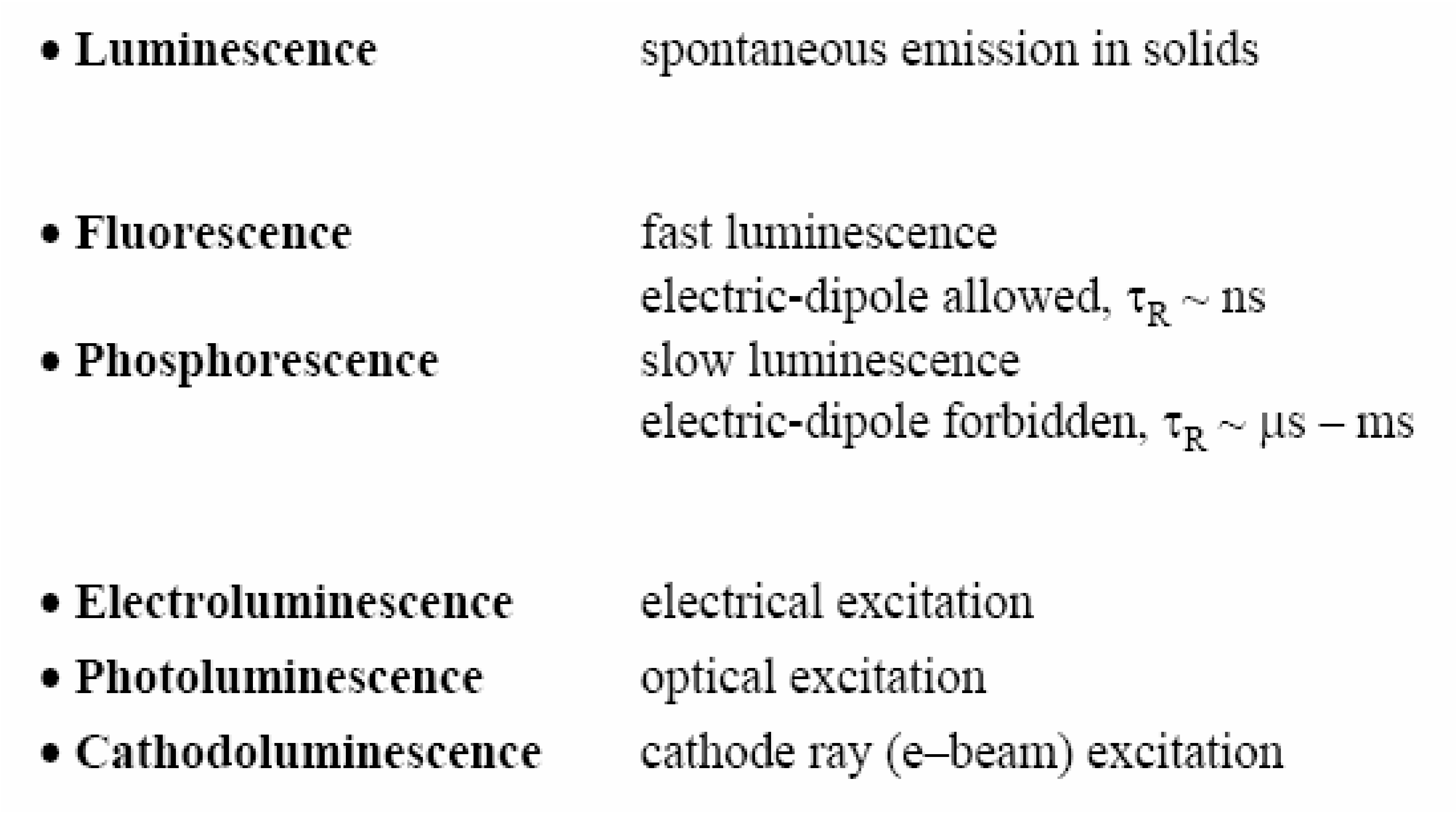
Lectures 23: Luminescence



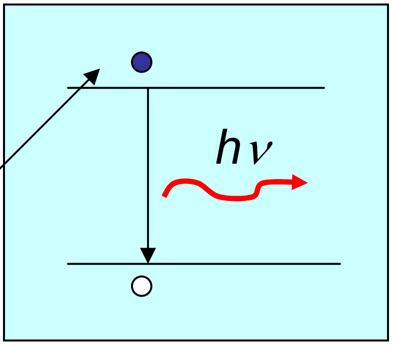
Luminescence	spontaneous emission in solids
Fluorescence	fast luminescence electric-dipole allowed, $\tau_R \sim$ ns
Phosphorescence	slow luminescence electric-dipole forbidden, $\tau_R \sim \mu s - ms$
Electroluminescence	electrical excitation
Photoluminescence	optical excitation
Cathodoluminescence	cathode ray (e–beam) excitation

Model: Occupancy Factors

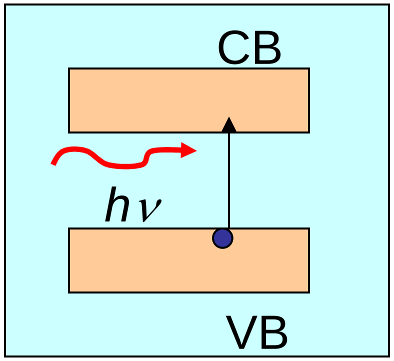
- **Two level system**:

$$\left(\frac{dN}{dt}\right)_{radiative} = -AN$$

$$N(t) = N(0)\exp(-At) = N(0)\exp(-t/\tau_R)$$



Intensity is determined by the occupancy factors *N*



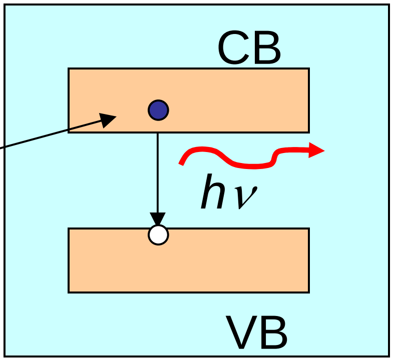
- **Absorption in a solid:**

$$W_{i\to f} = \frac{2\pi}{\hbar}|M|^2 g(\hbar\omega)$$

Matrix element M and the density of states *g*($h\nu$)

- **Emission in a solid:**

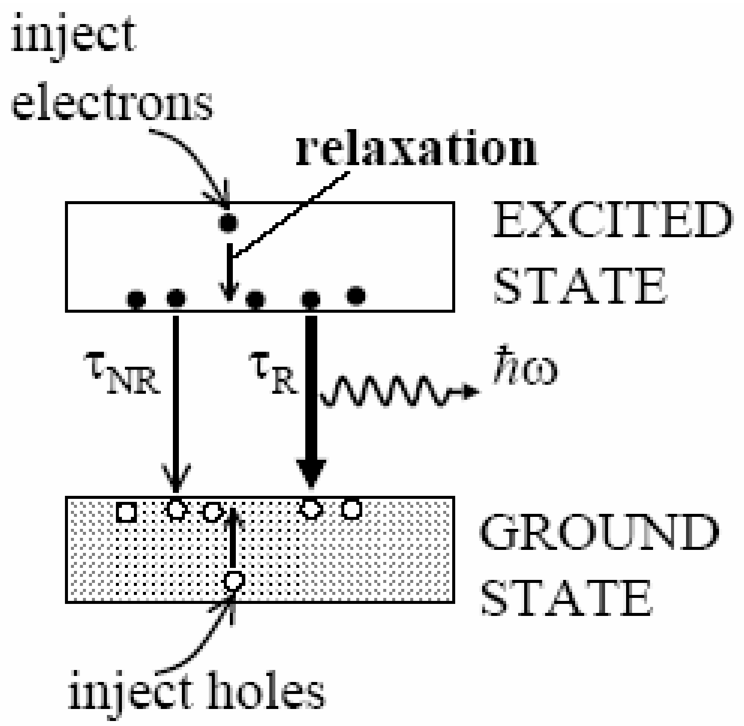
$$I(h\nu) \propto |M|^2 g(h\nu)\times level\_occupancy\_factors$$



Probability that the upper levels are occupied and the lower levels are empty

Model: Relaxation Path

Another difference with absorption: narrow emission band $h\nu \sim E_g$ due to fast relaxation

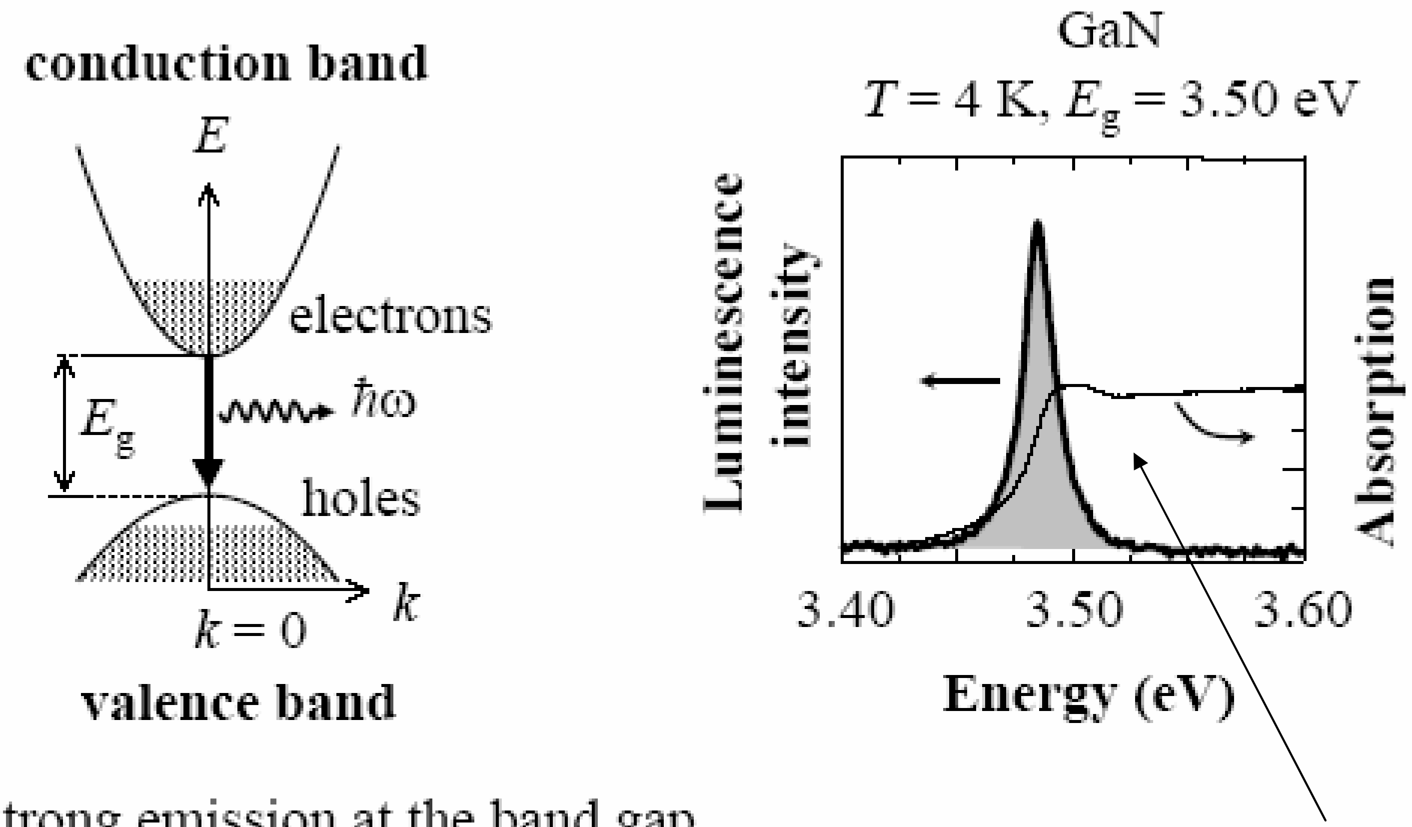


$$\eta_R = \text{radiative quantum efficiency} = \frac{\text{radiative transition rate}}{\text{total transition rate}}$$

$$\eta_R = \frac{1}{1 + \tau_R / \tau_{NR}}$$

- Radiative transition rate determined by Einstein A-coefficient
- $\tau_R = A^{-1}$
- τ_{NR} determined by phonon population, number of traps etc

