2021 Virtual School on Electron-Phonon Physics and the EPW code

June 14-18 2021

Lecture Wed.2

Phonon-assisted optical processes

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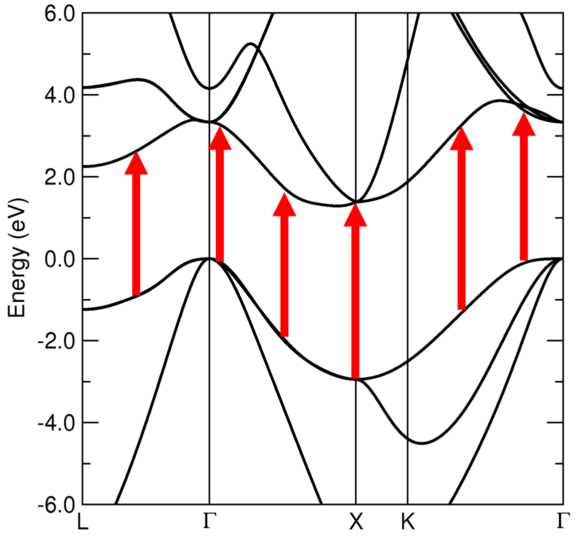
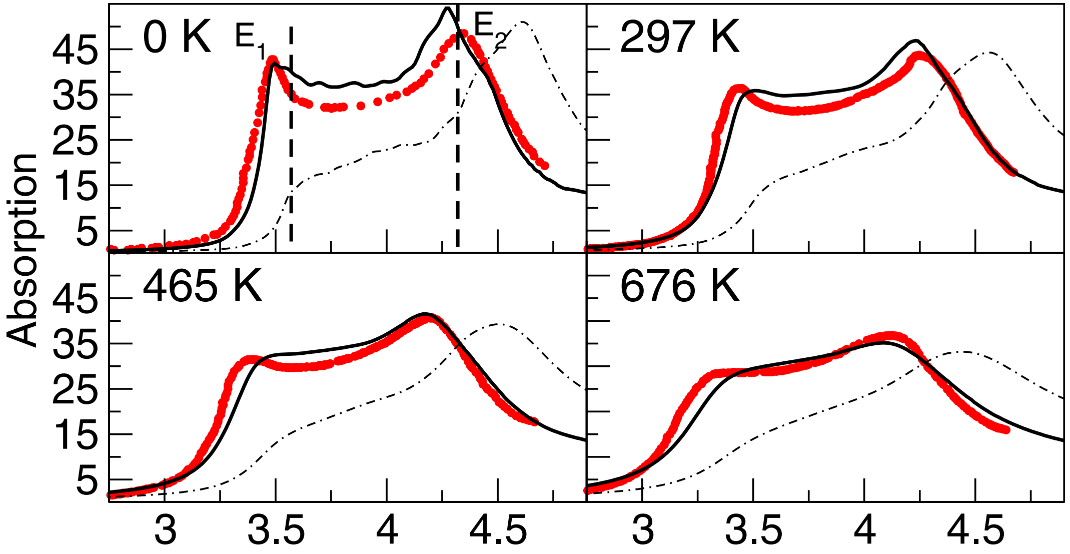
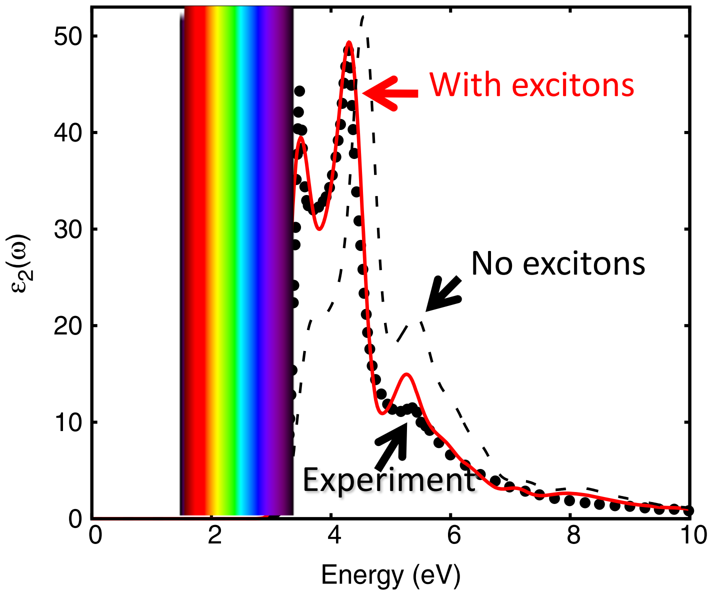
Motivation: optical absorption in Si



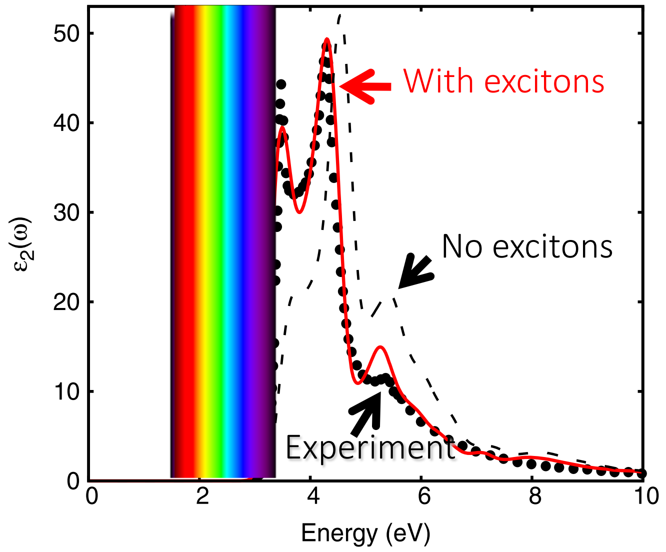




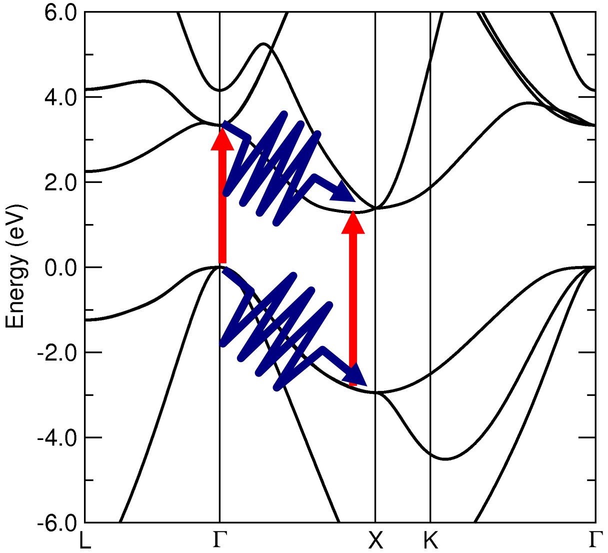
Direct absorption well understood, including excitons and temperature

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



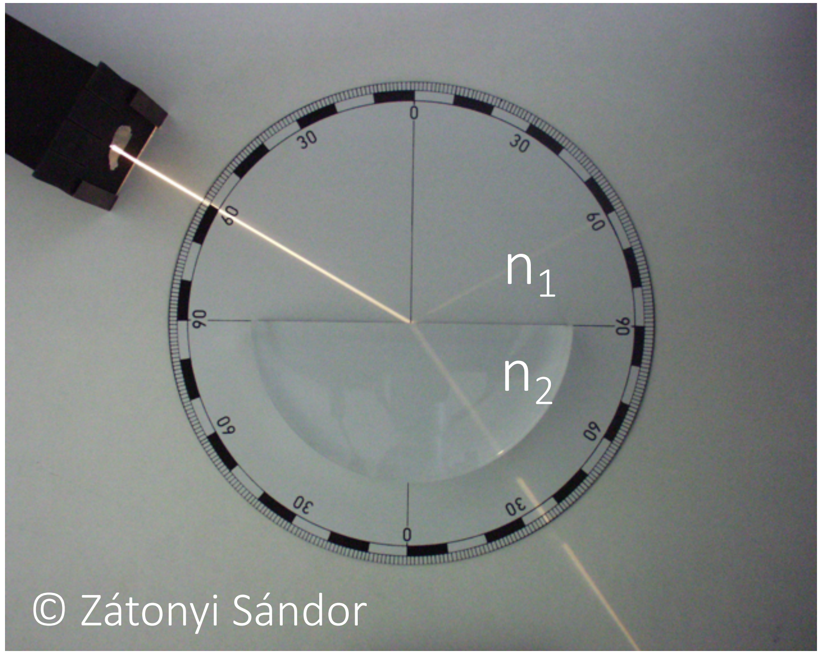
Deslippe et al. Comput. Phys. Commun. 183, 1269 (2012)

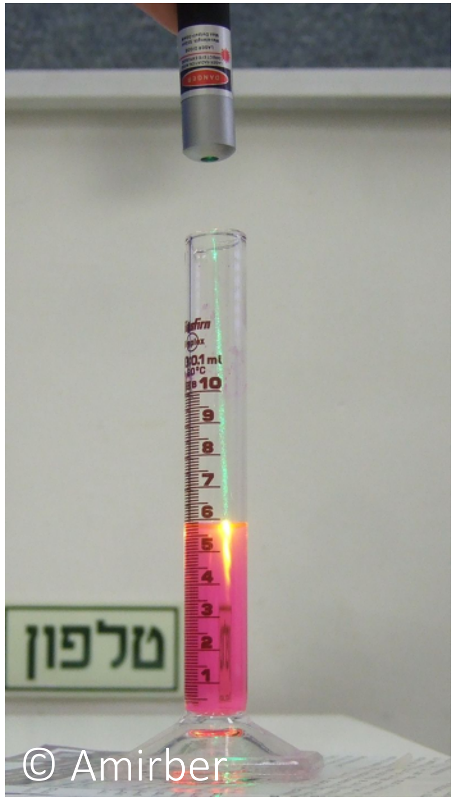


Gap of silicon is indirect (1.2 eV), minimum direct gap is 3.4 eV.
Direct optical absorption impossible in the visible.
Absorption in the visible is phonon-assisted, enables silicon solar cells.

