Semiconductors

Semiconductors are materials with a (relatively) small band gap (typically 1eV) between a filled valence band and an empty conduction band.

Chemical potential μ (often called Fermi energy) lies in the band gap.

Insulators at T=0, with a small density of electrons excited at finite temperatures.

Typical semiconductors are Silicon and Germanium
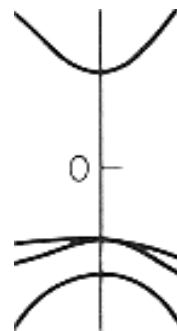
or III-V compounds such as GaAs

2 atoms in primitive basis have 4 electrons each (or 3 + 5); 8 electrons fill 4 bands made of s and p orbitals

Band Structure of Semiconductors

Plot Energy versus k. E_F separates filled and empty states
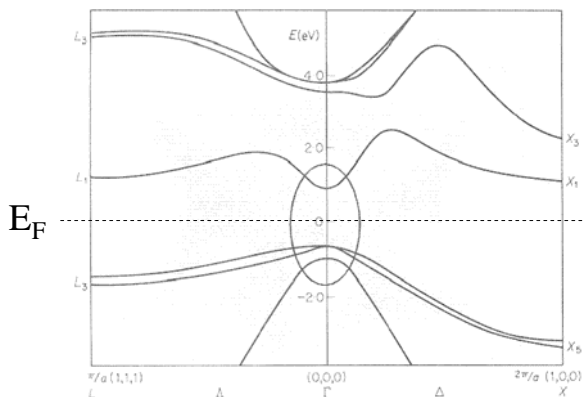
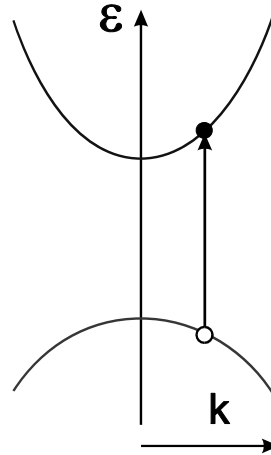Electrons are only excited in a very limited region of energy

E_F

Energy levels of electrons and holes

Close to the band edge minima and maxima we can write:

conduction band $\varepsilon = E_G + \dfrac{\hbar^2 k^2}{2m_e}$

valence band $\varepsilon = -\dfrac{\hbar^2 k^2}{2m_h}$

Band gap determines the optical properties - strong absorption when $h\nu > E_G$
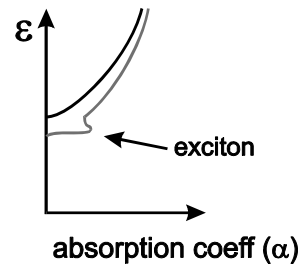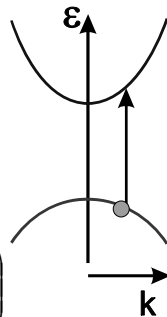
Optical absorption

Excitation promotes an electron from the valence band to conduction band.

An empty state left in valence band is known as a hole.

$\Delta\varepsilon = E_G + \dfrac{\hbar^2 k^2}{2m_e} - \left(-\dfrac{\hbar^2 k^2}{2m_h}\right)$

$\Delta\varepsilon = \left(E_G + \dfrac{\hbar^2 k^2}{2m_e}\right) + \dfrac{\hbar^2 k^2}{2m_h}$
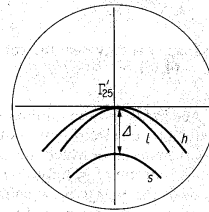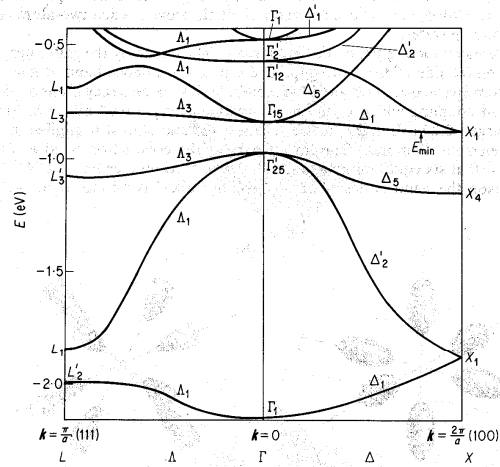
Electron energy   Hole energy

exciton

absorption coeff (α)

Absorption above the band gap is strong $\sim 10^6$ m^{-1}

If band minima and maxima are at different points then we have an indirect semiconductor.