Direct Gap Materials



- Strong emission at the band gap
- most III-V and II-VI semiconductors
- linewidth $\geq k_B T$

Emission and absorption spectra are different!

- **Small radiative lifetimes ~10^{-8} – 10^{-9} s and high efficiency**
- **k-vector conservation – vertical transitions**

Indirect Gap Materials

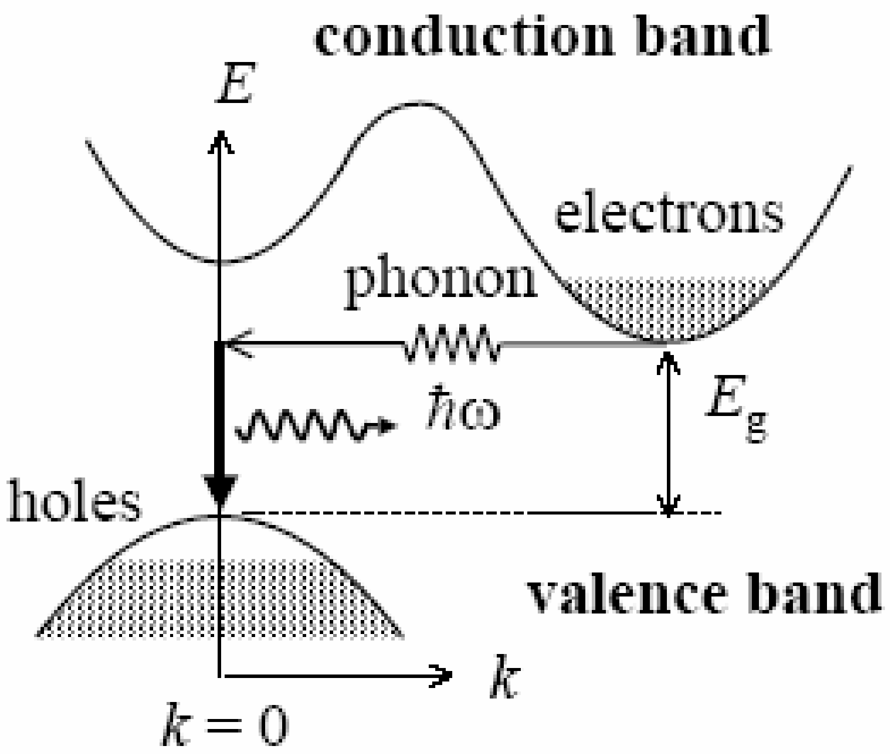
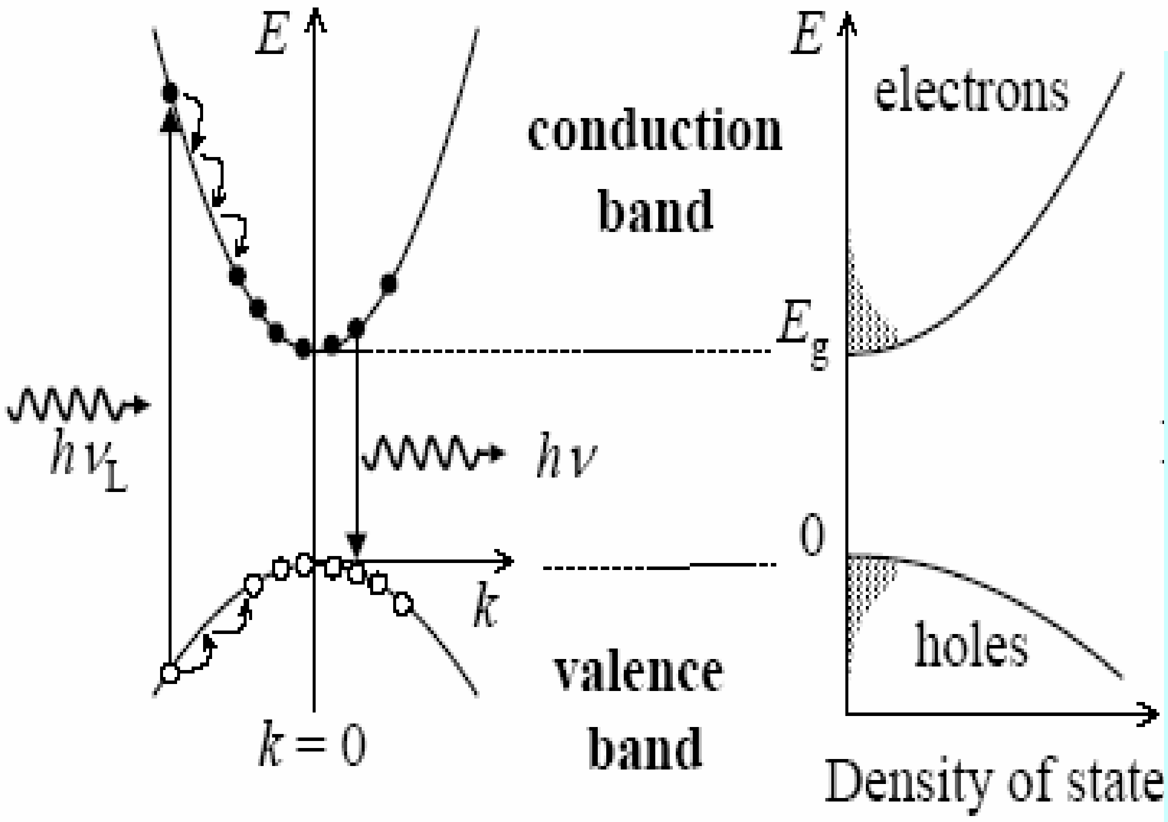


Figure 5.4

- Low emission probability (2nd order process)
- Long radiative lifetime ⇒ low radiative quantum efficiency
- diamond, silicon, germanium, AlAs

Photoluminescence



Hierarchy of time scales:

Excitation – fastest

Relaxation – fast (~100 fs or 10^{-13} s)

Thermalization – fast (~1ps or 10^{-12} s)

Radiative recombination ~ 1-10ns or 10^{-8}-10^{-9} s

Nonradiative recombination - slowest

- Excite using laser with photon energy > E_g
- electrons and holes relax to the bottom of their bands
- thermal distributions formed according to **statistical mechanics**
- emission from E_g to top of carrier distributions

Lectures 24: Luminescence (continued)

Attempting to reduce to two level system

$$N_e = \int_{E_g}^{\infty} g_c(E)\, f_e(E)\, dE$$

Convolution of density of states and filling factor

$$g_c(E) = \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{\frac{3}{2}}\left(E - E_g\right)^{\frac{1}{2}}$$

Straightforward consequence of 3-D case

$$f_e(E) = \left[\exp\left(\frac{E - E_F^c}{k_B T}\right) + 1\right]^{-1}$$

Fermi-Dirac distribution at *T*

$$N_e = \int_0^{\infty} \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{\frac{3}{2}} E^{\frac{1}{2}}\left[\exp\left(\frac{E - E_F^c}{k_B T}\right) + 1\right]^{-1} dE$$

$$N_h = \int_0^{\infty} \frac{1}{2\pi^2}\left(\frac{2m_h^*}{\hbar^2}\right)^{\frac{3}{2}} E^{\frac{1}{2}}\left[\exp\left(\frac{E - E_F^h}{k_B T}\right) + 1\right]^{-1} dE$$

Different Fermi levels for electrons (E_F^c) and holes (E_F^h) measured from the edges of the corresponding bands