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:

$$\tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2$$

Their connection:

$$n = \frac{1}{\sqrt{2}}\left(\varepsilon_1 + \left(\varepsilon_1^2 + \varepsilon_2^2\right)^{\frac{1}{2}}\right)^{\frac{1}{2}}$$

$$\kappa = \frac{1}{\sqrt{2}}\left(-\varepsilon_1 + \left(\varepsilon_1^2 + \varepsilon_2^2\right)^{\frac{1}{2}}\right)^{\frac{1}{2}}$$

Absorption coefficient:

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

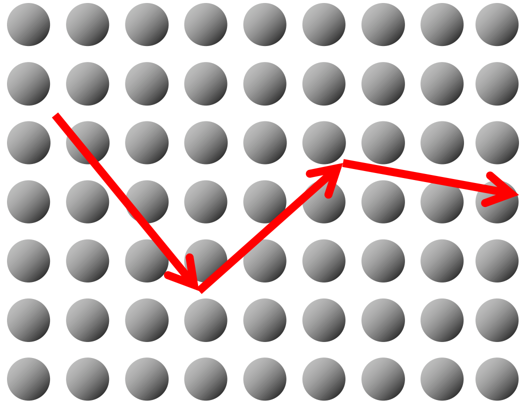
Classical theory of light absorption

Semiclassical Drude model:

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

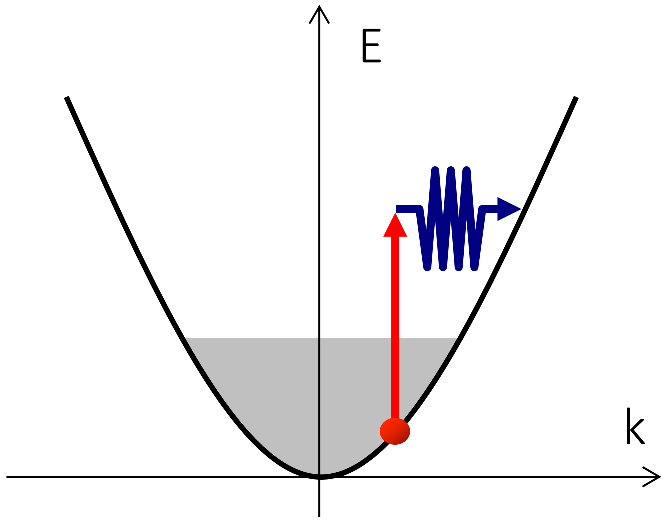
e.g., DC conductivity:

$$\sigma = \frac{ne^2\tau}{m^*}$$



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

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: $E_i = \epsilon_{i\boldsymbol{k}} + \hbar\omega, E_f = \epsilon_{j\boldsymbol{k}}$

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

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

Quantum theory of optical absorption

Absorption coefficient = energy absorbed per unit volume divided by energy flux

v = velocity matrix elements
λ = light polarization vector

$$\alpha(\omega) = \frac{\hbar\omega \sum_{i,j}(f_i - f_j)P_{i\to j}}{\frac{n_r^2 A^2 \omega^2}{2\pi c^2}\frac{c}{n_r}}$$

$$= 2\frac{4\pi^2 e^2}{n_r c\omega}\frac{1}{N_{\boldsymbol{k}}}\sum_{i,j,\boldsymbol{k}}(f_{i,\boldsymbol{k}} - f_{j,\boldsymbol{k}})\left|\boldsymbol{\lambda}\cdot\boldsymbol{v}_{ij}(\boldsymbol{k})\right|^2 \delta(\epsilon_{j\boldsymbol{k}} - \epsilon_{i\boldsymbol{k}} - \hbar\omega)$$

Dielectric function, imaginary part:

$$\varepsilon_2(\omega) = \frac{\alpha n_r c}{\omega} = 2\frac{4\pi^2 e^2}{\omega^2}\frac{1}{N_{\boldsymbol{k}}}\sum_{i,j,\boldsymbol{k}}(f_{i,\boldsymbol{k}} - f_{j,\boldsymbol{k}})\left|\boldsymbol{\lambda}\cdot\boldsymbol{v}_{ij}(\boldsymbol{k})\right|^2 \delta(\epsilon_{j\boldsymbol{k}} - \epsilon_{i\boldsymbol{k}} - \hbar\omega)$$

Real: from Kramers-Kronig relation:

$$\varepsilon_1(\omega) = 1 + 16\pi^2 e^2 \frac{1}{N_{\boldsymbol{k}}}\sum_{i,j,\boldsymbol{k}}(f_{i,\boldsymbol{k}} - f_{j,\boldsymbol{k}})\frac{\left|\boldsymbol{\lambda}\cdot\boldsymbol{v}_{ij}(\boldsymbol{k})\right|^2}{\epsilon_{j\boldsymbol{k}} - \epsilon_{i\boldsymbol{k}}}\frac{1}{(\epsilon_{j\boldsymbol{k}} - \epsilon_{i\boldsymbol{k}})^2/\hbar^2 - \omega^2}$$

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:

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

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

v = velocity matrix elements
g = electron-phonon coupling
λ = light polarization

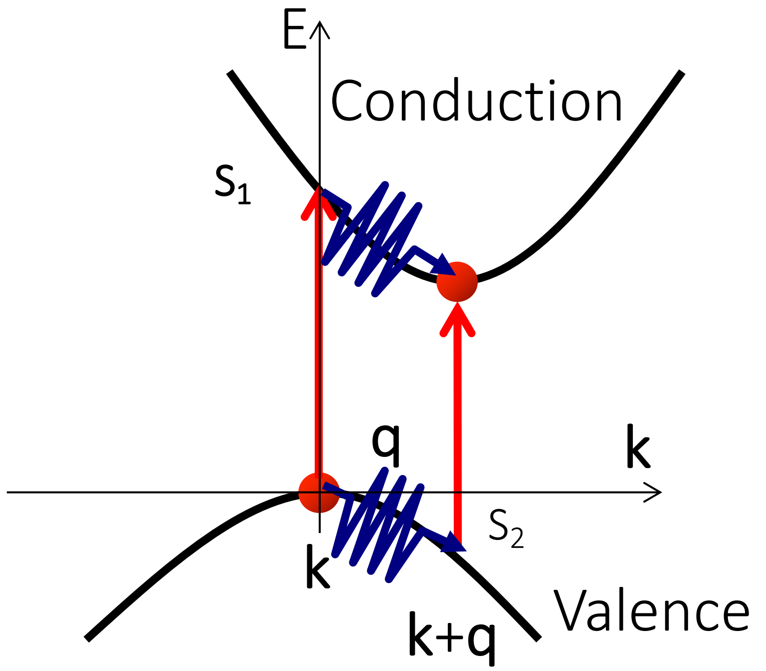
Two paths:

$$\boldsymbol{S}_1(\boldsymbol{k},\boldsymbol{q}) = \sum_m \frac{\boldsymbol{v}_{im}(\boldsymbol{k})g_{mj,\nu}(\boldsymbol{k},\boldsymbol{q})}{\epsilon_{m\boldsymbol{k}} - \epsilon_{i\boldsymbol{k}} - \hbar\omega}$$

$$\boldsymbol{S}_2(\boldsymbol{k},\boldsymbol{q}) = \sum_m \frac{g_{im,\nu}(\boldsymbol{k},\boldsymbol{q})\boldsymbol{v}_{mj}(\boldsymbol{k}+\boldsymbol{q})}{\epsilon_{m,\boldsymbol{k}+\boldsymbol{q}} - \epsilon_{i\boldsymbol{k}} \pm \hbar\omega_{\nu\boldsymbol{q}}}$$

Occupations:

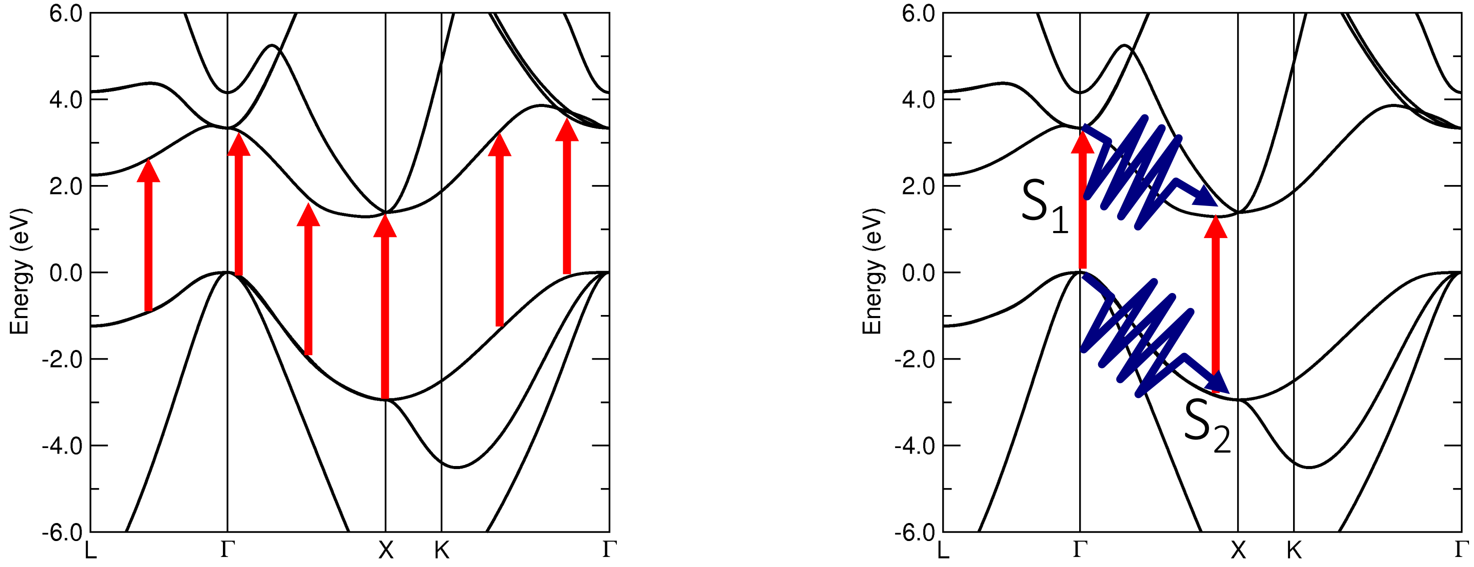
$$P = \left(n_{\nu\boldsymbol{q}} + \frac{1}{2} \pm \frac{1}{2}\right)(f_{i\boldsymbol{k}} - f_{j,\boldsymbol{k}+\boldsymbol{q}})$$



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

Computational challenge with phonon-assisted absorption

Direct absorption: **single sum** vs. *Phonon-assisted absorption*: **double sum**

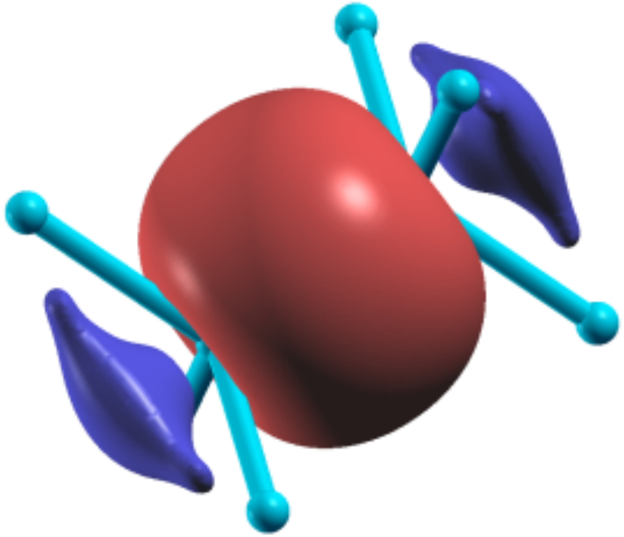


$$\alpha(\omega) \propto \sum_{i,j,\nu} P|\boldsymbol{S}_1 + \boldsymbol{S}_2|^2 \delta(\epsilon_j - \epsilon_i - \hbar\omega \pm \hbar\omega_\nu)$$

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

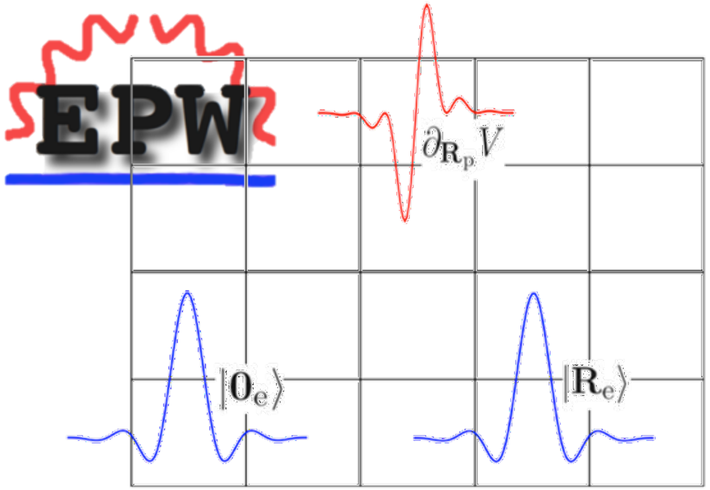


Interpolate quasiparticle energies, optical matrix elements.