The classic example is silicon.

This affects the optical properties such as absorption where $\Delta k \approx 0$

Hole picture

Remove one electron from a filled band and electricity can be conducted by the movement of all of the electrons present. The sum of this motion is equivalent to one positively charged particle: **a hole**

	filled band	Electron state removed	part-filled band	hole
crystal momentum	0	k_e	$-k_e$	$k_h = -k_e$
Energy	0	$\varepsilon_e(k_e)$	$-\varepsilon_e(k_e)$	$\varepsilon_h(k_h) = -\varepsilon_e(k_e)$

Holes and their properties

velocity
$$v_h = \frac{1}{\hbar}\frac{\partial \varepsilon}{\partial k} = v_e$$

Work done
by a force F
$$\frac{\partial \varepsilon}{\partial t} = F v_g = \frac{F}{\hbar}\frac{\partial \varepsilon}{\partial k}$$

$$= \frac{\partial \varepsilon}{\partial k}\frac{\partial k}{\partial t}$$

$$\therefore \ \hbar\frac{\partial k_e}{\partial t} = F = -\hbar\frac{\partial k_h}{\partial t}$$

Rate of change of momentum is *opposite* sign for holes

$$\hbar\frac{\partial k_e}{\partial t} = F = -e\,(\mathbf{E} + \mathbf{v}\times\mathbf{B}) \qquad \hbar\frac{\partial k_h}{\partial t} = +e\,(\mathbf{E} + \mathbf{v}\times\mathbf{B})$$

Effective masses

Force accelerates the electron or hole:

$$\frac{\partial v_g}{\partial t} = \frac{1}{\hbar}\frac{\partial^2 \varepsilon}{\partial k\,\partial t} = \frac{1}{\hbar}\frac{\partial^2 \varepsilon}{\partial k^2}\frac{\partial k}{\partial t} \qquad but \ \ F = \hbar\frac{\partial k}{\partial t}$$

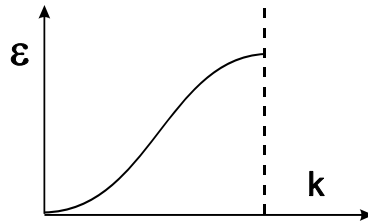$$\frac{\partial v_g}{\partial t} = \frac{1}{\hbar^2}\frac{\partial^2 \varepsilon}{\partial k^2}F = \frac{F}{m*}$$

Effective mass:
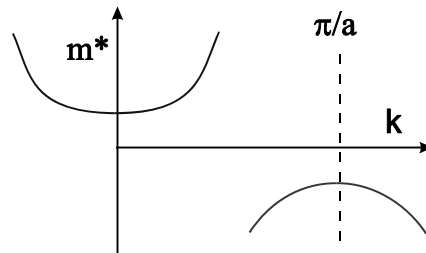Negative for holes unless
we say charge is positive

$$\boxed{\frac{1}{m*} = \frac{1}{\hbar^2}\frac{\partial^2 \varepsilon}{\partial k^2}}$$

Meaning of the effective mass

$$m^* = \hbar^2 \left(\frac{\partial^2 \varepsilon}{\partial k^2} \right)^{-1}$$

Effective mass changes as we move through a band in k-space

positive (electron-like) at the bottom, becoming **negative** (hole-like) at the top

Typical values in semiconductors are in the range 0.01 to 0.5 m_e

Concentrations of Electrons and Holes

Calculate carrier density from density of states and distribution function:

$$n = \int_{E_G}^{\infty} g(\varepsilon) \, f_{F-D}^e(\varepsilon) \, d\varepsilon \ , \quad \text{where } \varepsilon = E_G + \frac{\hbar^2 k^2}{2m_e}$$

