Doped Semiconductors

Dr. Katarzyna Skorupska

Doped semiconductors

- Increasing the conductivity of semiconductors by incorporation of foreign atoms

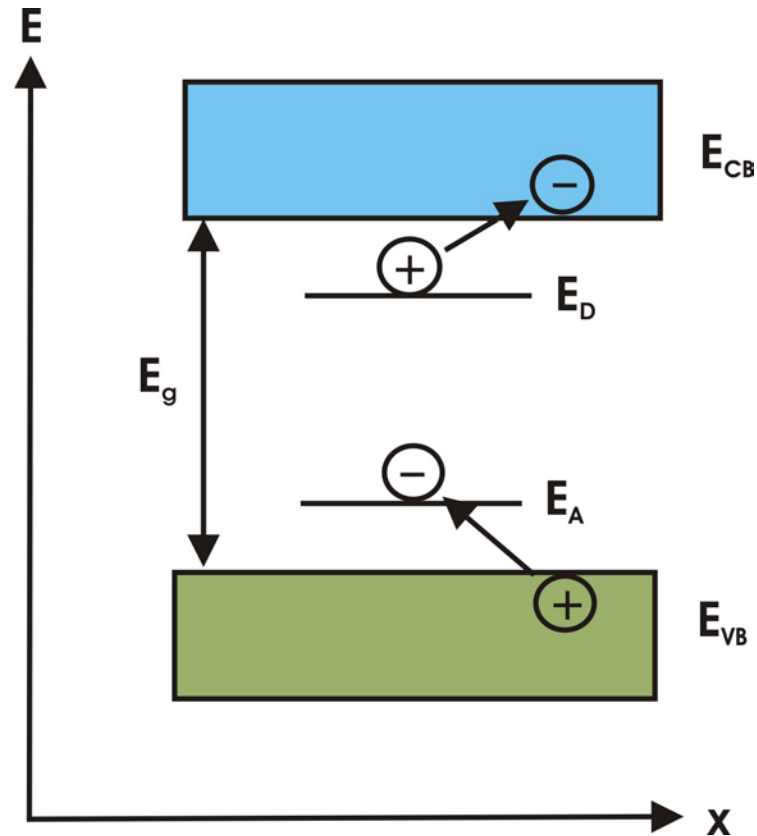… requires increase of the concentration of *mobile* charge carriers:

$$\sigma = e\,n\,\mu$$

σ- conductivity
n- carrier concentration
μ- mobility

- for thermal generation of mobile carriers in the bands, the energy levels of the foreign atoms must be located close to the band edges

Donors and acceptors

Donor: neutral if occupied with (outer) electron, positively charged if unoccupied

Acceptor: neutral if unoccupied by an electron, negatively charged if occupied

Due to the thermal ionization of the dopant atoms, the conductivity of the doped semiconductor increases

Schematic diagram of the energy levels of an
(a) n-type semiconductor
(b) a p-type semiconductor

Types of doping for Si

- Si crystallizes in the tetrahedral (diamond) structure
- each Si atom forms four mixed covalent and ionic bonds to its nearest neighbours

Types of doping

The extra atoms lead to spatially localized energy levels in the band gap (E_D)

If the energy levels are shallow enough for thermal excitation, the number of electrons in the conduction band increases

For donors, the number of electrons in the conduction band increase

The semiconductor attains n (negative) conductivity type

In an n-type semiconductor, electrons are *majority* carriers and holes are *minority* carriers

Dopants and traps

The energetic position of a defect level within the semiconductor energy gap deteremines ist function:

dopant: shallow level w.r.t. the band edges; thermal ionization of dopant likely

trap: deep level closer to the middle of the band gap; the thermal excitation is very slow; the site acts as a scavenger for mobile carriers in the bands;
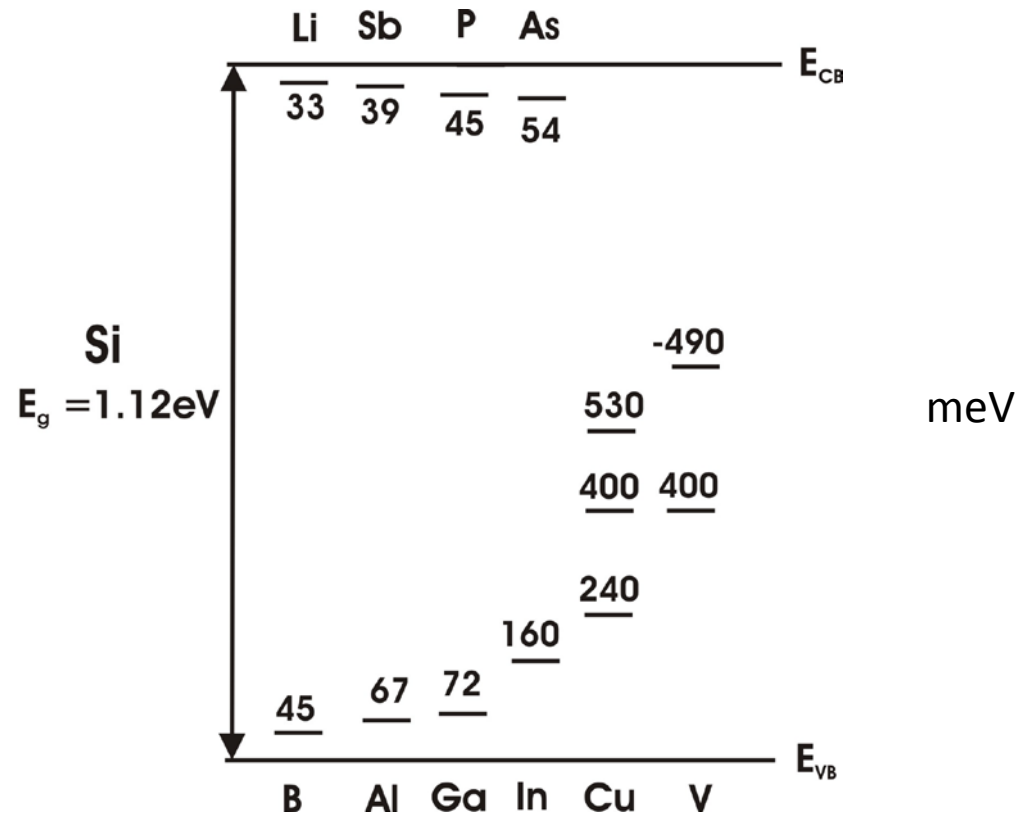
donor levels are Li, Sb, P and As in Si with energetic distance between 33 meV and 54 meV