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

Fourier

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

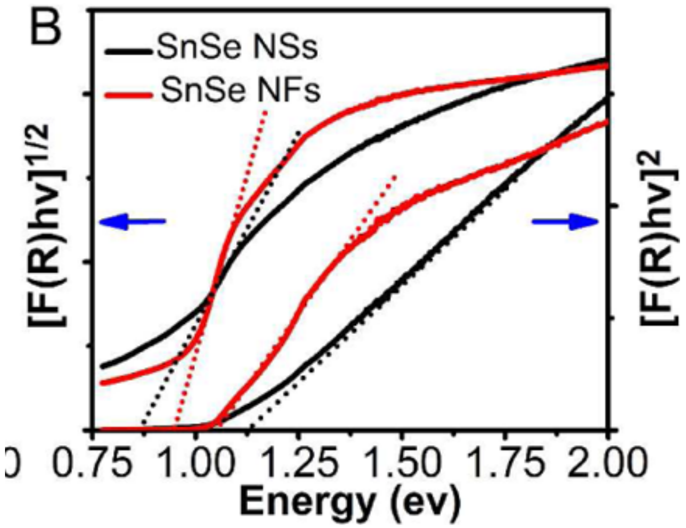


Interpolate electron-phonon matrix elements and optical (velocity) matrix elements

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

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

For direct absorption:

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

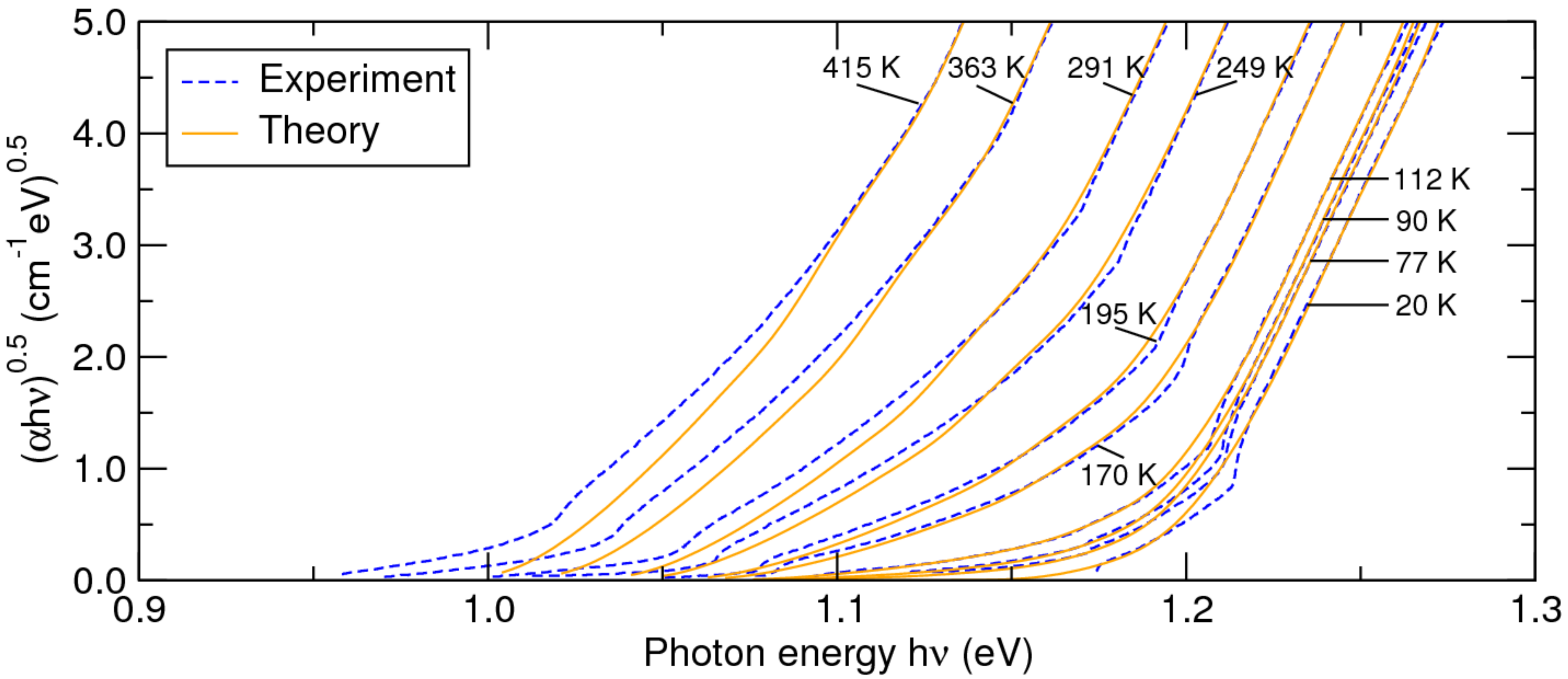
For indirect absorption:

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

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

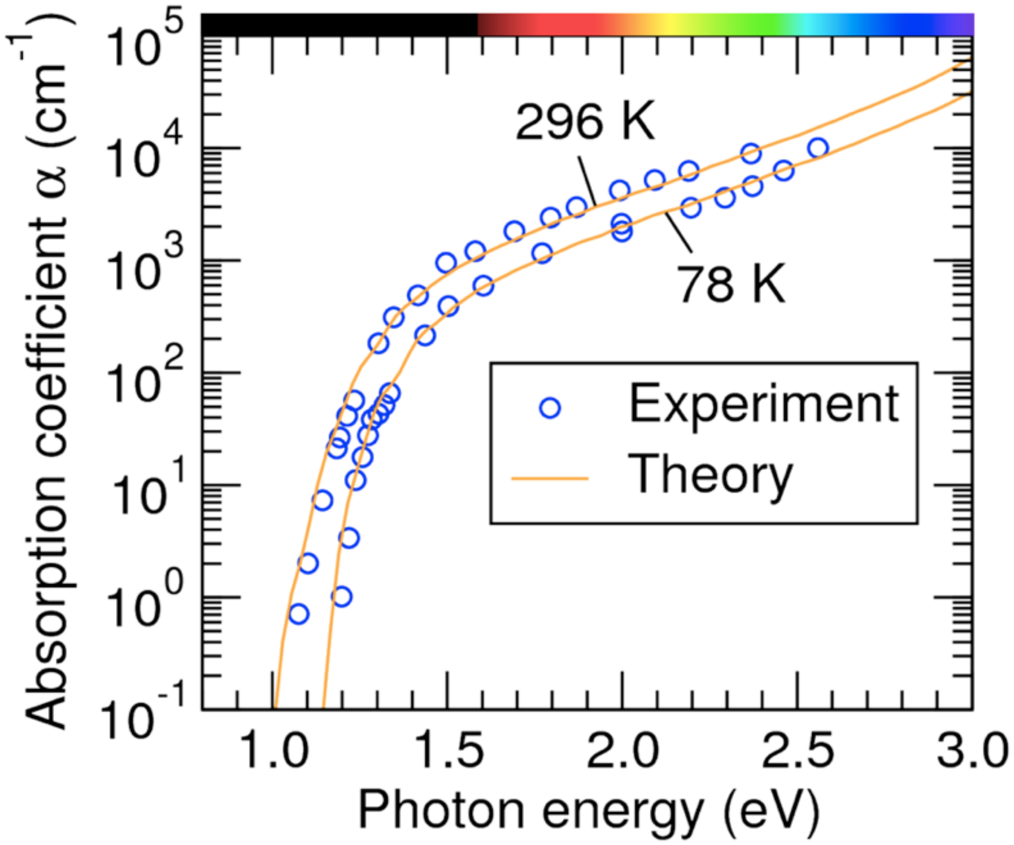
Exponent determines type and value of gap.
Two indirect terms for emission/absorption.

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



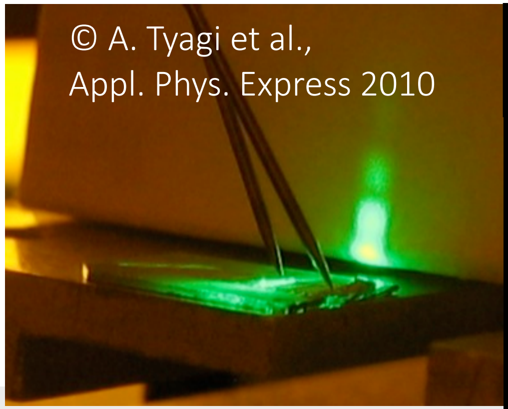
Noffsinger, Kioupakis, Van de Walle, Louie, and Cohen, *Phys. Rev. Lett*. **108**, 167402 (2012)
* Shifted the energy of onset to match experimental trend

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

Applications:

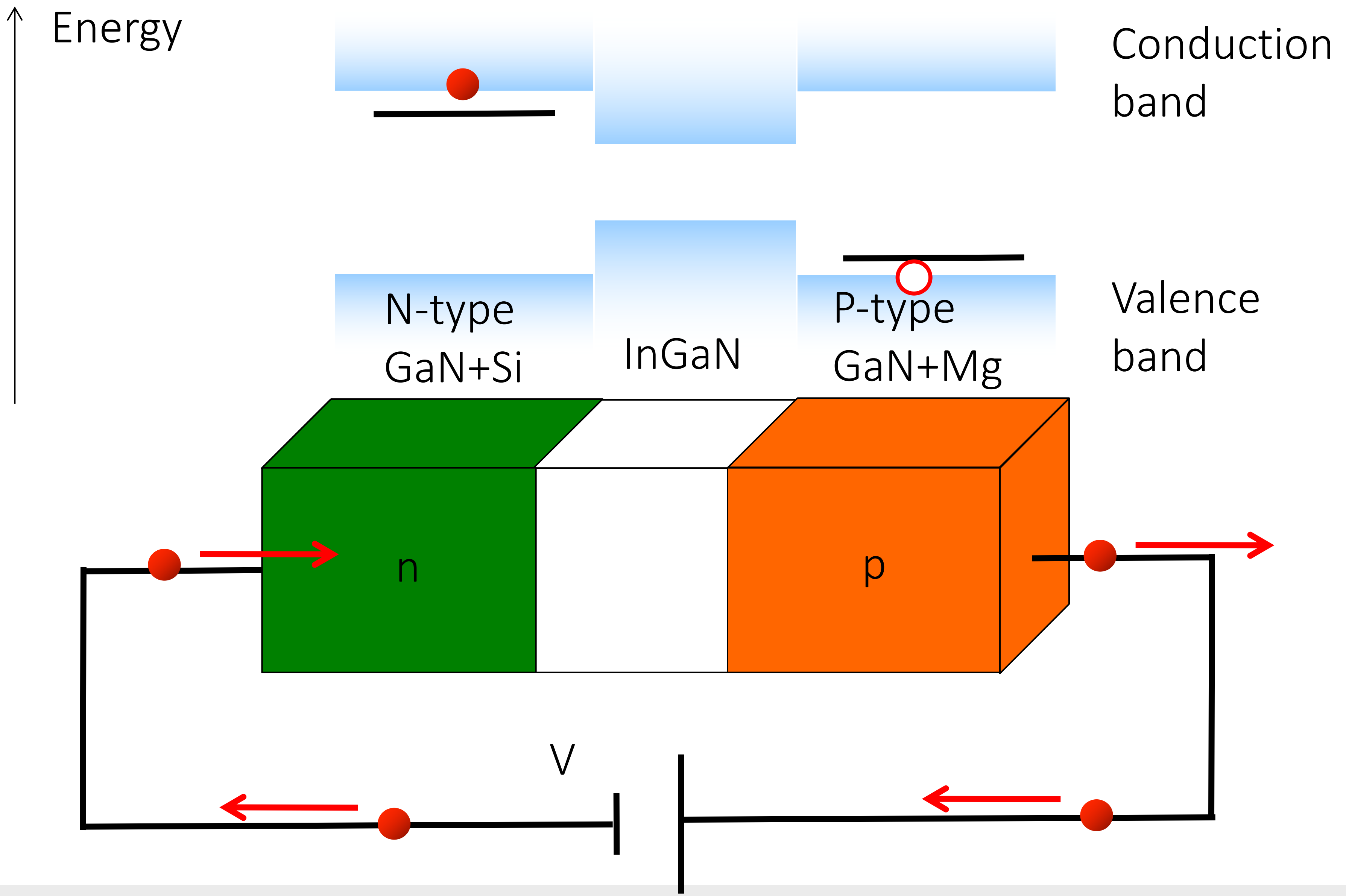
- Optical storage
- Laser projectors

Aim: high-power nitride green lasers.

