Lecture 5 – 08/10/2025

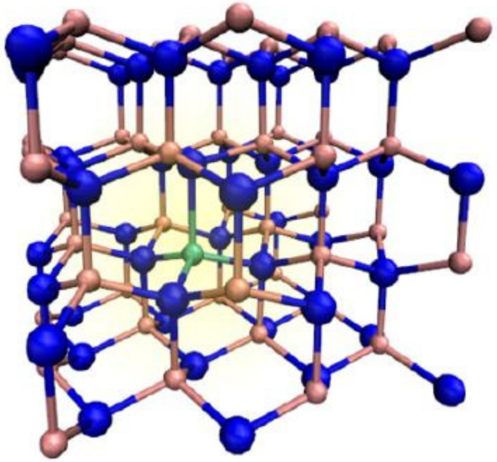
Donors and Acceptors

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

Density of states in the valence and conduction bands

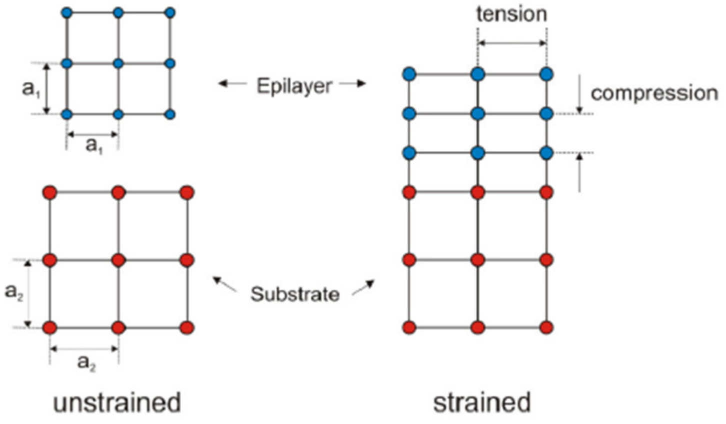
- Conductivity
- Density of states - generalities
- Density of states - calculations

Occupancy statistics and band filling



Summary Lecture 4

Epitaxial growth: crystal growth proceeds layer-by-layer and the layer structure complies with the substrate lattice



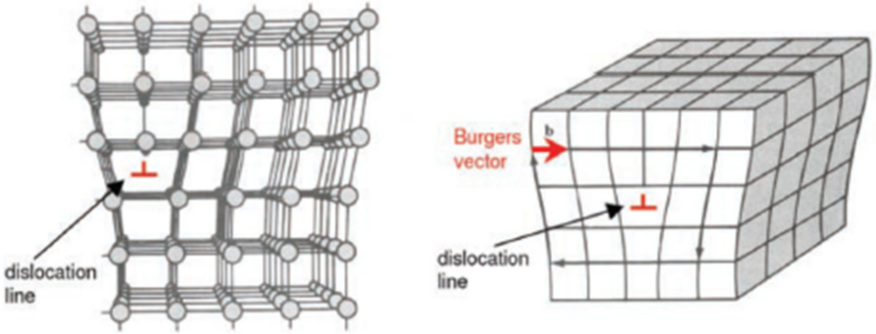
Example of heteroepitaxy

Burgers vector b: represents the magnitude & direction of the lattice distortion caused by a dislocation in a crystal lattice

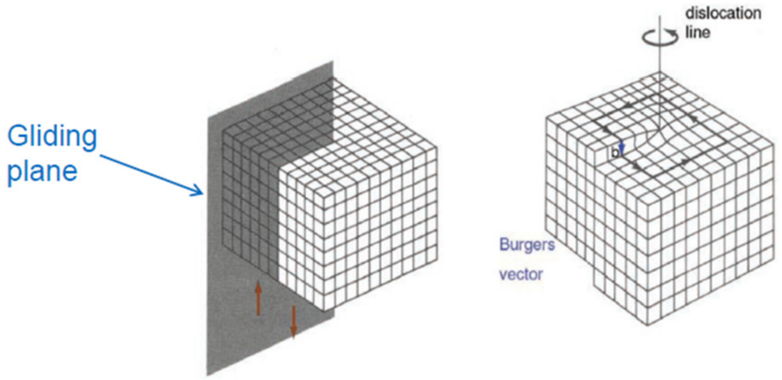
Critical thickness for plastic relaxation:

