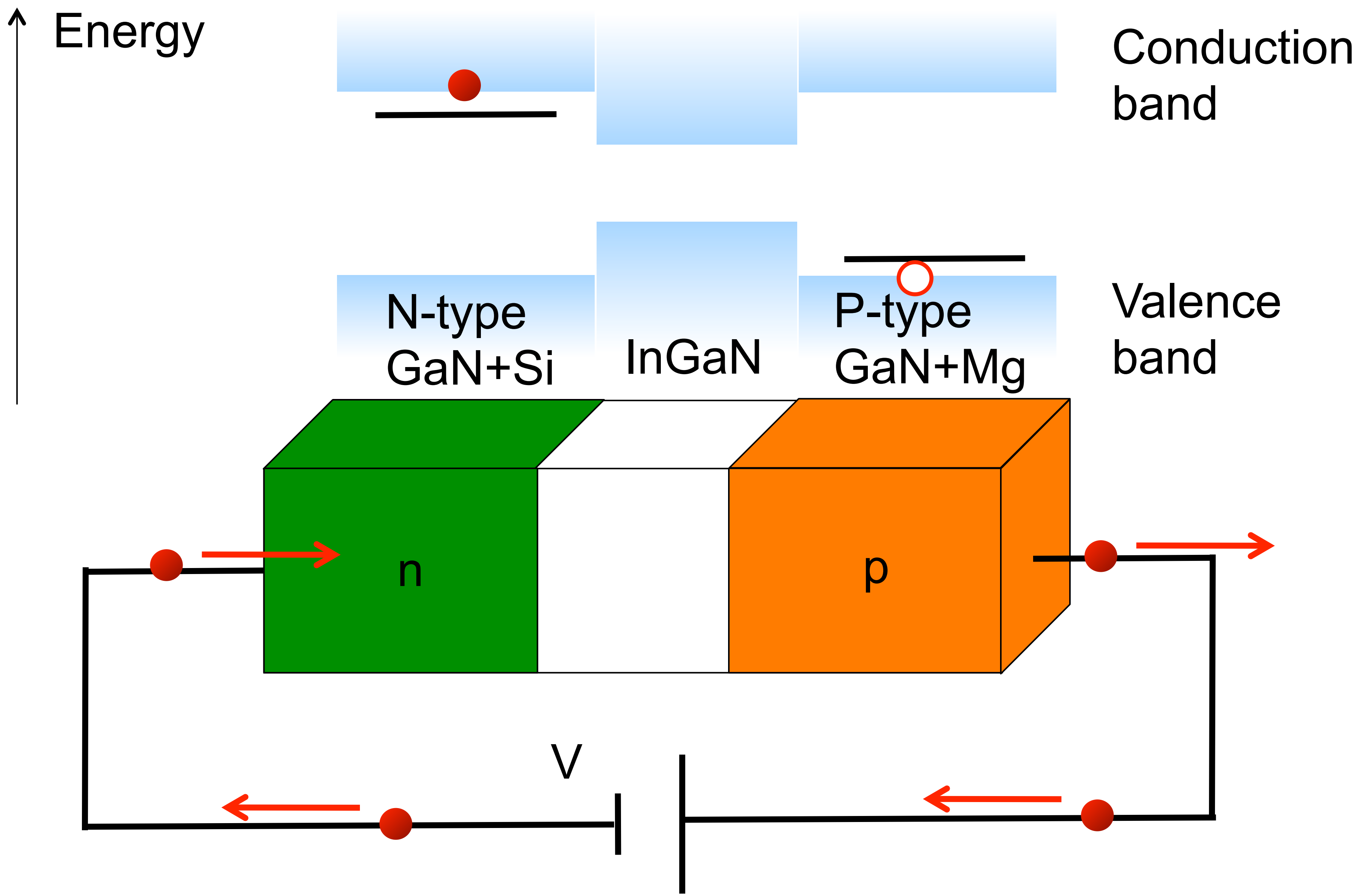
Applications:

- Optical storage
- Laser projectors

Aim: high-power nitride green lasers.



How nitride LEDs/lasers work



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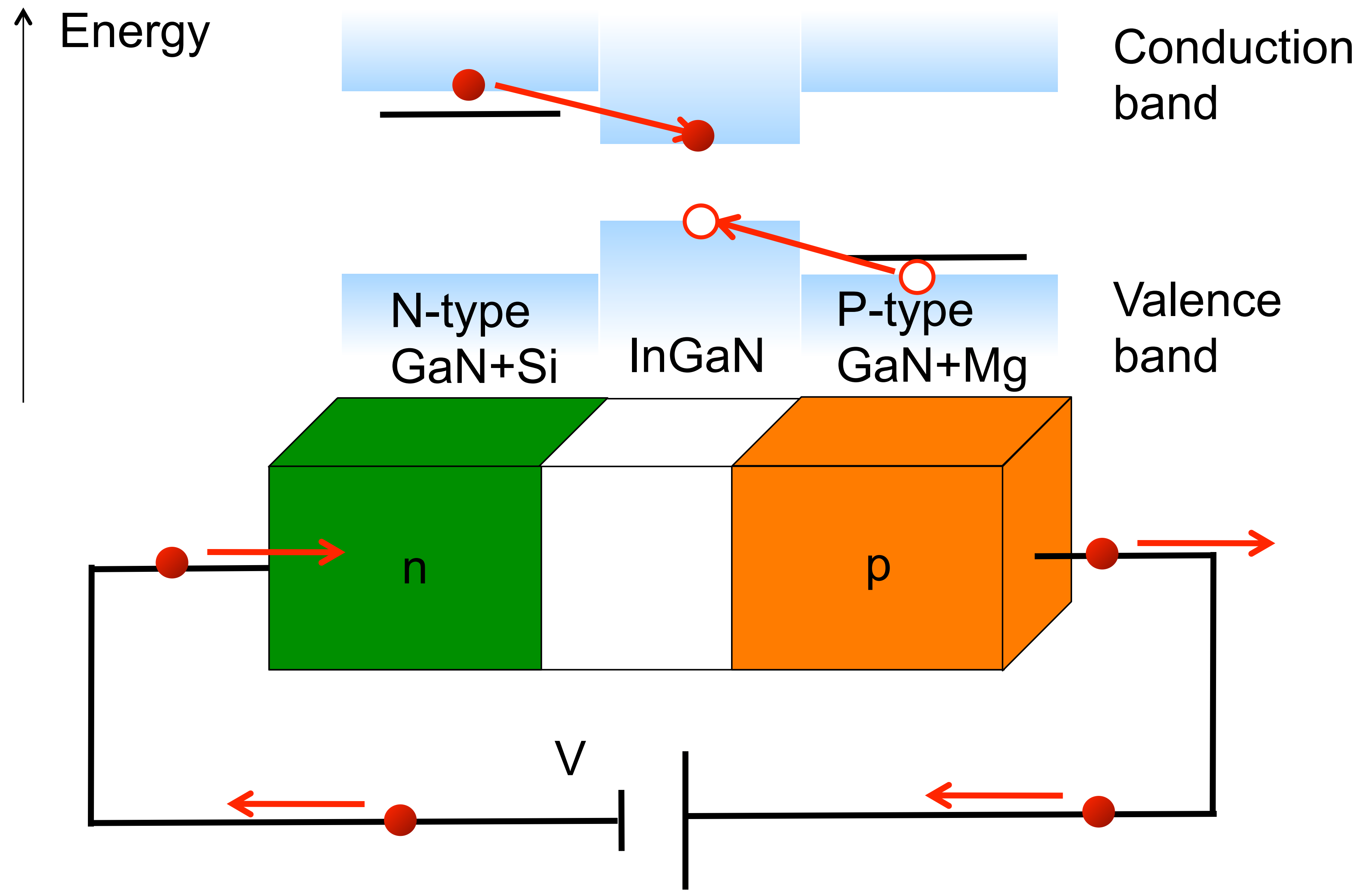