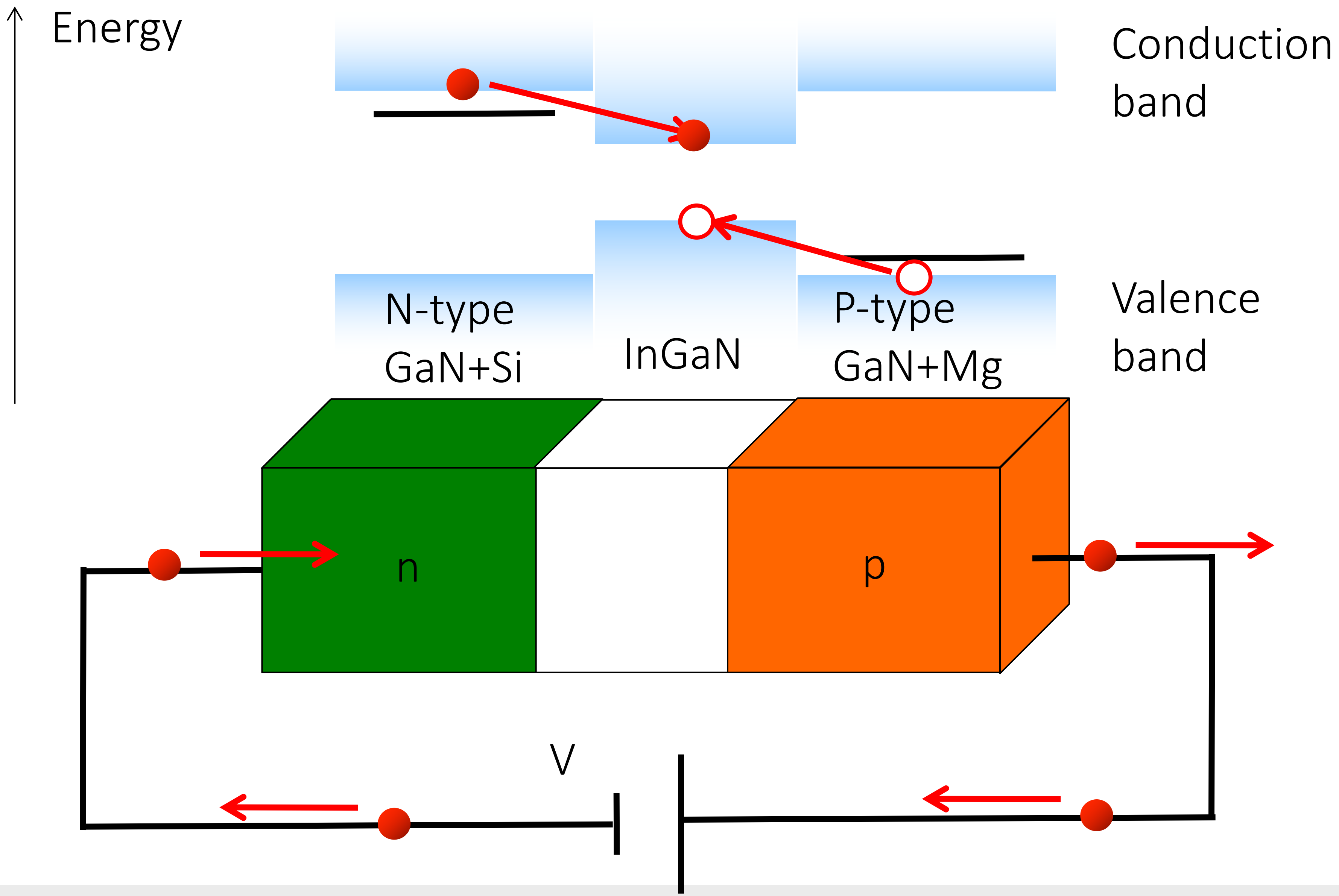


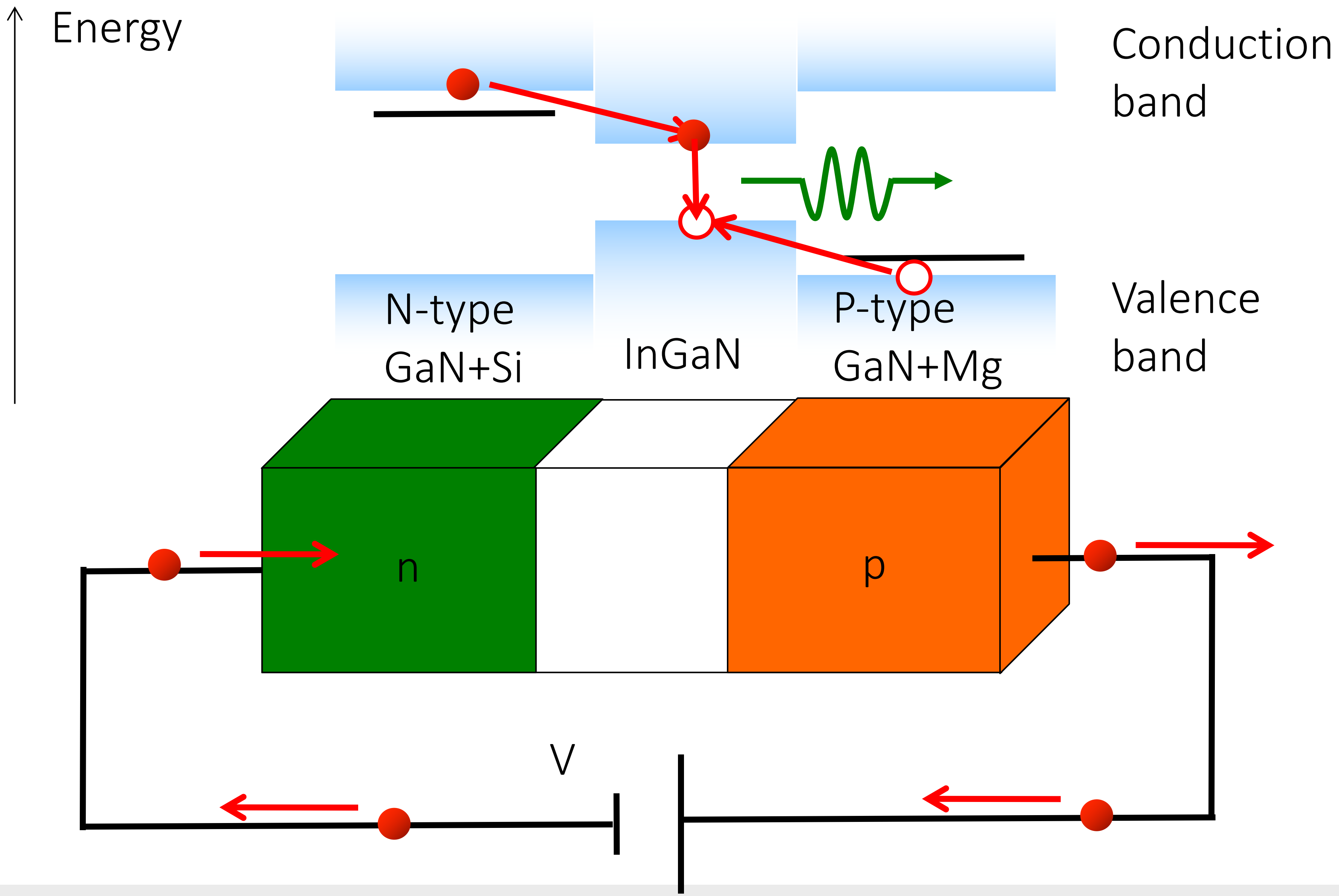
© A. Tyagi et al., Appl. Phys. Express 2010

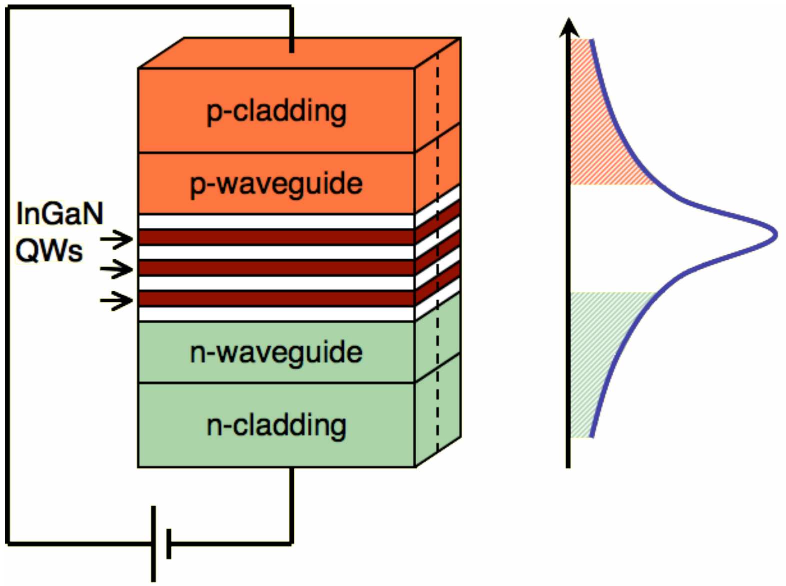
How nitride LEDs/lasers work



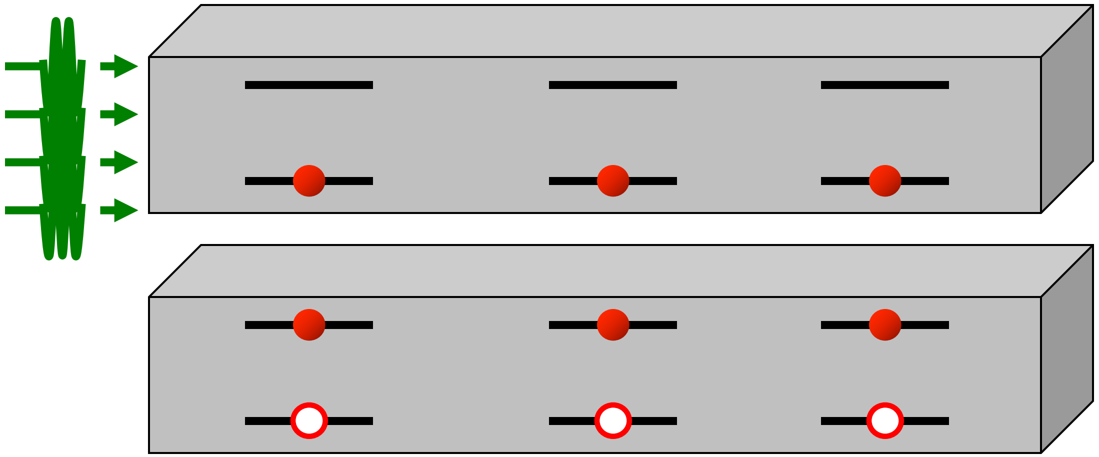
How nitride LEDs/lasers work




Energy
Conduction band
Valence band
N-type GaN+Si
InGaN
P-type GaN+Mg
n
p
V



Optical mode profile
(photon density)