$N_e = N_h$

Classical (Boltzmann) Statistics

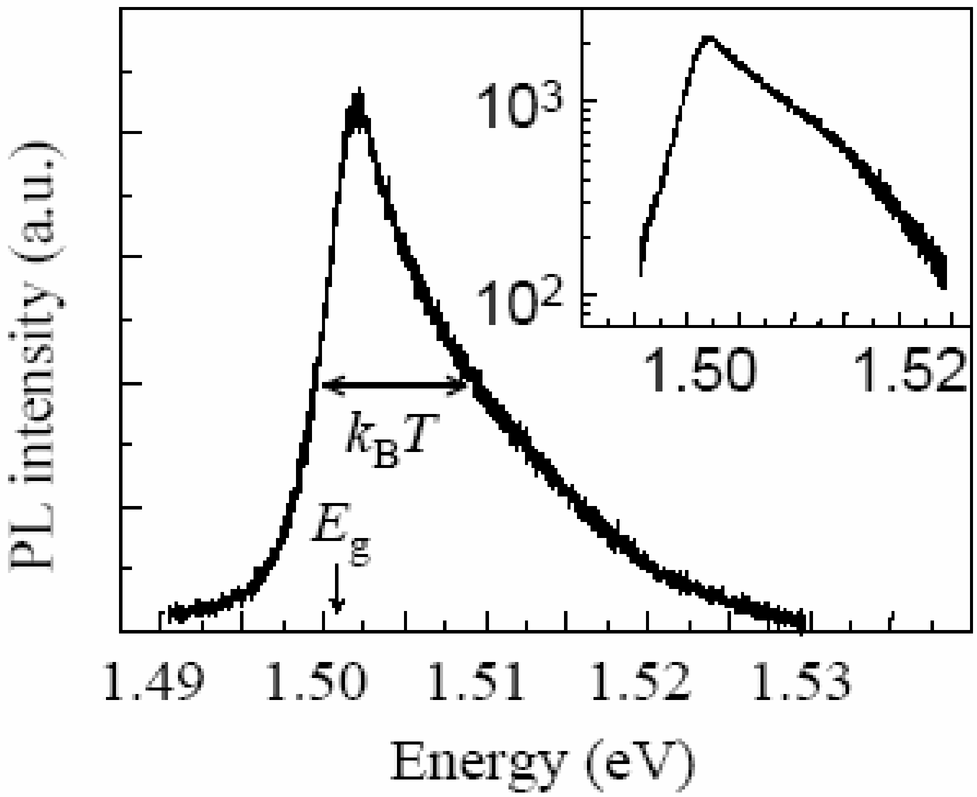


Figure 5.6

GaAs

$T = 100$ K

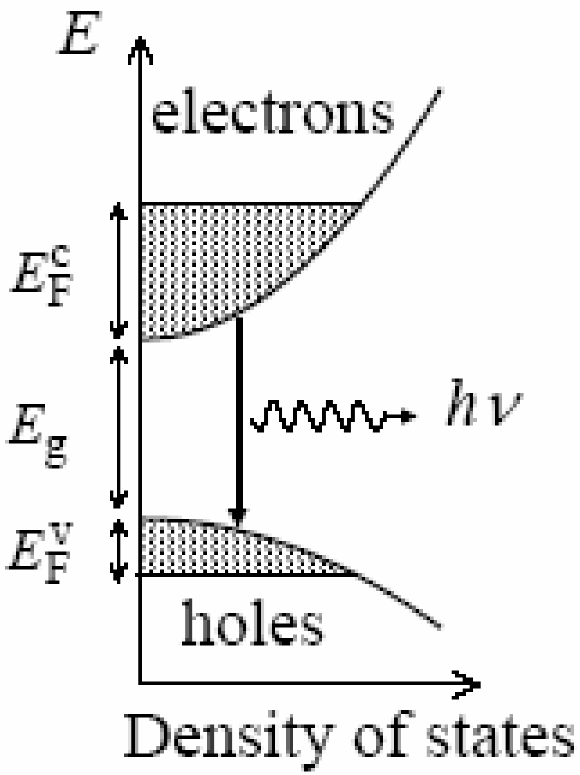
$k_BT = 8.6$ meV

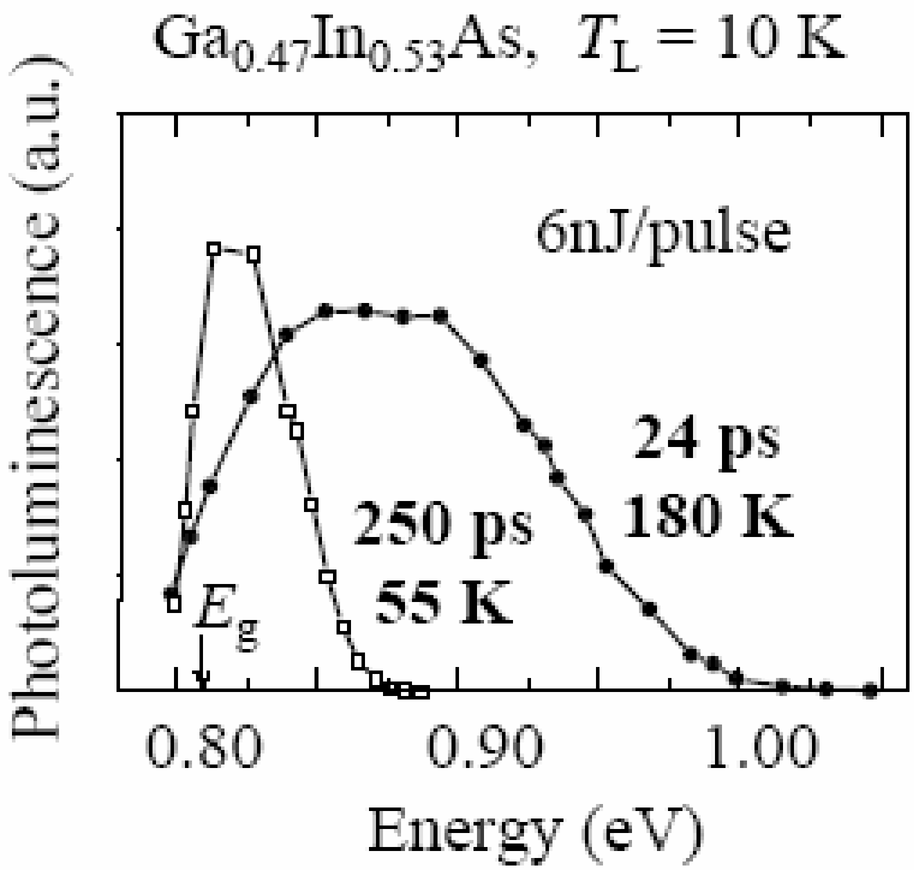
$E_g = 1.501$ eV

- Boltzmann statistics: $f(E) \propto \exp(-E/k_BT)$ **(occupancy factors)**
- $I(E) \propto$ Density of states $\times f_e(E)\, f_h(E)$
- PL rises sharply at E_g, then decays exponentially. Linewidth ~ k_BT

$$I(h\nu) \propto (h\nu - E_g)^{1/2} \exp\left(-\frac{h\nu - E_g}{k_BT}\right)$$

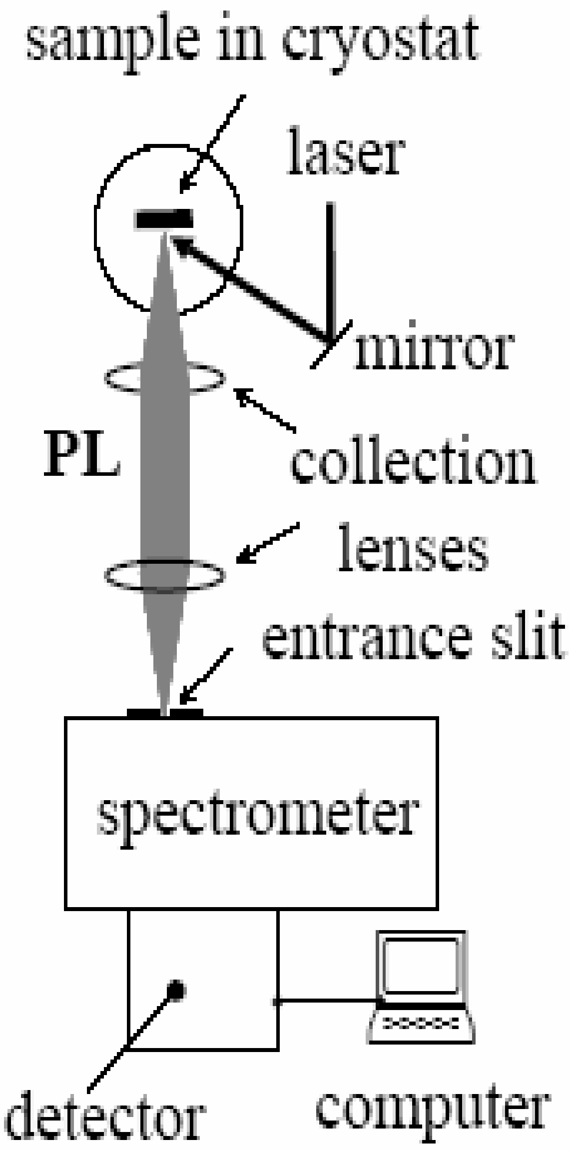
Degeneracy





- Degeneracy observed at high density and low temperatures
- Emission from E_g to $(E_g + E_F{}^c + E_F{}^v)$

Photoluminescence Spectroscopy



Photoluminescence (PL) spectroscopy

- fixed frequency laser, measure spectrum by scanning spectrometer

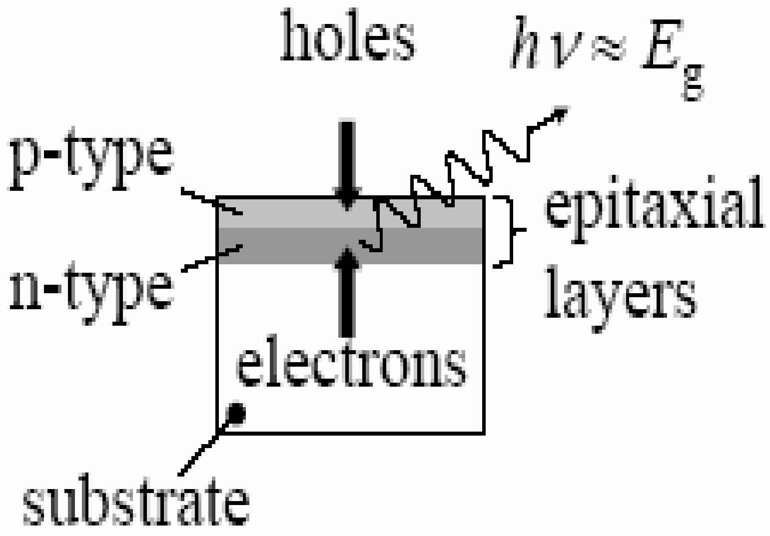
PL excitation spectroscopy (PLE)

- detect at peak emission, vary laser frequency
- effectively measures absorption

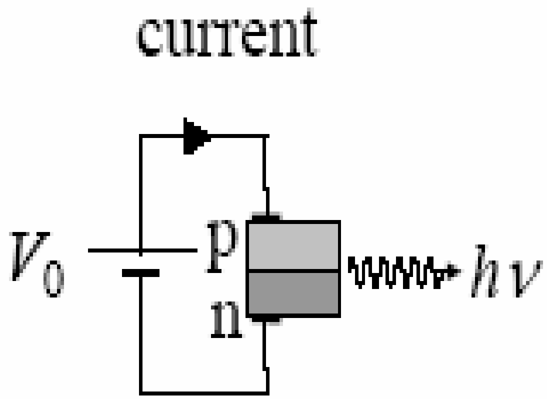
Time-resolved PL spectroscopy

- short pulse laser + fast detector
- measure lifetimes, relaxation processes

Electroluminescence



- Epitaxial growth of high purity light-emitting layers on substrate crystal
- MBE, MOCVD, LPE ….