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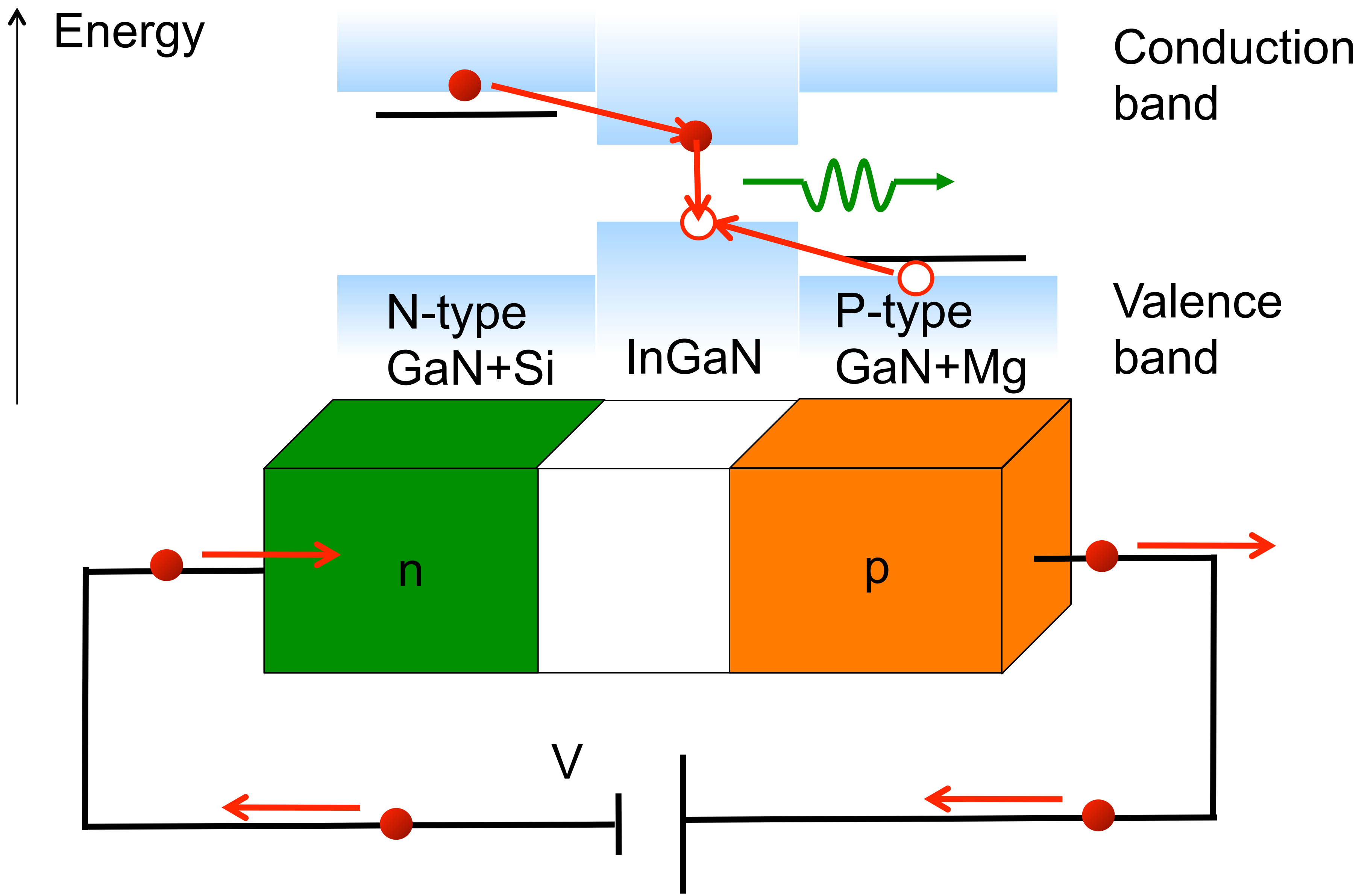
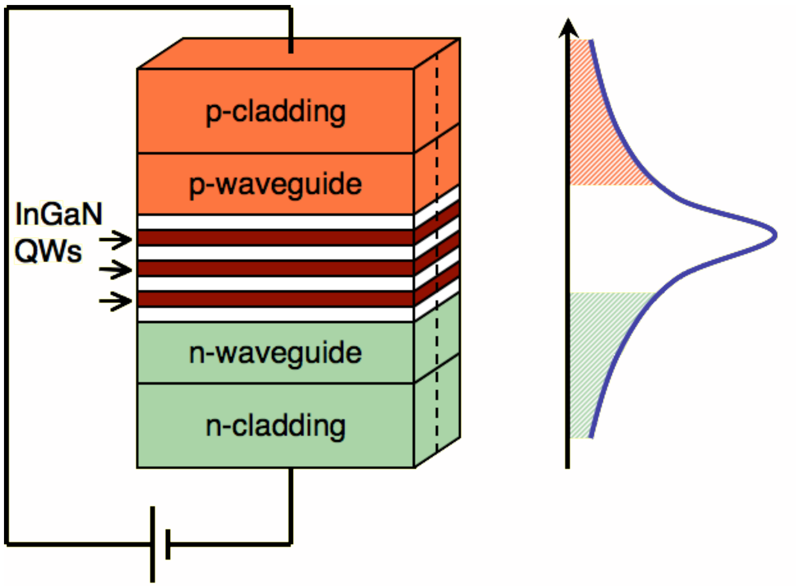
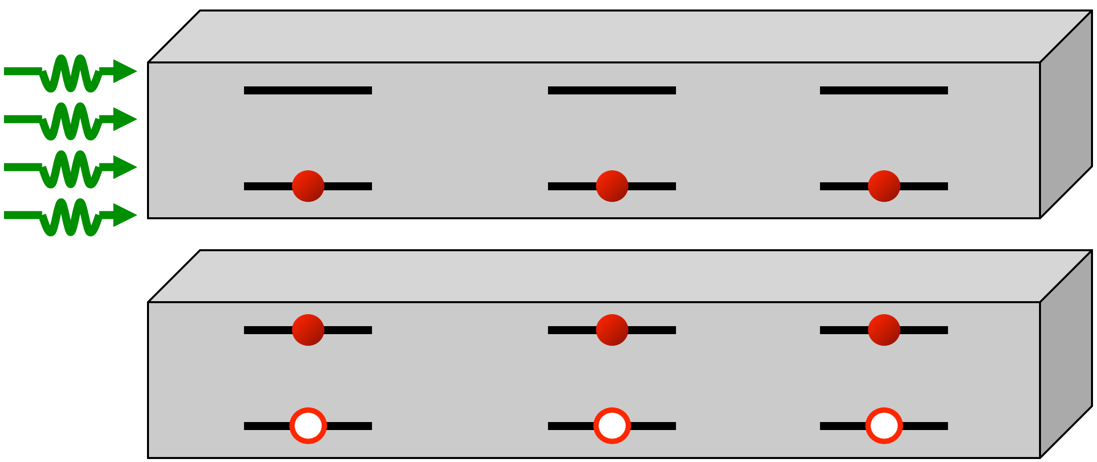


Absorption and gain



Optical mode profile (photon density)



Absorption:

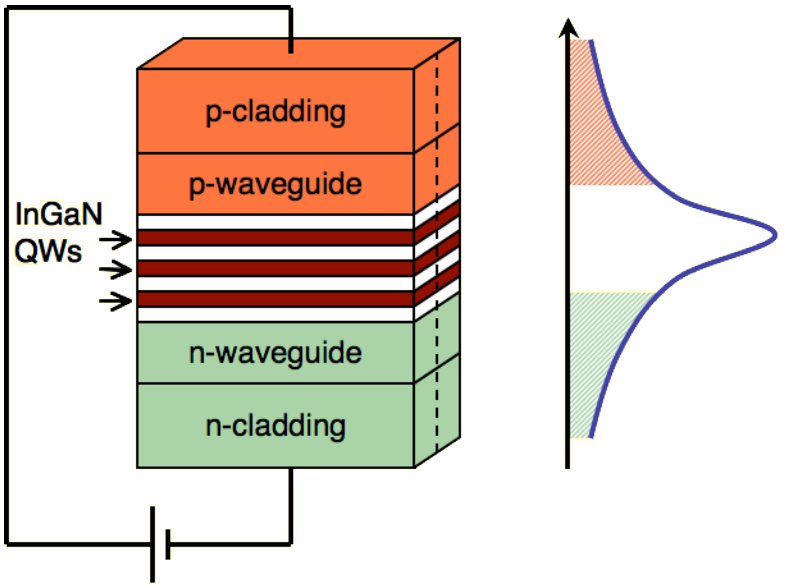
$$I(x) = I_0 e^{-\alpha x}$$

Gain in the QWs:

$$I(x) = I_0 e^{+gx}$$

Output = Gain – Absorption

Absorption and gain



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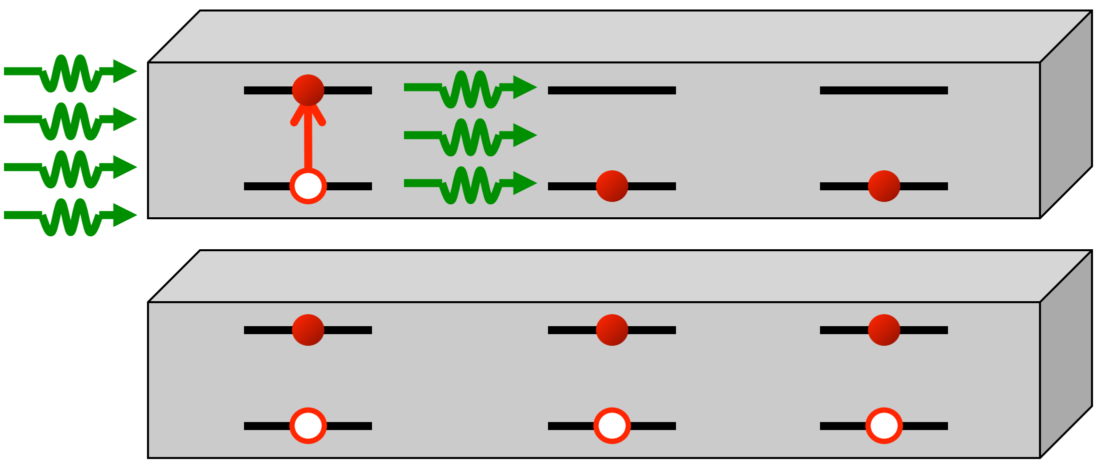

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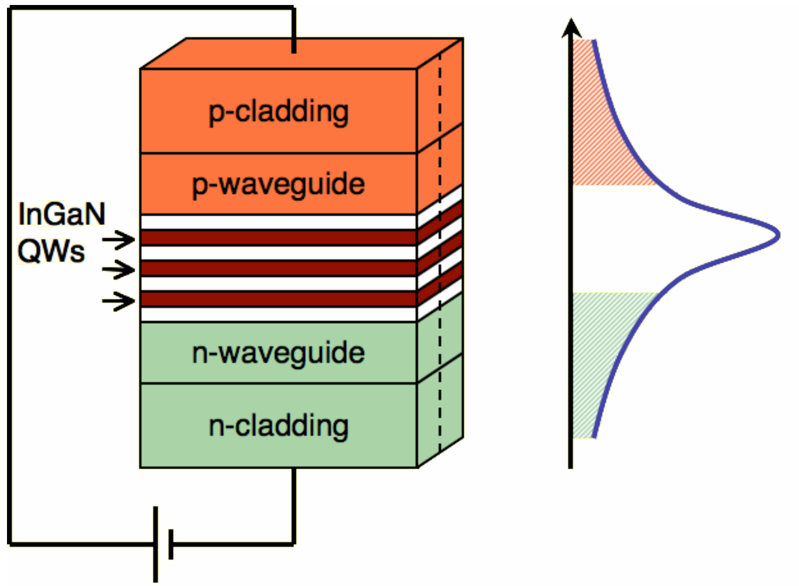

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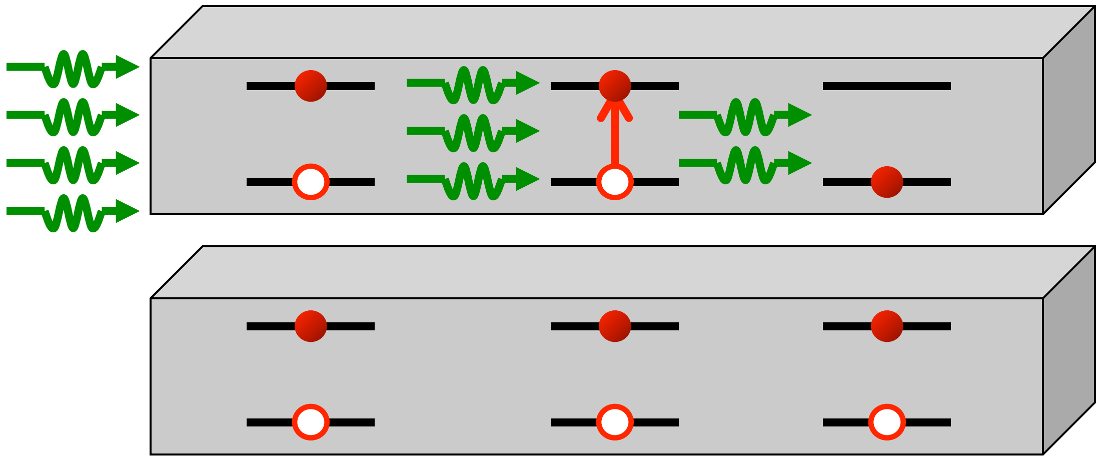

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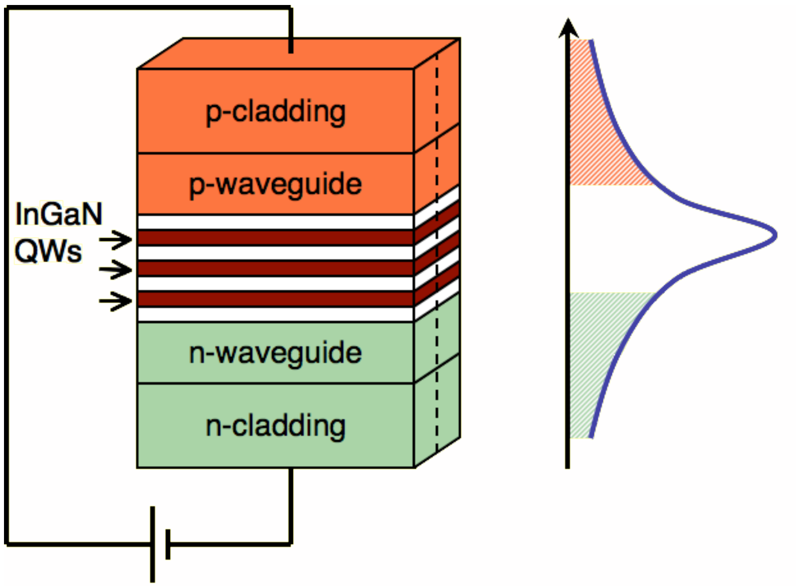