For most semiconductors the chemical potential, μ, (often also called the Fermi Energy (E_F)), lies in the band gap so:

$$f_{F-D}^e \approx \exp\left(\frac{\mu - \varepsilon}{k_B T}\right) \quad \text{and} \quad g(\varepsilon) = \frac{1}{2\pi^2} \left(\frac{2m_e}{\hbar^2} \right)^{3/2} (\varepsilon - E_G)^{1/2}$$

giving:

$$n = \frac{1}{2\pi^2} \left(\frac{2m_e}{\hbar^2} \right)^{3/2} e^{\left(\frac{\mu}{k_B T} \right)} \int_{E_G}^{\infty} (\varepsilon - E_G)^{1/2} \, e^{-\frac{\varepsilon}{k_B T}} \, d\varepsilon$$

$$n = \frac{1}{2\pi^2} \left(\frac{2m_e k_B T}{\hbar^2} \right)^{3/2} e^{\left(\frac{\mu - E_G}{k_B T} \right)} \int_0^\infty x^{1/2} e^{-x} dx, \quad \text{with} \quad x = \frac{\varepsilon - E_G}{k_B T}$$

$$n = 2 \left(\frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/2} e^{\left(\frac{\mu - E_G}{k_B T} \right)} = N_C e^{\left(\frac{\mu - E_G}{k_B T} \right)}$$

Effective number of conduction band states at $\varepsilon = E_g$

Now use same procedure for holes

$$p = \int_{-\infty}^0 g(\varepsilon) f_{F-D}^h(\varepsilon) d\varepsilon, \quad \text{where} \quad \varepsilon = -\frac{\hbar^2 k^2}{2m_h}$$

$$f_{F-D}^h = 1 - f_{F-D}^e = 1 - \frac{1}{e^{(\varepsilon - \mu)/k_B T} + 1} = \frac{1}{e^{(\mu - \varepsilon)/k_B T} + 1} \approx e^{(\varepsilon - \mu)/k_B T}$$

$$p = \frac{1}{2\pi^2} \left(\frac{2m_h}{\hbar^2} \right)^{3/2} e^{\left(\frac{-\mu}{k_B T} \right)} \int_{-\infty}^0 (-\varepsilon)^{1/2} e^{\frac{\varepsilon}{k_B T}} d\varepsilon$$

$$p = \frac{1}{2\pi^2} \left(\frac{2m_h k_B T}{\hbar^2} \right)^{3/2} e^{\left(\frac{-\mu}{k_B T} \right)} \int_0^\infty x^{1/2} e^{-x} dx, \quad \boxed{\text{with} \quad x = \frac{-\varepsilon_e}{k_B T} = \frac{\varepsilon_h}{k_B T}}$$

$$p = 2 \left(\frac{m_h k_B T}{2\pi \hbar^2} \right)^{3/2} e^{\left(\frac{-\mu}{k_B T} \right)} = N_V e^{\left(\frac{-\mu}{k_B T} \right)}$$

Effective number of valence band states at $\varepsilon = 0$

Law of Mass Action

Densities of electrons
and holes depend on μ

$$n = N_C e^{\left(\frac{\mu - E_G}{k_B T}\right)}, \qquad p = N_V e^{\left(\frac{-\mu}{k_B T}\right)}$$

μ is determined by density of charge introduced by impurities
(doping)

Product np is independent of μ: Law of Mass Action

$$np = 4\left(\frac{k_B T}{2\pi \hbar^2}\right)^3 (m_e m_h)^{3/2} e^{\left(\frac{-E_G}{k_B T}\right)} = N_C N_V e^{\left(\frac{-E_G}{k_B T}\right)}$$

Intrinsic Semiconductors

A semiconductor is said to be intrinsic if it is undoped, and
the only source of electrons and holes is by thermal
excitation from the valence band to the conduction band.

In this case:

$$n = p = n_i = \sqrt{N_C N_V}\; e^{\left(\frac{-E_G}{2k_B T}\right)} = 2\left(\frac{k_B T}{2\pi \hbar^2}\right)^{3/2} (m_e m_h)^{3/4} e^{\left(\frac{-E_G}{2k_B T}\right)}$$

We can use this relation to measure the Band Gap, by
measuring the carrier densities from the Hall Effect

At low temperatures $n_i \to 0$ and impurities are important

Doping Semiconductors

We can control the numbers of electrons and holes in a semiconductor by adding impurities which **dope** the material.

Donors donate an electron to make the material more n-type. A typical example is by adding a group V element (such as As or P) to a group IV semiconductor such as silicon.

Four of the electrons participate in the sp^3 bonds as if they were from silicon, but the fifth electron is left over. Extra charge on P nucleus creates a +ive core, and the fifth electron can be bound to this, but the binding is weak.