acceptors levels are B and Al are characterized by the smallest energetic distance to the valence band maximum

The role of traps

- reduce the majority carrier concentration

- act as recombination sites for light generated minority carriers

nature of traps besides impurity atoms:
lattice defects (point-planar- and 3-D defects),
stoichiometry deviations in compound semiconductors
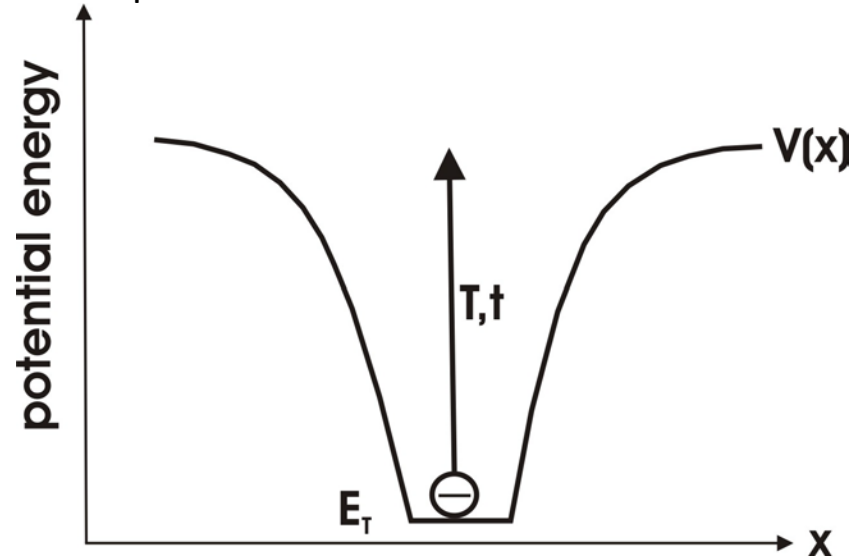
release time

$$t = t_0 \exp \frac{E_{CB} - E_T}{kT}$$

For so called deep traps ($E_{CB}-E_T$)>>kT the release time can exceed the lifetime of the conduction band electrons

Influence of doping on Fermi level position

donor and acceptors are present

$$n + N_A^- = p + N_D^+$$ electroneutrality conditions

N_D^+ – concentration of positively charged donors
N_A^- - concentration of negatively charged aceptors

$$\Delta E = E_{CB} - E_D \approx E_A - E_{VB} \leq kT$$ donors and acceptors will be ionized

$$n + N_A = p + N_D$$

$$n - (N_D - N_A) = p$$

multiplication by n $$n^2 - n(N_D - N_A) = np = n_i^2$$

$$np = n_i^2$$

$$n = \frac{1}{2}\left[(N_D - N_A) + \sqrt{(N_D - N_A)^2 + 4n_i^2}\right]$$

approximation
for n-type semiconductor

$$N_D \gg N_A \; so \; |N_D - N_A| \gg n_i$$

Effective doping concentration is much higher that the intrinsic carrier concentration