- Forward-biassed p-n junction
- Electrons and holes recombine at the junction
- photon energy ~ E_g

Lattice Matching

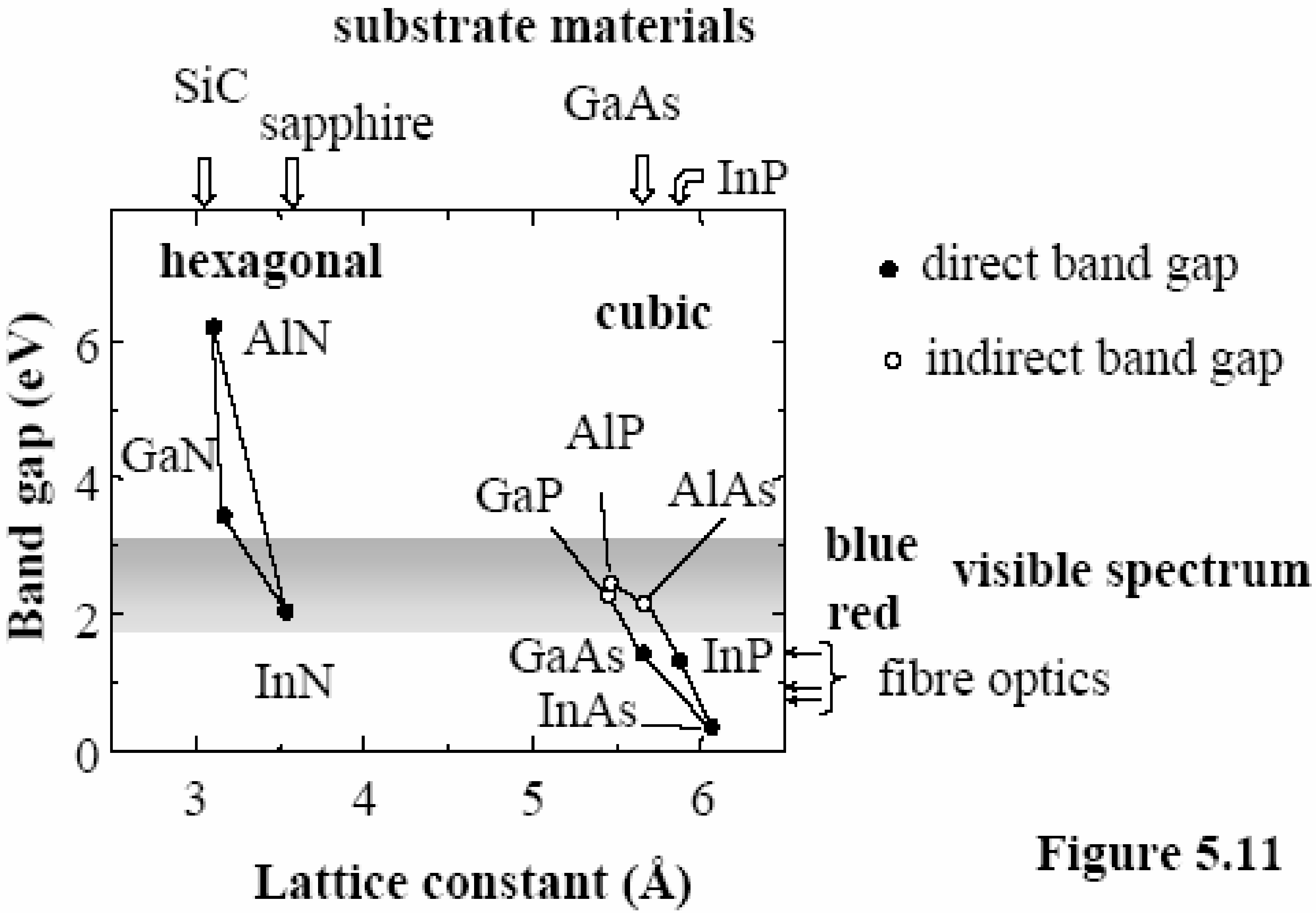
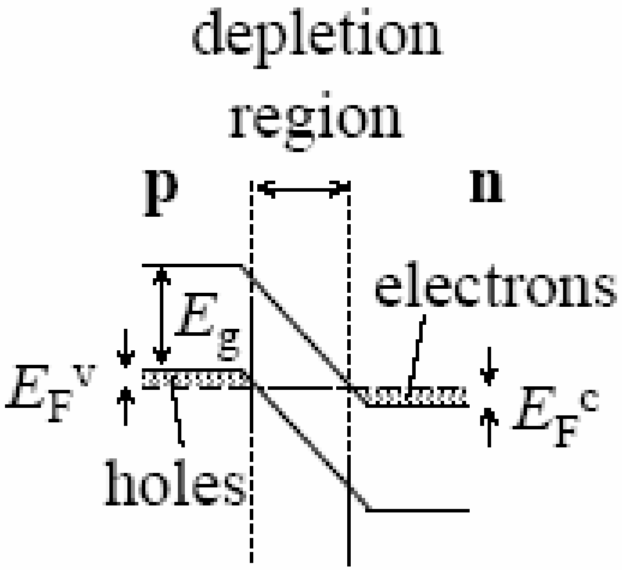