Absorption:

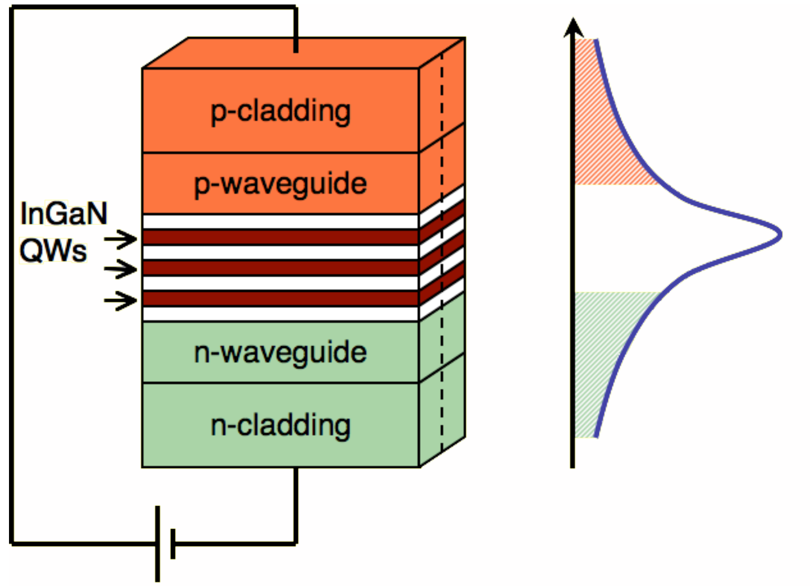
$$I(x) = I_0 e^{-\alpha x}$$

Gain in the QWs:

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

Output = Gain – Absorption

Absorption and gain



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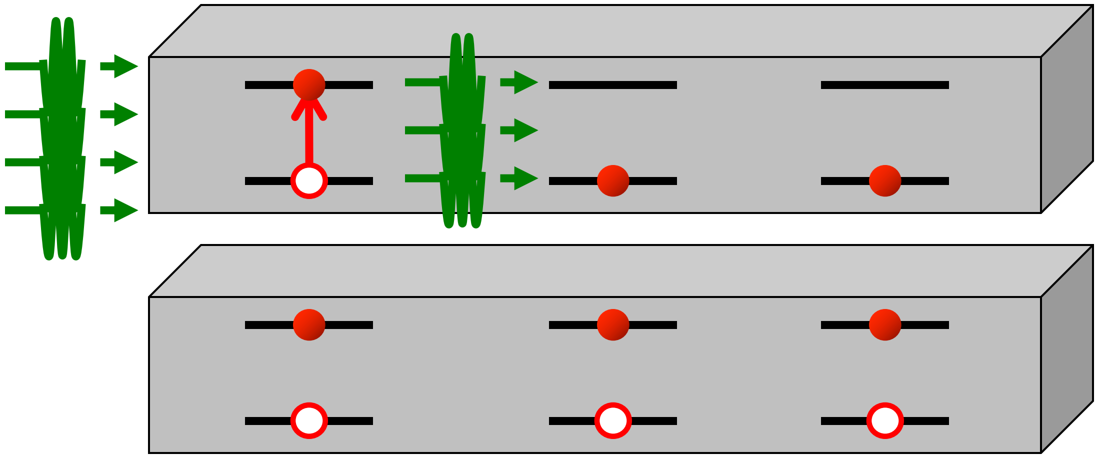

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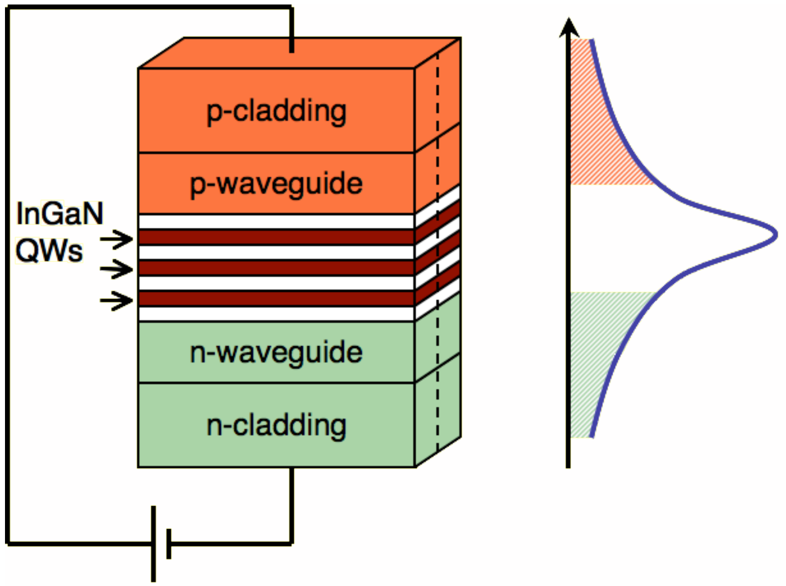

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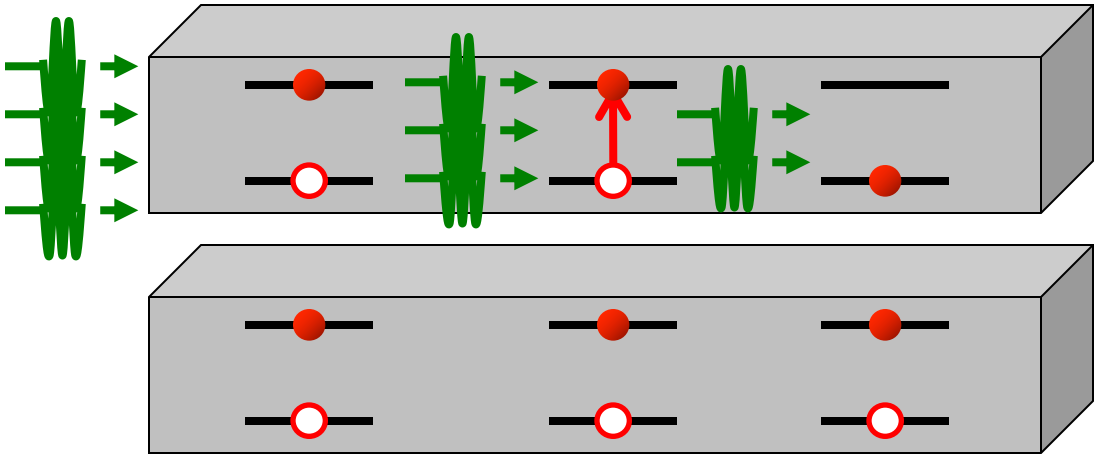

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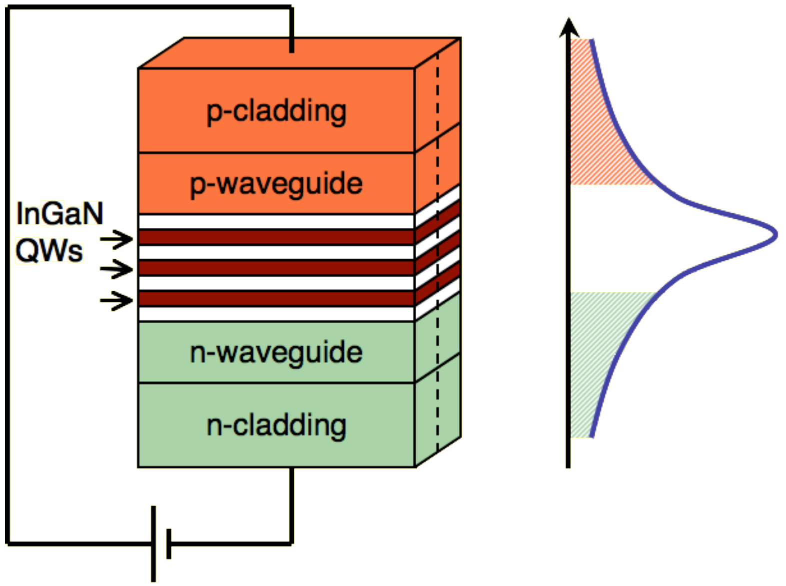

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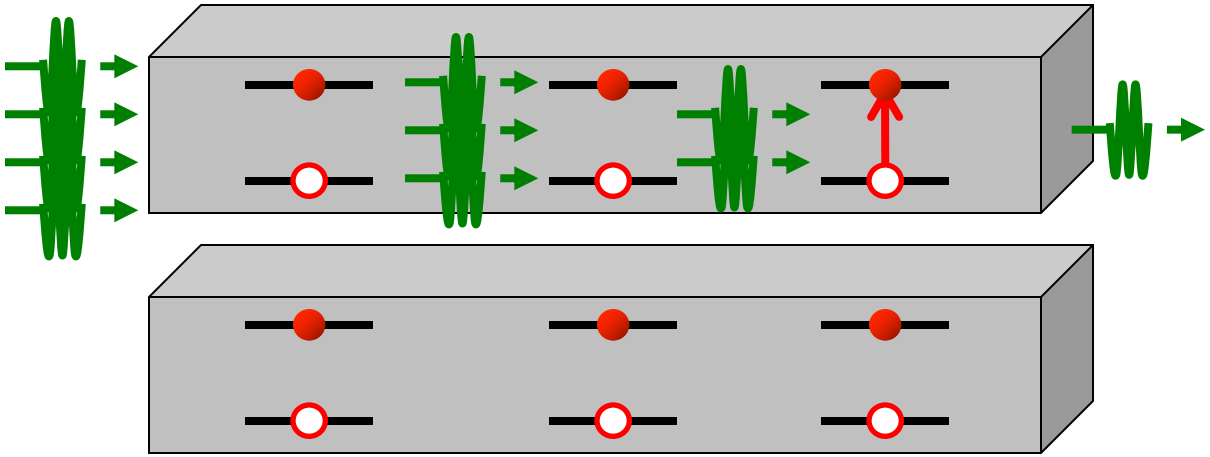

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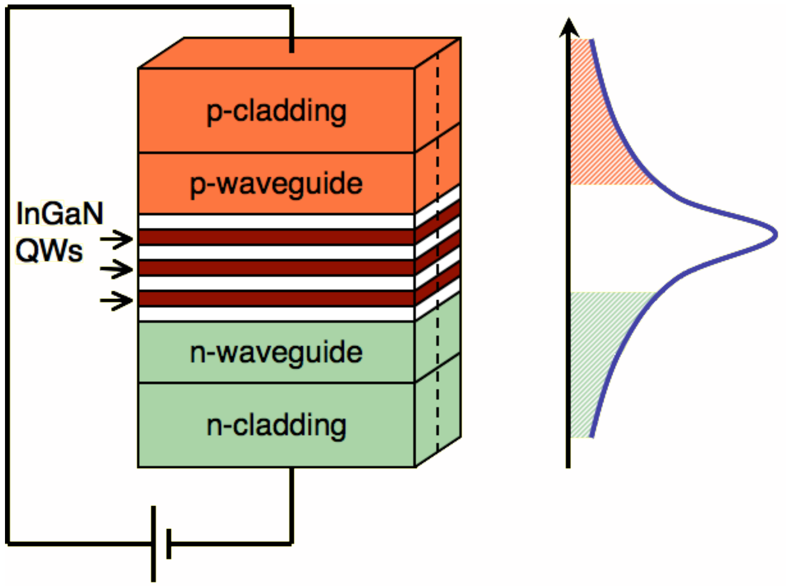