$$n = \frac{1}{2}\left(N_D + \sqrt{N_D^2}\right) = N_D$$

$$n = N_{CB} \exp\left(-\frac{(E_{CB} - E_F)}{kT}\right) = N_D \approx N_D^+$$

for n-type
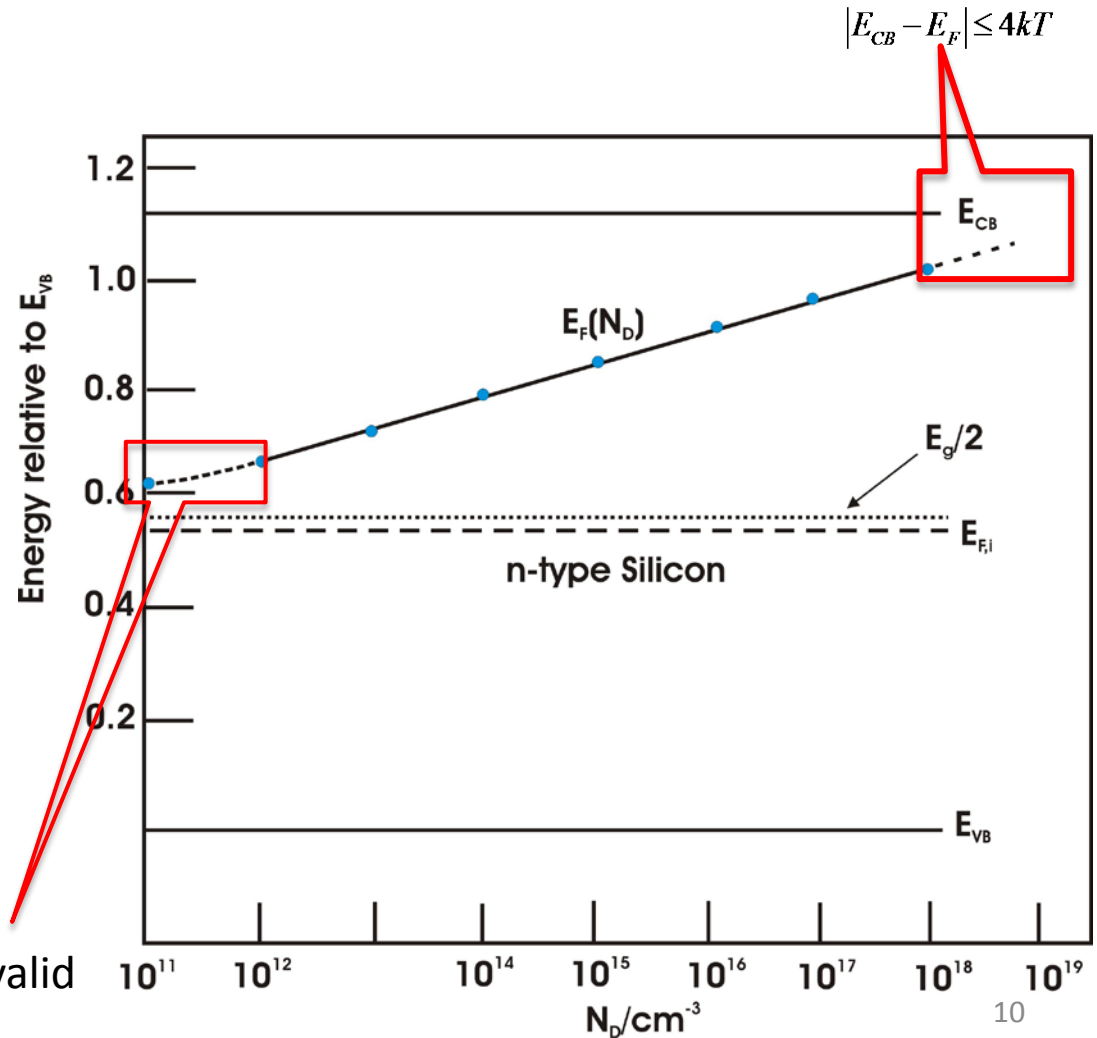
$$E_F = E_{CB} - kT \ln \frac{N_{CB}}{N_D}$$

for p-type

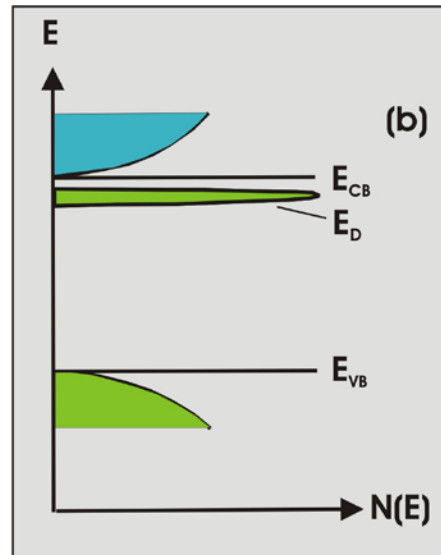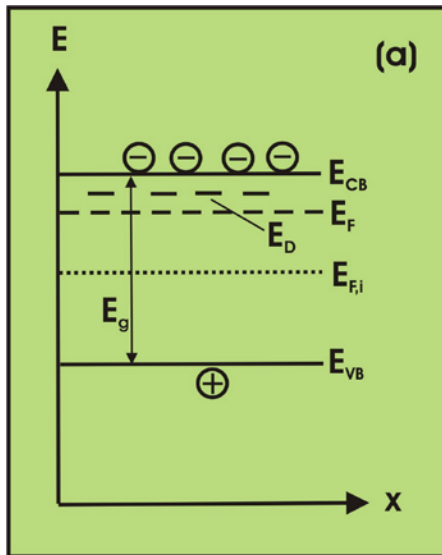$$E_F = E_{VB} + kT \ln \frac{N_{VB}}{N_A}$$

Intrinsic E_F located in midgap
$n_i = 1.45 \cdot 10^{10} \text{cm}^{-3}$

With exponential increase of doping concentration,
the Fermi level moves linearly towards the conduction band