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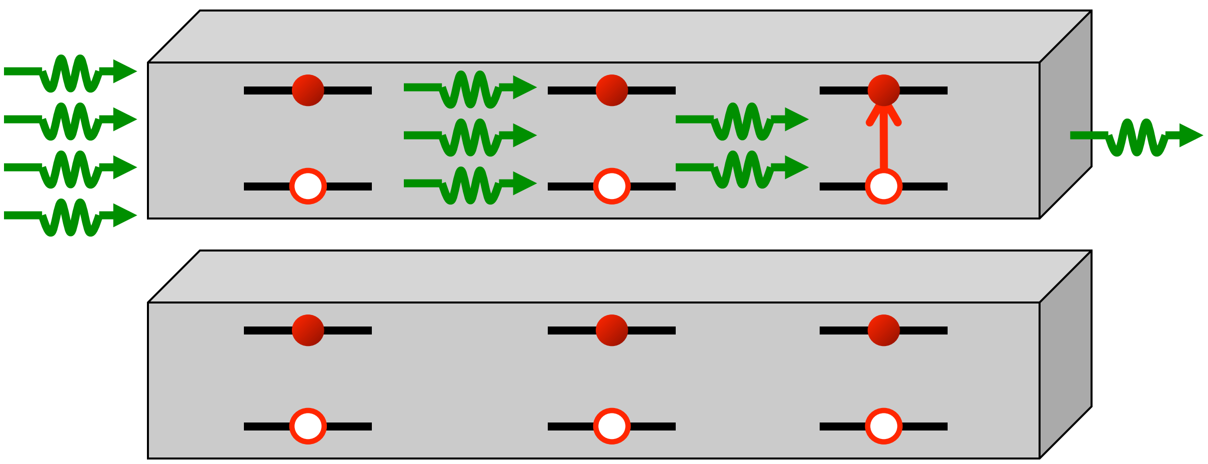

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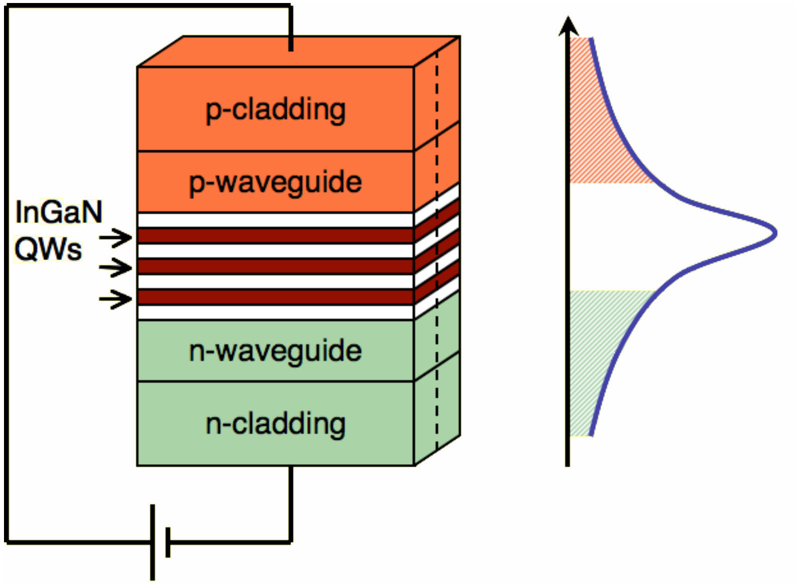
Absorption and gain



Optical mode profile
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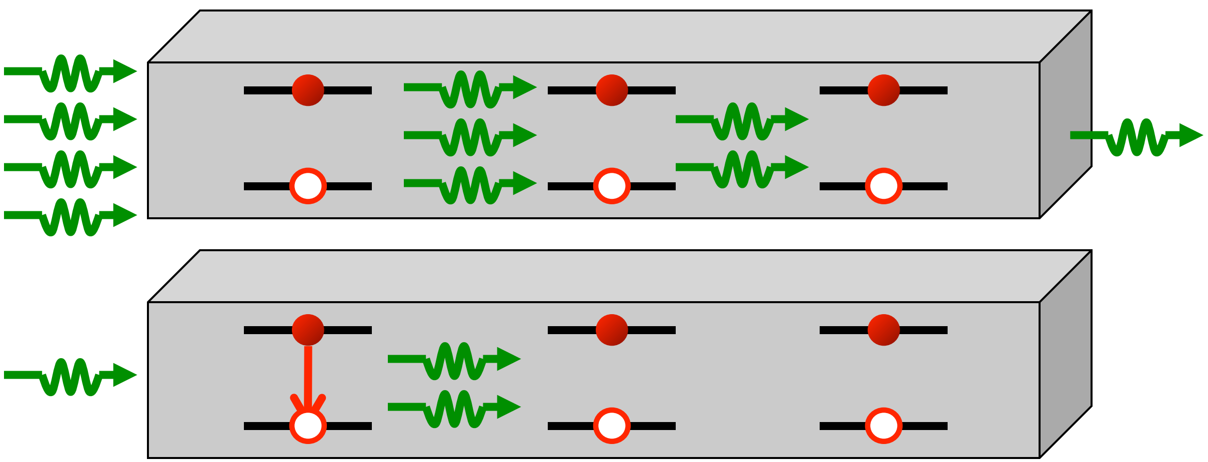

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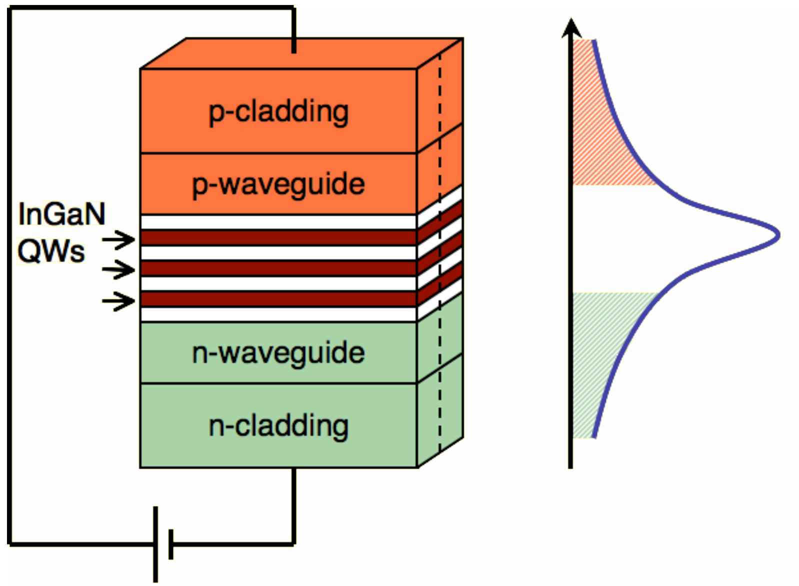
Absorption and gain



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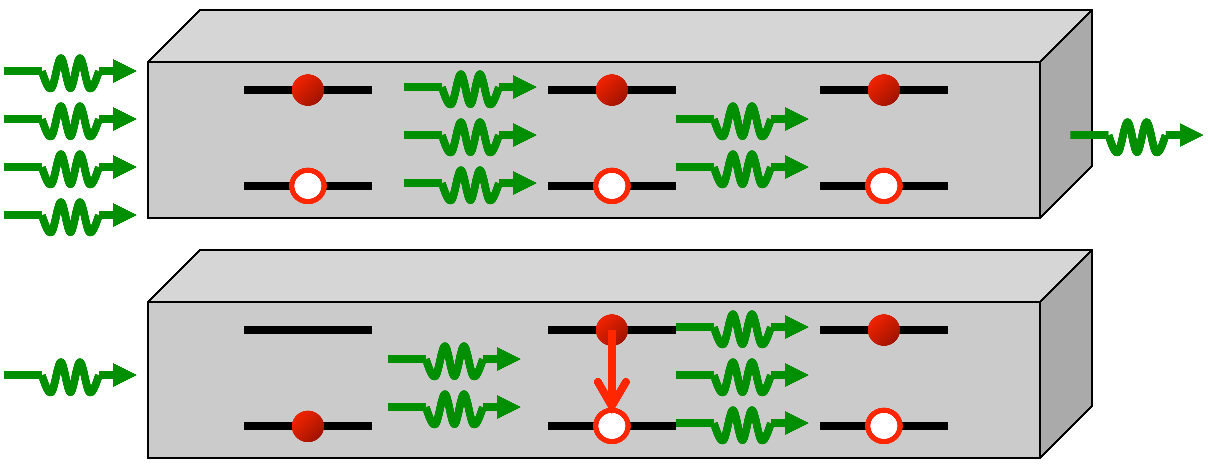
(photon density)