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

Edge type dislocation: $\mathbf{b} \perp$ dislocation line



Screw type dislocation: $\boldsymbol{b} \parallel$ dislocation line



Summary Lecture 4

Strain: define lattice mismatch: $\Delta a/a = (a_l - a_s)/a_s$

& in-plane strain: $\varepsilon_{\parallel} = (a_s - a_l)/a_l$

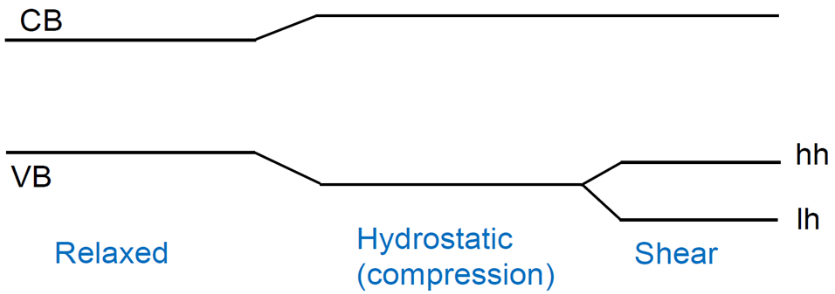
$\varepsilon_{//} < 0$	compressive strain
$\varepsilon_{//} > 0$	tensile strain

Elasticity theory: use Hooke's law: $\sigma_{kl} = C_{ijkl}\varepsilon_{ij}$ to describe deformation ε_{ij} w.r.t. stress σ_{ij}

Epitaxy layer is stress-free in growth direction, symmetrical and shear stress-free
e.g. for cubic SC along $[hkl] = [001]$ orientation: $\varepsilon_{\perp} = -(2C_{12}/C_{11})\varepsilon_{\parallel}$

Band structure: strain Hamiltonian $H = H_H + H_S$ impacted by deformations:

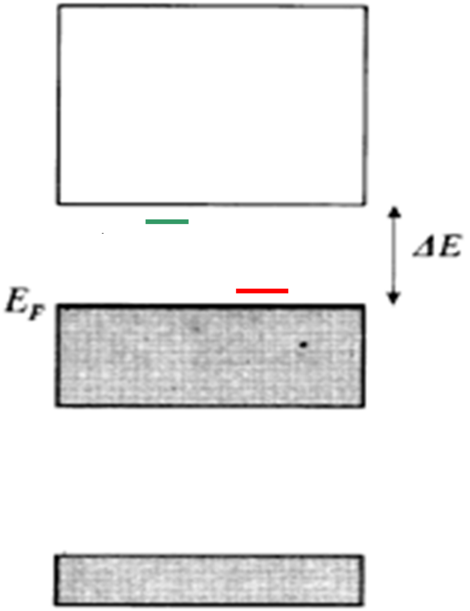
- volume dilatation → bandgap change
- shear strain → degeneracy lift of energy bands at high-symmetry points of the 1st-Brillouin zone