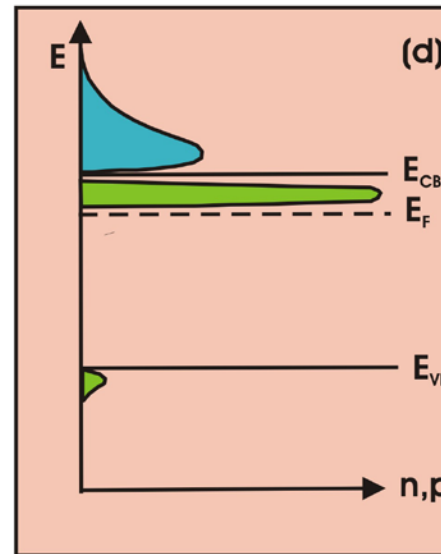Course of Fermi level with doping concentration for Si
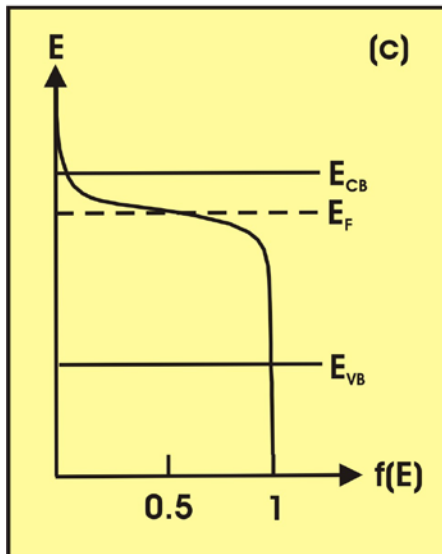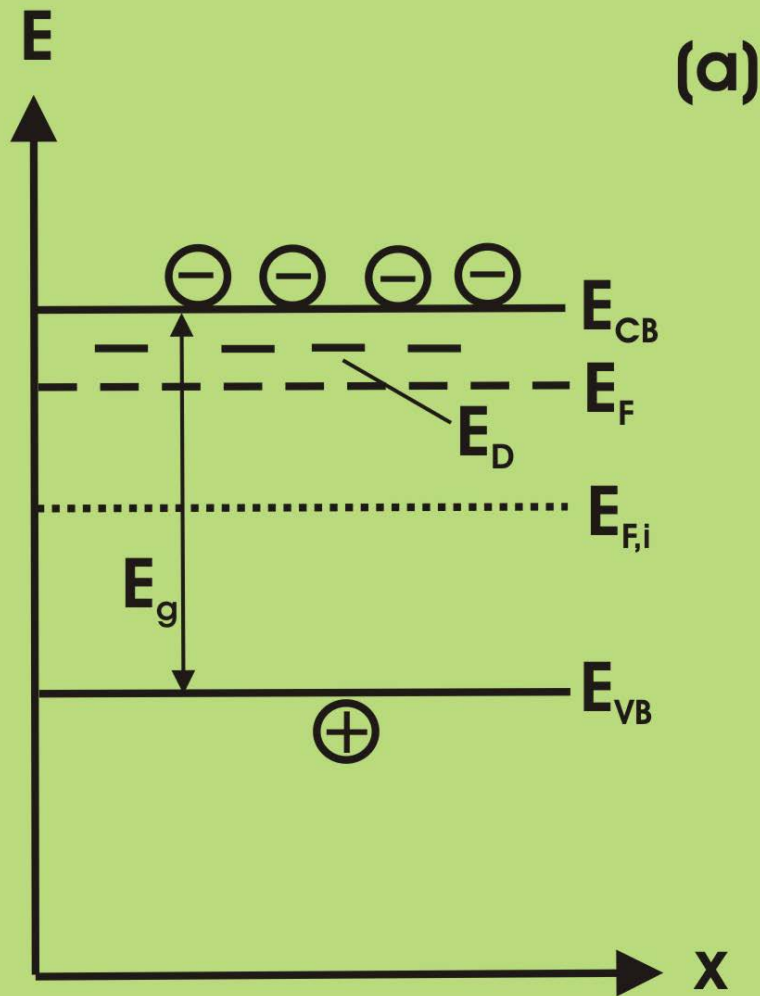
$$|E_{CB} - E_F| \le 4kT$$

$N_D \gg n_i$ not valid

Mobile carriers, DOS, Fermi level and carrier concentration for the doped semiconductor

Summarizing of properties of doped semiconductors
a) energy band diagram in space
b) energy dependence of the density of states
c) Fermi distribution function
d) carrier occupation density

