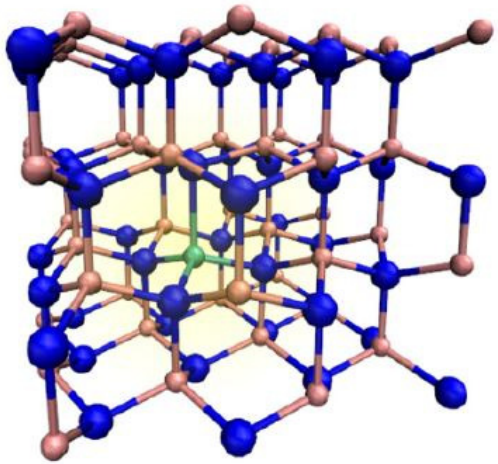
Lecture 5 – 09/10/2024

Donors and Acceptors

- *n*- and *p*-type species
- Binding energy



Density of states in the valence and conduction bands

- Conductivity
- Density of states - generalities
- Density of states - calculations

Occupancy statistics and band filling

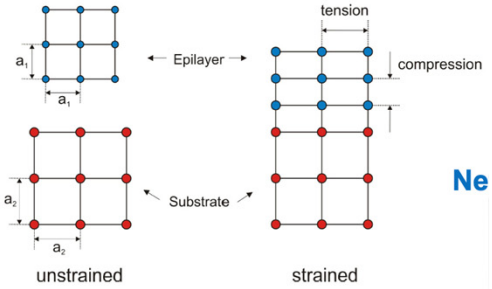
Summary Lecture 4

From epitaxy to deformation and their link to the energy gap

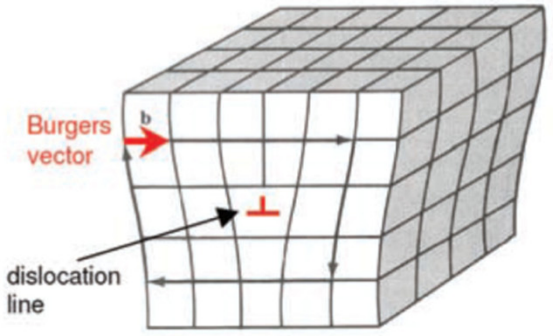
Stacking new types of atoms layer by layer on a substrate causes **deformation** due to **lattice-mismatch**.

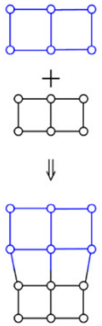
We study:

1. Deformation and stress,
2. And their impact at the level of the band gap.



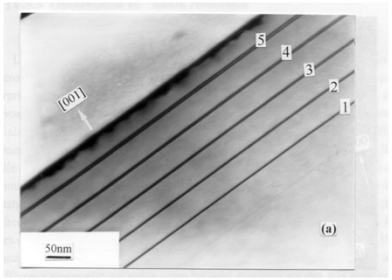
Ne





$$h_c = \frac{Kb^2}{4\pi B f_i b}_{,\text{edge}} \cdot \ln\left(h_c \alpha / b\right)$$

No dislocation

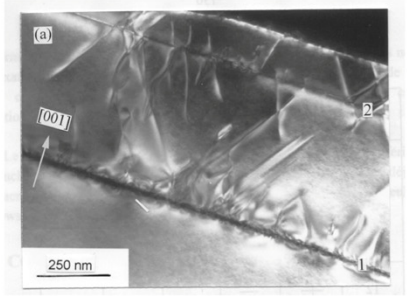


Elastic deformation

(Coherent growth)

TEM

Dislocations



Plastic deformation

Summary Lecture 4

Hooke's law provides a link between **deformation** and **stress** through **elastic constants**, while the deformation potentials and elastic constants contribute to the **strain Hamiltonian**.

$$\sigma_{kl} = C_{ijkl}\,\varepsilon_{ij}$$

$$\begin{pmatrix}\sigma_1\\ \sigma_2\\ \sigma_3\\ \sigma_4\\ \sigma_5\\ \sigma_6\end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0\\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0\\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0\\ 0 & 0 & 0 & C_{44} & 0 & 0\\ 0 & 0 & 0 & 0 & C_{44} & 0\\ 0 & 0 & 0 & 0 & 0 & C_{44}\end{pmatrix} \times \begin{pmatrix}\varepsilon_1\\ \varepsilon_2\\ \varepsilon_3\\ \varepsilon_4\\ \varepsilon_5\\ \varepsilon_6\end{pmatrix}$$

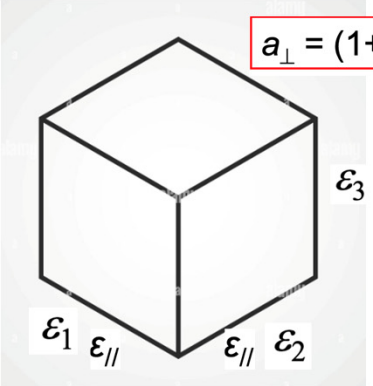
Practical use of Hooke's law:

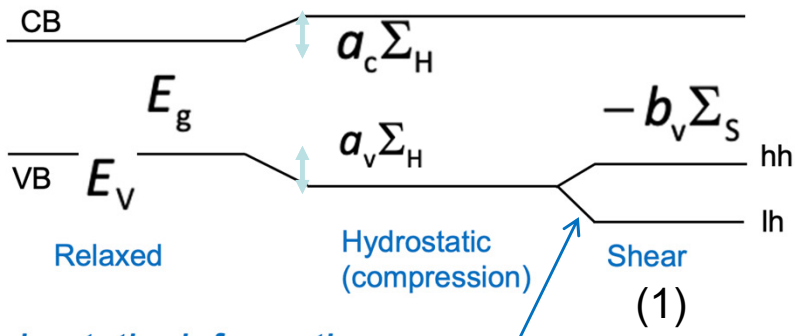
Relation between in-plane (//) and out of plane (⊥) deformation ([001] case for a cubic system)

$$\varepsilon_{13} = 0$$

$$\sigma_{11} = \sigma_{22} = \varepsilon_{\backslash\backslash}(C_{11} + 2C_{12})(C_{11} - C_{22})/C_{11}$$

$$\varepsilon_{\perp} = -2(C_{12}/\,C_{11})\;\varepsilon_{\backslash\backslash}$$





$\Sigma_H = 2\,(1\text{-}C_{12}/C_{11})\varepsilon_{//}$ *Hydrostatic deformation*

$\Sigma_S = -2\,(1+2C_{12}/C_{11})\varepsilon_{//}$ *Shear deformation*

Cubic semiconductor

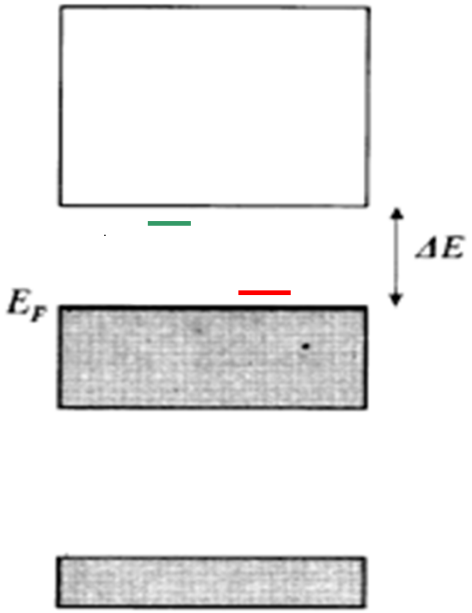
$$E_e = E_V + E_g + a_c\Sigma_H$$

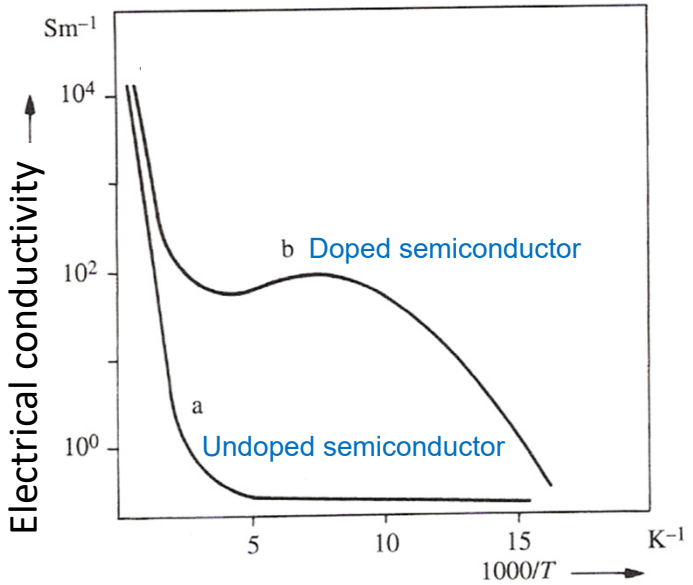
$$E_{hh} = E_V + a_v\Sigma_H - b_v\Sigma_S$$

$$E_{lh} = E_V + a_v\Sigma_H - \frac{\Delta_{SO} - b_v\Sigma_S - \sqrt{\left(\Delta_{SO} + b_v\Sigma_S\right)^2 + 8\left(b_v\Sigma_S\right)^2}}{2}$$