Shallow Donors

Impurity binding looks like a hydrogen atom

Binding energy
$$R^* = \frac{e^4 m_e^*}{2(4\pi\varepsilon_r\varepsilon_0\hbar)^2} = \frac{m_e^*/m_e}{\varepsilon_r^2} R_0$$

Binding energy is very small because:

(i) the effective mass is small (typically $m^* = 0.1\ m_e$)

(ii) The wavefunction is large (much more than the crystal unit cell), so we must include the relative dielectric constant of the medium ε_r, - typically ≈ 10.

$$\therefore\ R^* \approx 10^{-3} R_0 = 13.6\ meV\ (155\ K)$$

Acceptors

Dope semiconductors with holes by adding group III elements to a group IV material. e.g. put Ga into silicon.

One valence electron is missing. This creates a vacant state, a hole, which binds to the ion core of the Ga which is negatively charged.

Binding energy is:
$$R^* = \frac{e^4 m_h^*}{2(4\pi\varepsilon\varepsilon_0\hbar)^2} = \frac{m_h^*/m_e}{\varepsilon^2} R_0$$

Where is the energy level?

Ionized Acceptor or Donor is a free hole or electron at the top or the bottom of the band

$\therefore$ Acceptor is R* above the valence band edge

   Donor is R* below the conduction band edge

Extrinsic Carrier Densities

Density of impurities (e.g. Donors) usually much less than N_C, N_V. Impurities can be ionized N_d^+, or neutral N_d^0 so:
$$N_d = N_d^+ + N_d^0$$

Using charge neutrality we have:
$$n = p + N_d^+$$

Simple argument:

At high (e.g. Room) Temperature kT > R* therefore all donors will be ionized but the density of holes created by excitation across the band gap is still small

$$\therefore n \approx N_d^+ \approx N_d$$

Chemical Potential μ

At high (room) temperature most impurities are ionized

$$\therefore n \approx N_d^+ \approx N_d$$

μ lies below the Donor level so that most impurities are empty (ionized), but is still close to conduction band.

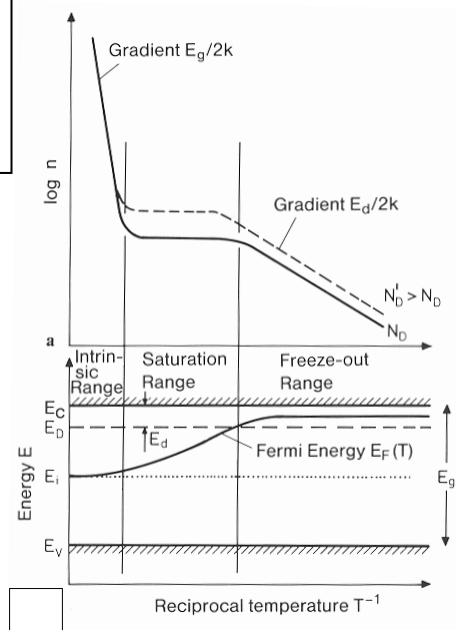**Minority Carriers**

By Law of Mass action the (very small) density of holes is:

$$p = n_i(T)^2/N_d$$

<table>
<tr><td>

Temperature dependent density and chemical potential

Density is constant in region around room temperature

High temperature gives intrinsic behaviour

</td><td>

</td></tr>
</table>

Conductivity of Semiconductors

$$\sigma = ne\mu_e + pe\mu_h , \quad \mu = \frac{e\tau}{m^*}$$

μ is the mobility, which is defined by $v = \mu E$, the dift velocity per unit electric field.
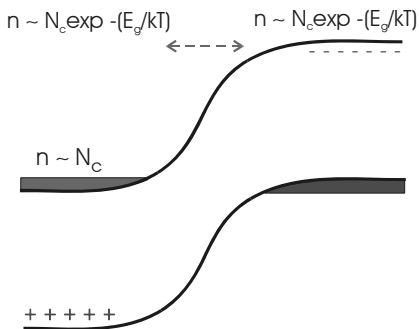
Conductivity is dominated by variation in densities.