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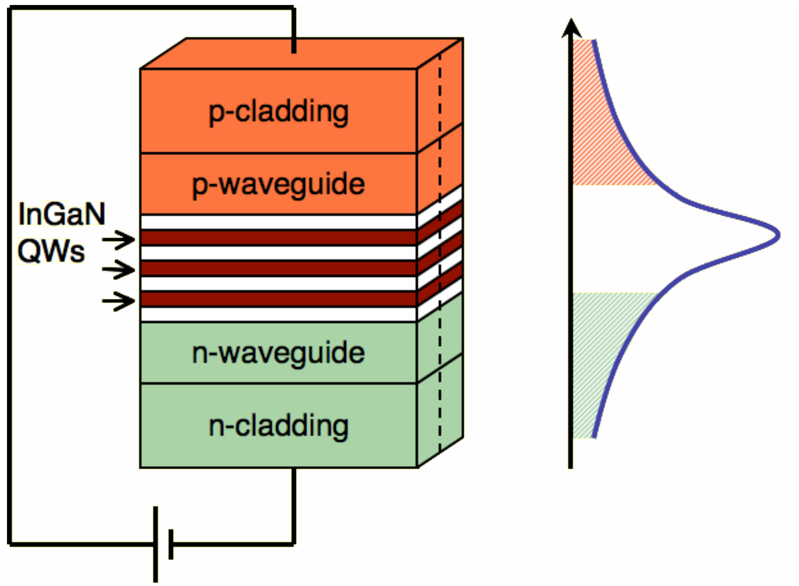
Absorption and gain



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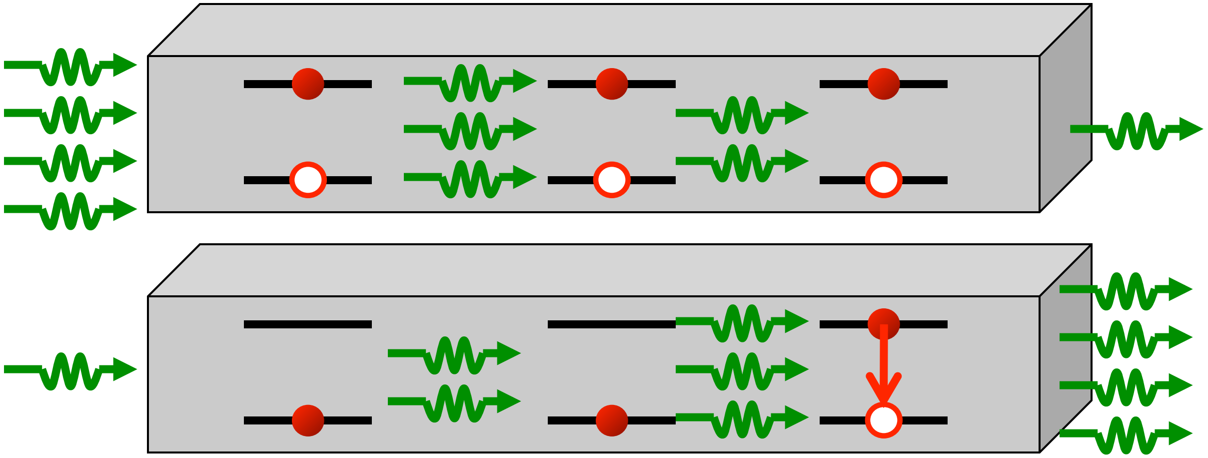

Absorption:

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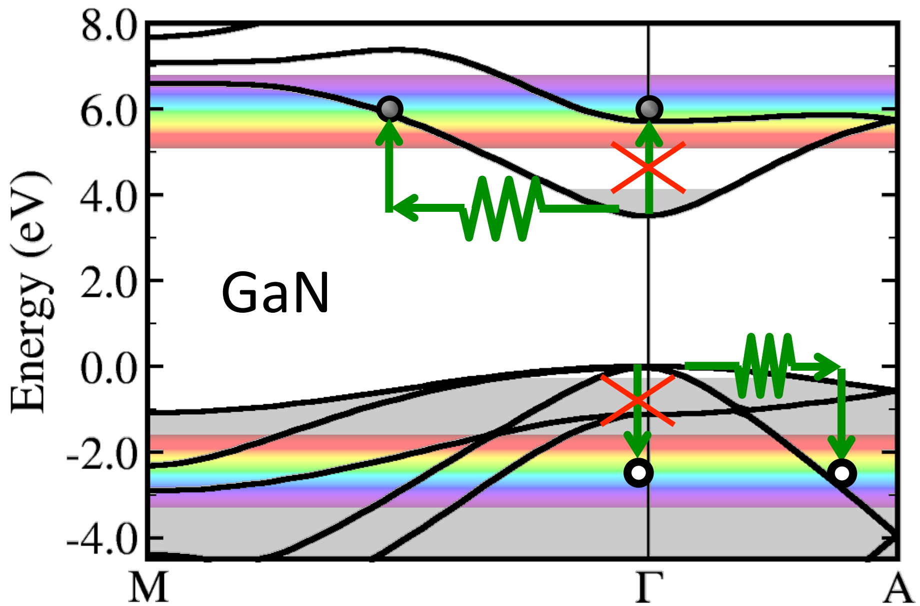
Gain in the QWs:

$$I(x) = I_0 e^{+gx}$$

Output = Gain – Absorption

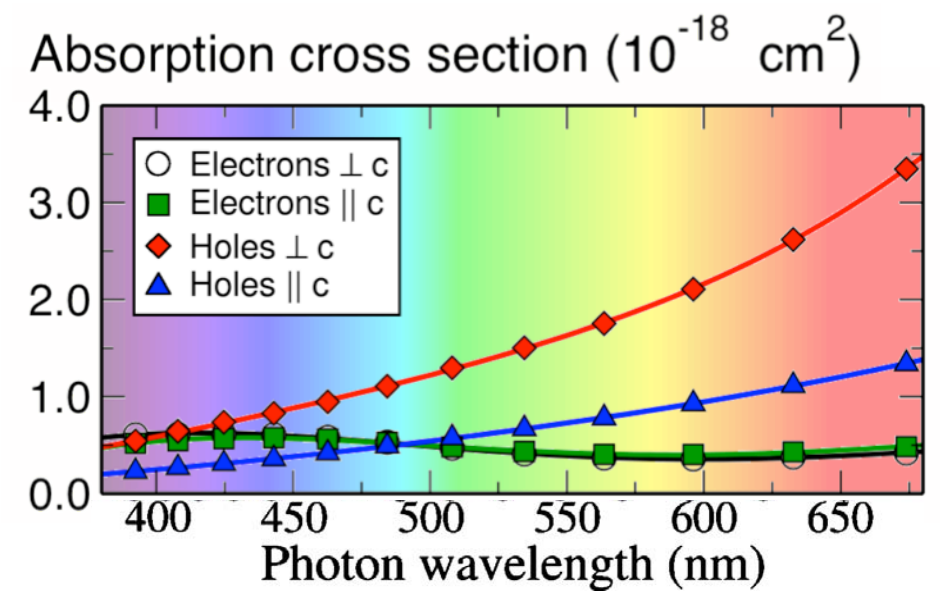
Free-carrier absorption

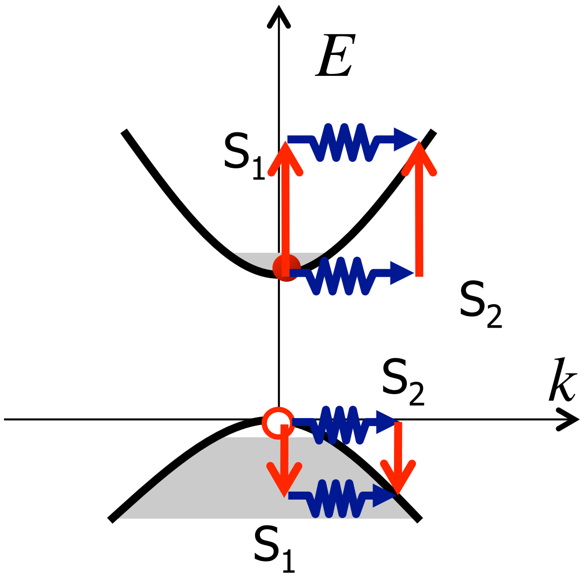
Band gap wider than photon energy, no absorption across gap
High concentration of free carriers in lasers,
free-carrier absorption a potential source of loss