Donors and acceptors

Donors and acceptors

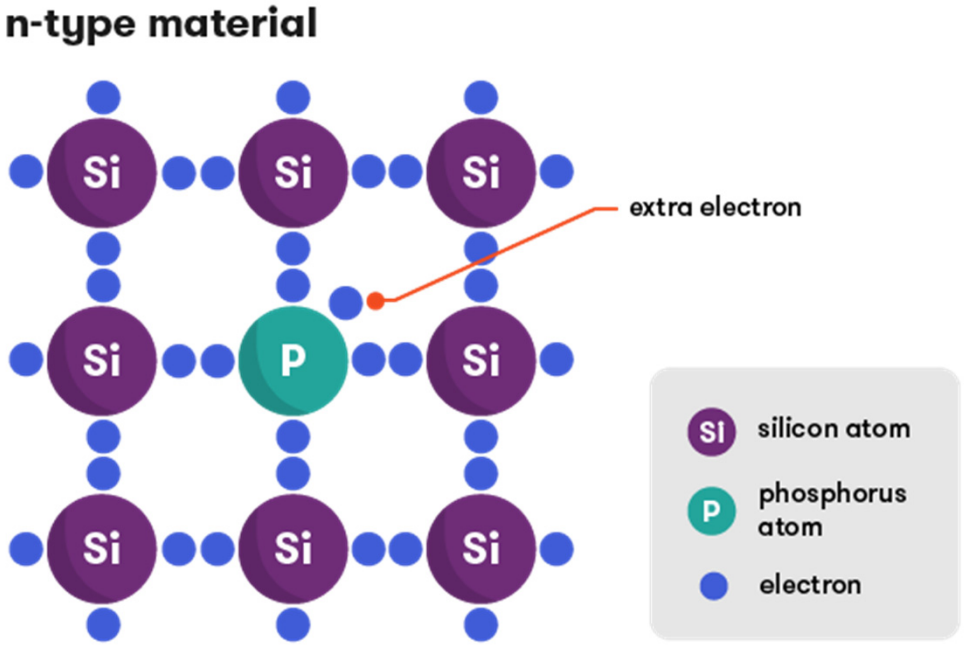


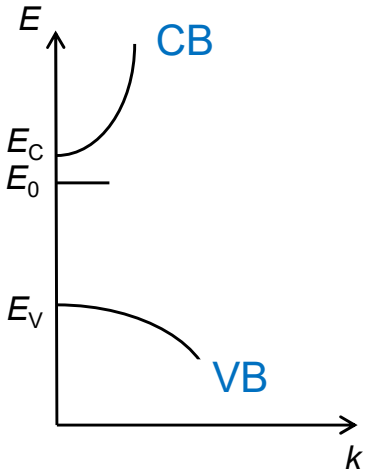


The control of the conductivity is achieved by incorporating exogen atomic species in the crystal:

- donor species: provide at least 1 electron to the lattice
- acceptor species: trap at least 1 electron of the lattice

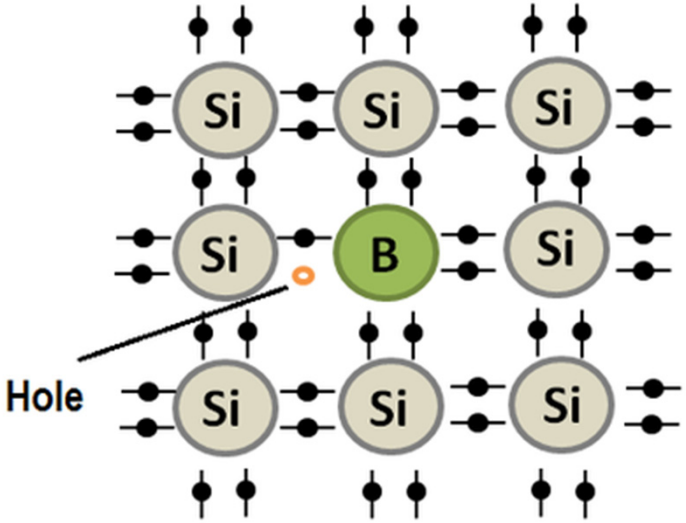
Donors

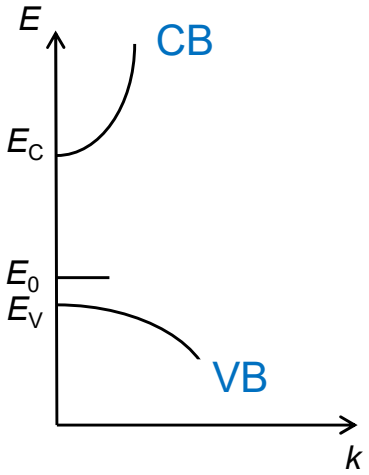




Can you explain qualitatively why the concept of doping is valid for both direct and indirect bandgap semiconductors?

Acceptors





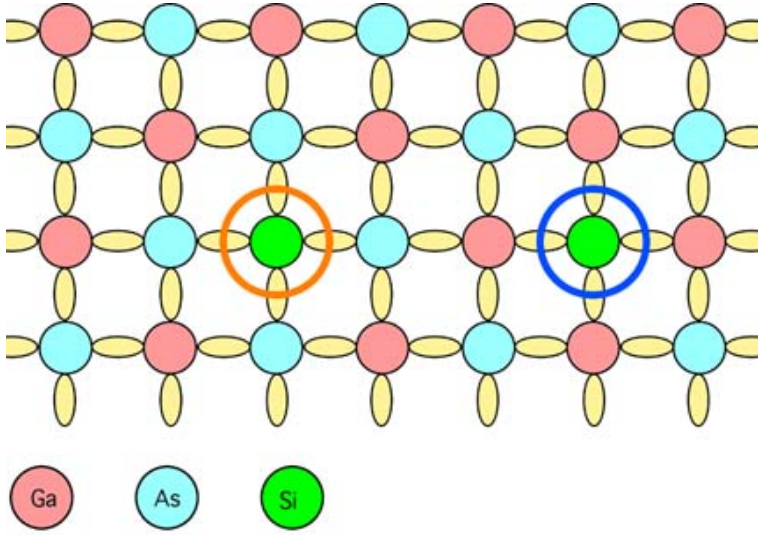
Donors and acceptors

Donors/Acceptors for Si and Ge, and GaAs?