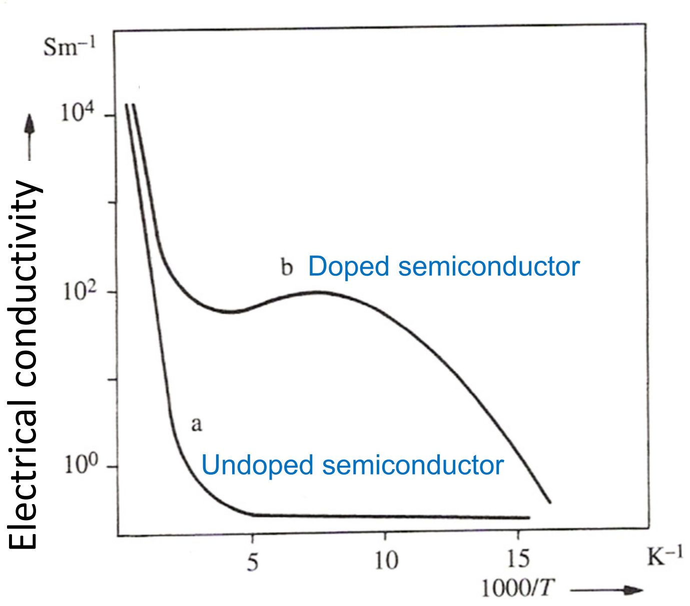


Example of compressive strain

Donors and acceptors

Donors and acceptors

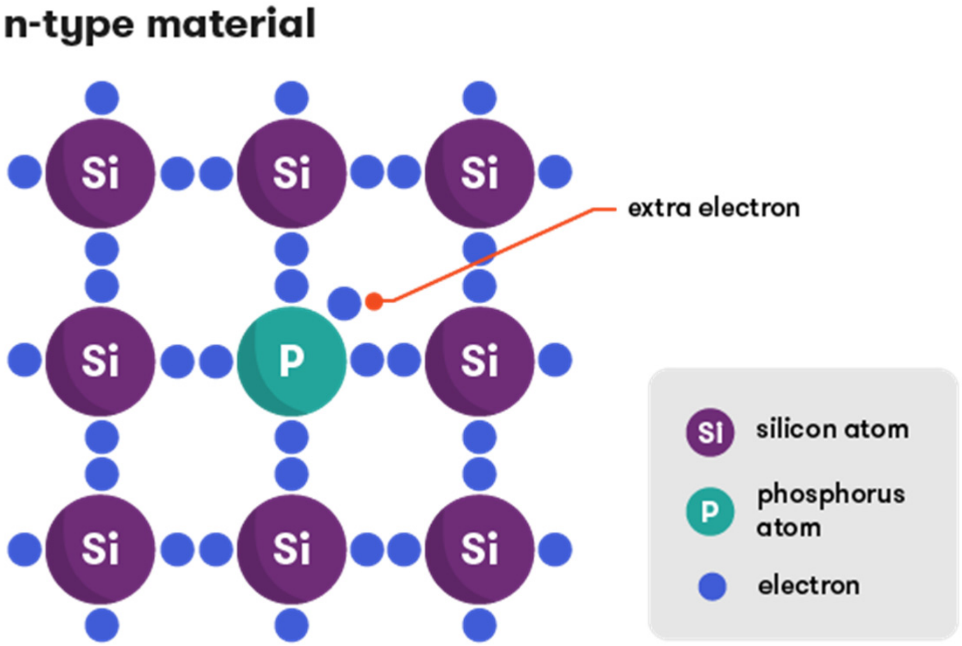


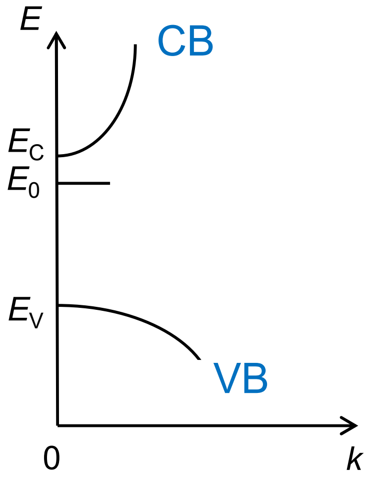


The control of the conductivity is achieved by incorporating exogen atomic species in the crystal:

- donor species: provide at least 1 free conduction electron to the lattice
- acceptor species: trap at least 1 valence electron of the lattice (which leads to the formation of a free conduction hole among the states near the top of the valence band)