- Direct absorption is weak:
  - Holes: impossible
  - Electrons: dipole-forbidden
- Phonon-assisted absorption: Possible for every photon energy

Phonon-assisted free-carrier absorption



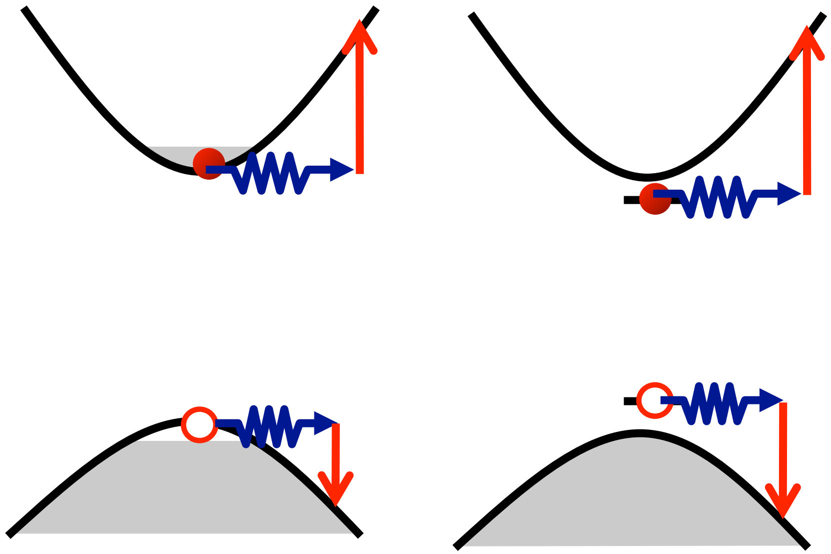


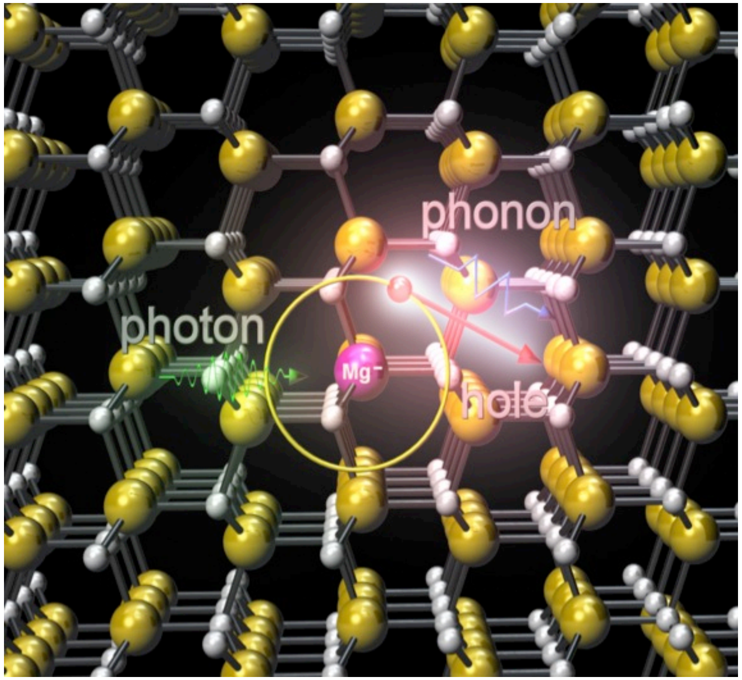
Absorption cross section σ: $\alpha = n\sigma$

For n = 10^{19} cm^{-3} (lasers under operating conditions): α = 10 cm^{-1}
Contrast with direct gap materials: α = 10^5–10^6 cm^{-1}

Absorption by non-ionized Mg in p-GaN

Absorption by carriers bound to dopants





Free carriers *vs.* donor/acceptor bound

Activation energies:

GaN:Si : 50 meV

GaN:Mg : 200 meV

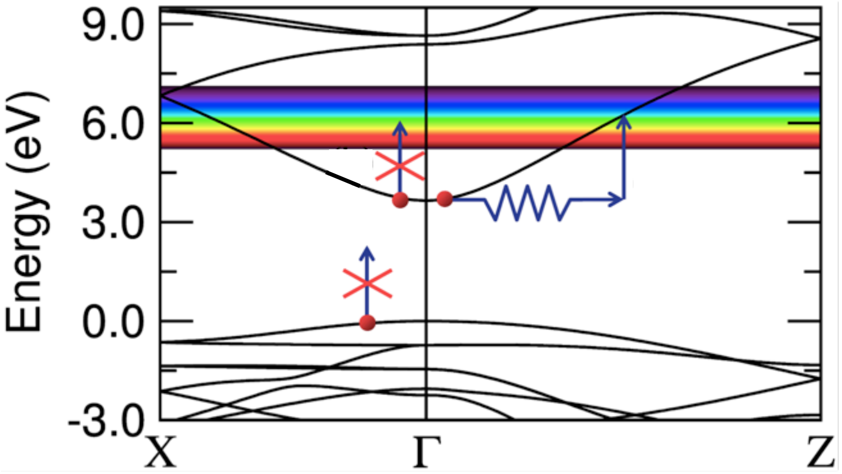
Large concentration (10^{19} cm^{-3}) of non-ionized Mg in p-GaN, causes internal absorption loss, more important at longer wavelengths

1.) Kioupakis, Rinke, Schleife, Bechstedt, & Van de Walle, *Phys. Rev. B* **81**, 241201 (2010)

2.) Kioupakis, Rinke, & Van de Walle, *Appl. Phys. Express* **3,** 082101 (2010)

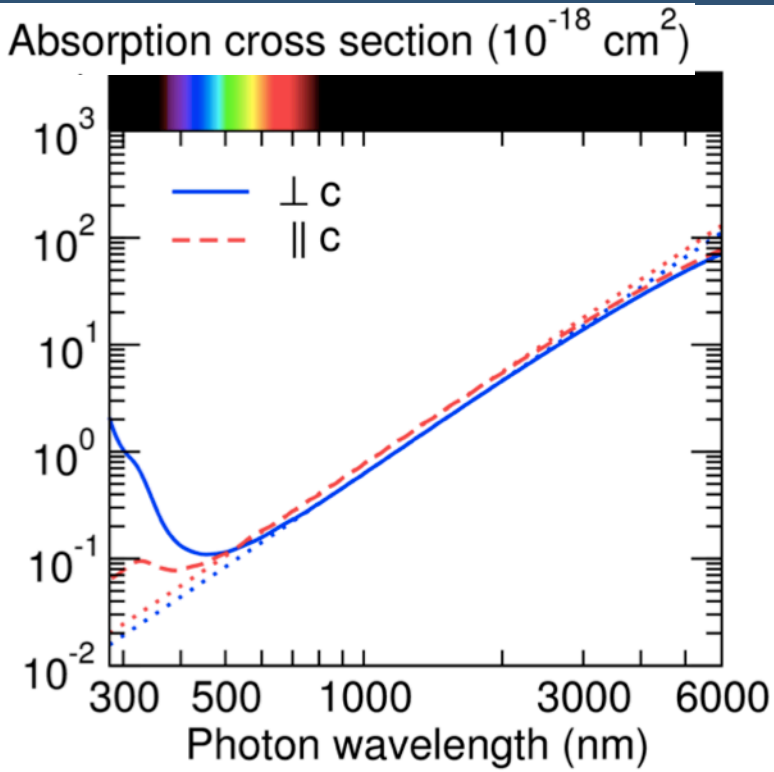
Absorption in transparent conducting oxides

