Lecture contents

- Semiconductor statistics

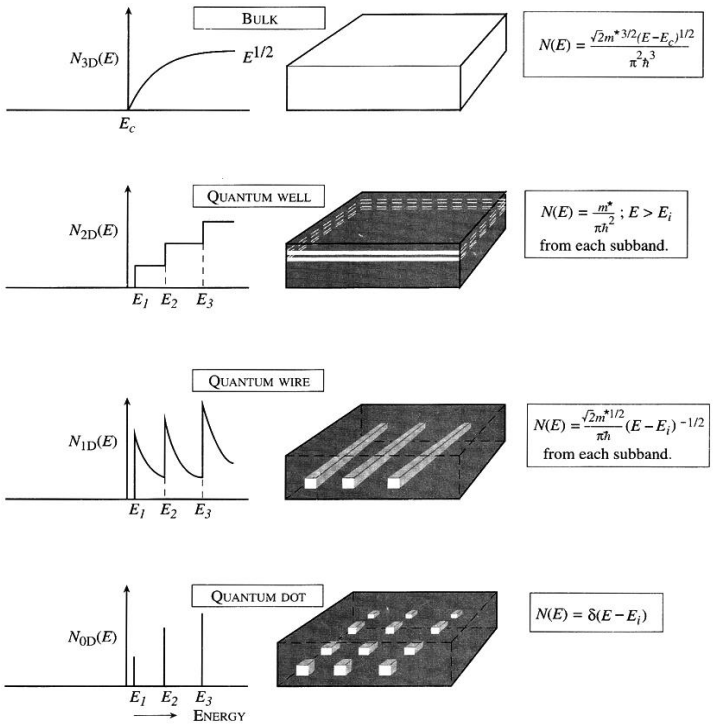
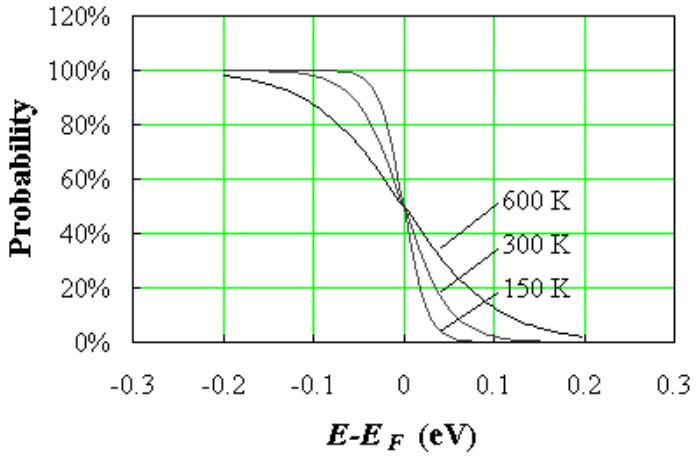


Figure 3.13: A schematic of how the density of states change as a function of dimensionality.



Filling the empty bands: Distribution function

- Electron concentration at the energy *E* (Density of states) x (distribution function):

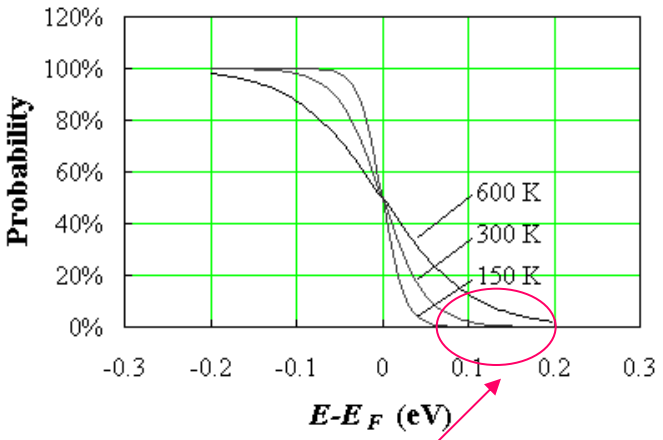
$$n(E) = N(E)\, f(E)$$

- Pauli Exclusion Principle: No two electrons (fermions) can have identical quantum numbers.

- Electrons follow Fermi-Dirac statistics.

- Fermi-Dirac distribution function:

$$f_{FD}(E) = \frac{1}{e^{\frac{E-E_F}{k_B T}} + 1}$$



In the non-degenerate case (electron energies are far from E_F):
Boltzmann distribution function may be used:

$$E - E_F >> k_B T$$

$$f_B(E) = e^{-(E-E_F)/k_B T}$$

Statistics of carriers: General

Electron concentration at the energy E (Density of states) x (distribution function):

$$n(E) = N(E)\,f(E)$$

Electron concentration in the energy range E to $E+dE$ close to the conduction band minimum:

$$n(E)dE = \frac{\sqrt{2}m_e^{*3/2}}{\pi^2\hbar^3}\frac{(E-E_C)^{1/2}dE}{\exp\left(\frac{E-E_F}{k_BT}\right)+1}$$

Total electron concentration in the conduction band

$$n = \frac{\sqrt{2}m_e^{*3/2}}{\pi^2\hbar^3}\int_{E_c}^{\infty}\frac{(E-E_C)^{1/2}dE}{\exp\left(\frac{E-E_F}{k_BT}\right)+1} \equiv \frac{\sqrt{2}m_e^{*3/2}}{\pi^2\hbar^3}(k_BT)^{3/2}\int_0^{\infty}\frac{x^{1/2}dx}{\exp(x-\eta_c)+1} =$$

$$x = \frac{E-E_C}{k_BT} \qquad \eta_c = \frac{E_F-E_C}{k_BT}$$

$$= 2\left(\frac{m_e^*k_BT}{2\pi\hbar^2}\right)^{3/2}\frac{2}{\sqrt{\pi}}\int_0^{\infty}\frac{x^{1/2}dx}{\exp(x-\eta_c)+1}$$

General equation for **3D** carrier concentration (effective density of states) x (Fermi integral of ½ order):

$$n = N_C\Phi_{1/2}(\eta_c)$$

General equation for **2D** carrier concentration (effective density of states) x (Fermi integral of zero order):

$$n_s = \frac{m_e^*}{\pi\hbar^2}(k_BT)\ln\left(1+\exp(\eta_c)\right)$$

DOS Effective DOS

Statistics of carriers: General

The same is true for holes in the valence band:

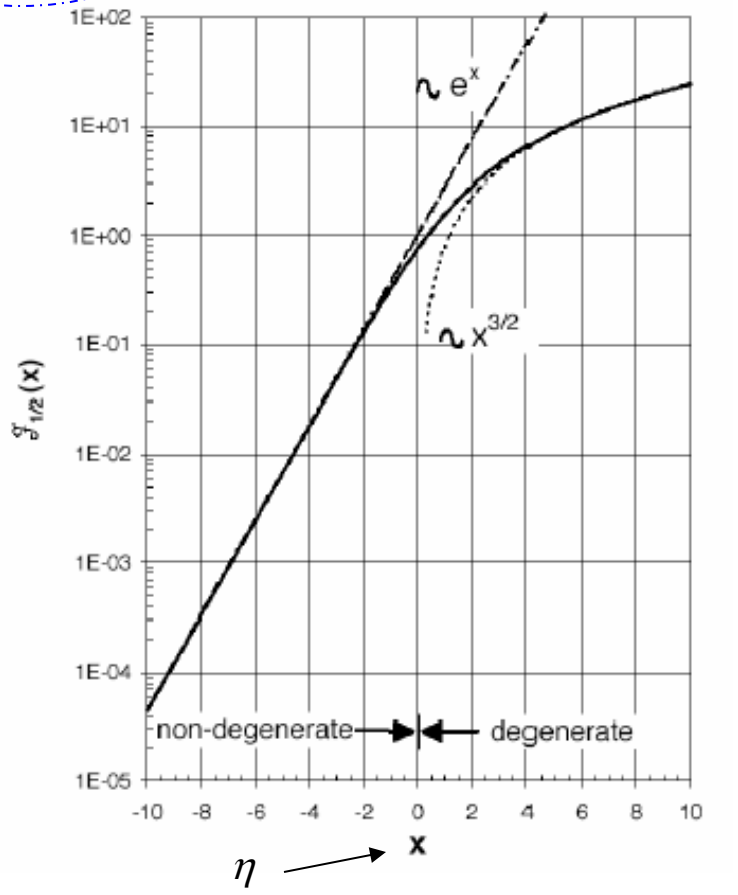
$$p = 2\left(\frac{m_h^* k_B T}{2\pi\hbar^2}\right)^{3/2} \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2}\,dx}{\exp(x-\eta_V)+1}$$

$$\Phi_{1/2}(\eta)$$

$$p = N_V \Phi_{1/2}(\eta_V)$$

Effective density of states of electrons (or holes)

$$N_c = 2.512 \times 10^{19} \left(\frac{m_{dn}}{m_e}\right)^{3/2} \left(\frac{T}{300}\right)^{3/2} \left(cm^{-3}\right)$$



One-to-one correspondence

Concentration of mobile (band) carriers	⇔	Fermi level position

Statistics of carriers: Non-degenerate system

General equation: $$n = N_C \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2} dx}{\exp(x-\eta_c)+1} \qquad x = \frac{E - E_C}{k_B T} \qquad \eta_c = \frac{E_F - E_C}{k_B T}$$

If all the C.B. energies are far from Fermi level:
$E_C - E_F >> k_B T$ $(> 3\, k_B T)$:

$$\exp(x-\eta_c) >> 1$$

$$\int_0^\infty \frac{x^{1/2} dx}{\exp(x-\eta_c)+1} = \int_0^\infty e^{-(x-\eta_c)} x^{1/2} dx = e^{\eta_c} \int_0^\infty e^{-x} x^{1/2} dx = e^{\eta_c} \frac{\sqrt{\pi}}{2}$$

Concentration of band carriers

General case:

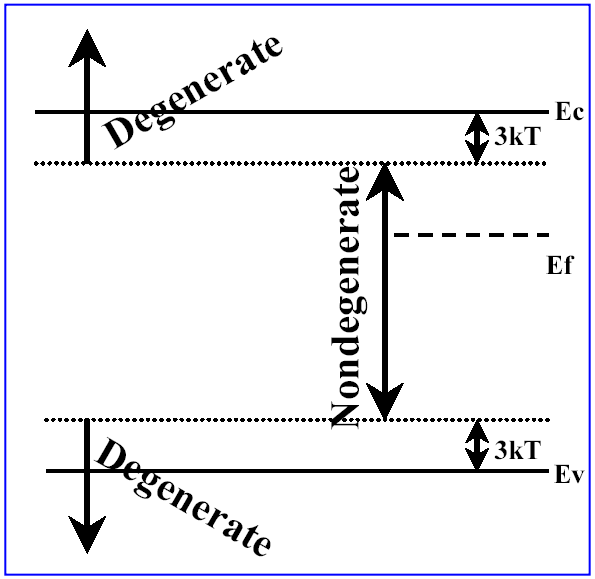
$$n = N_C \Phi_{1/2}(\eta_c)$$

$$p = N_V \Phi_{1/2}(\eta_V)$$

Non-generate system:

$$n = N_C \exp\left(\frac{E_F - E_C}{k_B T}\right)$$

$$p = N_V \exp\left(\frac{E_V - E_F}{k_B T}\right)$$

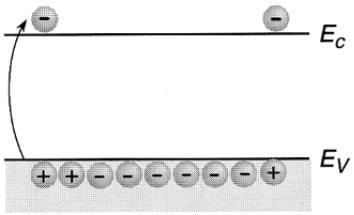


$$np = N_C N_V \exp\left(-\frac{E_g}{k_B T}\right) \equiv n_i^2$$

→ Definition of intrinsic carrier concentration

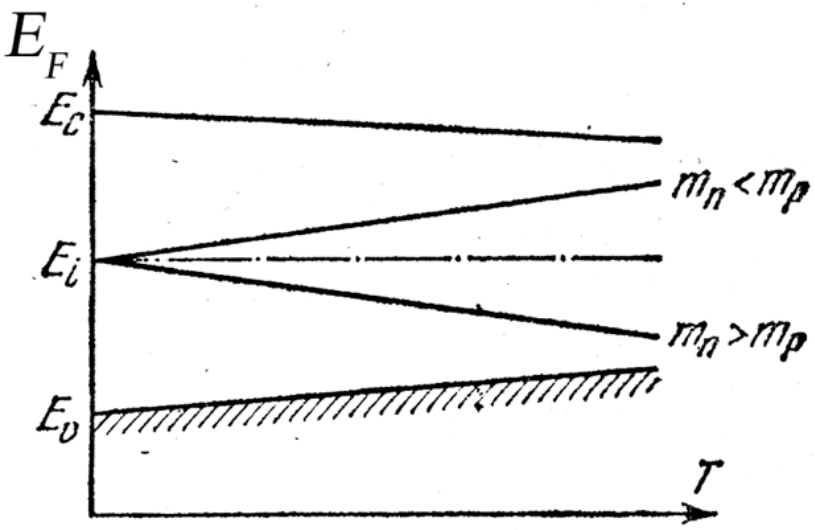
Carriers in intrinsic semiconductors

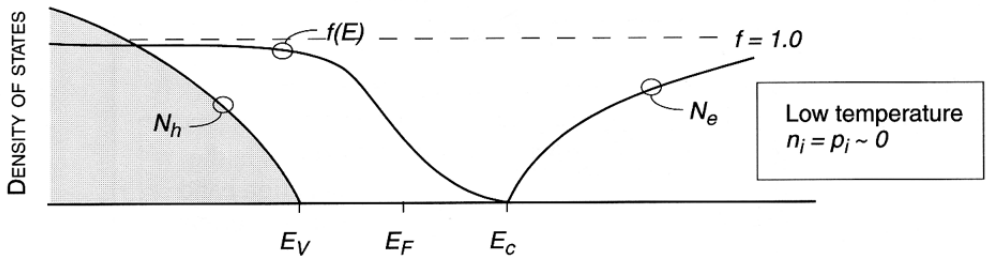
Material	Conduction band effective density (N_C)	Valence band effective density (N_V)	Intrinsic carrier concentration ($n_i = p_i$)
Si (300 K)	2.78×10^{19} cm^{-3}	9.84×10^{18} cm^{-3}	1.5×10^{10} cm^{-3}
Ge (300 K)	1.04×10^{19} cm^{-3}	6.0×10^{18} cm^{-3}	2.33×10^{13} cm^{-3}
GaAs (300 K)	4.45×10^{17} cm^{-3}	7.72×10^{18} cm^{-3}	1.84×10^{6} cm^{-3}



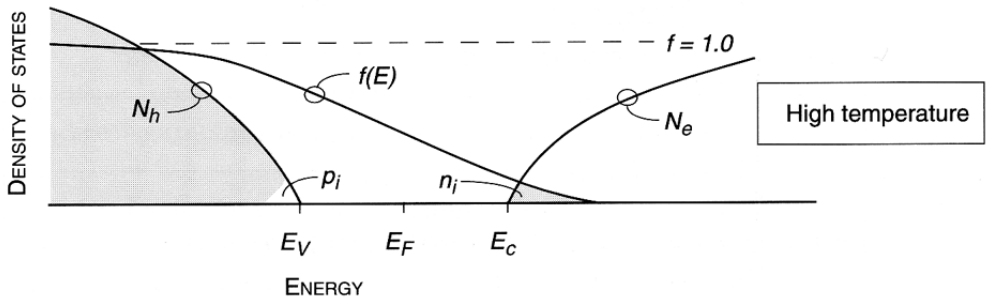
Pure semiconductors
$n = p = n_i = p_i$

Fermi level position in intrinsic semiconductor





Low temperature
$n_i = p_i \sim 0$



High temperature

Effective mass approximation

Small perturbation of periodicity: shallow impurities,
most of "hand-made" structures,
external forces

One-electron Schrödinger equation with weak and slow varying perturbation V_i (Effective mass approximation):

$$\left[\frac{p^2}{2m_0} + V(r) + V_i(r)\right]\psi(r) = E_i\psi(r)$$

And as usual build a solution as a wave packet of Bloch wavefunctions :

$$\psi(r) = \sum_{n,k} c_n(k) e^{ikr} u_{nk}(r)$$

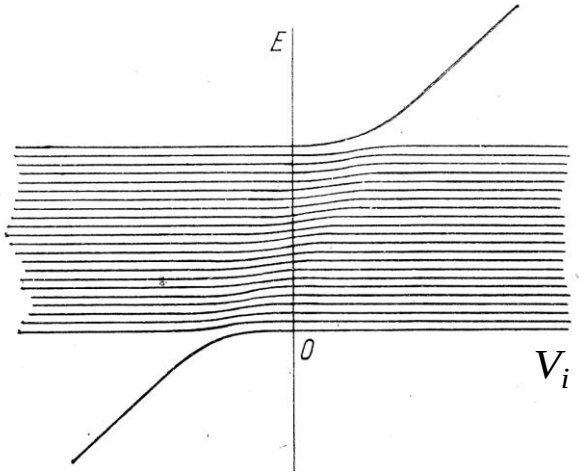
Bloch wave packet: $\psi(r) \approx F(r)u_0(r)$

With dimensions in real and k-space

$$\Delta r \approx \frac{1}{\Delta k} >> a_0$$

Large perturbation of periodicity → other bands need to be considered: deep impurities

Depending on sign of the perturbation, the top-most or bottom-most state splits from the band :



Example of EMA: Hydrogen-like impurity (donor)

Hydrogen-like impurity = shallow impurity

Schrödinger equation for Hydrogen atom with effective mass and screened Coulomb potential:

$$V_i(r) = -\frac{e^2}{\varepsilon r}$$

$$\left[\frac{p^2}{2m^*} - \frac{e^2}{\varepsilon r}\right] F(r) = (E - E_C) F(r)$$

Solution for energy :

$$E_d = \frac{e^4 m^*}{2\varepsilon^2 \hbar^2}\frac{1}{n^2} = Ry\frac{m^*}{m}\frac{1}{\varepsilon^2}\frac{1}{n^2}$$

Effective Ry* :

Envelope function of the ground state :

$$F(r) = \frac{1}{\left(\pi a_B^3\right)^{1/2}} \exp\left(-\frac{r}{a_B}\right)$$

Semiconductor	Binding energy from (4.24) [meV]	Experimental binding energy of common donors [meV]
GaAs	5.72	Si_{Ga}(5.84); Ge_{Ga}(5.88) S_{As}(5.87); Se_{As}(5.79)
InP	7.14	7.14
InSb	0.6	Te_{Sb}(0.6)
CdTe	11.6	In_{Cd}(14); Al_{Cd}(14)
ZnSe	25.7	Al_{Zn}(26.3); Ga_{Zn}(27.9) F_{Se}(29.3); Cl_{Se}(26.9)

From Yu and Cordona, 2003

$$a_B = \frac{\hbar^2}{m_0 e^2}\frac{m_0}{m^*}\varepsilon$$

For donors in GaAs (m^*=0.07m: and ε = 12.6):

Ry* =6.6 meV, a_B = 91 A

When effective mass approximation is applicable ?

Width of the band

$$V_{pert} \ll \langle \psi_0(r) | \Delta V | \psi_0(r-R) \rangle = -\gamma$$

$$\Delta r \approx \frac{1}{\Delta k} >> a_0$$

EMP works fine when perturbation of crystal periodic potential is small in value and large in scale:

- Potentials in device structures
  - Electrostatic potentials
  - Heterostructures
- "Shallow" impurities = Hydrogen-like impurities: those with similar covalent radius that do not disturb periodicity significantly and have similar valence states

When EMA works poorly:

- Impurities and defects with strong disturbance of crystal periodicity = deep levels or deep impurities: vacancies, group I, VII in III-V's, d-metals, low radius.