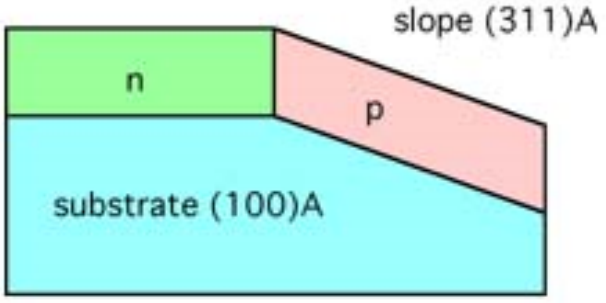
II	III	IV	V	VI
	B	C	N	O
	Al	Si	P	S
Zn	Ga	Ge	As	Se
Cd	In	Sn	Sb	Te

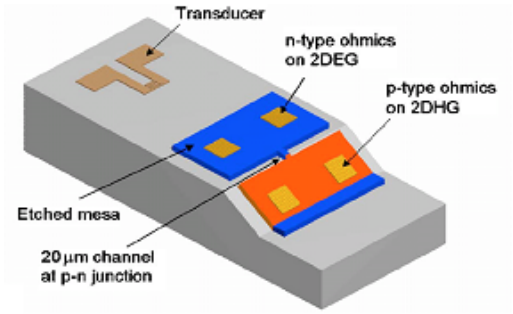
Donors and acceptors

Amphoteric properties of silicon



Cationic vs anionic sites!





Cambridge Univ.

Binding energy

- **Hydrogenic model**

$$\mathrm{H} = \frac{p^2}{2m^*} - \frac{e^2}{4\pi\varepsilon_0\varepsilon_r r}$$

Coulomb interaction between the nucleus and the electron ⇒ similar situation to the one existing in the H atom, except that this occurs in the crystal. This is accounted for by introducing the dielectric constant of the medium $\left(\varepsilon = \varepsilon_r\varepsilon_0\right)$ ⇒ mean field treatment (≡ effective mass theory for the present case)

The eigenenergies are then given by:

"Mean field correction term"

$$E_n = -\frac{\hbar^2}{2m_0 a_0^2} \times \frac{m^*/m_0}{\varepsilon_r^2} \times \frac{1}{n^2} = -13.6\ \mathrm{eV} \times \frac{m^*/m_0}{\varepsilon_r^2} \times \frac{1}{n^2}$$

Bohr radius of the hydrogen atom

The ionization energy of a donor corresponds to the difference between the lowest energy level (n = 1) and the conduction band level where the electron is free to move in the crystal lattice (the equivalent situation can be transposed to the case of acceptors)

Binding energy

- The binding energy (or ionization energy) is strongly reduced with respect to the case of the H atom due to dielectric screening effects in the crystal ($\varepsilon_r > 10$)

- **In this model, the binding energy is independent of the impurity species.** *The relevant parameter is the effective mass of free carriers in the semiconductor.* This model will depict the behavior of *shallow* donors and acceptors.

Semiconductors	P	As	Sb	Bi
Ge	12	12.7	9.6	
Si	44	49	39	69

Experimental binding energies (in meV)

Remark: **Bi** $\Rightarrow$ does not follow the general trend (failure of the hydrogenic model)

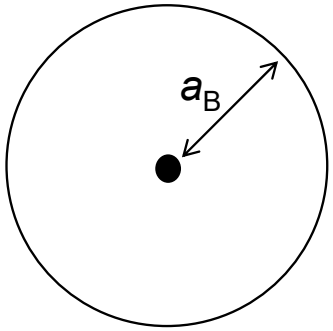
Bohr radius of an impurity

$$a_B = \frac{4\pi\varepsilon\hbar^2}{e^2 m^*} = \frac{\varepsilon_r}{m_r^*} a_0$$

with $m^* = m_r^* m_0$, m_r^* *the effective reduced mass* and a_0 the Bohr radius of the H atom (0.53 Å)

"Mean field correction term"

a_B = 24 Å in silicon



The electron is delocalized over several crystal unit cells

This description is valid only if the impurity is not ionized (i.e., usually at low temperature)

Donors and acceptors

- Relatively small binding energy for most of the semiconductors
  $\Rightarrow$ full ionization expected at RT

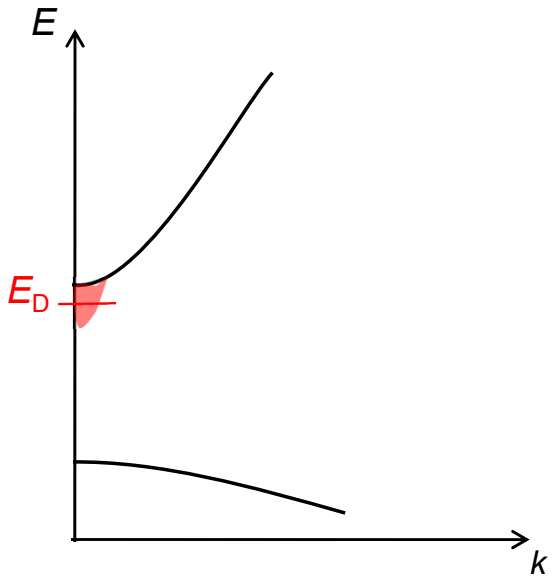
- No longer the case for wide bandgap semiconductors (e.g., GaN, diamond)