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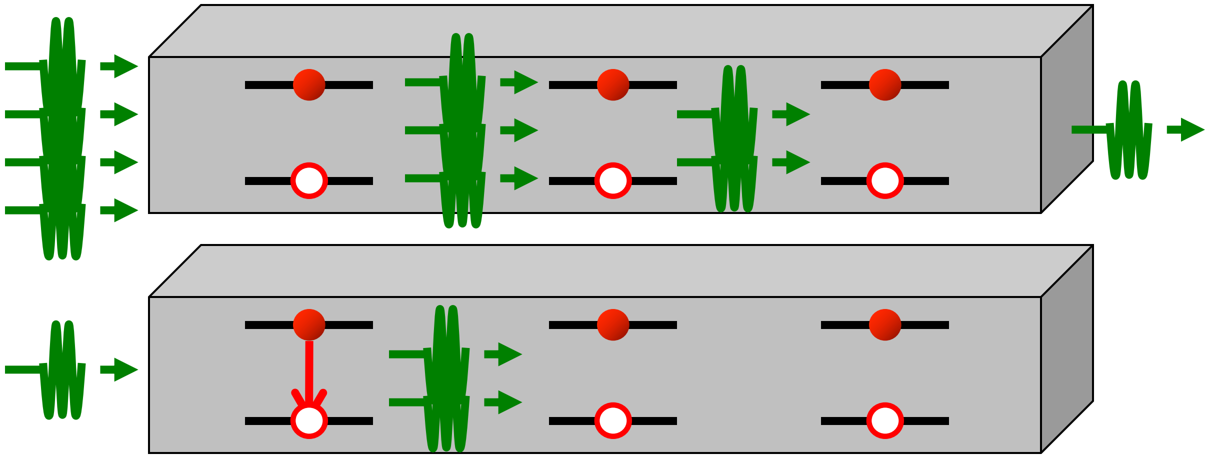

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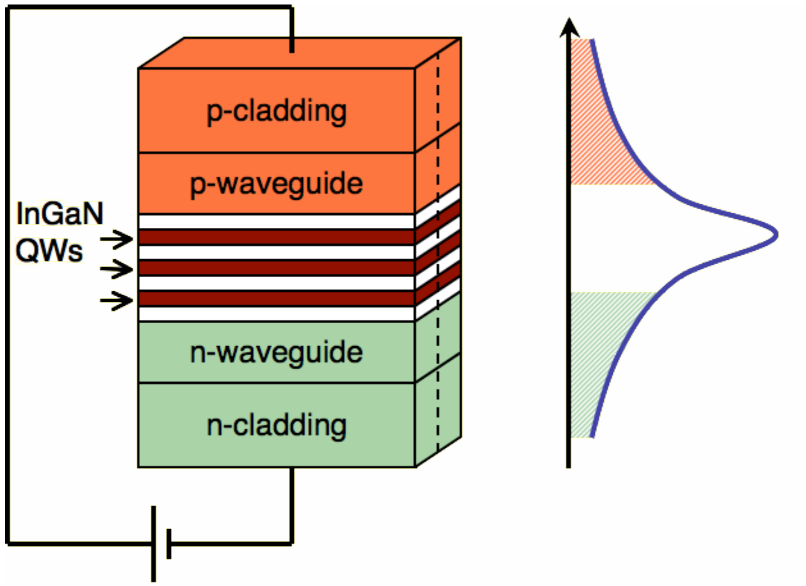

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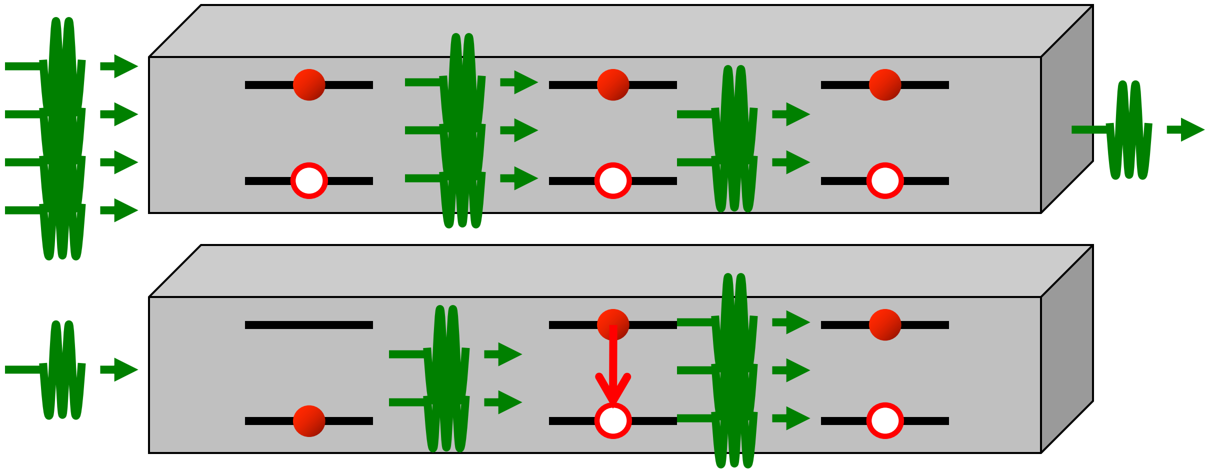

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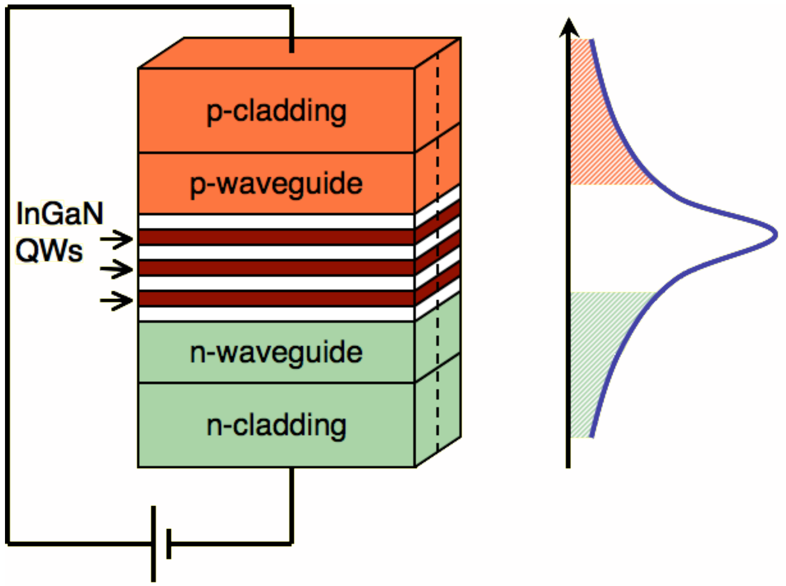

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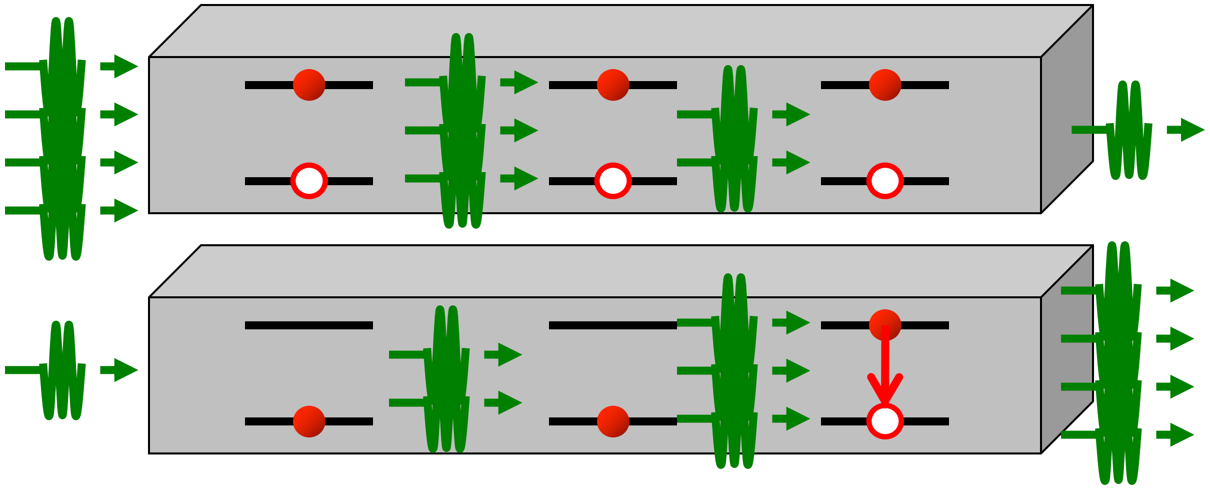

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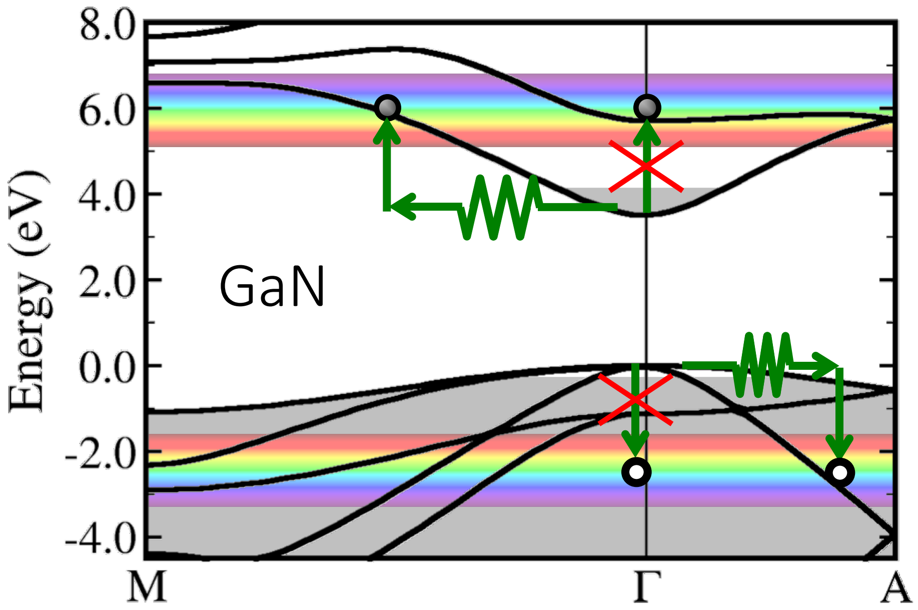
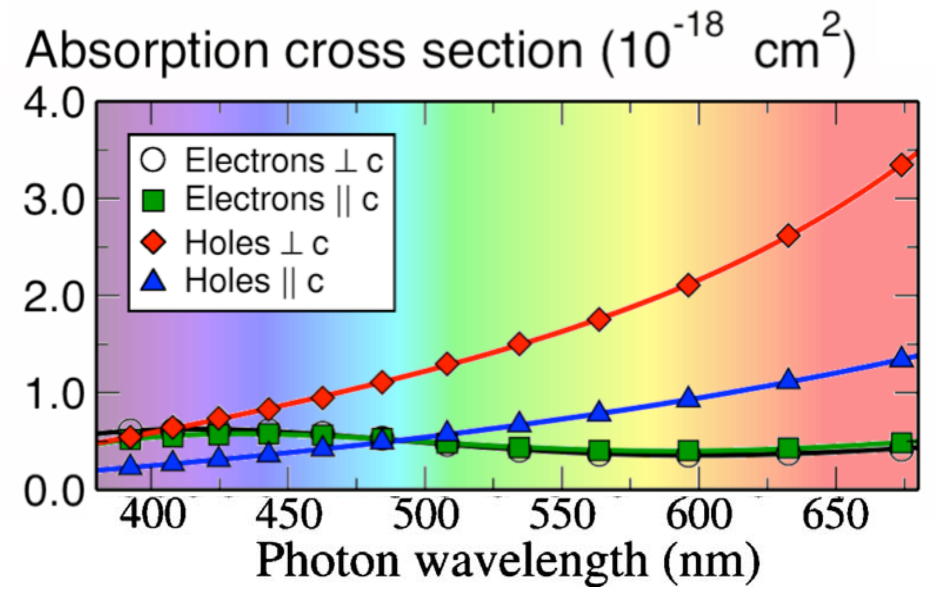
Output = Gain – Absorption