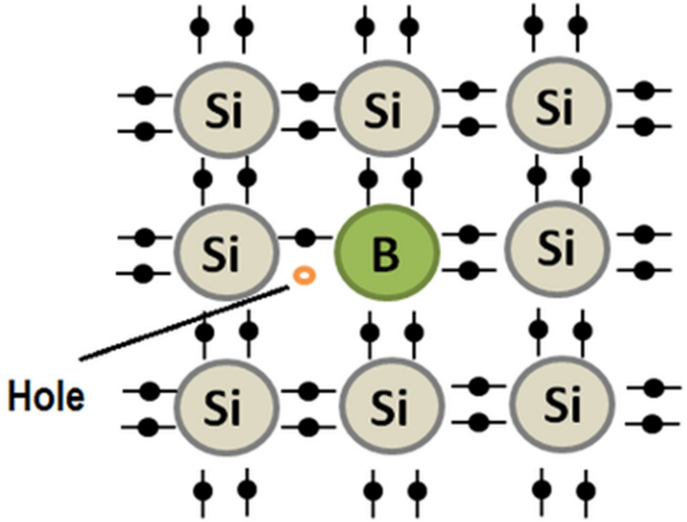
Donors

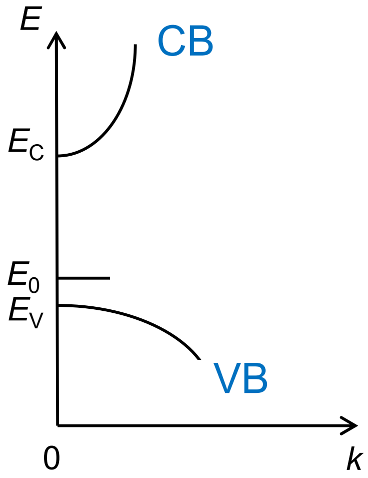




Can you explain qualitatively why the concept of doping is valid for both direct and indirect bandgap semiconductors?

Acceptors





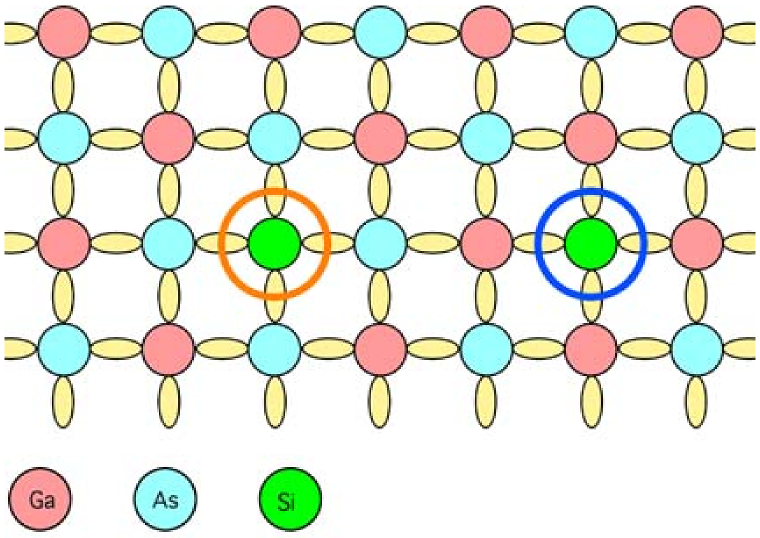
Donors and acceptors

Donors/Acceptors for Si and Ge, and GaAs?

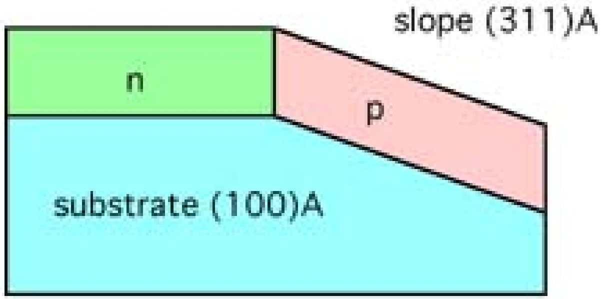
II	**III**	**IV**	**V**	**VI**
	B	C	N	O
	Al	Si	P	S
Zn	Ga	Ge	As	Se
Cd	In	Sn	Sb	Te

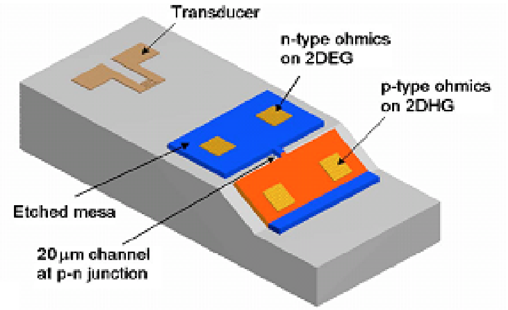
Donors and acceptors

Amphoteric properties of silicon



Cationic vs anionic sites!