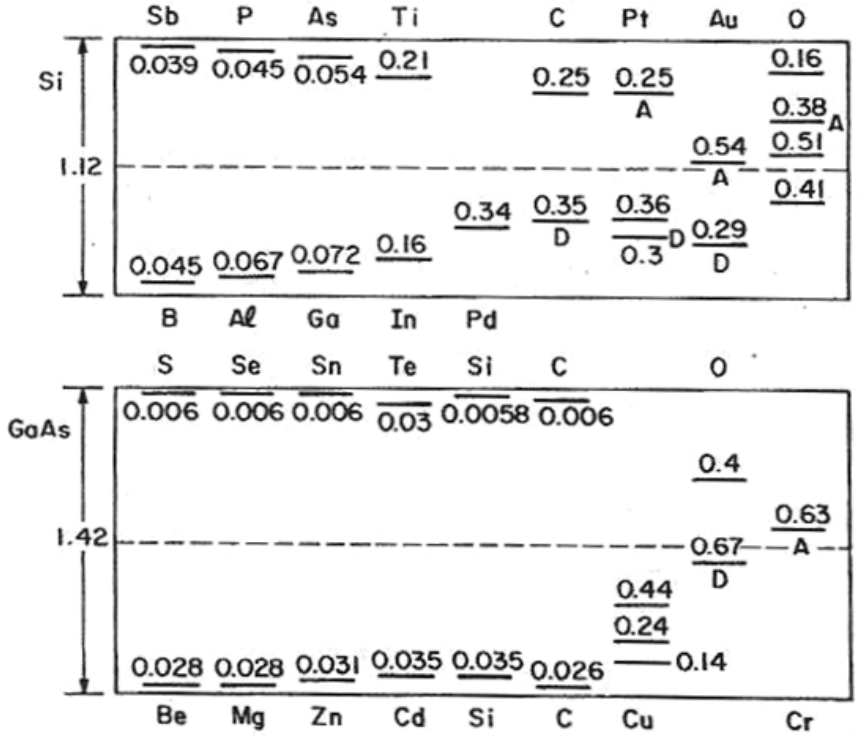
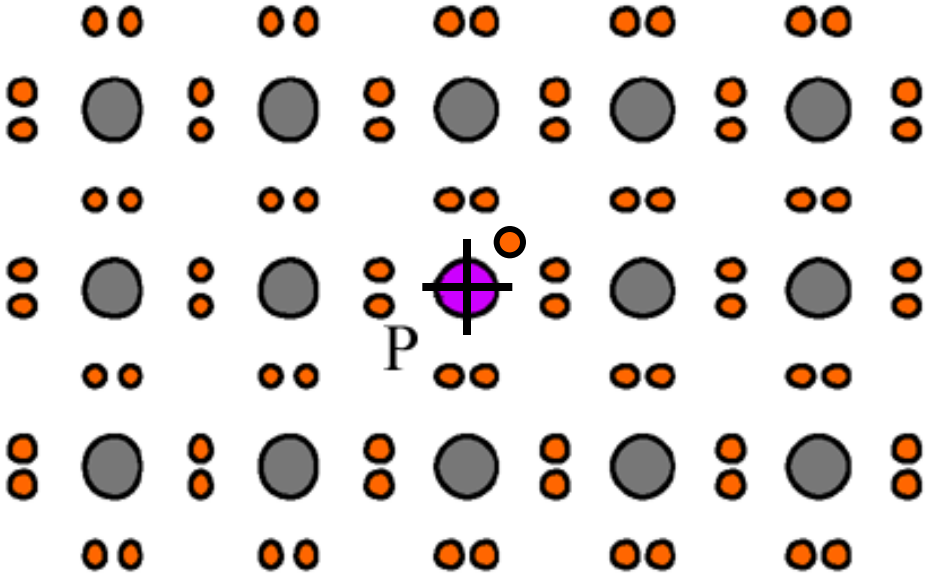


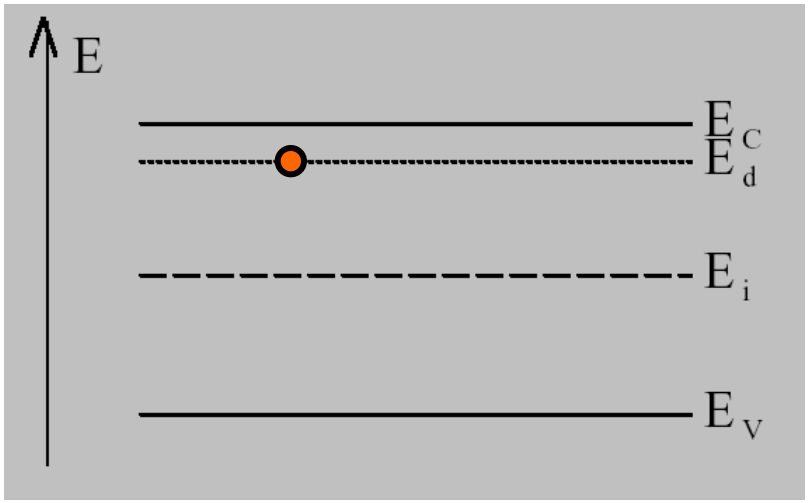
Fig. 18 Measured ionization energies for various impurities in Si and GaAs. The levels below the gap center are measured from the top of the valence band and are acceptor levels unless indicated by D for donor level. The levels above the gap center are measured from the bottom of the conduction band and are donor levels unless indicated by A for acceptor level.[5]

From Milnes, 1973

Donors

Shallow donors:
- usually group V elements in Si and Ge (P, As, Sb)
- group IV elements on group III sublattice in III-V's (Si, Sn in GaAs)
- group VI elements on group V sublattice in III-V's (S, Te, Se in GaAs)