n-type semiconductor, characterized by dopants (donors) located at an energy E_D within the energy gap and a Fermi level position energetically below E_D; accordingly, most donors are empty i.e. ionized. The imbalance of the carrier concentration in the respective bands is expressed by the different absolute number of electrons and holes. Electrons are majority carriers; holes are minority carriers in n-type material.
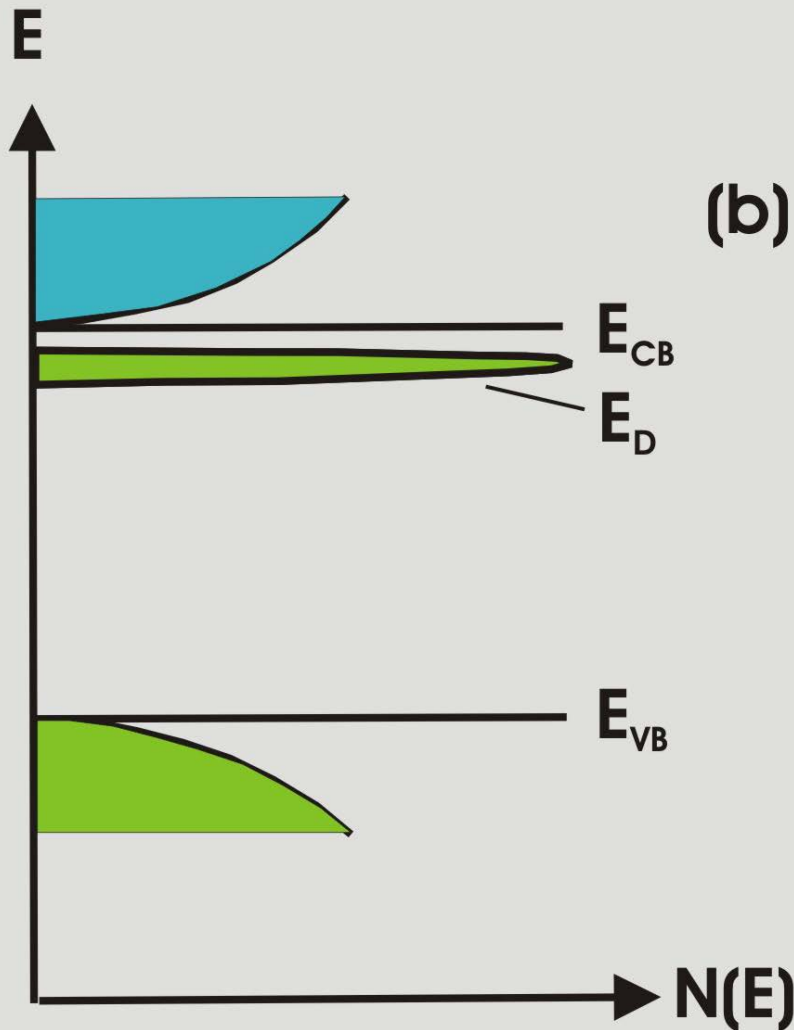
The DOS for the carriers in the conduction and valence band is displayed.

It corresponds to the DOS of the intrinsic semiconductor. The ionized donors, however, exhibit a high density of states in the energy range of their levels, indicated by the peaked curve around E_D.

The conservation of charge neutrality leads to the upward shift of the Fermi level of the n-type semiconductor compared to the intrinsic one.
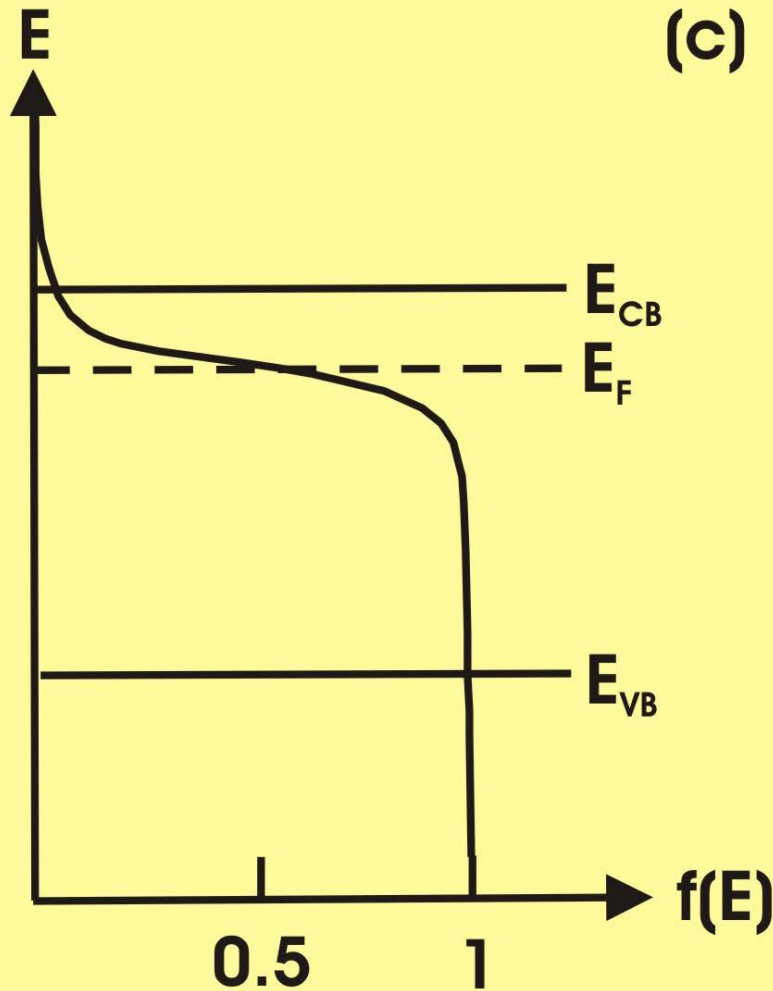
Assume Si doping with a concentration of $N_D = 10^{16}$cm^{-3}

$$N_D = 10^{16}\, cm^{-3}$$

$$n_i \approx N_D$$

$$n_i = 1.45 \cdot 10^{10}\, cm^{-3}$$

$$p = \frac{n_i^2}{N_D} = 2.1 \cdot 10^4\, cm^{-3}$$

Hole concentration is lower by about 6 orders of magnitude compared to the intrinsic carrier concentration.