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Binding energy

- **Hydrogenic model**

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

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 $\left(\varepsilon = \varepsilon_\mathrm{r}\varepsilon_0\right)$ ⇒ mean field treatment (≡ effective mass theory for the present case)

The eigenenergies are then given by:

"Mean field correction term"

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

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** ⇒ does not follow the general trend (failure of the hydrogenic model)

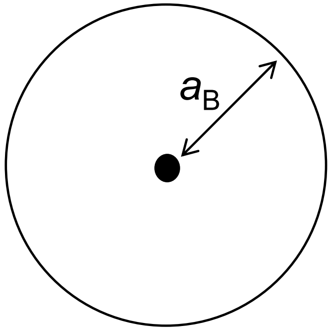
Bohr radius of an impurity

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

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

  ⇒ full ionization expected at RT

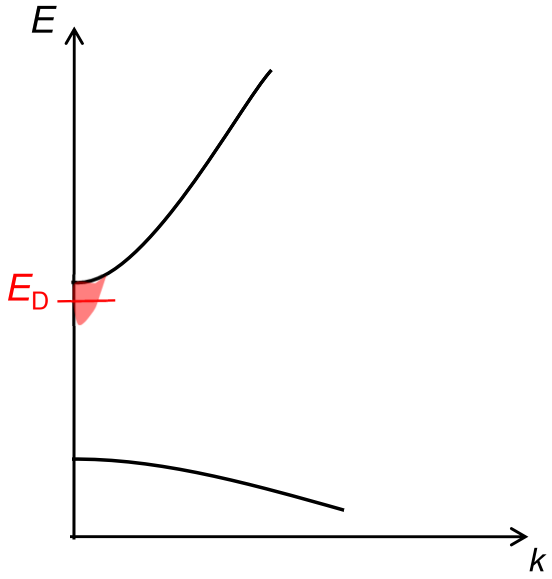
- No longer the case for wide bandgap semiconductors (e.g., GaN, diamond)

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 ⇒ formation of an impurity band due to wavefunction overlap

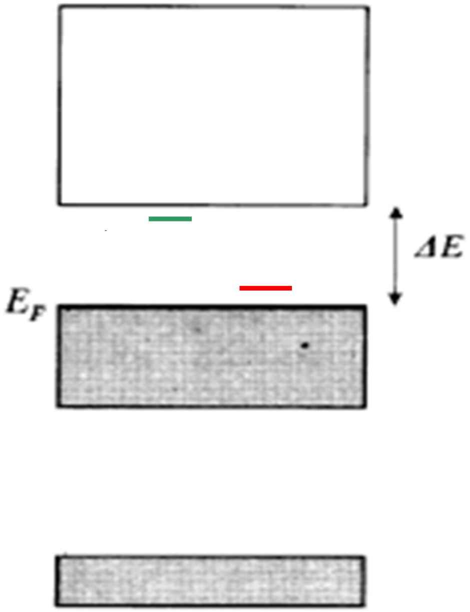
Donors and acceptors

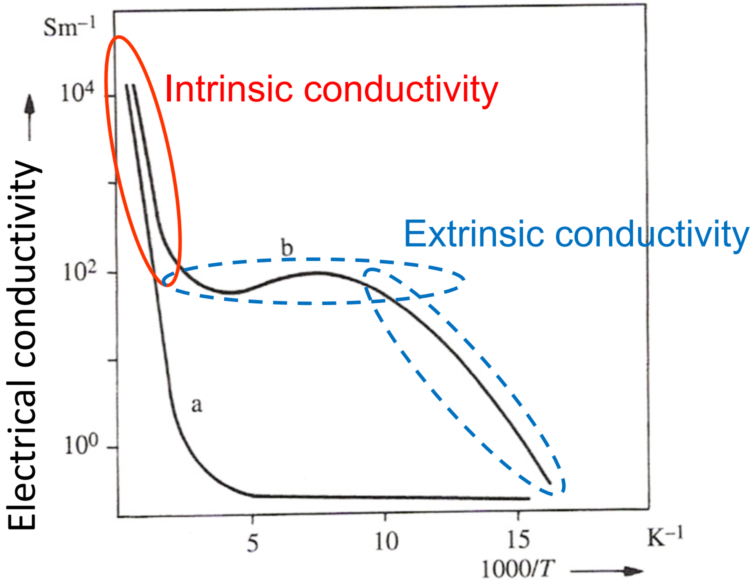
High concentration ⇒ interaction between dopant wavefunctions