Mobility is determined by scattering rate:

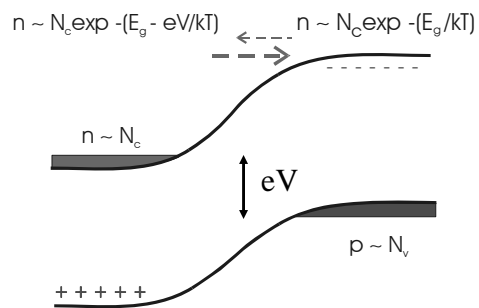Low T: impurity scattering gives $\mu \sim T^{3/2}$

High T: phonon scattering gives $\mu \sim T^{-3/2}$

p-n junction

- Unbiased junction

- Forward bias of V

$n \sim N_c \exp -(E_g/kT)$ $n \sim N_c \exp -(E_g/kT)$

$n \sim N_c$

$+ + + + +$

$n \sim N_c \exp -(E_g - eV/kT)$ $n \sim N_c \exp -(E_g/kT)$

$n \sim N_c$

eV

$p \sim N_v$

$+ + + + +$

p-n junctions

What is current flow across junction? $\quad j = ne\text{v}$

What is v? - due to diffusion of carriers with
diffusion coefficient D and lifetime τ.

Diffusion length $L = \sqrt{D\tau} \quad$ so $\quad v = \dfrac{L}{\tau} = \sqrt{\dfrac{D}{\tau}}$

Electron current/area from:

(i) p $\rightarrow$ n $\qquad j^e_{p\rightarrow n} = e\sqrt{\dfrac{D}{\tau}}\, N_C\, e^{-\frac{E_G}{k_B T}}$

(ii) n $\rightarrow$ p $\qquad j^e_{n\rightarrow p} = e\sqrt{\dfrac{D}{\tau}}\, N_C\, e^{-\frac{E_G}{k_B T}}$

(iii) Total $\qquad j^e_{Total} = e\sqrt{\dfrac{D}{\tau}}\, N_C\, e^{-\frac{E_G}{k_B T}}\,(1-1) = 0$

Add bias voltage V - This only affects electron current
from n $\rightarrow$ p

Electron current/area from:

(i) p $\rightarrow$ n $\quad j^e_{p\rightarrow n} = e\sqrt{\dfrac{D}{\tau}}\, N_C\, e^{-\frac{E_G}{k_B T}}$

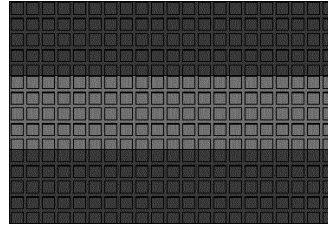(ii) n $\rightarrow$ p $\quad j^e_{n\rightarrow p} = e\sqrt{\dfrac{D}{\tau}}\, N_C\, e^{\frac{-E_G + eV}{k_B T}}$

(iii) Total $\quad j^e_{Total} = e\sqrt{\dfrac{D}{\tau}}\, N_C\, e^{-\frac{E_G}{k_B T}}\,(e^{\frac{eV}{k_B T}} - 1) = I_0\,(e^{\frac{eV}{k_B T}} - 1)$

An equivalent pair of currents flows for holes with the

same formulae, except for masses and lifetimes of holes

$$\left(D = \mu k_B T / e, \text{ the Einstein relation}\right)$$

Low Dimensional Structures and Materials

- Anisotropic Materials
- Artificial layered structures - Quantum Wells and Superlattices

Layers may be only a few atoms thick

- Electric or Magnetic Fields applied in one direction.
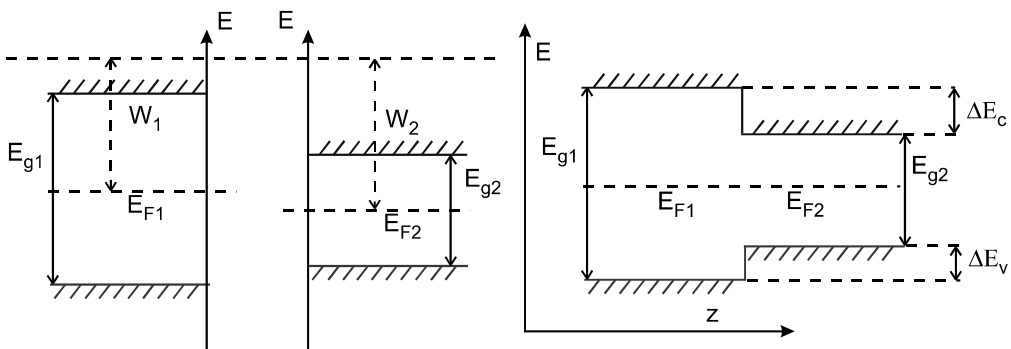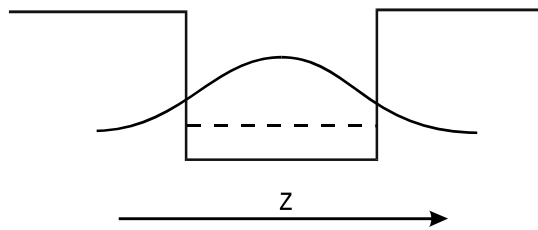
Heterojunctions