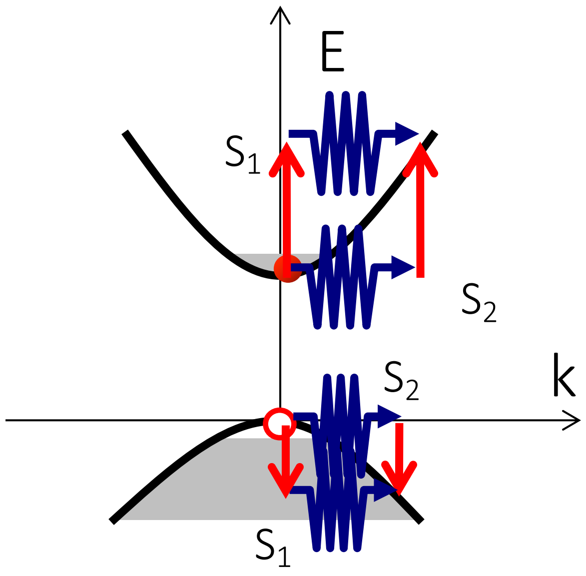
Band gap wider than photon energy, no absorption across gap
High concentration of free carriers in lasers,
free-carrier absorption a potential source of loss



- 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: $\alpha = n\sigma$

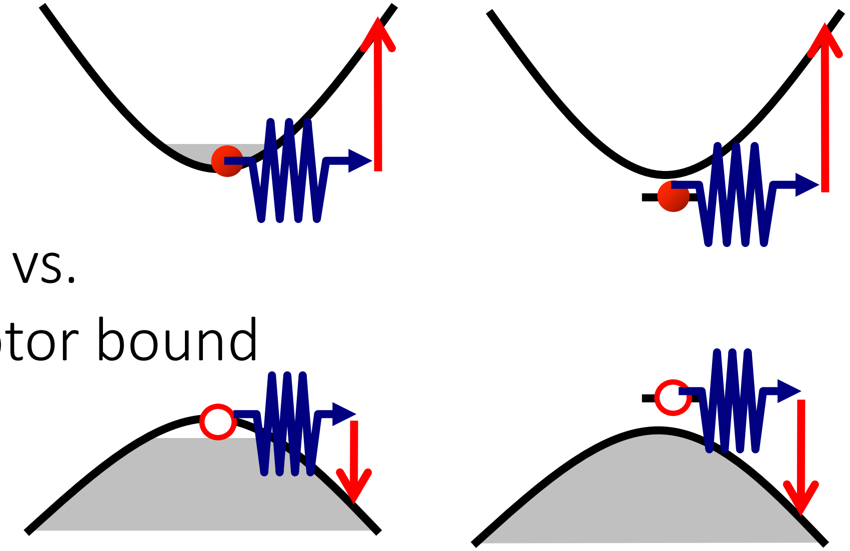
For $n = 10^{19}$ cm^{-3} (lasers under operating conditions): $\alpha = 10$ cm^{-1}

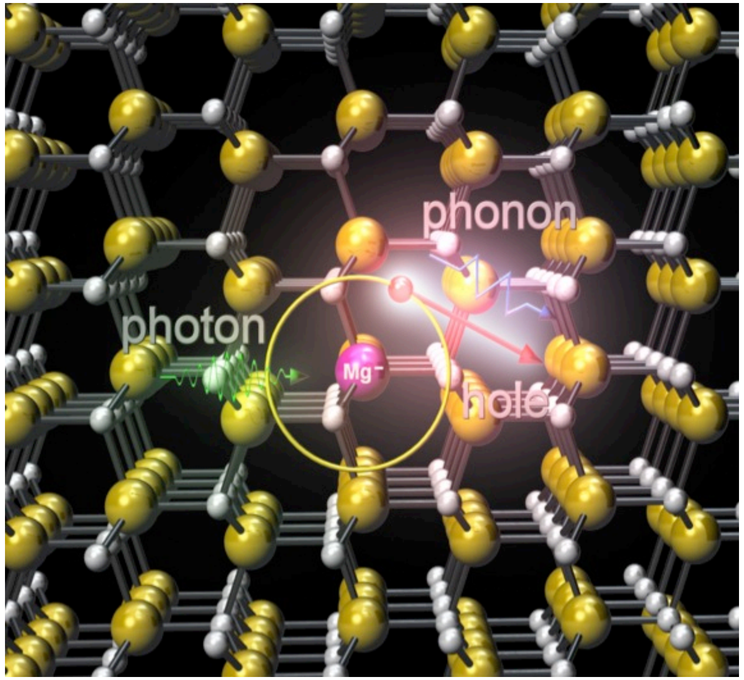
Contrast with direct gap materials: $\alpha = 10^5$–10^6 cm^{-1}

Absorption by non-ionized Mg in p-GaN

Absorption by carriers bound to dopants

Free carriers vs.
donor/acceptor bound



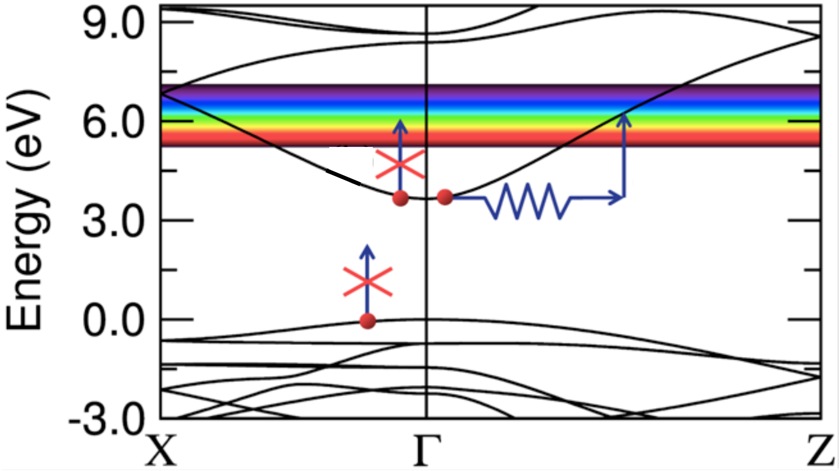


Activation energies:
GaN:Si : 50 meV
GaN:Mg : 200 meV

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)

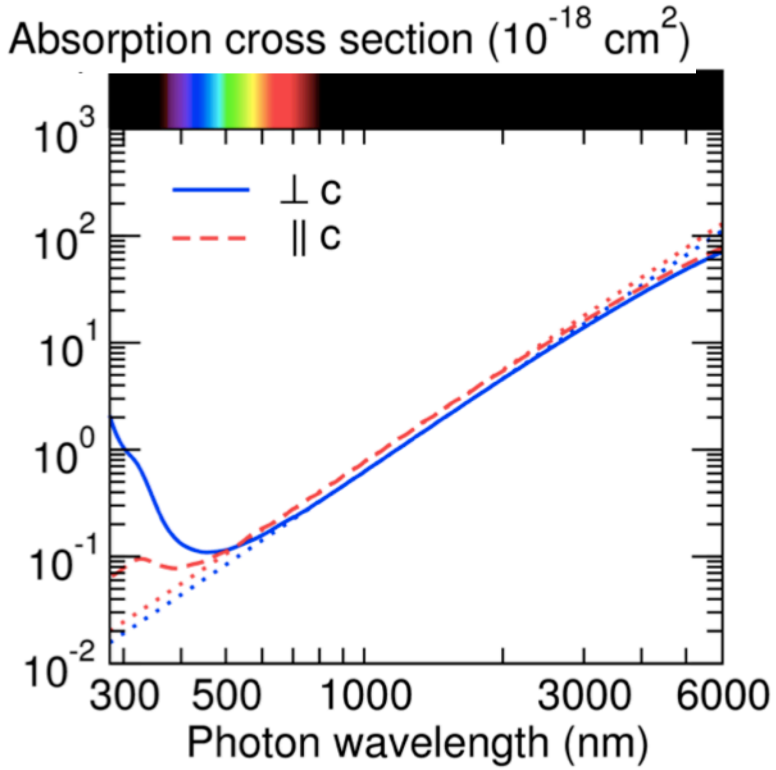
Large concentration (10^{19} cm^{-3}) of non-ionized Mg in p-GaN, causes internal absorption loss, more important at longer wavelengths

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

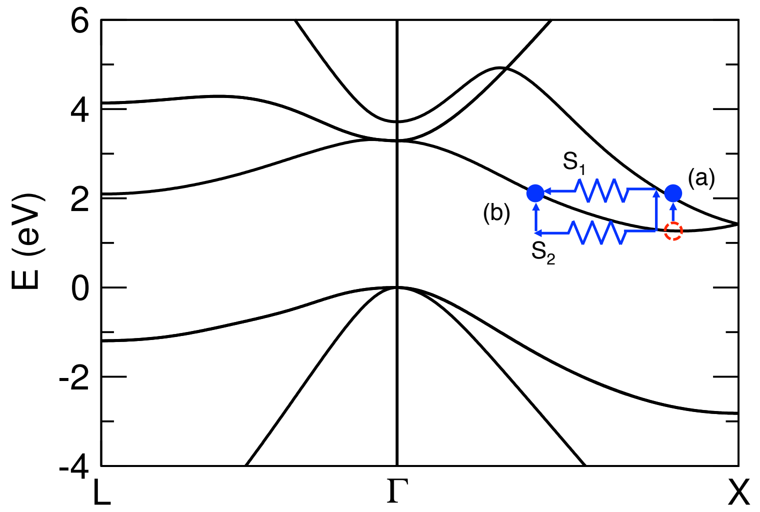


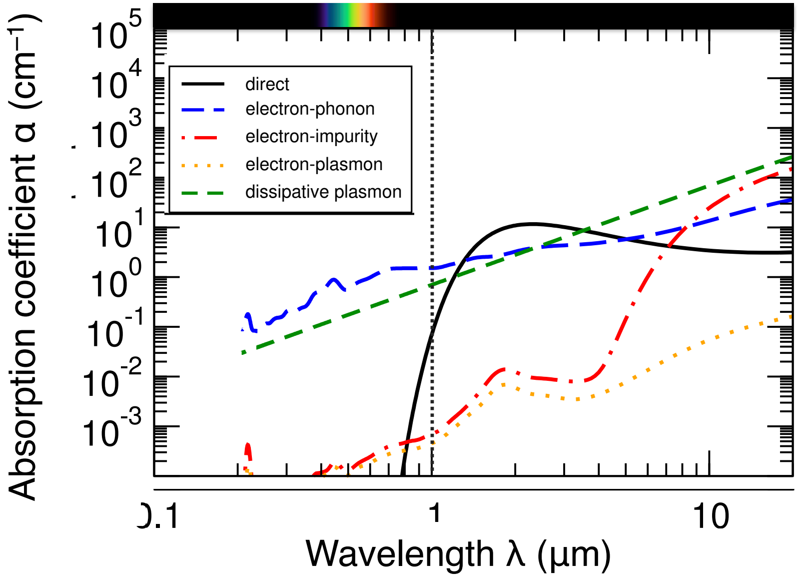
Fundamental limits on optical transparency of transparent conducting oxides: free-carrier absorption in SnO_2