Band tailing effect

Conductivity





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

Density of states

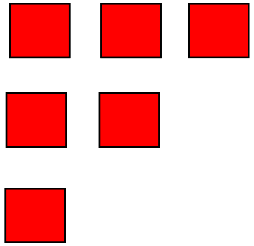
Density of states in the VB and the CB

Density of states in the VB and CB

⇒ 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 (true for intrinsic and non-degenerate semiconductors (cf. lecture 6))*

Density of states

1D: linear chain of N atoms ⇒ 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 ⇒ $1/V_r$
- density of states in the reciprocal space per unit volume

  ⇒ $[1/V_r]$ / 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 ±1/2)

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

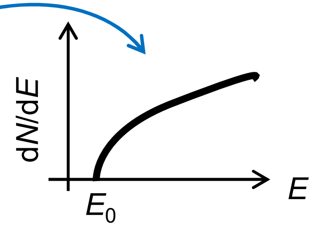
$$= \frac{1}{3\pi^2}\left(\frac{2m^*}{\hbar^2}\left(E - E_0\right)\right)^{3/2}$$

Density of states per energy unit

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

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

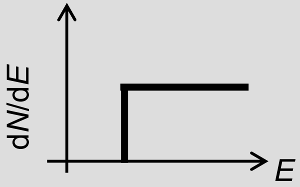
$$\rho_{3D}(E) = \frac{dN_{3D}(E)}{dE} = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\sqrt{E-E_0}$$

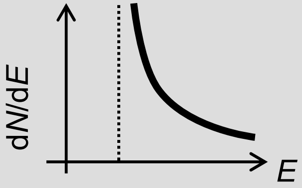


- **3D density of states (DOS) per energy unit varies as the square root of *E***
- **3D DOS per energy unit varies as the effective mass with the exponent 3/2**

Key role when defining the magnitude of the absorption coefficient (lecture 12): concept of joint-DOS

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)

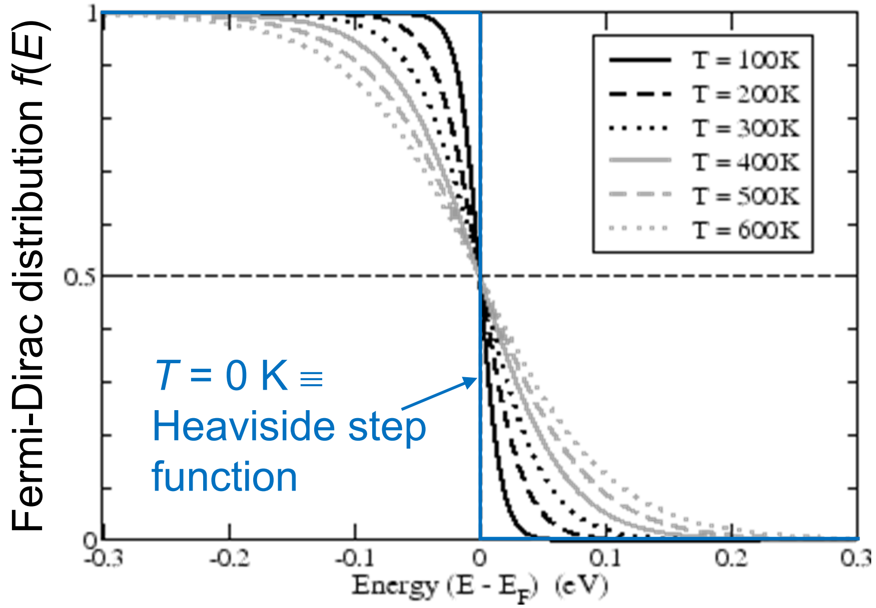
The probability that an energy state E is filled by 1 electron at a temperature T is given by the Fermi-Dirac distribution:

$$f(E) = \frac{1}{1 + e^{(E - E_\mathrm{F})/k_\mathrm{B}T}}$$

- 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 $f(E_\mathrm{F}) = ½$ whatever the temperature**