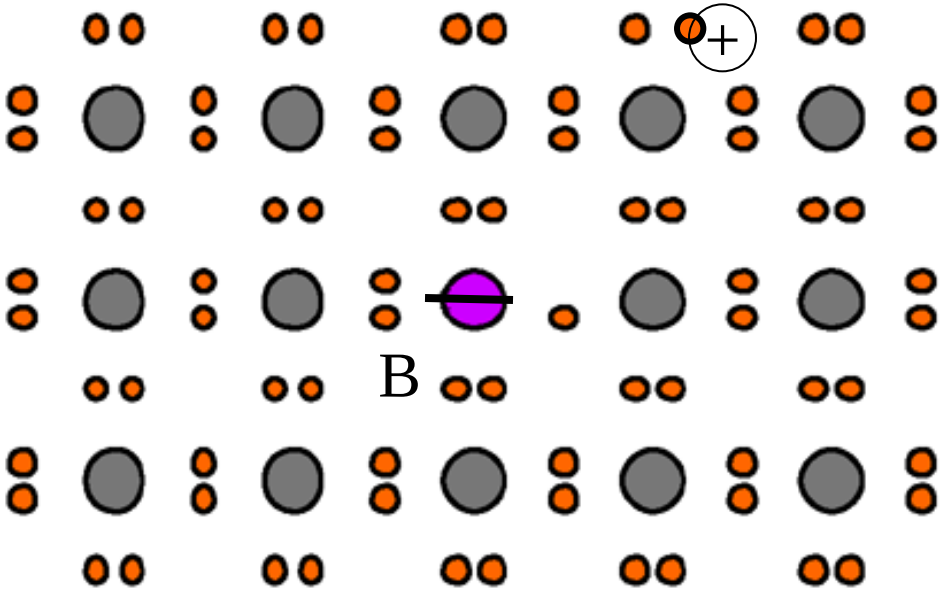


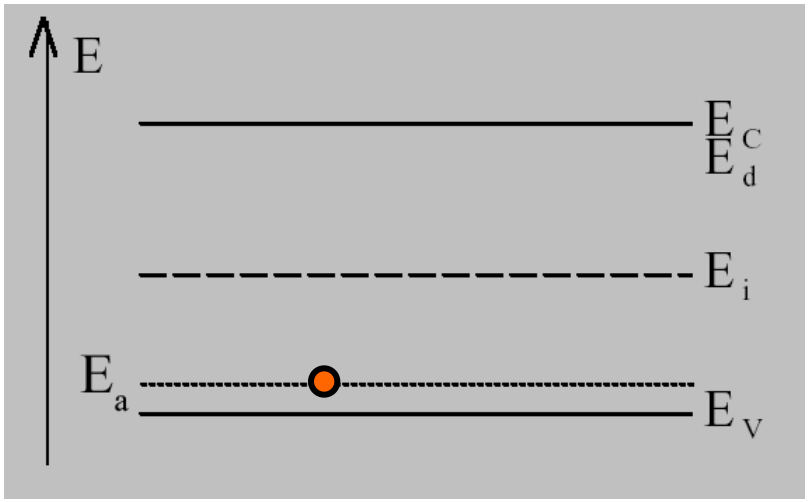


Acceptors

Shallow acceptors: - usually group III elements in Si and Ge (B, Al, Ga, In)
- group II elements on group III sublattice in III-V's (Be, Mg, Zn in GaAs)
- group IV elements on group V sublattice in III-V's (C, Si, Ge in GaAs)

Group IV impurities in III-V's are often amphoteric.





Adding impurities: Extrinsic semiconductors

Simple impurity with two charge states, e.g. simple donor:

$d^0 \leftrightarrow d^+ + e$,

Total donor concentration:

$$N_d = N_d^+ + N_d^0$$

Concentration of neutral (filled with electron) and ionized donors:

$$N_d^0 = gN_d f_{FD}(E_d)$$

$$N_d^+ = N_d(1 - gf_{FD})$$

$$f_{FD}(E) = \frac{1}{e^{\frac{E-E_F}{k_BT}} + 1}$$

d^0 has a degeneracy factor *g*

Ratio of neutral to charged donors:

$$\frac{N_d^0}{N_d^+} = \frac{gf_{FD}}{1 - gf_{FD}} = ge^{\frac{E_F - E_d}{k_BT}}$$

g=2 for simple donors and
g=4 for simple acceptors

Ionization ratio for donors

$$\frac{N_d^+}{N_d} = \frac{1}{1 + g_d e^{\frac{E_F - E_d}{k_BT}}}$$

and acceptors:

$$\frac{N_a^-}{N_a} = \frac{1}{1 + g_a e^{\frac{E_a - E_F}{k_BT}}}$$

Extrinsic semiconductors: no compensation

What happens with Fermi level if semiconductors contains impurities?

In extrinsic semiconductors charge neutrality condition includes ionized impurities (instead of $n = p$ in intrinsic semiconductors):

$$n + N_a^- = p + N_d^+$$

When impurity of one type (say donors) are present:

$$n = p + N_d^+ \approx N_d^+ ; \quad if \ p \ll n$$

Then general equation for Fermi level (needs to be solved for degenerate semiconductors) :

$$N_c \Phi_{1/2}\left(\frac{E_F - E_c}{k_B T}\right) = \frac{N_d}{1 + g_d e^{\frac{E_F - E_d}{k_B T}}}$$

And in non-degenerate case (Δ – ionization energy):

$$n = \frac{N_d}{1 + g_d \frac{n}{N_c} e^{\frac{\Delta_d}{k_B T}}}$$

or

$$n = \frac{n_1}{2}\left(\sqrt{\frac{4N_d}{n_1} + 1} - 1\right) \quad \text{with} \quad n_1 = \frac{N_c}{g_d} e^{-\frac{\Delta_d}{k_B T}}$$

Fermi level position (non-degenerate) using $n = N_C \exp\left(\frac{E_F - E_C}{k_B T}\right)$

$$E_F = E_C + k_B T \ln \frac{n_1}{2N_c}\left(\sqrt{\frac{4N_d}{n_1} + 1} - 1\right)$$

Extrinsic semiconductors: no compensation

At high temperatures ($k_B T > \Delta_d$), for $\frac{4N_d}{n_1} << 1$

$$n = N_d$$

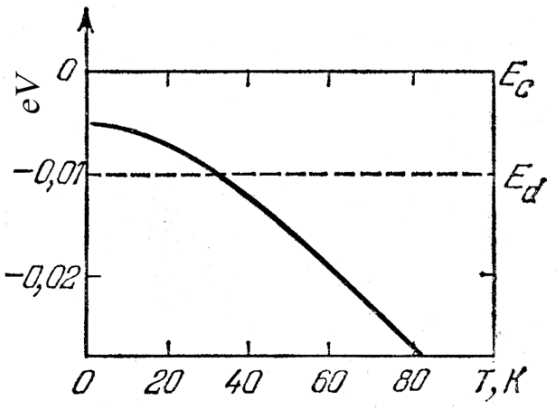
At low temperatures, for

$$\frac{4N_d}{n_1} >> 1, \quad or \quad n << N_d$$

Fermi level position in n-Ge (uncompensated)

Fermi level

$$E_F = E_C - \frac{\Delta_d}{2} + \frac{k_B T}{2} \ln \frac{N_d}{g_d N_C}$$



and concentration

$$n = \sqrt{\frac{N_d N_C}{g_d}} e^{-\frac{\Delta_d}{2k_B T}}$$

Carriers are "freezing out"

Extrinsic semiconductors with compensation (results for a non-degenerate case)

At high temperatures, for $\frac{4(N_d - N_A)n_1}{(N_A + n_1)^2} >> 1$ and $n_1 >> N_A$

$$n = N_d - N_A$$

What is the accuracy of assumption $p << n$?