The area under the curve for the electron concentration in the conduction band (negative charges) must be equal the area of the hole concentration in the valence band plus the area under the ionized donors (positive charges).

Energy integration of the curve in the conduction band gives the electron concentration and the analogue integration along the valence band energies yields the hole concentration.
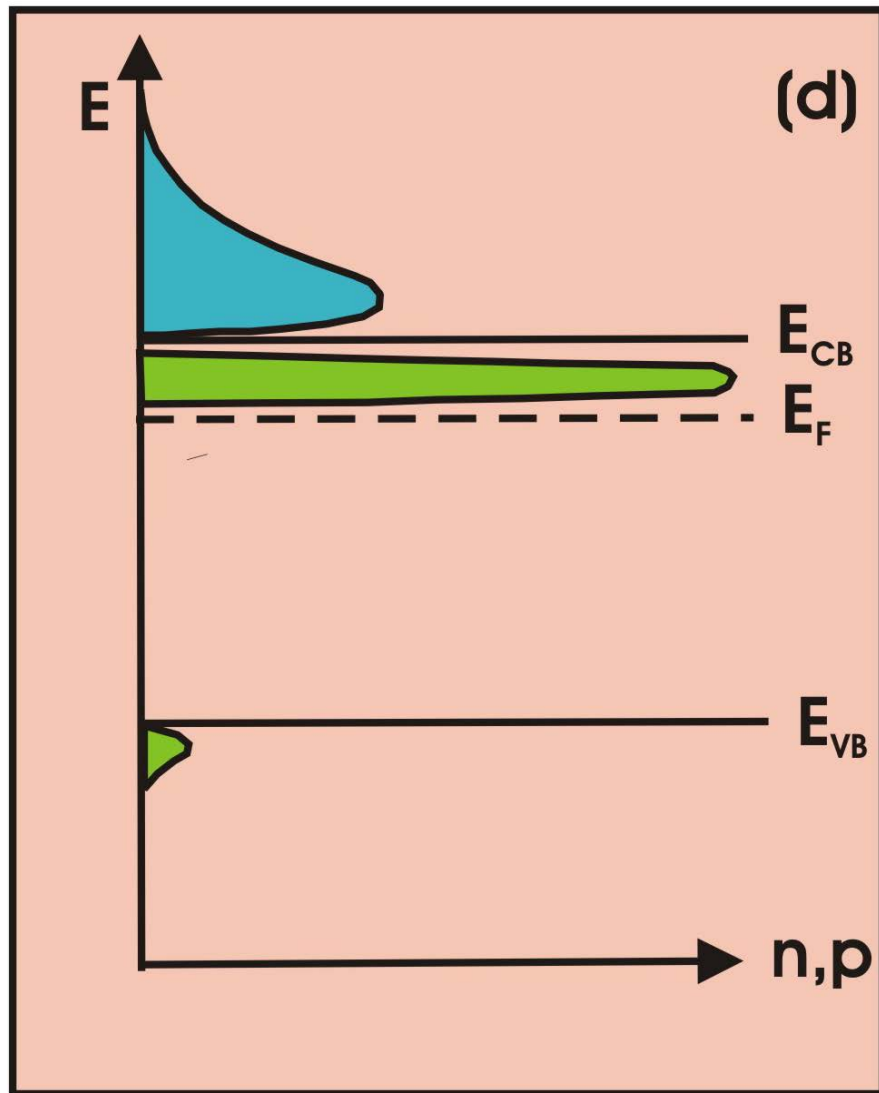
The product of DOS and distribution function gives again the energetic dependence of the number of carriers in the bands and here also in the defect levels. The shift of the Fermi distribution to higher energies in direction of the conduction band results in a drastic reduction of the number of holes in the valence band, actually below the value for the intrinsic case.