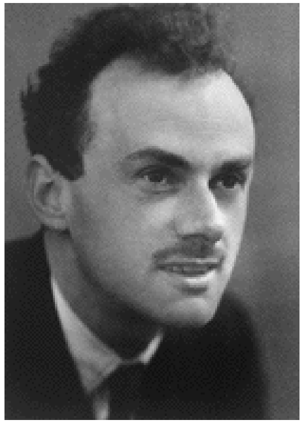
Band filling

Fermi-Dirac distribution



$T = 0$ K ≡ Heaviside step function

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., $f_c(E)+f_v(E) = 1$

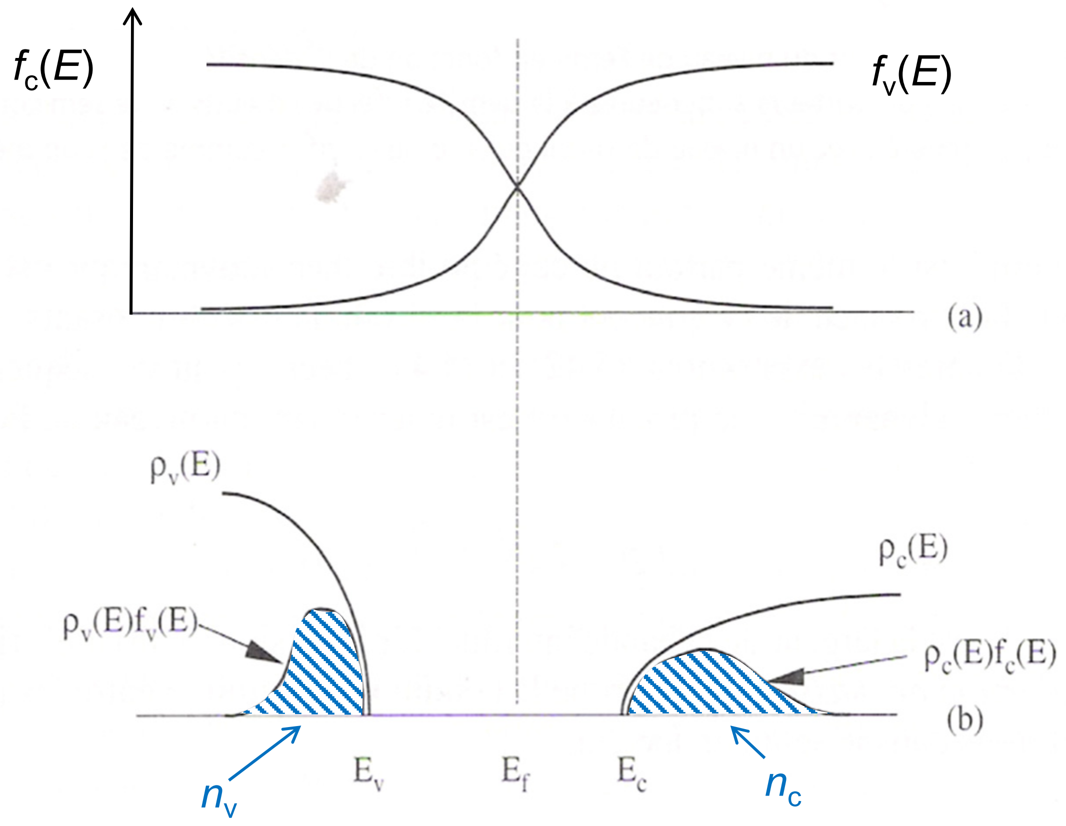
The total concentration of electrons (holes) in the CB (VB) is obtained by integrating the carrier density $n_{c(v)}$ over the bands