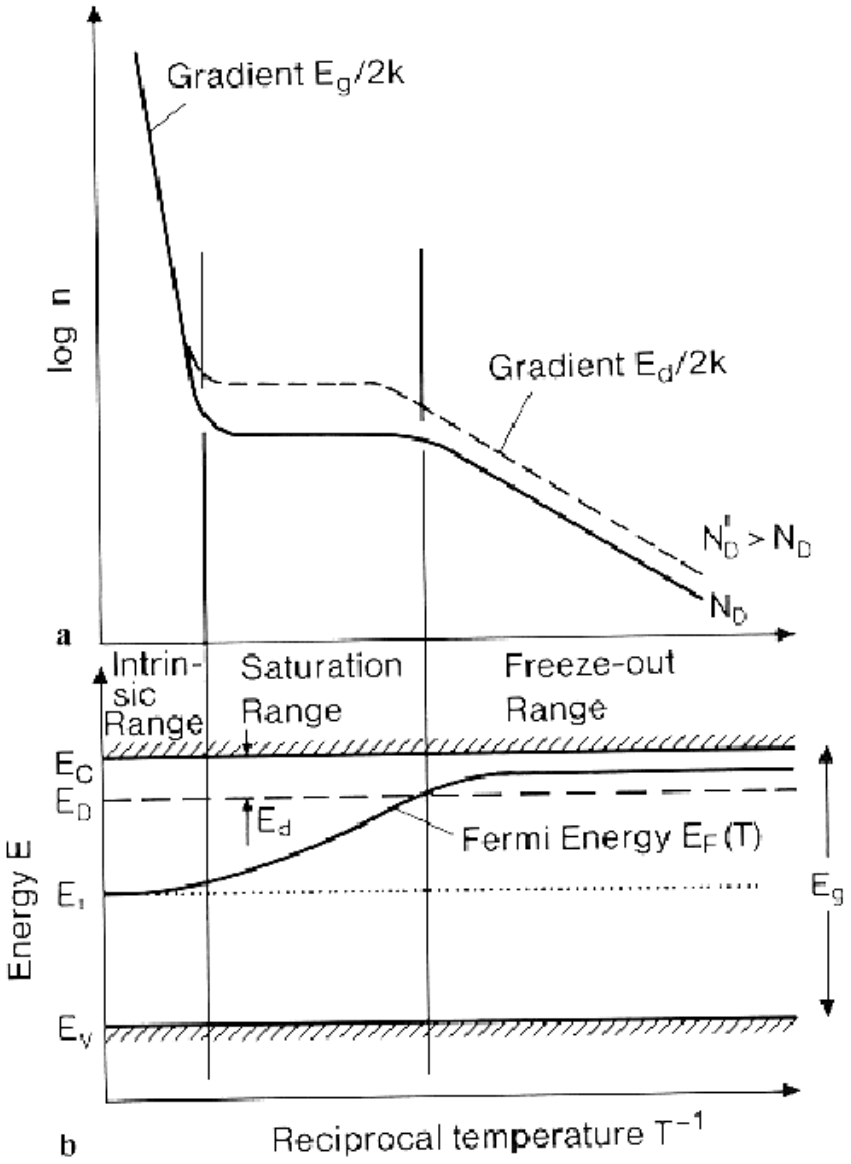
For n-type material: $n = \frac{n_i^2}{n} + N_d - N_a$ $\quad n = \frac{N_d\text{-}N_a}{2} + \sqrt{\frac{(N_d\text{-}N_a)^2}{4} + n_i^2}$

At low temperatures, for $n << N_A, \quad N_d - N_A$

Fermi level $E_F = E_d - k_B T \ln \frac{N_A}{g_d (N_d - N_A)}$

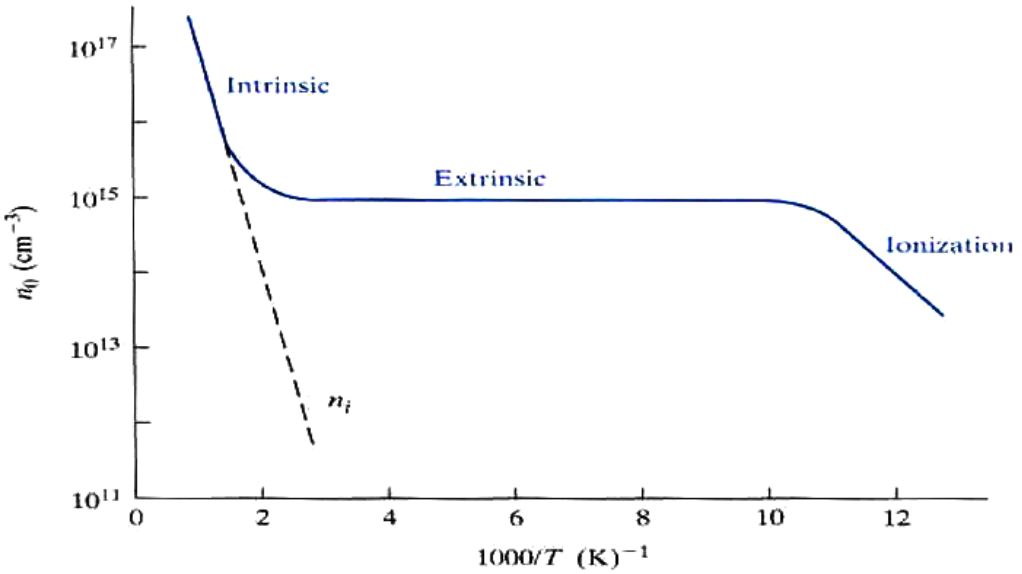
and concentration $n = \frac{N_d - N_A}{N_A} \frac{N_C}{g_d} e^{-\frac{\Delta_d}{k_B T}}$

Doped semiconductors: Temperature dependence



Carrier concentration vs. temperature curve has 3 distinct regions (4 regions in compensated semiconductor)

Typical dependence for Si



Strong non-degeneracy: metals again

Strong degeneracy, i.e. Fermi level lies in the conduction (or valence) band:

$$\exp\left(\frac{E_C - E_F}{k_B T}\right) << 1 \quad or \quad E_F > E_C$$

Carrier concentration:

$$n = N_C \Phi_{1/2}(\eta_c) \qquad \eta_c = \frac{E_F - E_C}{k_B T}$$

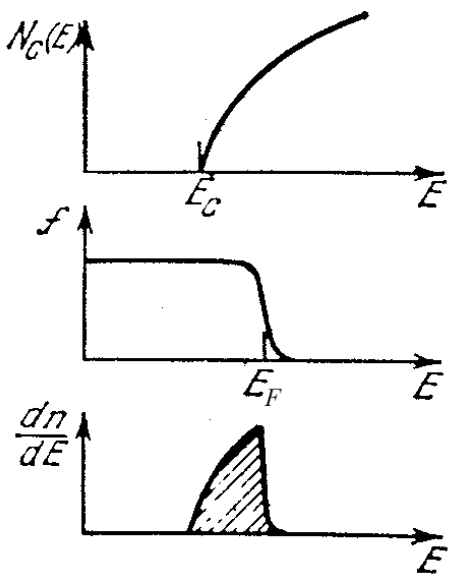
Substituting Fermi function by step function (good for $E_F - E_C > 3k_B T$)

$$n = N_C \frac{2}{\sqrt{\pi}} \int_0^{\infty} \frac{x^{1/2} dx}{\exp(x - \eta_c) + 1} \approx N_C \frac{2}{\sqrt{\pi}} \int_0^{\frac{E_F - E_C}{k_B T}} x^{1/2} dx =$$