Energy levels for 2 different semiconductors

Energy line up at junction of two (undoped) materials

Reduced Dimensionality

Quantum Well removes 1 Dimension by quantization

z

Electron is bound in well and can only move in plane

2-D system - motion in x, y plane

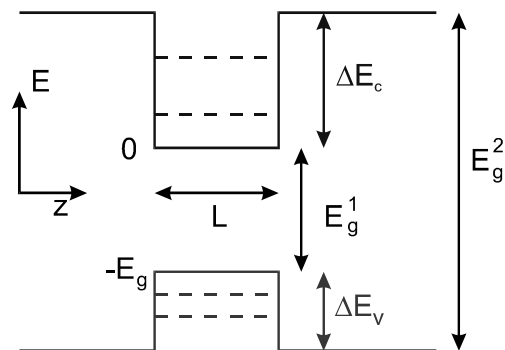# Quantum Well - Type I

Typical Materials:

1: GaAs   2: $(Al_{0.35}Ga_{0.65})As$
(E_g = 1.5 eV)   (E_g = 2.0 eV)

Energy levels are quantized in z-direction with values E_n for both electrons and holes $\therefore$

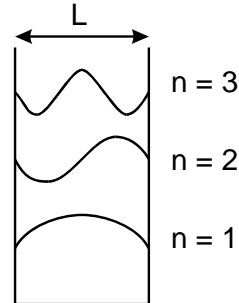$$E = E_n + \hbar^2 k_\perp^2/2m^*$$

$\uparrow$ $\uparrow$

1-D   2-D

Infinite well - Particle in a box

- 1-D Motion in z-direction

$$-\frac{\hbar^2}{2m^*}\frac{d^2\psi}{dz^2}=E\psi \qquad \psi_n=A\sin\frac{n\pi z}{L}$$

$$E_n=\frac{\hbar^2}{2m^*}\left(\frac{n\pi}{L}\right)^2+\frac{\hbar^2 k_\perp^2}{2m^*}$$

L

n = 3

n = 2

n = 1

Typical values   L = 10 nm, m_e^* = 0.07 m_e $\rightarrow$ E_n = 54 n^2 meV

∴System is Two-Dimensional when:	
E_2 - E_1	> kT
162 meV	25 meV at 300 K

Density of States   g(k)dk   g(ε)dε

Travelling waves
e^{ikx} ($e^{i\mathbf{k.r}}$)

Periodic boundary condit.
$\psi(x) = \psi(x + L)$

∴ $e^{ikL} = 1$ $\rightarrow$ k = $\pm 2n\pi/L$
$\rightarrow$ $\delta k = 2\pi/L$

$\varepsilon = \hbar^2 k^2/2m^*$,
$d\varepsilon = (\hbar^2/2m^*)$ 2k dk

3-D

$$\frac{4\pi k^2 dk}{(2\pi/L)^3} \qquad \frac{V}{(2\pi)^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\varepsilon^{1/2}d\varepsilon$$

2-D

$$\frac{2\pi k\ dk}{(2\pi/L)^2} \qquad \frac{A}{4\pi}\left(\frac{2m^*}{\hbar^2}\right)d\varepsilon$$

1-D

$$\frac{2dk}{2\pi/L} \qquad \frac{L}{2\pi}\left(\frac{2m^*}{\hbar^2}\right)^{1/2}\varepsilon^{-1/2}d\varepsilon$$
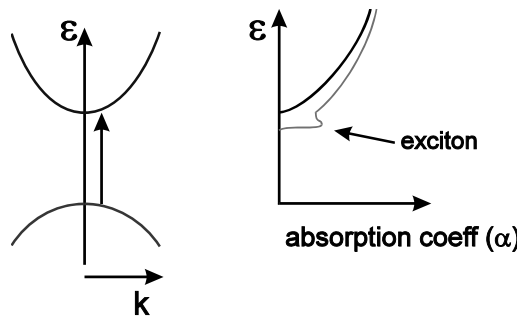
ε

g(ε)