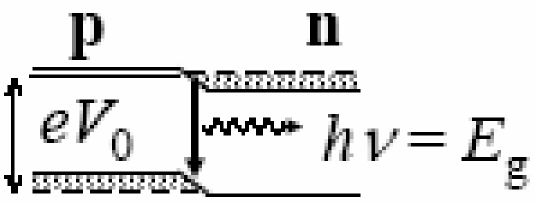
Figure 5.11

Lectures 25: Diode Lasers

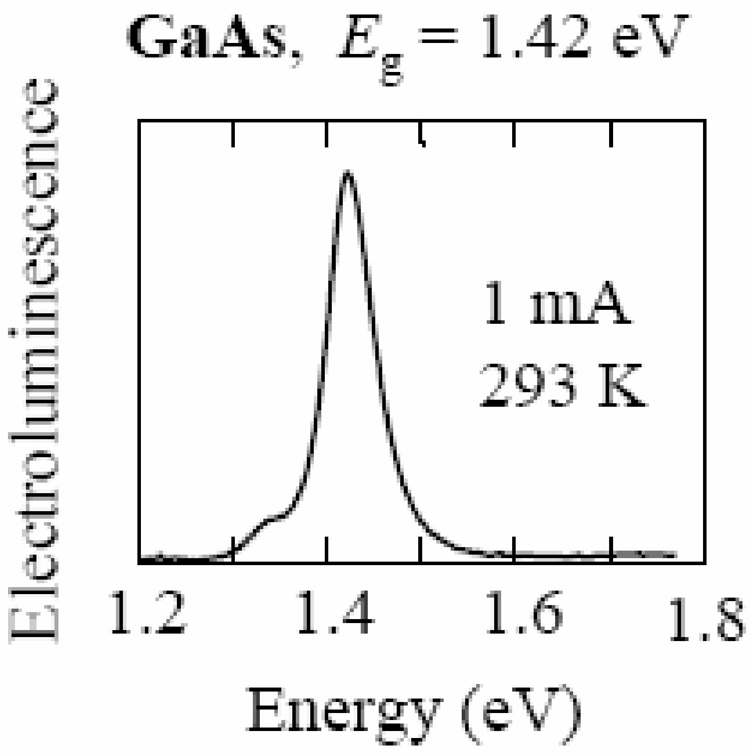
Junction Electroluminescence



(a) $V_0 = 0$

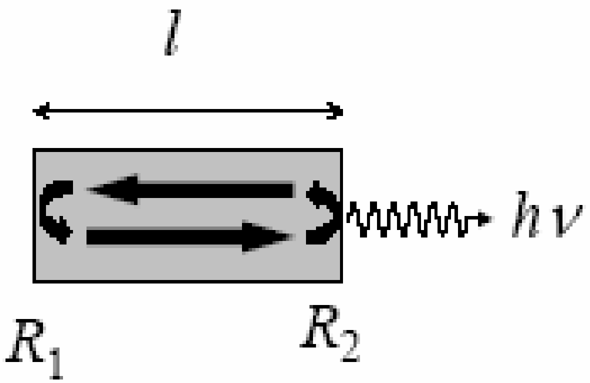


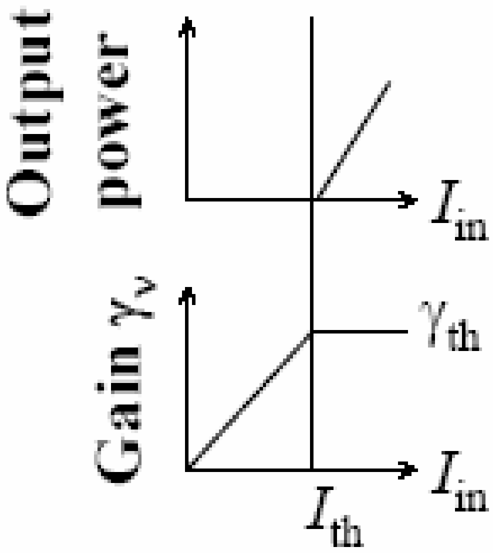
(b) $V_0 \approx +E_g/e$

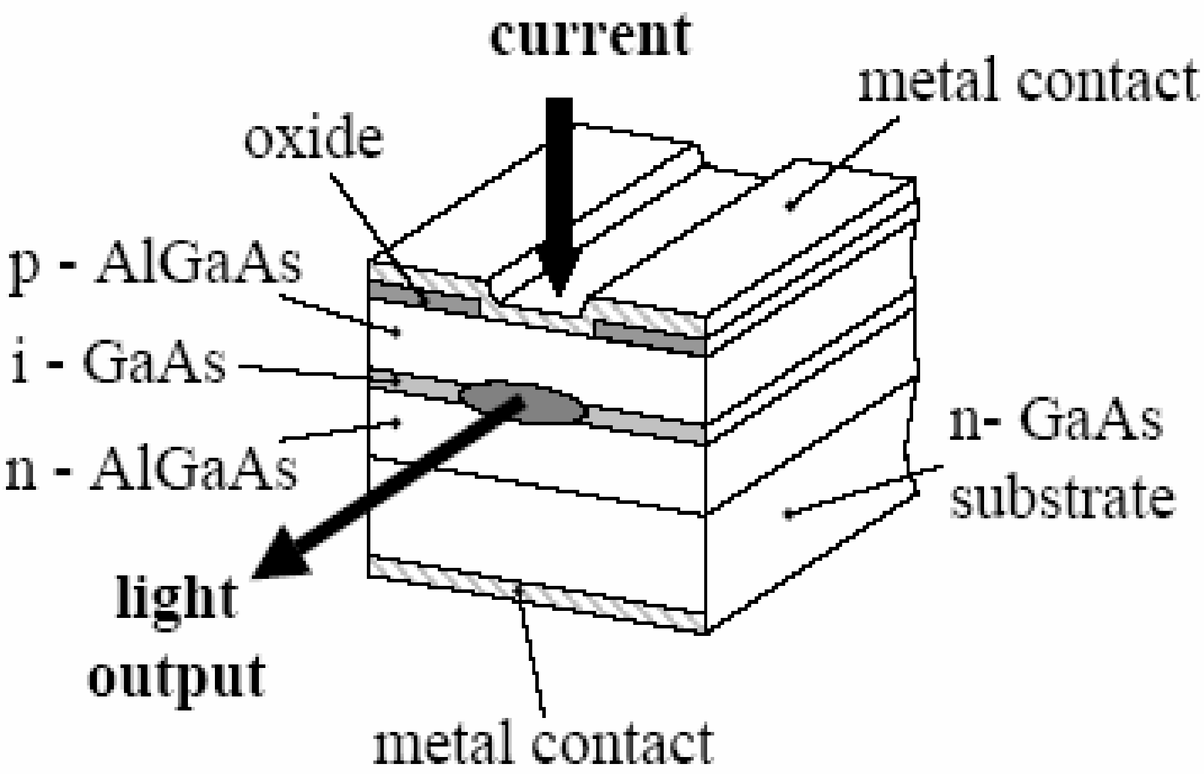


- Emission at E_g
- Operating voltage ~ E_g / e
- Spectral width ~ $k_B T$

Diode Lasers







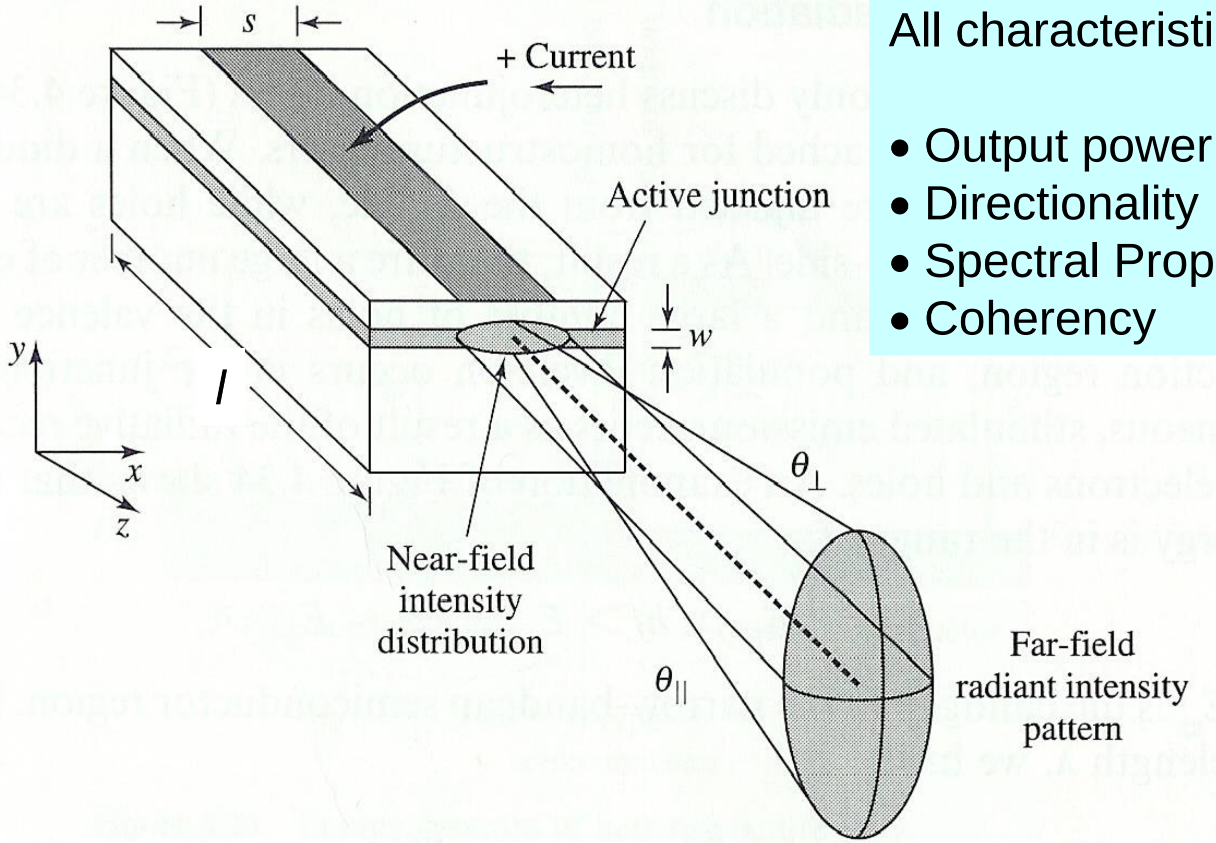
- Mirrors formed by "facets" (i.e. edges) of chip
- Emission wavelength ~ hc / E_g
- Linewidth determined by cavity modes

Diode Lasers

- Threshold current I_{th}
- Below the threshould – spontaneous emission
- Above the threshould – stimulated emission

All characteristics are changed at I_{th}:

- Output power
- Directionality
- Spectral Properties
- Coherency



Diode Lasers

$$m \times \frac{\lambda'}{2} = l, where\_\lambda' = \lambda / n$$

$$\nu = m \times \frac{c}{2nl}$$

$$dI = +\gamma_\nu dx \times I(x)$$

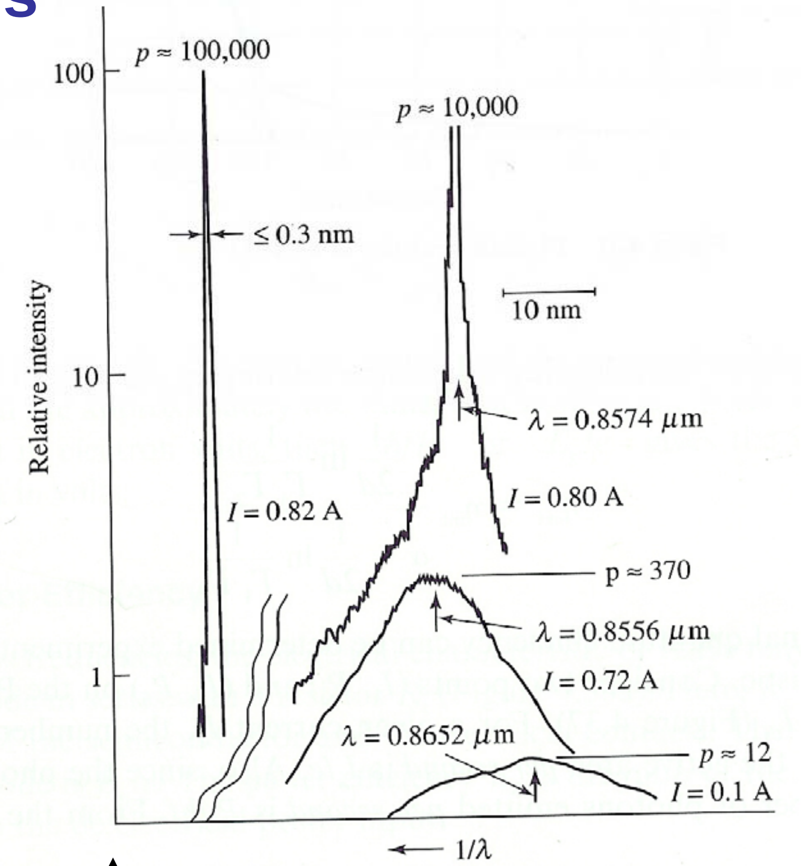
$$I(x) = I_0 e^{\gamma_\nu x}$$

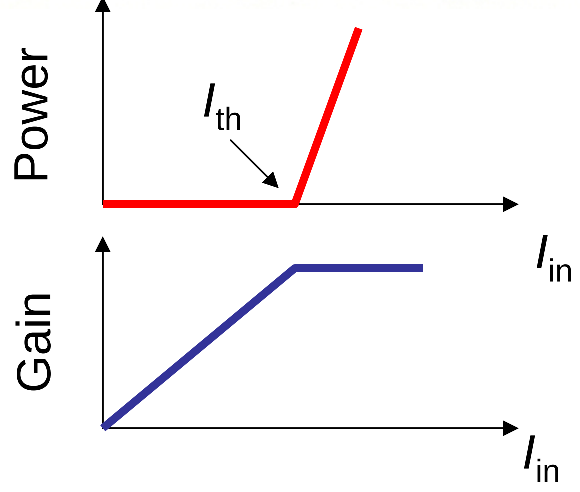
$$R_1 R_2 e^{2\gamma_\nu x} e^{-2\alpha_b l} = 1$$

$$\gamma_{th} = \alpha_b - \frac{1}{2l}\ln(R_1 R_2)$$

$$P_{out} = \eta \frac{h\nu}{e}(I_{in} - I_{th})$$

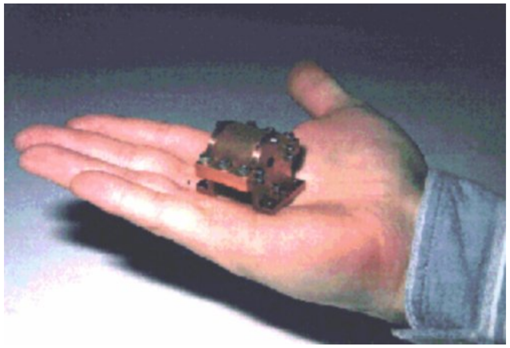
$$Slope\_efficiency = \frac{P_{out}}{(I_{in} - I_{th})} = \frac{\eta h\nu}{e}$$