Note, however, that the GaN:Mg acceptor level positioned 150-200 meV above the VB maximum can still be described using the effective-mass approximation

- When the impurity concentration increases $\Rightarrow$ formation of an impurity band due to wavefunction overlap

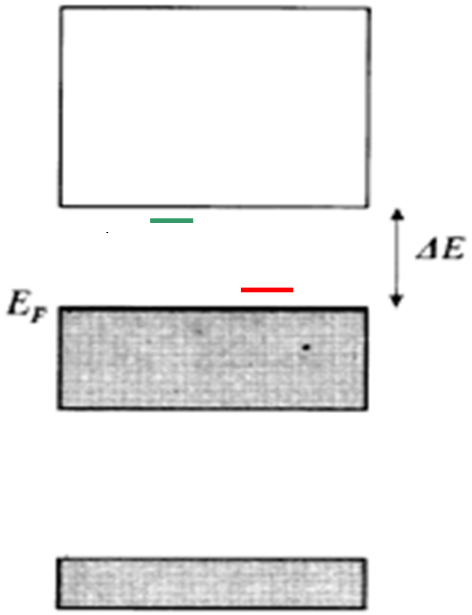
Donors and acceptors

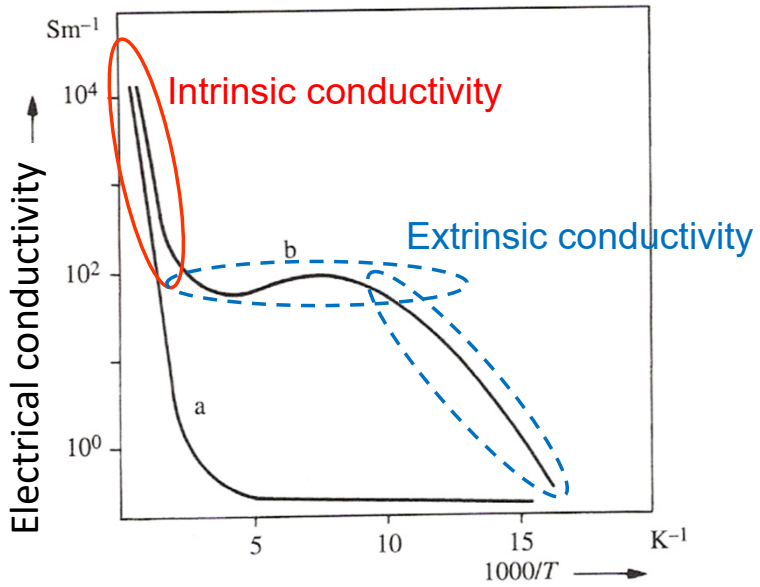
High concentration $\Rightarrow$ interaction between dopant wavefunctions



Band tailing effect

Conductivity





The conductivity of a semiconductor critically depends on the free carrier population

Density of states

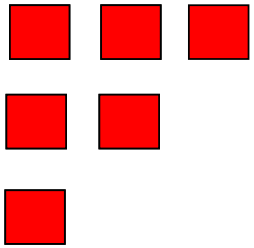
Density of states in the VB and the CB

Density of states in the VB and CB

$\Rightarrow$ number of states of different energies available for carriers

It only depends on the energy

The temperature is responsible for the band filling



Remarks:

- *2 electrons of opposite spin per level at most*
- *at T = 0 K, no carriers in the CB*

Density of states

1D: linear chain of N atoms $\Rightarrow$ N values of k between $-\pi/a$ and $+\pi/a$, separated by $2\pi/Na$

$$k = \frac{2n\pi}{Na}$$

3D: to each k value corresponds a volume in reciprocal space $V_r = (2\pi/Na)^3$, or $V_r = 8\pi^3/V$, with $V=N^3a^3$ the volume of the crystal in real space

Density of states for the electrons in *k*-space:

- density of states in the reciprocal space $\Rightarrow 1/V_r$
- density of states in the reciprocal space per unit volume
  $\Rightarrow [1/V_r]$ / crystal volume $(V) = (V/8\pi^3)/V = 1/8\pi^3$

The density of states is constant over each *k* interval

However, the density of states over each energy interval increases due to the quadratic relation between E and k

Density of states

Density of states as a function of *E*

$$E = E_0 + \frac{\hbar^2 k^2}{2m^*}$$

Expression valid nearby an energy band extremum only (parabolic band approximation)

$$\Rightarrow k = \sqrt{2m^* \left(E - E_0\right) / \hbar^2}$$

How many states are packed in a sphere of radius *k*?