ε

g(ε)

ε

g(ε)

Optical Properties

3-D

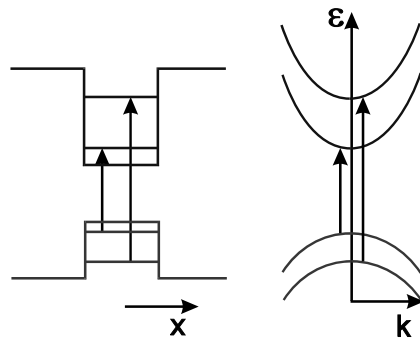Absorption coefficient is proportional to the density of states:

$$\therefore \alpha \sim \varepsilon^{1/2}$$

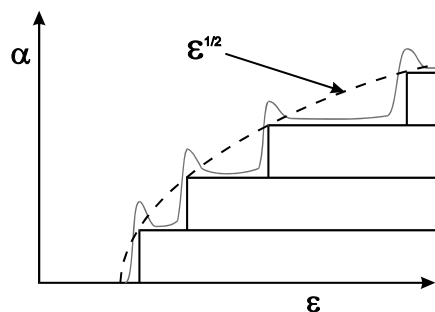Modified close to the band gap due to '**excitons**'

Multiple Band gaps -
    Band gap shift -
    Sharper edge

2-D - Big Changes

For wide wells the sum of many 2-D absorptions becomes equivalent to the 3-D absorption shape ($\varepsilon^{1/2}$)
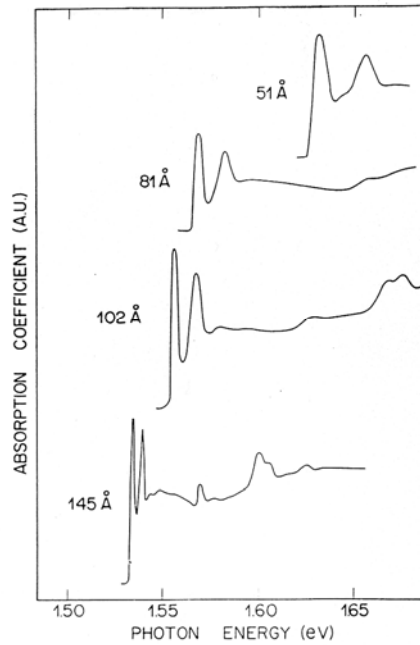
Correspondence principle.

GaAs/Al$_{0.35}$Ga$_{0.65}$As Quantum Well absorption

- Sharp peaks due to excitons
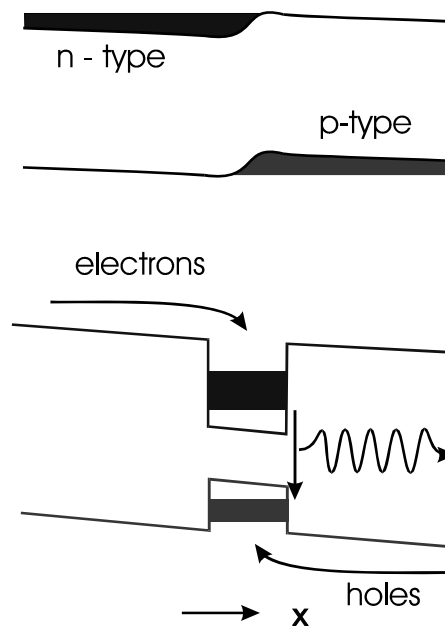- peaks doubled due to heavy and light holes

- Sharp peaks due to excitons
- peaks doubled due to heavy and light holes

Semiconductor lasers

Forward biased p-n junction

Quantum Well laser
Fibre Optic Communications,
CD players, laser pointers

How do we achieve low dimensionality?

Naturally anisotropic crystals

Controlled growth of layers   and/or   apply external potential

Deposit thin layers of single crystals to create
    'heterostructures'

Two Main techniques:

I) Molecular Beam Epitaxy (MBE)

II) Metal Organic Vapour Phase Epitaxy (MOVPE)

**Molecular Beam Epitaxy
    (MBE)**

- Ultra High Vacuum
  evaporation of molecular
  species of elements
  (<u>Molecular Beam</u>)

- <u>Epitaxy</u>   - maintaining
  crystal structure of the
  'substrate' - which is a
  single crystal