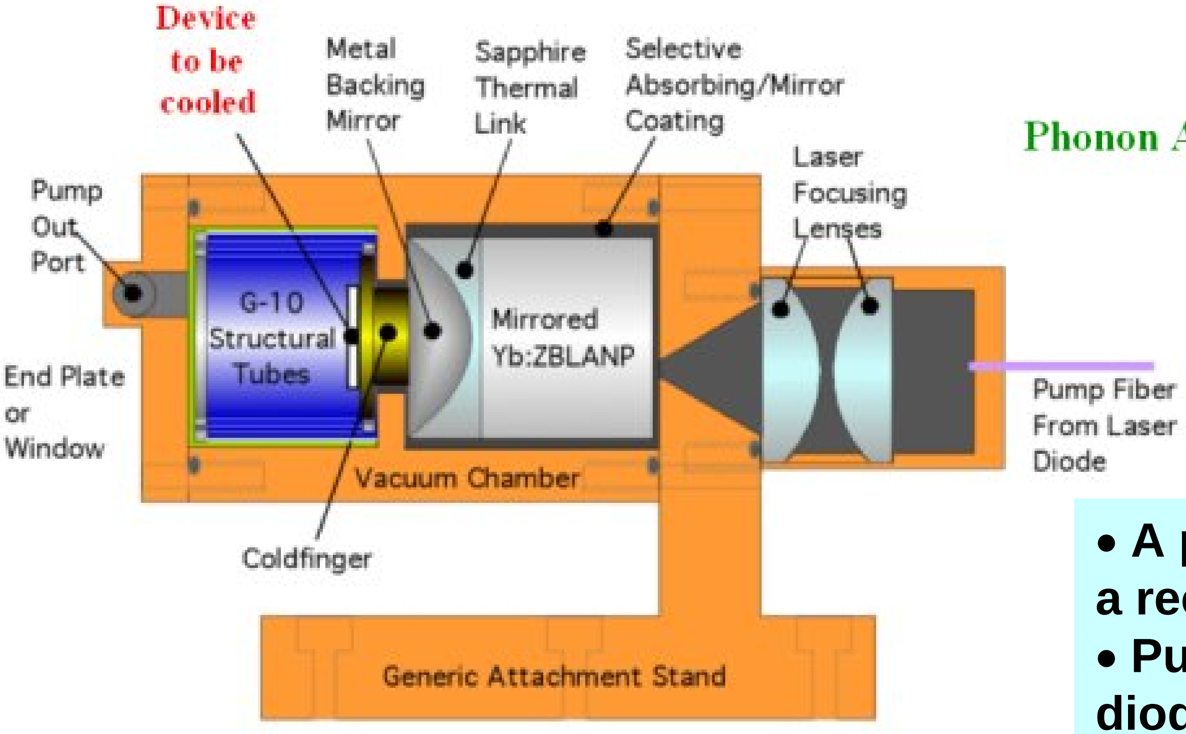


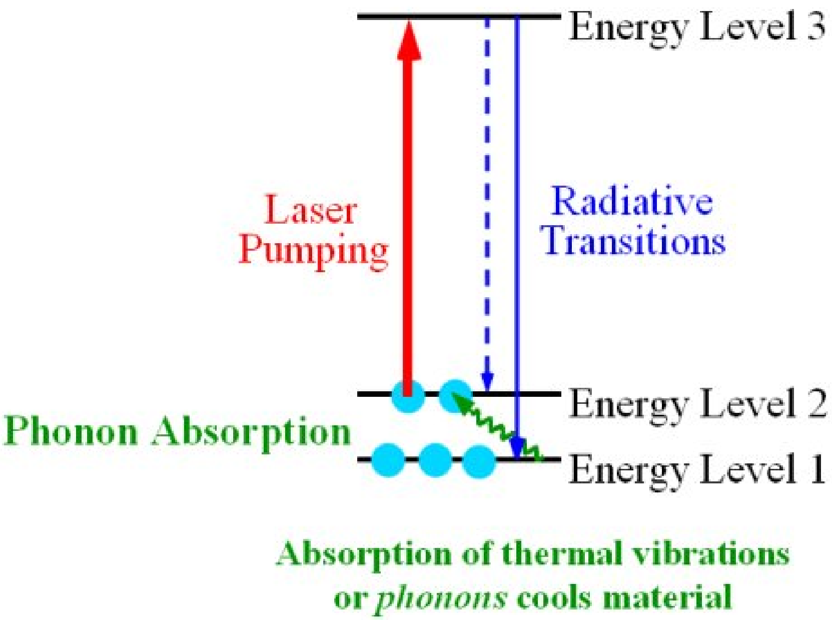


Optical Refrigerating Breaks Record

J. Thiede, J. Distel, S. R. Greenfield, and R. I. Epstein
Applied Physics Letters **86** 154107 (2005)







Absorption of thermal vibrations or *phonons* cools material

- **A prototype laser fridge cools to a record low temperature of 208 K**
- **Pumped with up to 11 W of diode-pumped Yb:YAG laser**

Lectures 26-27: Quantum Confined Structures

$$\Delta p_x \sim \frac{\hbar}{\Delta x}$$

Confinement energy > thermal energy

$$E_{confinement} = \frac{(\Delta p_x)^2}{2m} \sim \frac{\hbar^2}{2m(\Delta x)^2} > \frac{1}{2}k_B T$$

$$\Delta x < \sqrt{\frac{\hbar^2}{m k_B T}}$$

$$\Delta x < \lambda_{deB} \equiv p_x / h$$

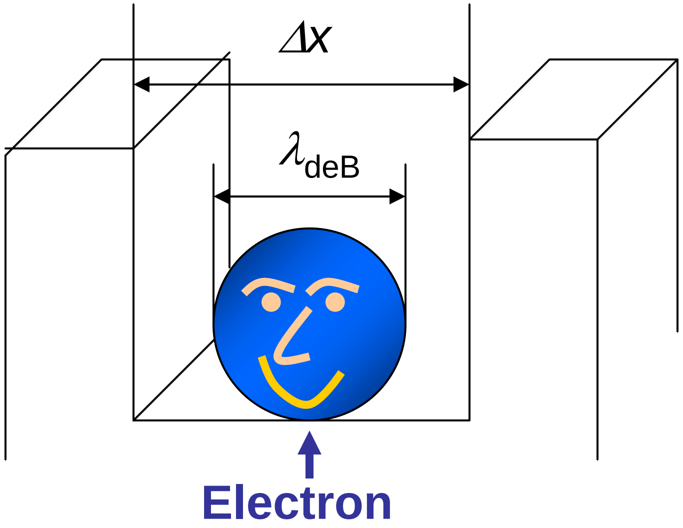
Size quantization

To observe quantum confinement effects:

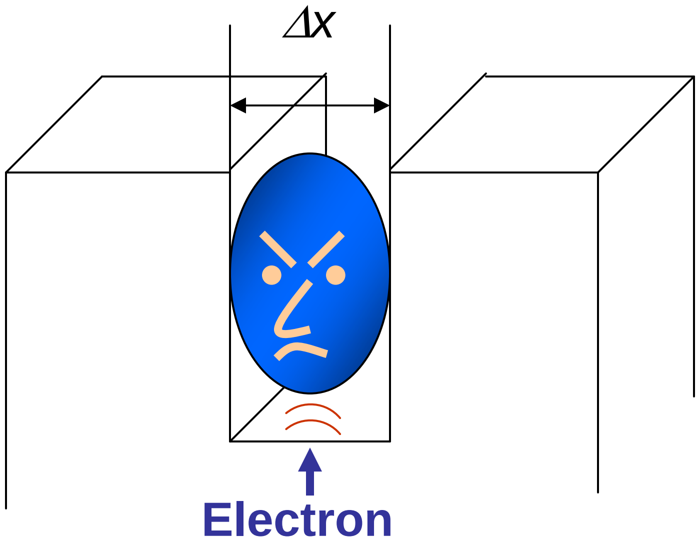
$\Delta x < \lambda_{deB}$

- Quantum wells (1-D) confinement (epitaxial growth)
- Quntum wires (2-D) confinement (etching of QWs or patterned substrates)
- Quantum dots (3-D) confinement (self-organized III-V dots, doped glasses)

No size quantization: $\Delta x > \lambda_{deB}$



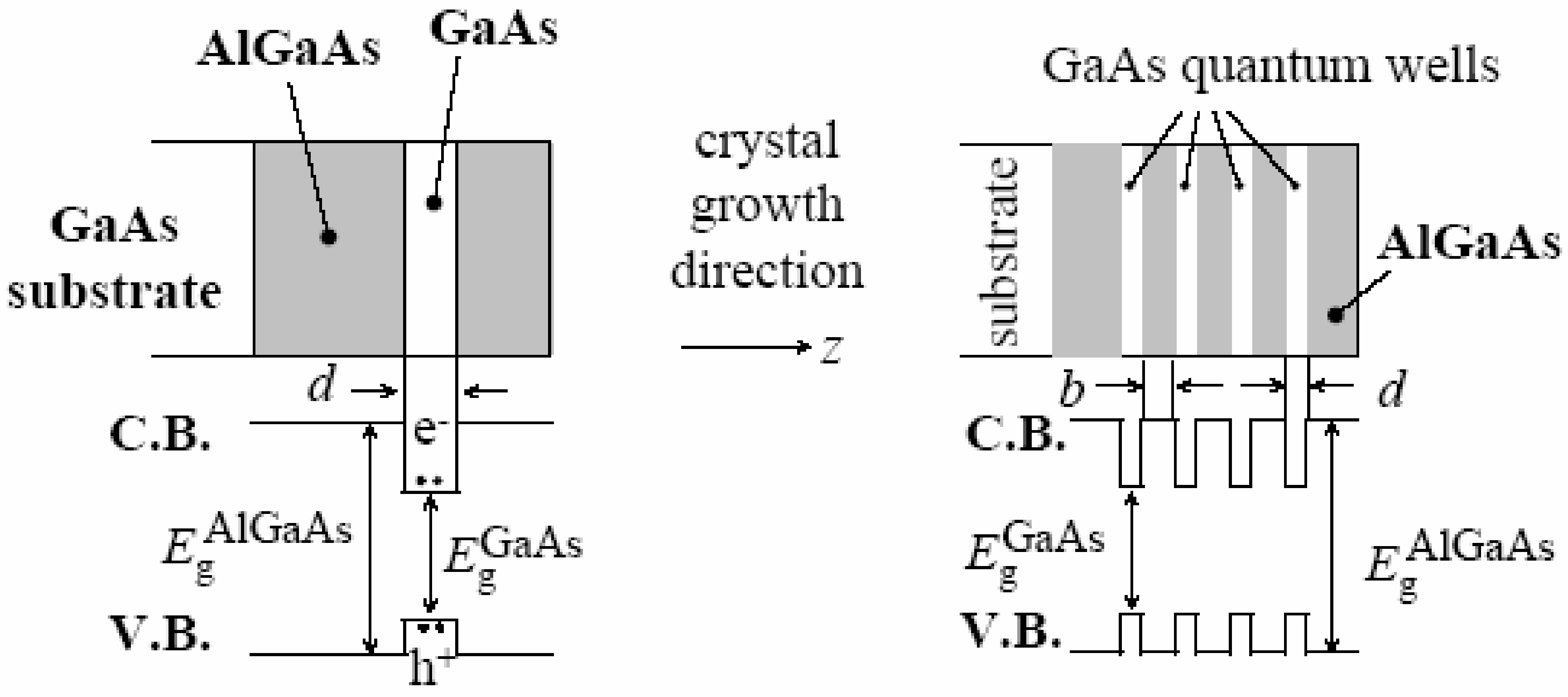
Size quantization: $\Delta x < \lambda_{deB}$



Semiconductor Quantum Wells

Quantization along *z*
Free motion along *x,y*

Multi-QWs: b ≥ 10-20nm
Superlattice: b < 10nm



Single quantum well

MQW or superlattice

growth methods
- Molecular beam epitaxy (MBE)
- Metal-organic chemical vapour deposition (MOCVD)