Conducting oxides (e.g. SnO_2) used for transparent electrical contacts



Fundamental *transparency limit* due to free-carrier absorption

Free-carrier absorption in n-SnO_2

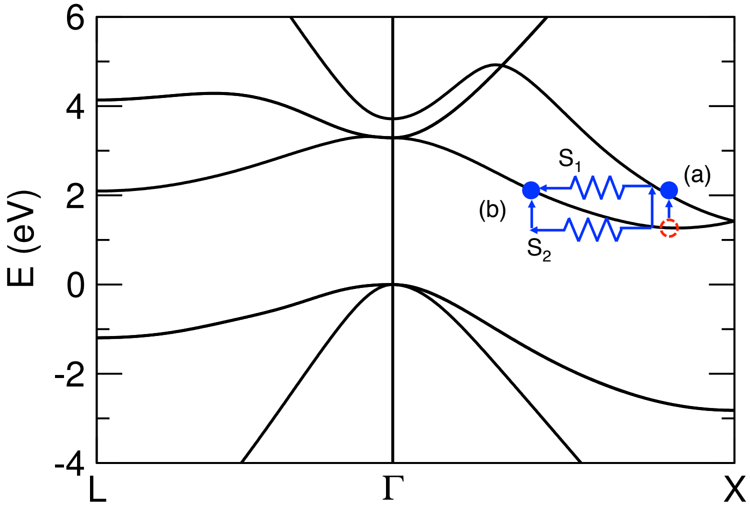


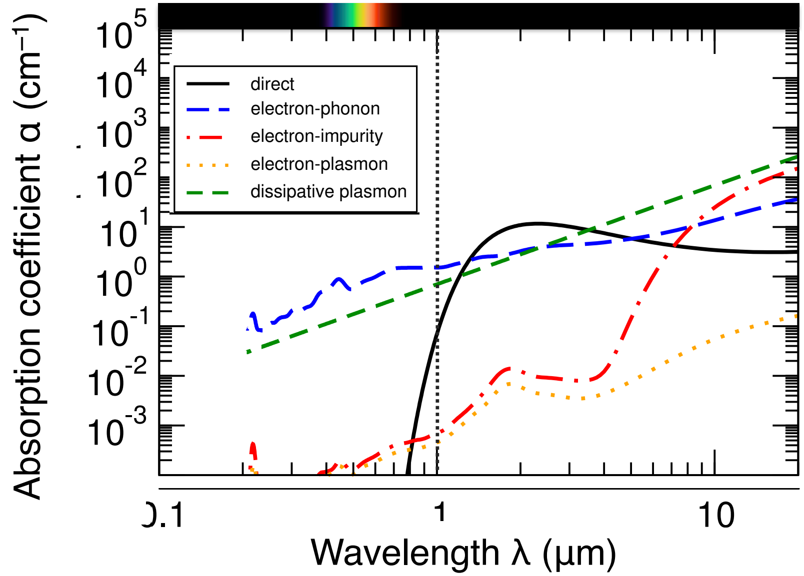
Fundamental limits on optical transparency of transparent conducting oxides: free-carrier absorption in SnO_2

H. Peelaers, E. Kioupakis, and C. G. Van de Walle

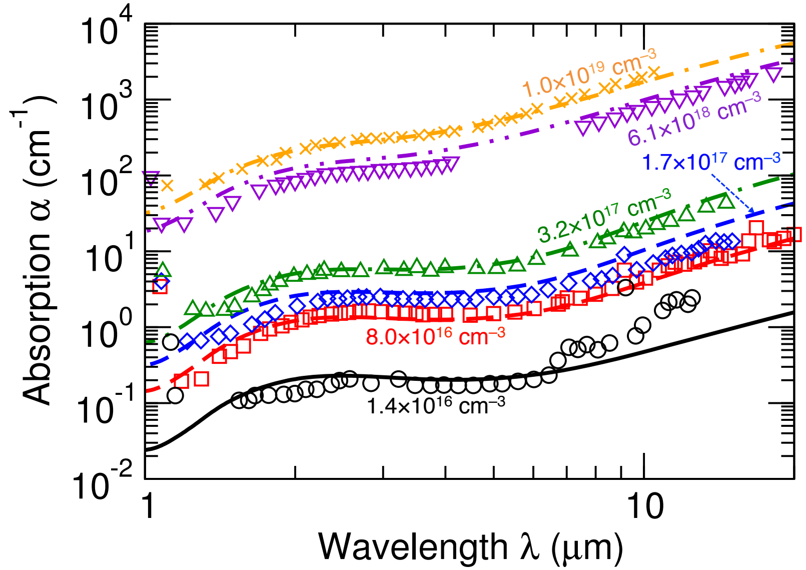
- Appl. Phys. Lett. **100**, 011914 (2012)
- Phys. Rev. B **92**, 235201 (2015)

Free-carrier absorption in n-type silicon



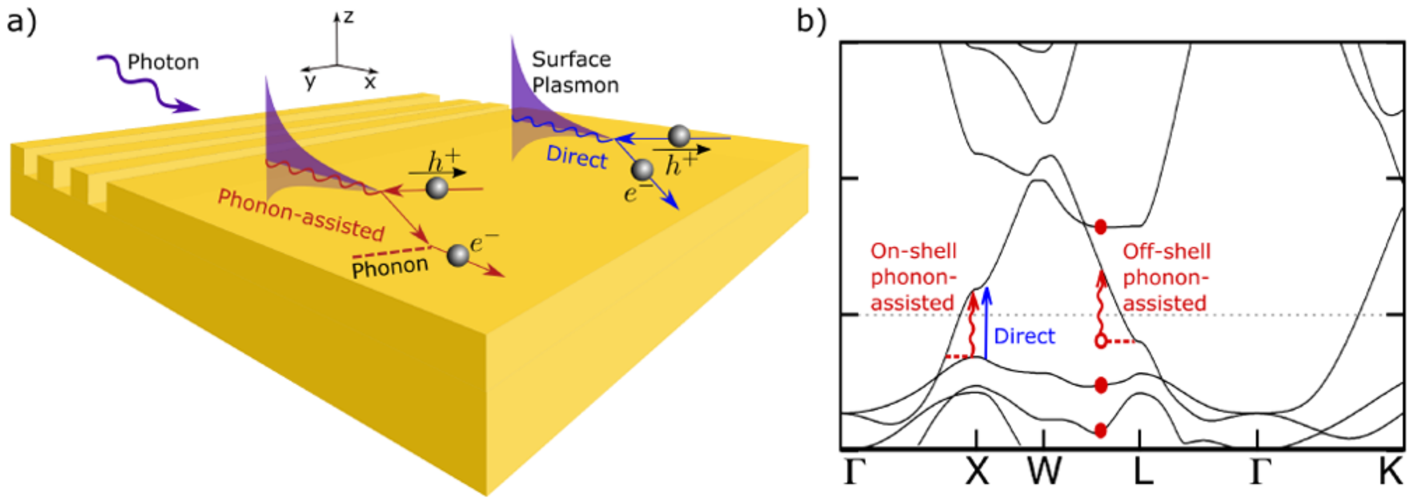


- Absorption of light in n-type silicon competes with interband absorption.
- Also: absorption in the infrared.
- Direct + indirect absorption possible.
- Results for α vs. doping in good agreement with experiment.