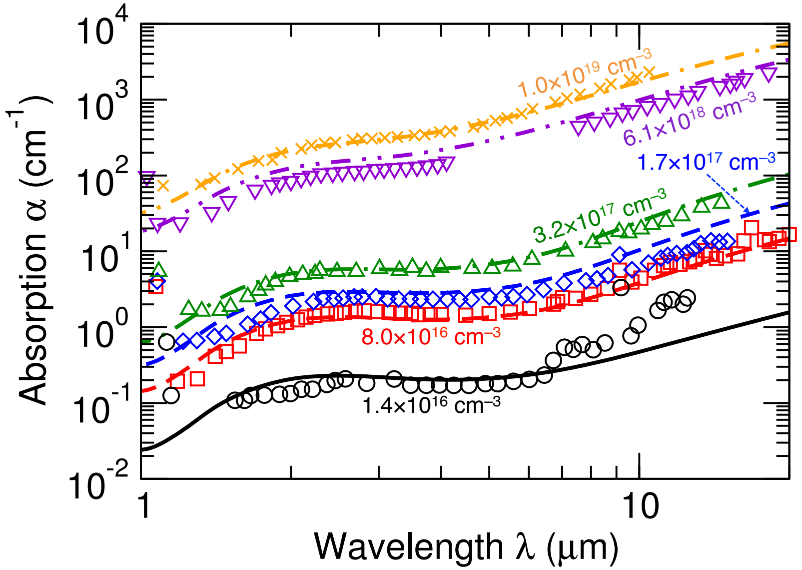
H. Peelaers, E. Kioupakis, and C. G. Van de Walle

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

Free-carrier absorption in n-type silicon



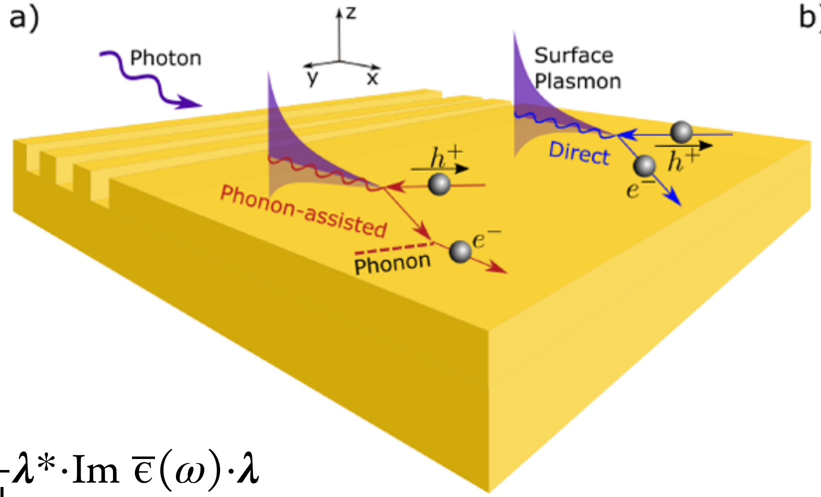


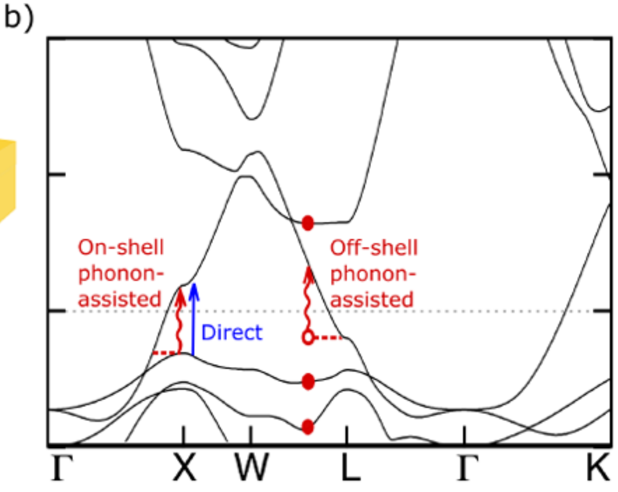


- Absorption of light in n-type silicon competes with interband absorption.
- Also: absorption in the infrared.
- Direct + indirect absorption possible.
- Results for α vs. doping in good agreement with experiment.

X Zhang, G. Shi and E. Kioupakis, in preparation

Plasmon decay in metals





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

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

Strong contribution from phonon-assisted terms

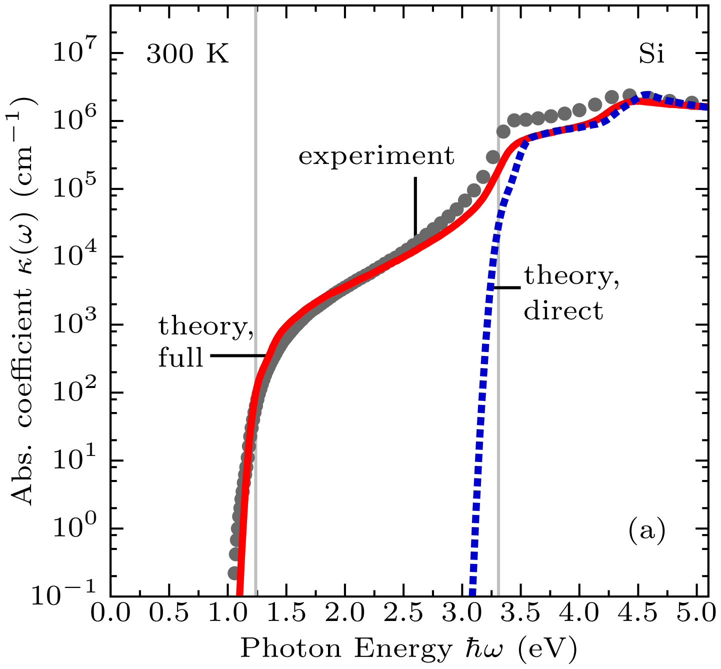
Brown et al., ACS Nano 10, 957–966 (2016)

$$\boldsymbol{\lambda}^*\cdot\mathrm{Im}\,\bar{\epsilon}_{\mathrm{phonon}}(\omega)\cdot\boldsymbol{\lambda} = \frac{4\pi^2e^2}{m_e^2\omega^2}\int_{\mathrm{BZ}}\frac{\mathrm{d}\mathbf{q}'\mathrm{d}\mathbf{q}}{(2\pi)^6}\sum_{n'n\alpha\pm}(f_{\mathbf{q}n}-f_{\mathbf{q}'n'})\left(n_{\mathbf{q}'-\mathbf{q},\alpha}+\frac{1}{2}\mp\frac{1}{2}\right)\delta(\varepsilon_{\mathbf{q}'n'}-\varepsilon_{\mathbf{q}n}-\hbar\omega\mp\hbar\omega_{\mathbf{q}'-\mathbf{q},\alpha})\times\left|\boldsymbol{\lambda}\cdot\sum_{n_1}\left(\frac{g^{\mathbf{q}'-\mathbf{q},\alpha}_{\mathbf{q}'n',\mathbf{q}n_1}\langle\mathbf{p}\rangle^{\mathbf{q}}_{n_1n}}{\varepsilon_{\mathbf{q}n_1}-\varepsilon_{\mathbf{q}n}-\hbar\omega+i\eta}+\frac{\langle\mathbf{p}\rangle^{\mathbf{q}'}_{n'n_1}g^{\mathbf{q}'-\mathbf{q},\alpha}_{\mathbf{q}'n_1,\mathbf{q}n}}{\varepsilon_{\mathbf{q}'n_1}-\varepsilon_{\mathbf{q}n}\mp\hbar\omega_{\mathbf{q}'-\mathbf{q},\alpha}+i\eta}\right)\right|^2$$

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, …

See Marios Zacharias talk on Friday and
[Phys. Rev. Research 2, 013357 (2020)]



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

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

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

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

$$l_\nu = (\hbar/2M_p\Omega_\nu)^{1/2}$$

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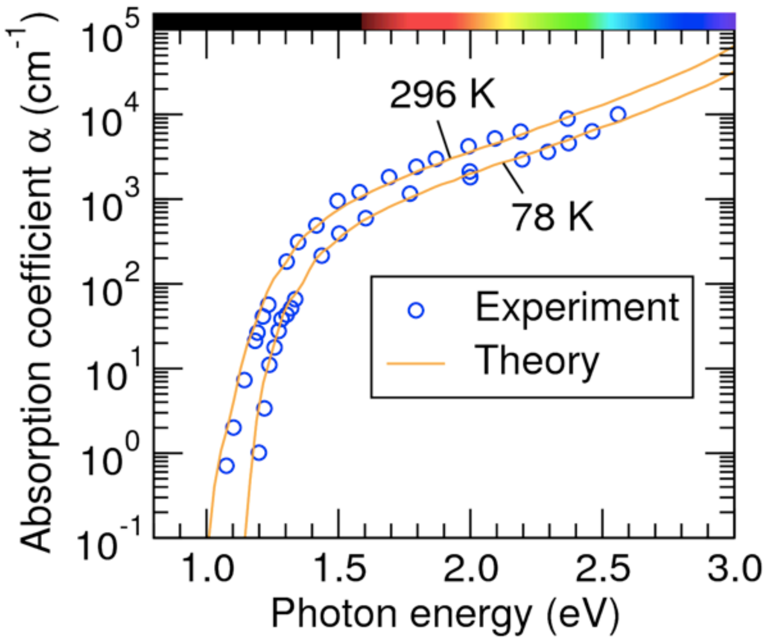

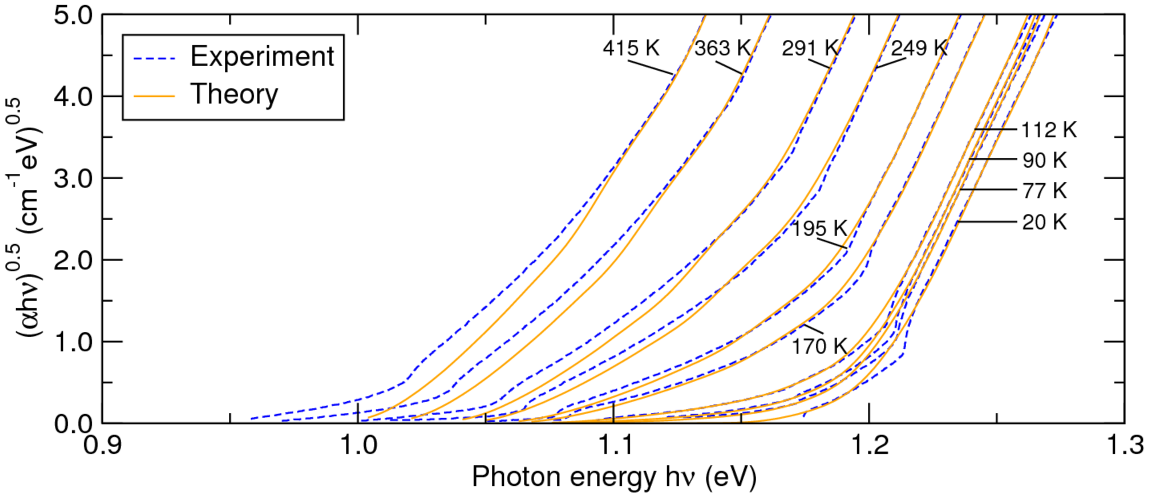

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Thank you for your attention