Separation of Variables

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z)=E^{total}\psi(x,y,z)$$

Free electron gas

$$\psi(x,y,z)=\psi(x,y)\varphi(z)$$

Motion along *x* and *y* is independent of *z*

$$E^{total}(n.\mathbf{k})=E_n+E(\mathbf{k})$$

$$\psi_k(x,y)=\frac{1}{\sqrt{A}}e^{i\mathbf{k}\cdot\mathbf{r}}$$

Plane waves in *xy* plane

$$E(k)=\frac{\hbar^2k^2}{2m^*}$$

k-vector for motion in *xy* plane

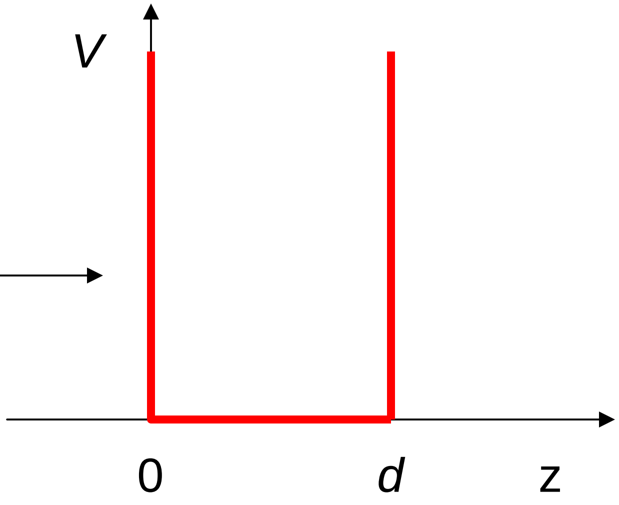
$$E^{total}(n,\mathbf{k})=E_n+\frac{\hbar^2\mathbf{k}^2}{2m^*}$$

Infinite Quantum Wells: 1-D problem (z)

$$-\frac{\hbar^2}{2m}\frac{d^2\varphi(z)}{dz^2}+V(z)\varphi(z)=E\varphi(z)$$

$$\left.\begin{aligned}&V(z)=\infty\_z<0\\&=0\_0<z<d\\&=\infty\_z>d\end{aligned}\right]$$

Potential



$$\varphi(z)=0\_z<0$$

$$\varphi(z)=0\_z>d$$

$$Inside\_the\_box\_(V(z)=0):$$

$$\frac{d^2\varphi(z)}{dz^2}+\frac{2mE}{\hbar^2}\varphi(z)=0$$

$$There\_is\_no\_solution\_for\_E<0:$$

$$\frac{d^2\varphi(z)}{dz^2}-k^2\varphi(z)=0,\_where\_k^2=2m|E|/\hbar^2$$

Infinite Quantum Wells: 1-D problem (continued)

$$For\_E>0\_and\_k^2=\frac{2mE}{\hbar^2}$$

$$\frac{d^2\varphi(z)}{dz^2}+k^2\varphi(z)=0$$

$$General\_solution:$$

$$\varphi(z)=A\sin kz+B\cos kz$$

$$Since\_\varphi(0)=0\Rightarrow\varphi(z)=A\sin kz$$

$$Since\_\varphi(d)=0\Rightarrow kd=n\pi,\_n=1,2,3,\ldots$$

$$k_n=n\frac{\pi}{d}$$

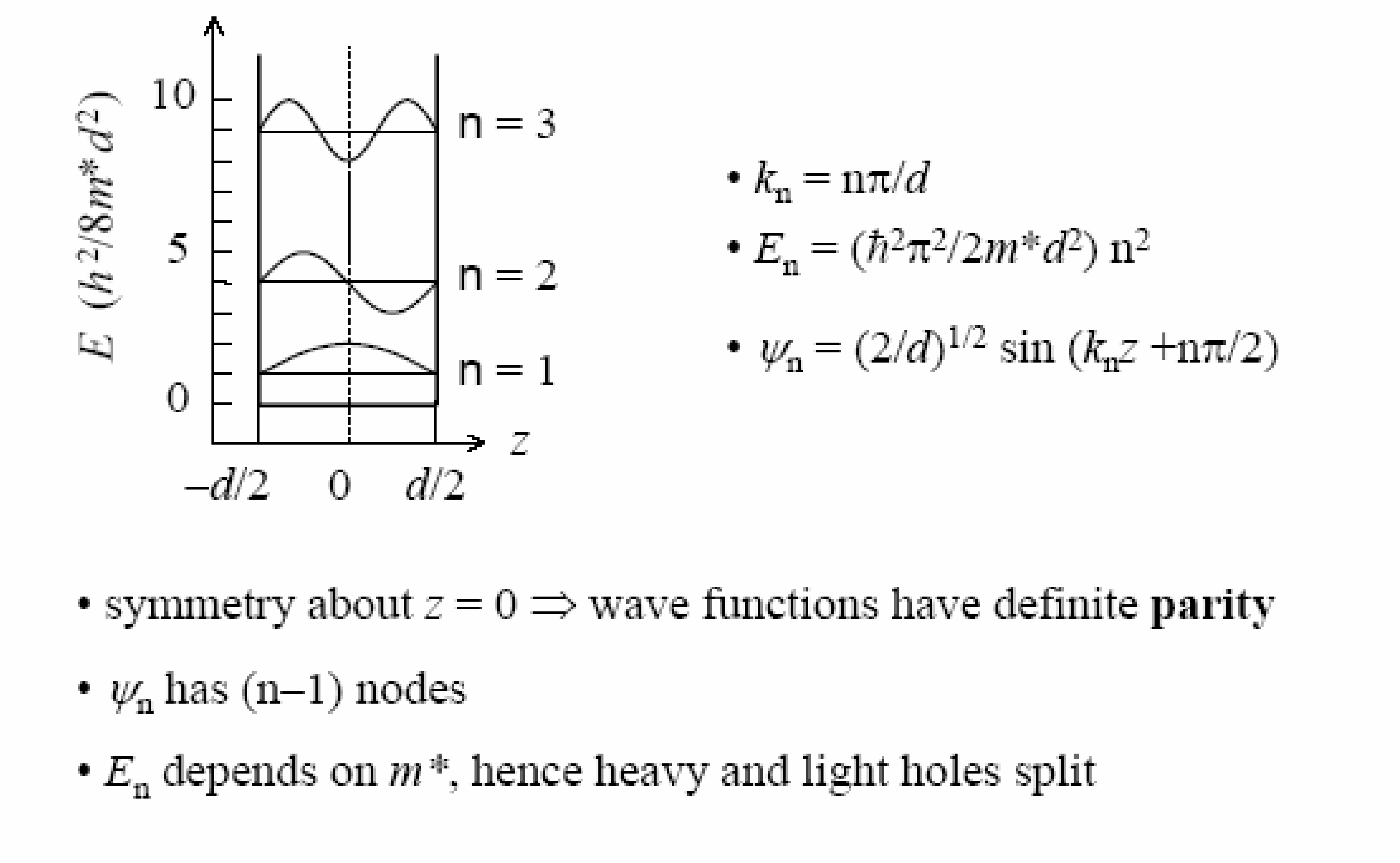
$$Thus:$$

$$E_n=\frac{\hbar^2k_n^2}{2m}=\frac{\hbar^2\pi^2n^2}{2md^2},\_n=1,2,3,\ldots$$

$$\varphi_n(z)=\sqrt{\frac{2}{d}}\sin k_nz=\sqrt{\frac{2}{d}}\sin\frac{n\pi z}{d}$$

If we select 0 in the middle of the well:

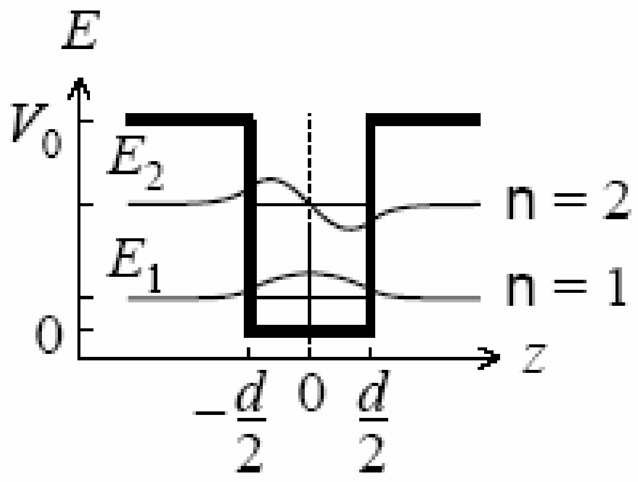
$$\varphi_n(z)=\sqrt{\frac{2}{d}}\sin k_n z\rightarrow\sqrt{\frac{2}{d}}\sin\left(k_n z+\frac{n\pi}{2}\right)$$



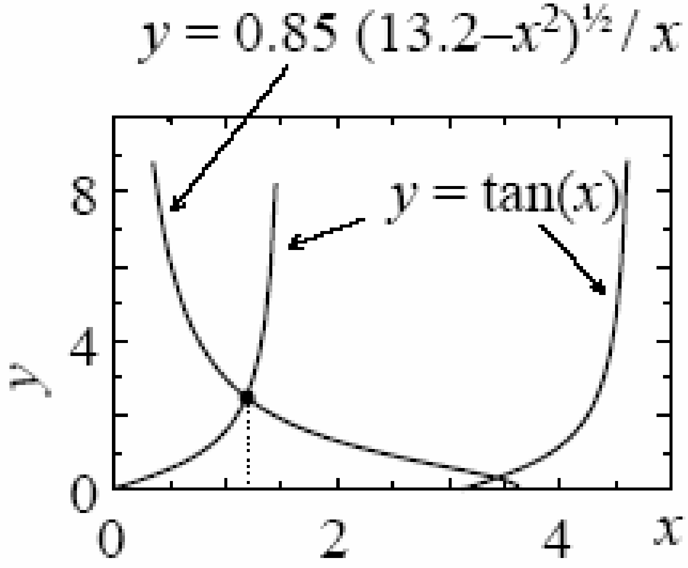
- $k_n = n\pi/d$
- $E_n = (\hbar^2\pi^2/2m^*d^2)\, n^2$
- $\psi_n = (2/d)^{1/2} \sin (k_n z + n\pi/2)$

- symmetry about $z = 0 \Rightarrow$ wave functions have definite **parity**
- ψ_n has (n–1) nodes
- E_n depends on m^*, hence heavy and light holes split

Finite QWs



- Wave functions tunnel into the barrier
- wave function still identified by parity and number of nodes
- Confinement energy reduced compared to infinite well
- graphical solution to find E_n