G. Shi and E. Kioupakis, *in preparation*

Plasmon decay in metals



$$\Gamma = \frac{\omega}{2L(\omega)|\gamma(z<0)|}\boldsymbol{\lambda}^{*}\cdot\mathrm{Im}\,\overline{\epsilon}(\omega)\cdot\boldsymbol{\lambda}$$

Imaginary part of dielectric function also describes plasmon energy loss in metals

$$\boldsymbol{\lambda}^{*}\cdot\mathrm{Im}\,\overline{\epsilon}_{\mathrm{phonon}}(\omega)\cdot\boldsymbol{\lambda} = \frac{4\pi^2 e^2}{m_e^2\omega^2}\int_{\mathrm{BZ}}\frac{\mathrm{d}\mathbf{q}'\mathrm{d}\mathbf{q}}{(2\pi)^6}\sum_{n'n\alpha\pm}(f_{\mathbf{q}n}-f_{\mathbf{q}'n'})\left(n_{\mathbf{q}'-\mathbf{q},\alpha}+\frac{1}{2}\mp\frac{1}{2}\right)\delta(\varepsilon_{\mathbf{q}'n'}-\varepsilon_{\mathbf{q}n}-\hbar\omega\mp\hbar\omega_{\mathbf{q}'-\mathbf{q},\alpha})\times\left|\boldsymbol{\lambda}\cdot\sum_{n_1}\left(\frac{g^{\mathbf{q}'-\mathbf{q},\alpha}_{\mathbf{q}'n',\mathbf{q}n_1}\langle\mathbf{p}\rangle^{\mathbf{q}}_{n_1 n}}{\varepsilon_{\mathbf{q}n_1}-\varepsilon_{\mathbf{q}n}-\hbar\omega+i\eta}+\frac{\langle\mathbf{p}\rangle^{\mathbf{q}'}_{n'n_1}g^{\mathbf{q}'-\mathbf{q},\alpha}_{\mathbf{q}'n_1,\mathbf{q}n}}{\varepsilon_{\mathbf{q}'n_1}-\varepsilon_{\mathbf{q}n}\mp\hbar\omega_{\mathbf{q}'-\mathbf{q},\alpha}+i\eta}\right)\right|^2$$

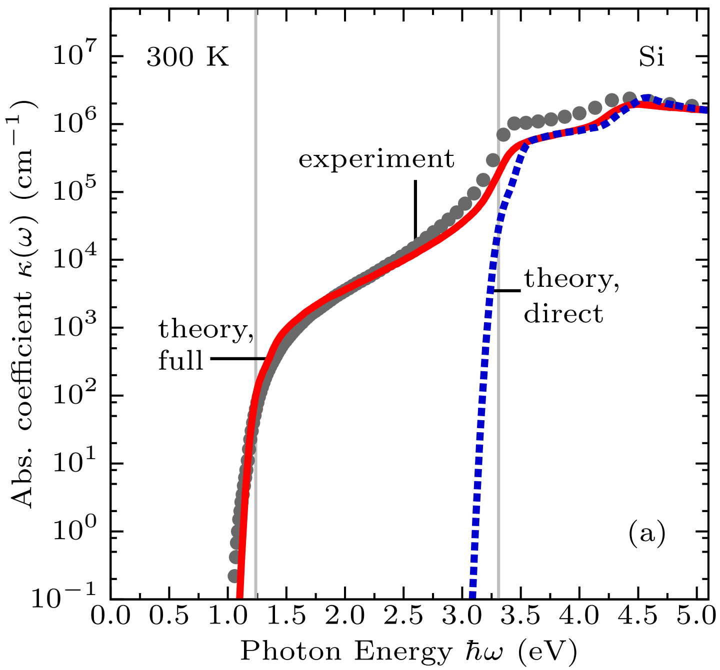
Strong contribution from phonon-assisted terms

Brown et al., *ACS Nano* **10**, 957–966 (2016)

Alternative method: Zacharias and Giustino

Calculate direct optical absorption in a single optimal supercell with atoms displaced according to a linear combination of the phonon modes

Advantages:
- Avoids divergence
- No need for Wannier interpolation
- T-dependence of eigenvalues, band gap, and Urbach tail.
- Can be generalized for other functionals, excitons, …



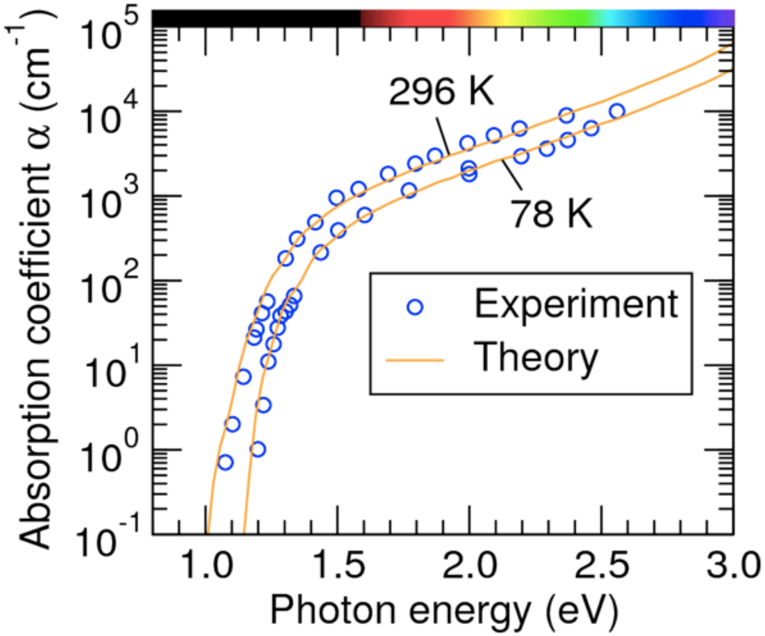
Zacharias and Giustino
Physical Review B 94, 075125 (2016)

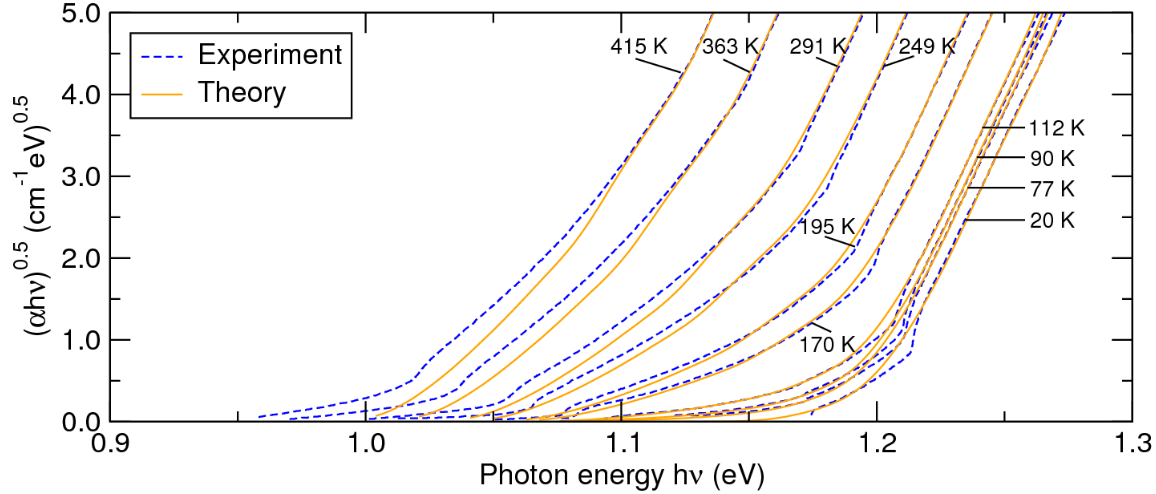
$$\Delta\tau_{\kappa\alpha} = (M_{\rm p}/M_\kappa)^{\frac{1}{2}} \sum_\nu (-1)^{\nu-1} e_{\kappa\alpha,\nu}\, \sigma_{\nu,T}.$$

$$\sigma^2_{\nu,T} = (2n_{\nu,T} + 1)\, l^2_\nu,$$

$$n_{\nu,T} = [\exp(\hbar\omega_\nu/k_{\rm B}T) - 1]^{-1}$$

$$l_\nu = (\hbar/2M_{\rm p}\Omega_\nu)^{1/2}$$





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Thank you for your attention