The area under the curve for the electron concentration in the conduction band (negative charges) must be equal the area of the hole concentration in the valence band plus the area under the ionized donors (positive charges).
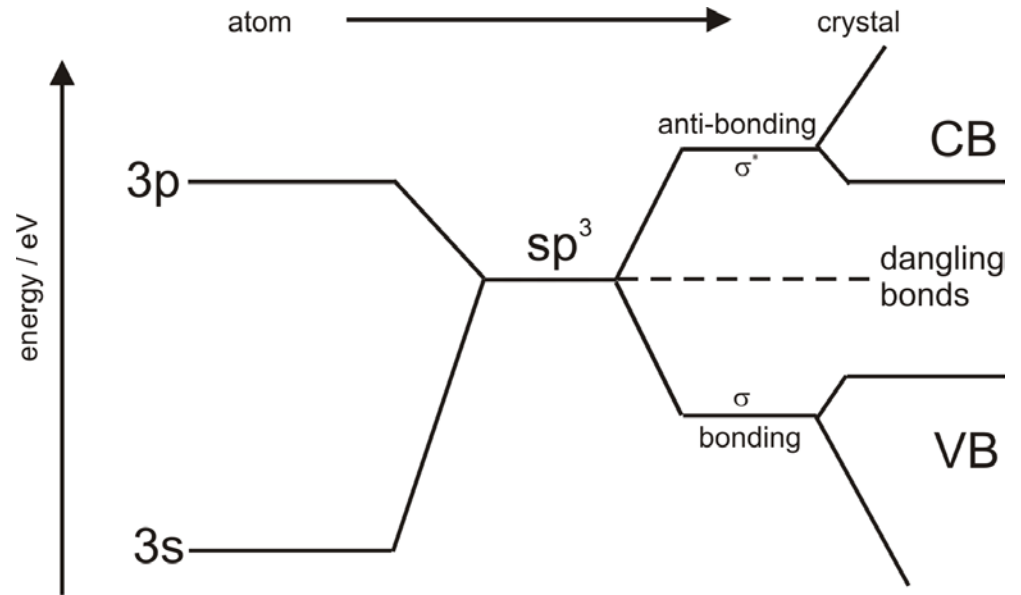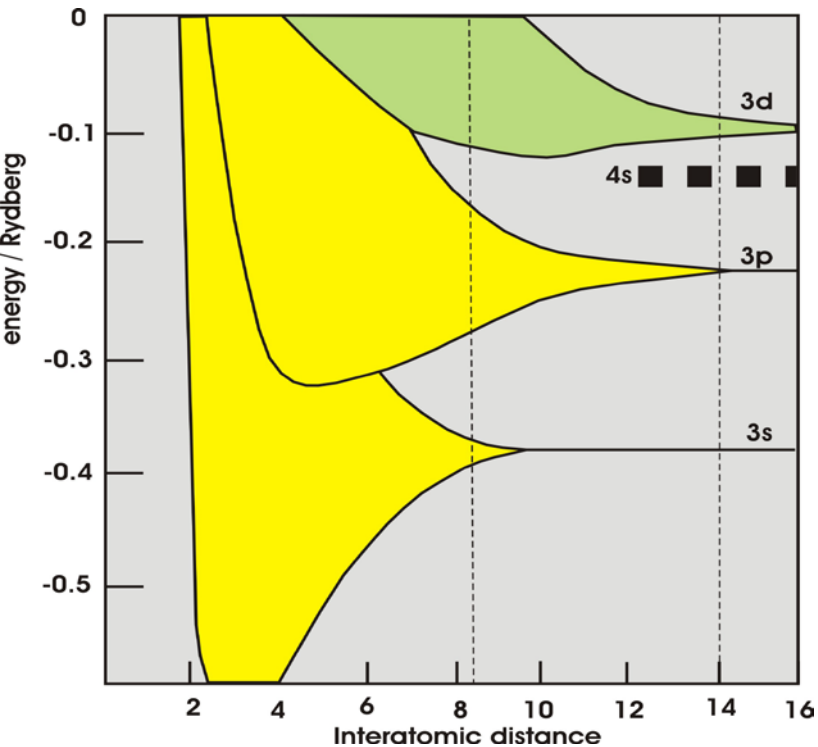
Intrinsic Semiconductors

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Transition from electron energy levels in isolated atom to band structure ion crystalline solid

Decreasing distance leads to increasing overlap of atomic potentials and wave functions

Semiconductors

- insulator for deep temperatures (T = 0)

- conduction band at low temperatures as good as empty, valence band almost full

- band gap $0.3eV < E_g < 3eV$

- T ↑ → resistivity ↓   (intrinsic semiconductor)

- Electrons can stay in the conduction band for about 10^{-3} - 10^{-9} s
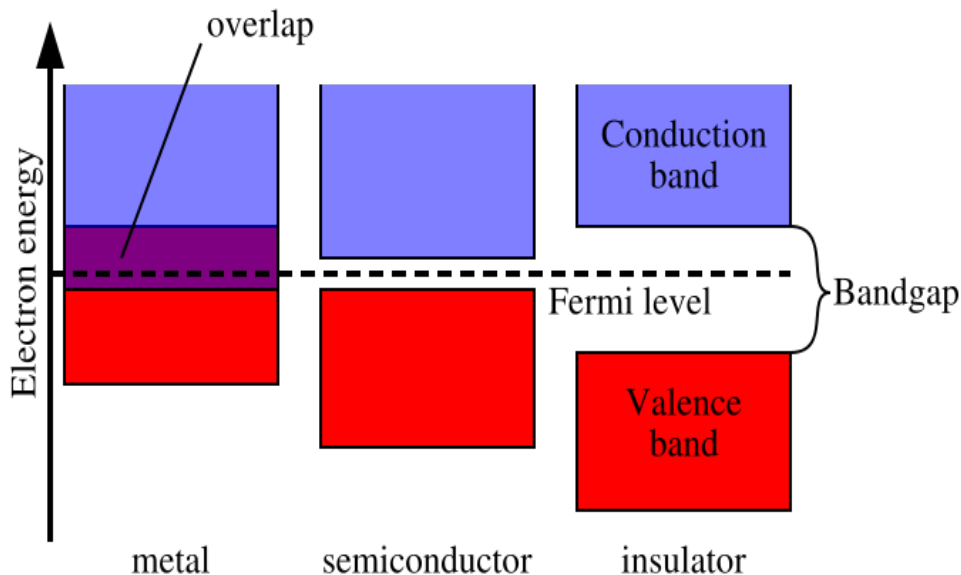
Metals: no energy gap
Semiconductors: $0.3 < E_g < 3$ eV
Isolators: $E_g > 3$ eV