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

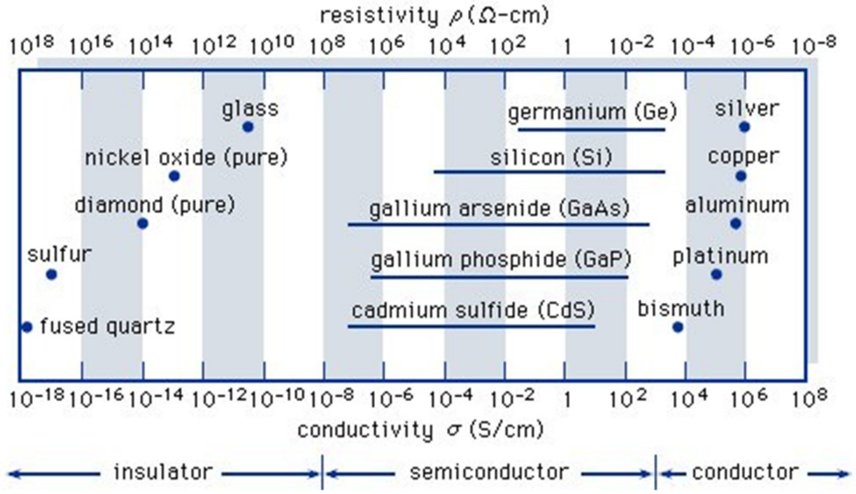
$$n_v = \int_{-\infty}^{E_V} \rho_v(E) f_v(E)\, dE = \int_{-\infty}^{E_V} \rho_v(E)[1 - f_c(E)]\, dE$$

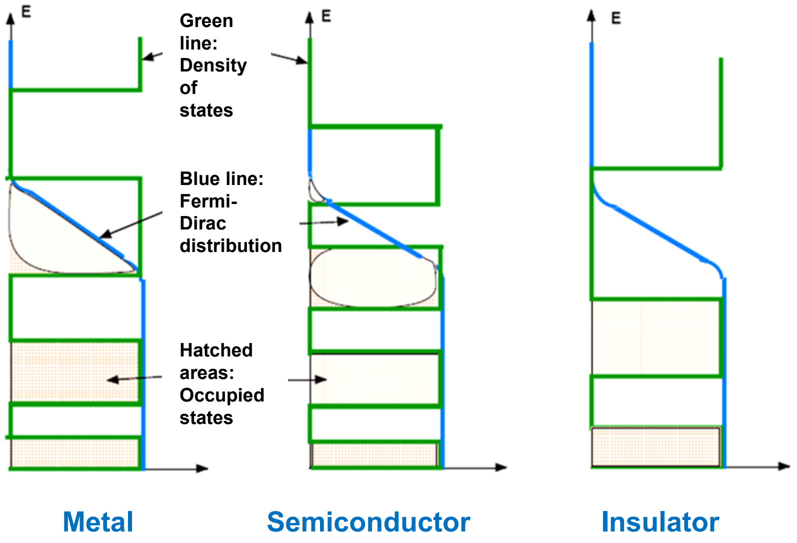
Band filling

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

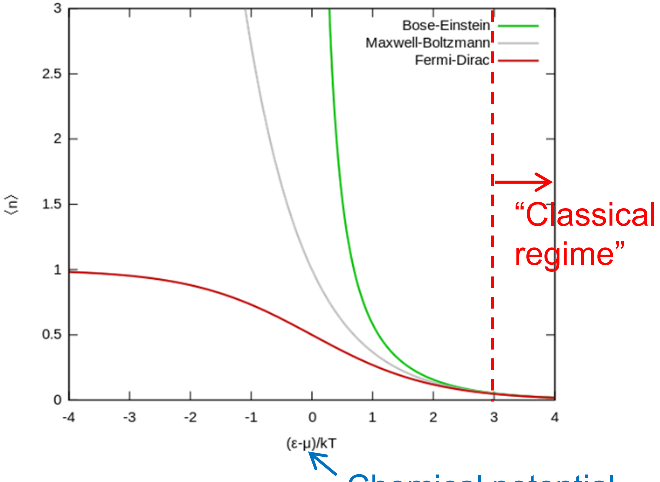
Then it comes $|E-E_F| >> k_BT$ (300 K: $k_BT \approx 25$ meV to be compared to $E_g/2 > 500$ meV (see, e.g., the case of Si, GaAs, GaN, etc.))

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

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

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

Occupancy statistics



Chemical potential

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 ⇒ a band can be described by a discrete level with a concentration N_c and filled with a probability $\exp[-(E_c-E_F)/k_B T]$

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