Finally:

$$n = N_C \frac{4}{3\sqrt{\pi}} \left(\frac{E_F - E_C}{k_B T}\right)^{3/2}$$

Which is similar to simple metal



Quantum confinement: Quantum Wells

Schrödinger equation under effective mass approximation (with envelope function ψ):

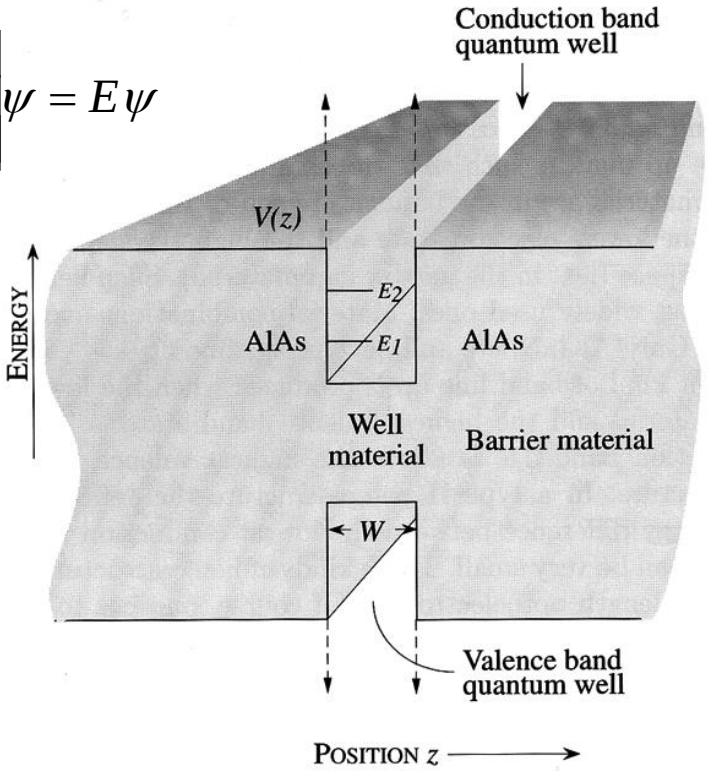
$$\left[-\frac{\hbar^2}{2m^*}\nabla^2 + V(z)\right]\psi = E\psi$$

Electrons (or holes) are "free" along *x* and *y*:

$$\psi = e^{ik_x x} e^{ik_y y} f(z)$$

We return to a problem of a "particle in a well"

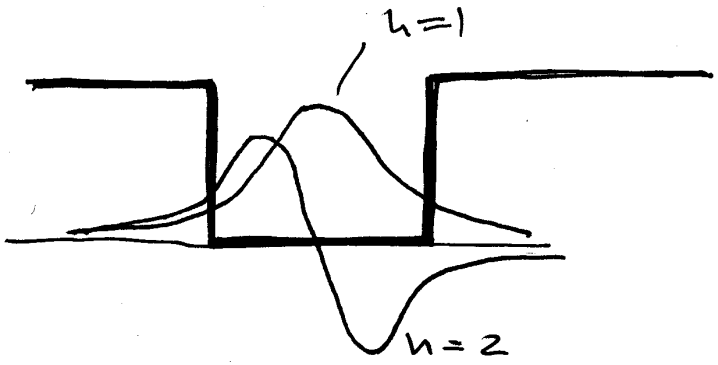
$$\left[-\frac{\hbar^2}{2m^*}\nabla^2 + V(z)\right] f(z) = E f(z)$$



From Singh, 2003

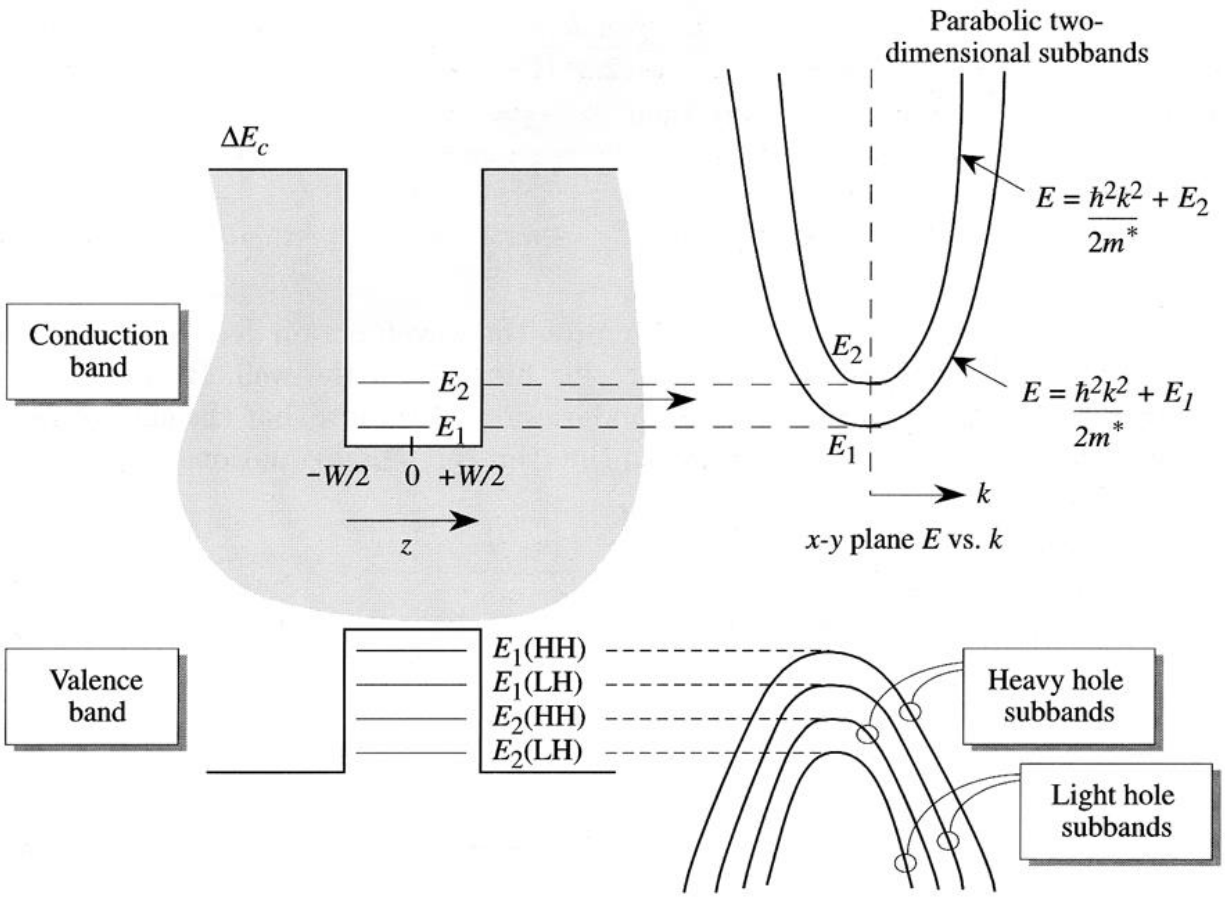
Solution:

- Finite number of discrete energy levels
- Sinusoidal wavefunction inside the well
- Exponential decay in the barrier



Quantum Wells

- Each level in 1D well corresponds to a 2D band with parabolic dispersion
- *E(k)* dispersion corresponds to an effective mass in *x-y* plane
- Hole 2D bands split according to their effective masses (light and heavy holes)
- For better accuracy for holes use Kohn-Luttinger valence band structure

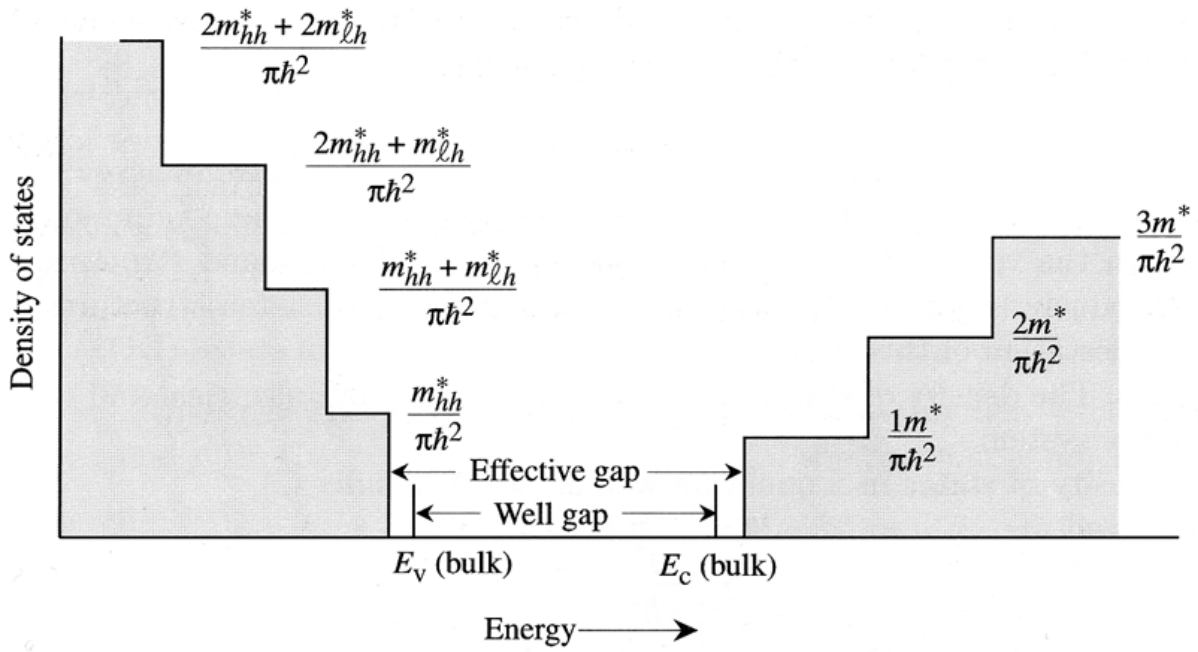


From Singh, 2003

Density of states in Quantum Wells

- Density of states in 2D band (a single subband in the interval E to $E+dE$ number of states per unit "volume")

$$N(E) = \frac{m}{\pi\hbar^2}$$

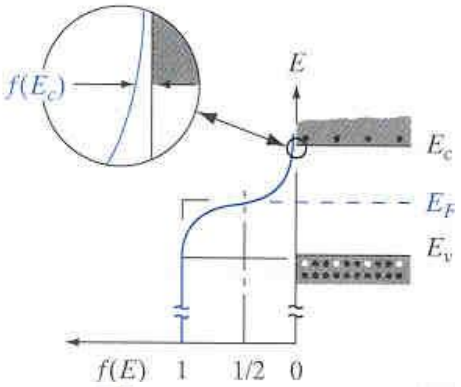


From Singh, 2003

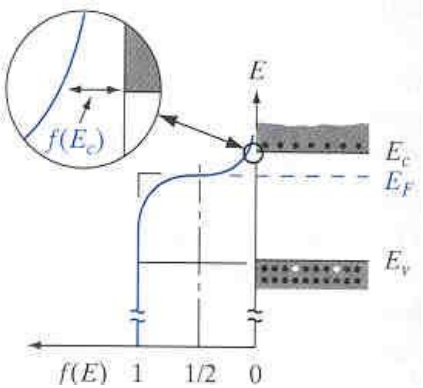
2D Carrier concentration in a single subband [cm^{-2}]

$$n_s = \frac{m_e^*}{\pi\hbar^2}(k_B T)\ln\left(1+\exp(\eta_c)\right)$$

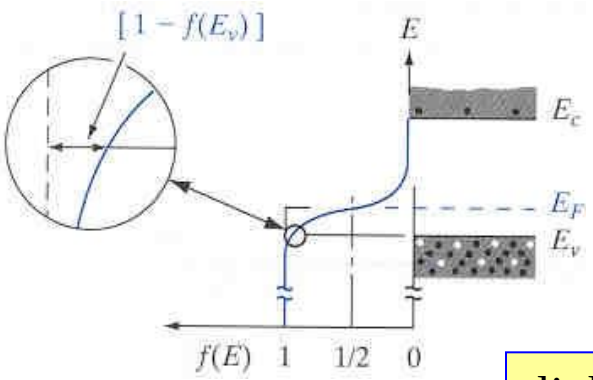
Summary of carrier statistics in semiconductors



Intrinsic



n-type



p-type

Importance of doping:

Si	Resistivity
Undoped	2 x 10^5 Ω-cm
Doped w/ 10^{15} As atoms/cm^3	5 Ω-cm

5 order of magnitude resistivity change due to 1 in 50 million impurities !

10^{15} As atoms/cm^3 in 5x10^{22} Si atoms/cm^3

- Electronic properties are extremely sensitive to impurities, defects, fields, stresses …
- Fermi level determines static carrier concentrations
- General equations can be simplified in non-degenerate and strongly degenerate cases

link to Java applets
http://jas.eng.buffalo.edu

Lecture recap

- In semiconductors, statistics generally applied to parabolic bands
- DOS depends on dimensionality of the system
- Band curvature (effective mass tensor) is the primary property, other effective masses (m^*_{DOS}, $m^*_{conductivity}$) are derived from it
- General *n(E)* =DOS x Distr.Func. , total *n* through Fermi integral
- Two cases approximated differently: non-degenerate and degenerate semiconductor
- Doping used to control carrier density = Fermi level position