$N_{3D}(E)$ = V_{sphere} x DOS per unit volume x 2 (spins $\pm 1/2$)

= $4/3\ \pi k^3$ x $1/8\pi^3$ x 2

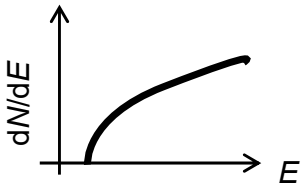
$$= \frac{1}{3\pi^2}\left(\frac{2m^*}{\hbar^2}\left(E - E_0\right)\right)^{3/2}$$

Density of states per energy unit

Density of states per energy unit at energy $E \Rightarrow \mathrm{d}N(E)/\mathrm{d}E$

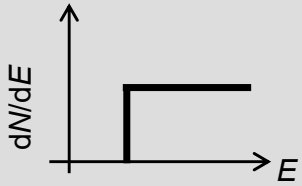
$$N_{3D}(E) = \frac{1}{3\pi^2}\left(\frac{2m^*}{\hbar^2}(E - E_0)\right)^{3/2}$$

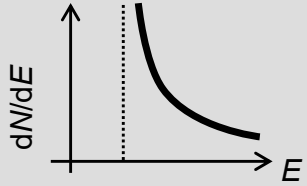
$$\rho_{3D}(E) = \frac{dN_{3D}(E)}{dE} = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\sqrt{E - E_0}$$



- **3D density of states (DOS) per energy unit varies as the square root of *E***
- **3D DOS per energy unit varies as the effective mass with the exponent 3/2**

Exercise: calculate the DOS per energy unit for the 2D and 1D cases (series)





Band filling

Electrons and holes obey the Fermi-Dirac distribution (fermions)

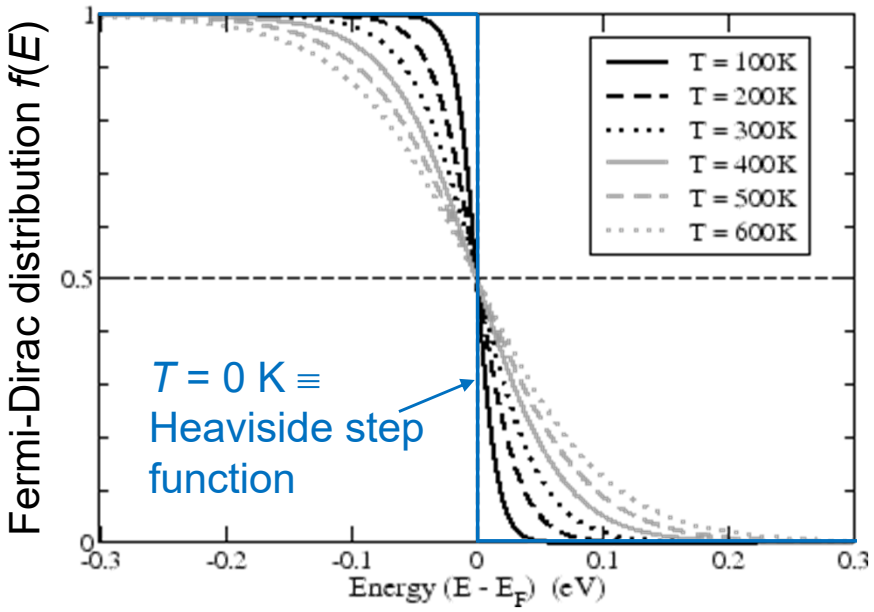
The probability that an energy state E is filled by 1 electron at a temperature T is given by the Fermi-Dirac distribution:

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

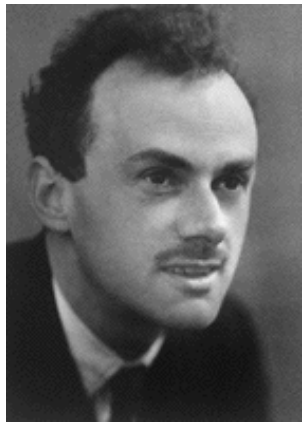
- E_F is the Fermi level $\Rightarrow$ at T = 0 K, this is the highest energy level, which is occupied
- E_F is also the chemical potential
- **E_F corresponds to a certain energy for which $f(E_F)$ = ½ whatever the temperature**

Band filling

Fermi-Dirac distribution



E. Fermi (1901-1954)



P. A. M. Dirac (1902-1984)

Note that $f(E) = 0.5$ when $E = E_F$ whatever T(K)

Named after Fermi and Dirac who derived this distribution independently in 1926!