Example : GaAs/AlGaAs

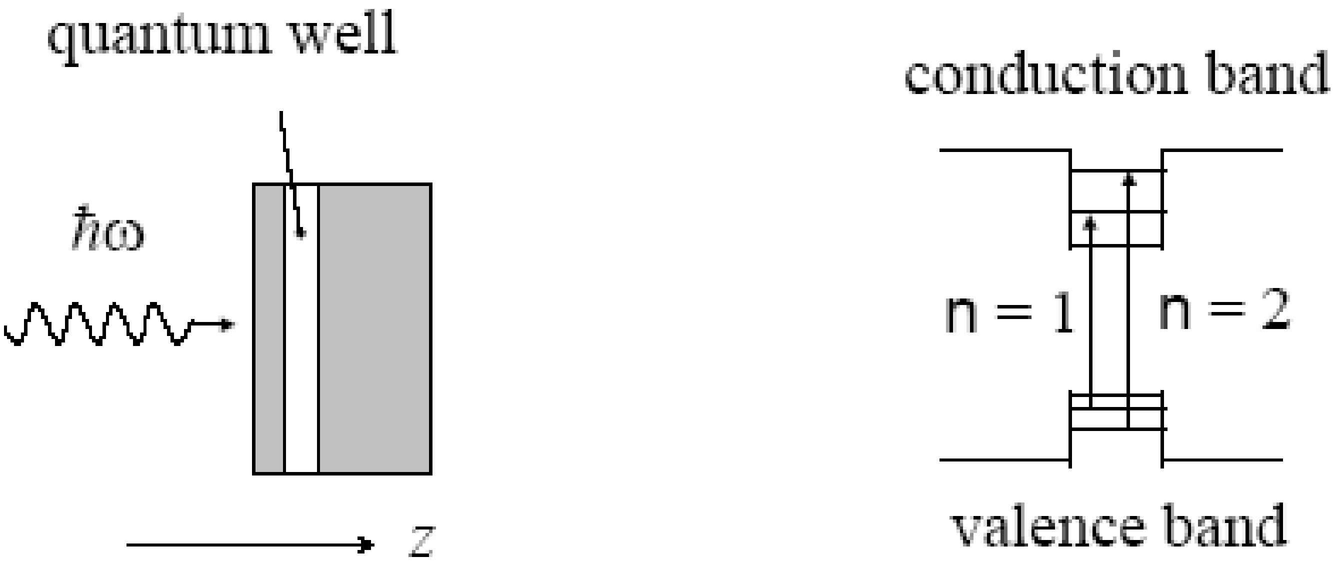
$V_0 = 0.3$ eV, $d = 10$ nm

$m_w^* = 0.067 m_e$, $m_b^* = 0.092 m_e$

$E_1 = 31.5$ meV

c.f. infinite well: $E_1 = 57$ meV

Optical Transitions



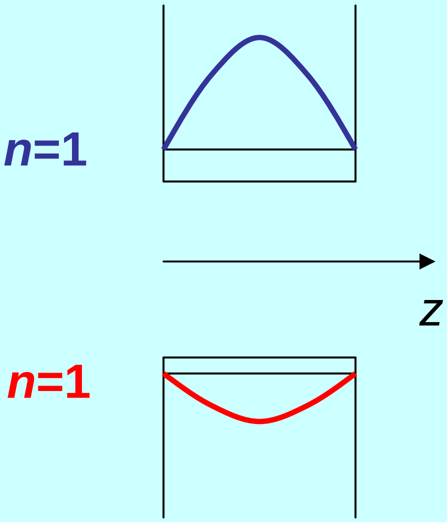
- Light polarized in *x,y* plane for normal incidence
- Parity selection rule: Δn = even number
- Infinite well selection rule: $\Delta n = 0$

Selection Rules

$$M_{nn'} = \int_{-\infty}^{\infty} \varphi^{*}_{en'}(z)\varphi_{hn}(z)dz = \frac{2}{d}\int_{-d/2}^{d/2} \sin(k_n z + \frac{n\pi}{2})\sin(k_{n'} z + \frac{n'\pi}{2})dz$$

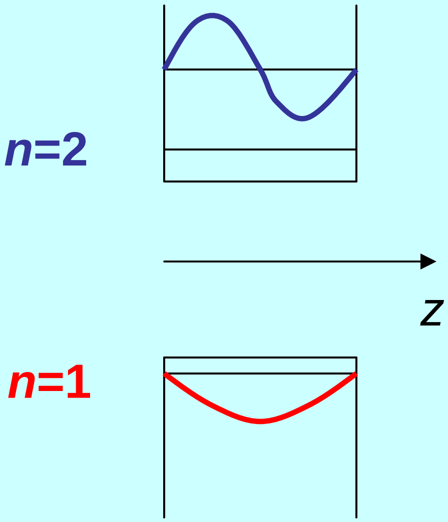
$$\int \quad = 1\_if\_n = n'$$

Good spatial overlap along *z* between electron and hole



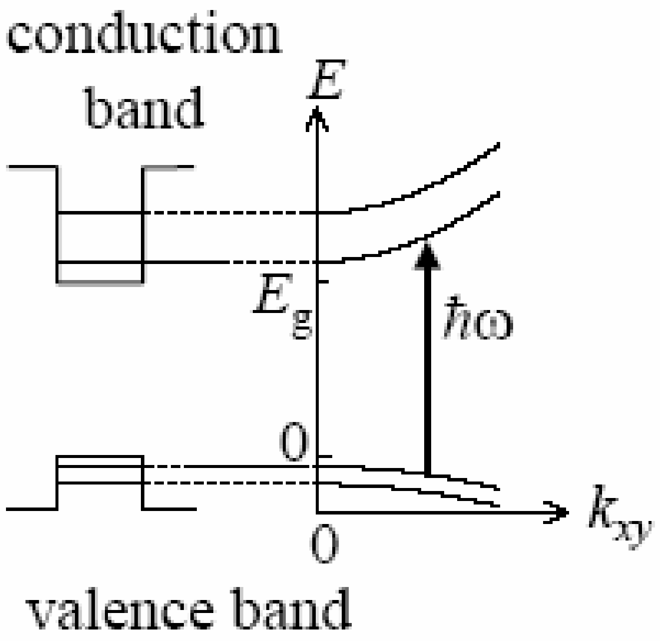
$$\int \quad = 0\_if\_n \neq n'$$

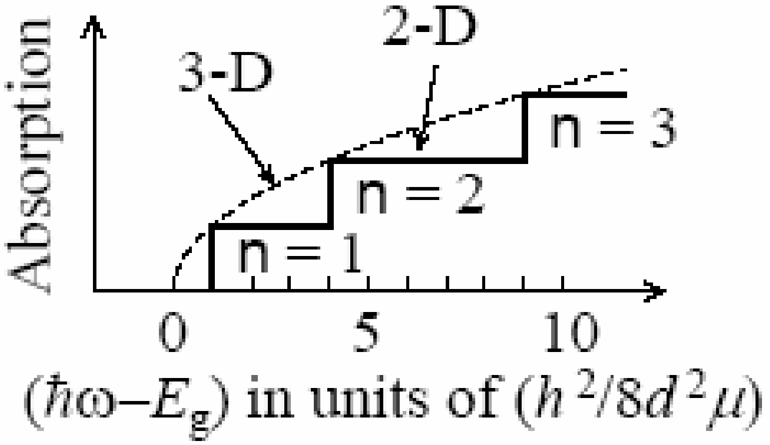
Poor spatial overlap along *z* between electron and hole



The selection rule *Δn* = 0 appears as a result of maximizing the matrix element proportional to the overlap of the electron and hole states.

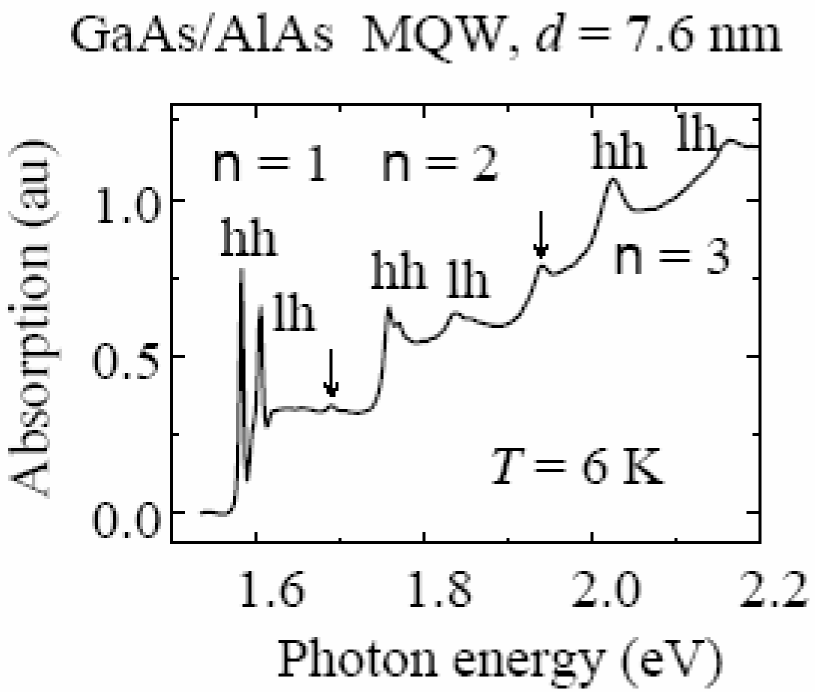
Optical Absorption

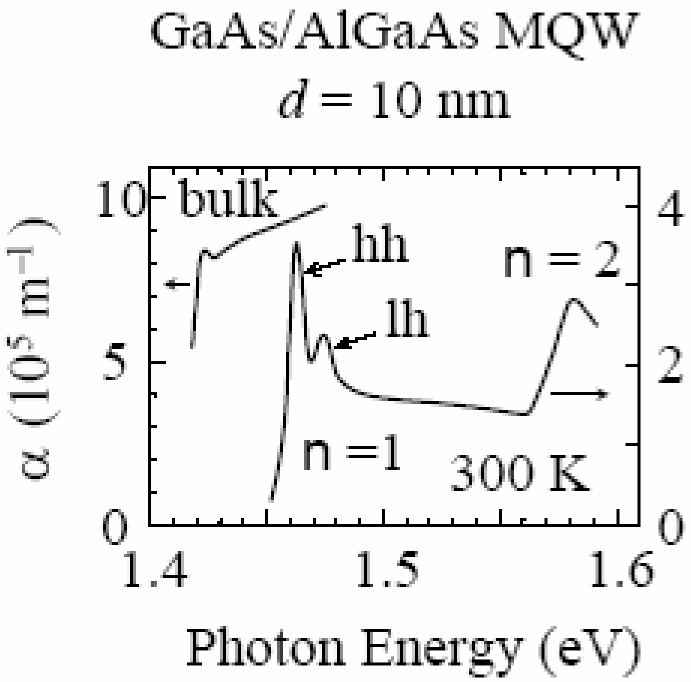




- Absorption $\propto$ density of states
- Density of states constant in 2-D: $g_{2D}(E) = m / \pi\hbar^2$
- Thresholds whenever $\hbar\omega$ exceeds $(E_g + E_{en} + E_{hn})$
- Band edge shifts to $(E_g + E_{e1} + E_{hh1})$

GaAs Quantum Wells


GaAs/AlAs MQW, *d* = 7.6 nm


GaAs/AlGaAs MQW
d = 10 nm

- Excitonic effects enhanced in quantum wells: strong at room temp
- Pure 2-D: $R_X^{2D} = 4 \times R_X^{3D}$
- Typical GaAs quantum well: $R_X \sim 10$ meV $\sim 2.5 \times R_X$ (bulk GaAs)
- Splitting of heavy and light hole transitions