Illustrative example

At 300 K, for $E - E_F = 0.05$ eV $\Rightarrow f(E) = 0.12$

for $E - E_F = 7.5$ eV $\Rightarrow f(E) = 10^{-129}$

Band filling

In the CB, the density of electrons at an energy E per unit energy is given by the product of the DOS $\rho_c(E)$ by the occupation probability $f_c(E)$

$$n_c(E) = f_c(E)\rho_c(E)$$

In the VB, the density of holes writes similarly considering the occupation probability $f_v(E)$ of an empty state

$$n_v(E) = f_v(E)\rho_v(E) = [1-f_c(E)]\rho_v(E)$$ i.e., $f_c(E)+f_v(E) = 1$

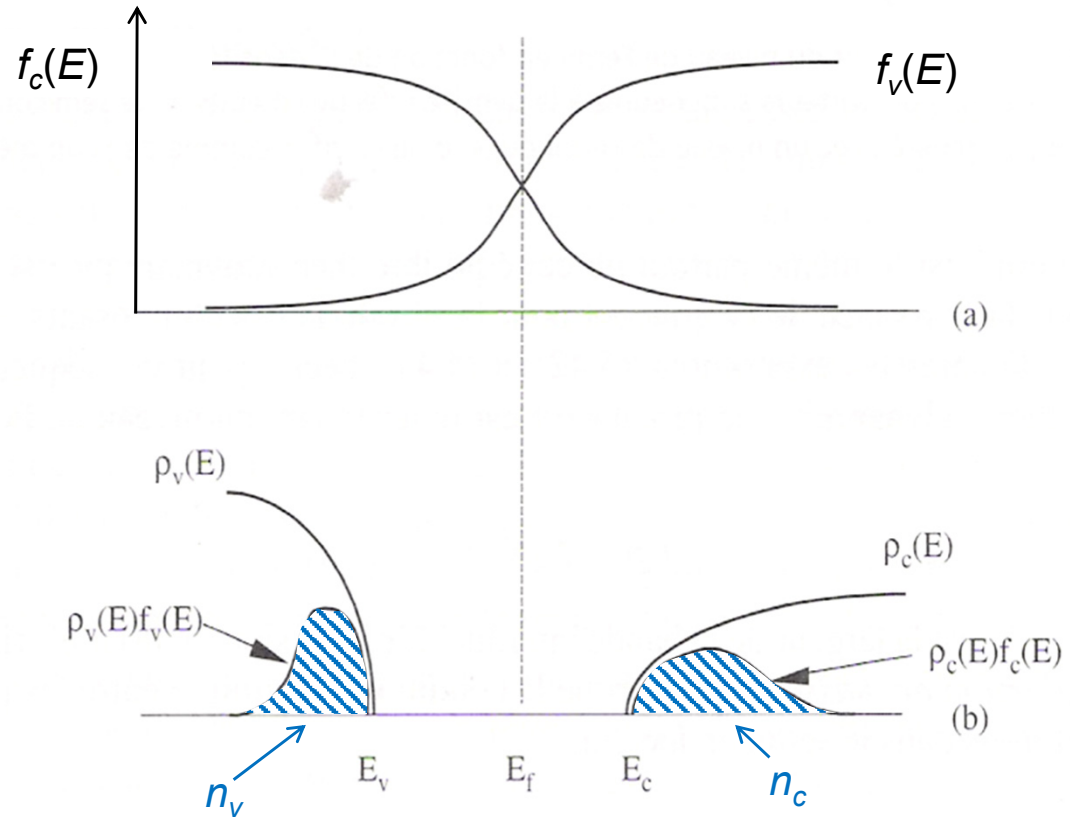
The total concentration of electrons (holes) in the CB (VB) is obtained by integrating the carrier density $n_{c(v)}$ over the bands

$$n_c = \int_{E_c}^{+\infty} \rho_c(E) f_c(E) dE$$

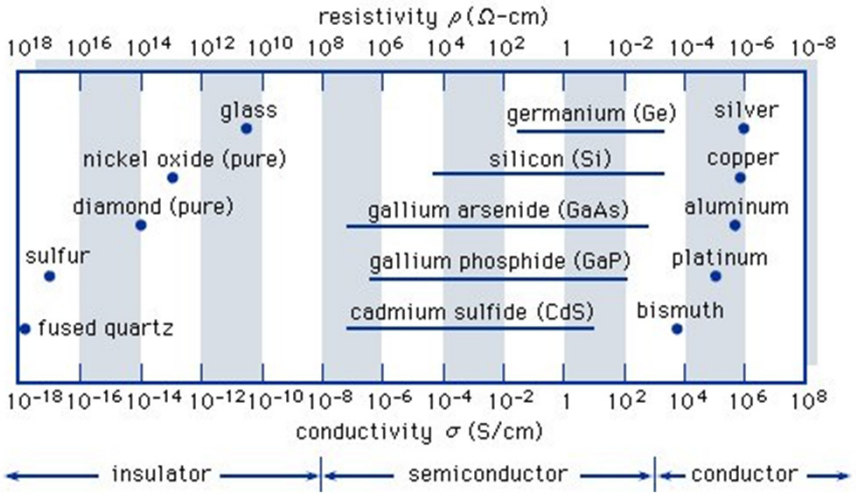
$$n_v = \int_{-\infty}^{E_v} \rho_v(E) f_v(E) dE = \int_{-\infty}^{E_v} \rho_v(E)[1 - f_c(E)] dE$$

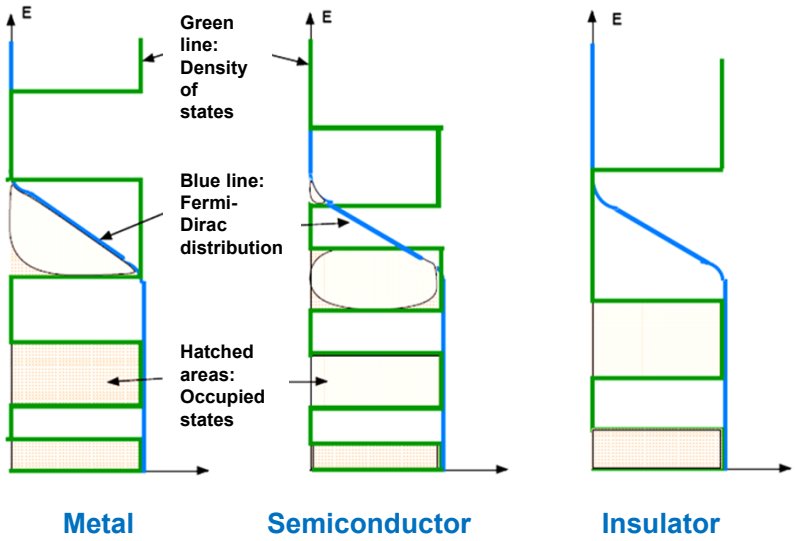
Band filling

The Fermi level usually lies close to mid-gap for undoped and perfect semiconductors



Insulator-metal-semiconductor





- What dictates whether we are dealing with an insulator or a semiconductor is not so much the value of the bandgap than the ability to modify the conductivity/resistivity through the introduction of exogen species
- It is understood that those dopants will allow to tune in a *controllable* manner the position of the Fermi level toward the valence or the conduction bands
- As an illustration, AlN, whose bandgap is ~6.1-6.2 eV, is a semiconductor!

Non-degenerate semiconductors

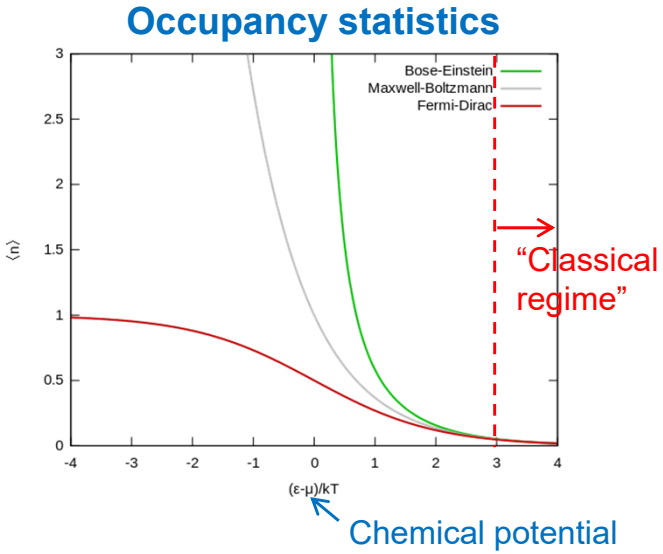
Non-degenerate semiconductor ⇒ the Fermi level lies within the bandgap, and is generally close to the mid-gap

Then it comes $|E\text{-}E_F| >> k_B T$ (300 K: $k_B T \approx 25$ meV to be compared to $E_g/2 > 500$ meV (see, e.g., the case of Si, GaAs, GaN, etc.))

⇒ **Boltzmann approximation** (i.e., the carrier number is low enough so that Pauli exclusion principle does not apply). The occupancy statistics becomes:

$$f_c(E) = \frac{1}{1+e^{(E-E_F)/k_B T}} \Rightarrow f_c(E) \approx e^{-(E-E_F)/k_B T}$$

$$f_v(E) = 1 - f_c(E) \approx e^{-(E_F-E)/k_B T}$$



Non-degenerate semiconductors

One then integrates using $\rho_{3D}(E) = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\sqrt{E-E_0}$ **3D-DOS per energy unit**

$$n_c = \int_{E_c}^{+\infty} \rho_c(E) f_c(E) dE \quad \Rightarrow \quad n = N_c e^{-(E_C - E_F)/k_B T}$$

$$n_v = \int_{-\infty}^{E_v} \rho_v(E) f_v(E) dE \quad \Rightarrow \quad p = N_v e^{-(E_F - E_V)/k_B T}$$

$$N_{c(v)} = 2\left(\frac{2\pi m^* k_B T}{h^2}\right)^{3/2} = cst \cdot \left[\frac{m^*}{m_0} T\right]^{3/2}$$

$$= 2.5\times 10^{19}\left(\frac{m^*}{m_0}\right)^{3/2}\left(\frac{T}{300}\right)^{3/2} \text{ cm}^{-3}$$

$N_{c(v)}$ are the effective density of states

Non-degenerate semiconductors

Effective density of states $\Rightarrow$ a band can be described by a discrete level with a concentration N_c and filled with a probability $\exp[-(E_c-E_F)/k_BT]$

Effective density of states ($N_{c(v)}$) *at 300 K for different semiconductors*

	N_C (10^{19} cm^{-3})	N_V (10^{19} cm^{-3})
Si	2.8	1.0
Ge	1	0.4
GaAs	0.04	1.2