E_{CB}-energy of conduction band
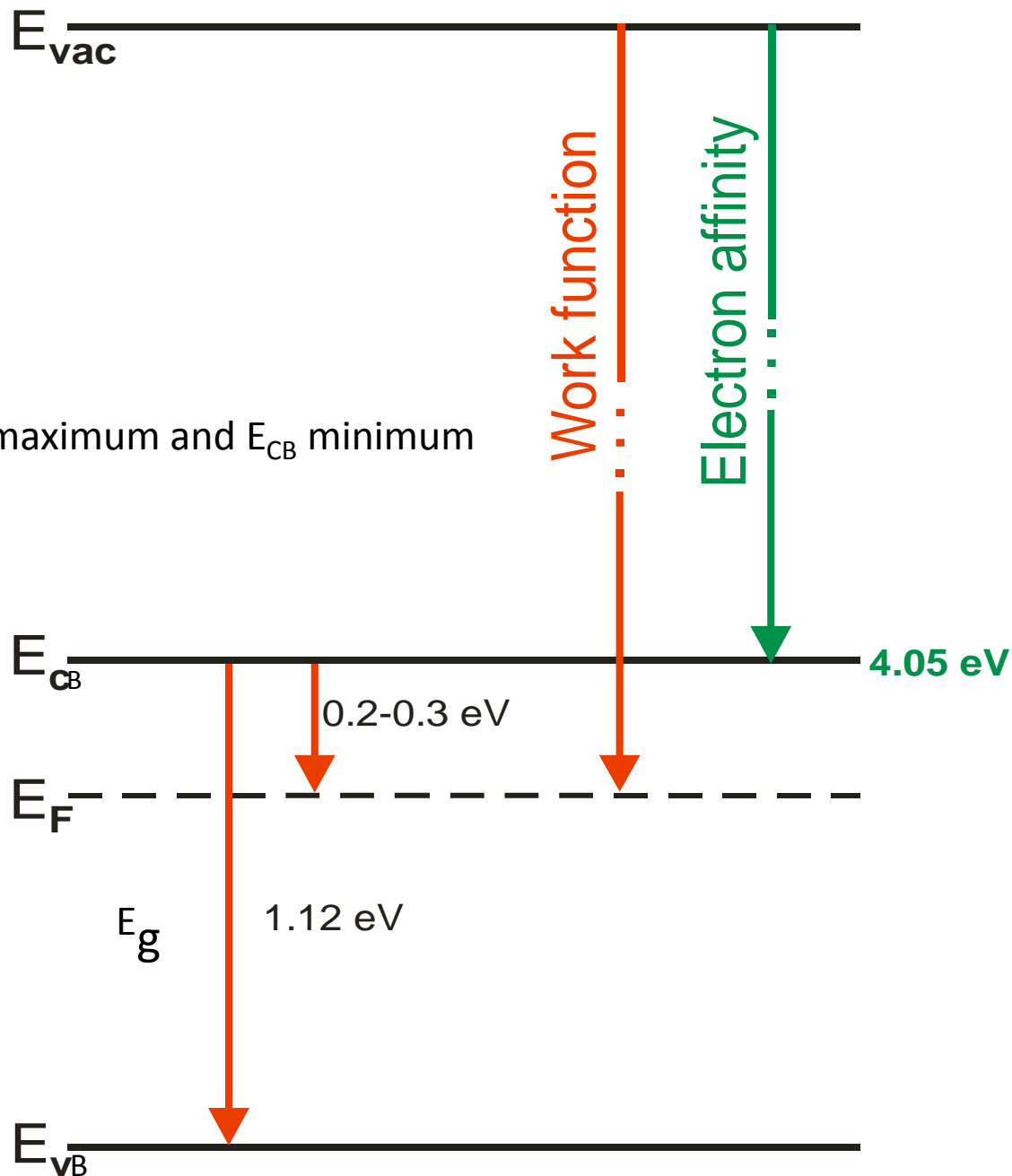 lowest unoccupied level
E_{VB}- energy of valence band
  highest occupied level
E_g- band gap
  energy distance between E_{VB} maximum and E_{CB} minimum
E_F- Fermi level

E_{vac}

Work function

Electron affinity

E_{CB} 4.05 eV

0.2-0.3 eV

E_F

E_g 1.12 eV

E_{VB}

The **vacuum level**

is the energy of electron at rest far from the influence of the potential of the solid.

The **electron affinity**

for semiconductor is the energy required to remove an electron from the bottom of the conduction band to the vacuum level.

The **work function**

is the energy required to take an electron from the Fermi level to the vacuum.

Intrinsic semiconductors

Carrier generation by **thermal excitation**; INTRINSIC CONDUCTIVITY

The energetic width of the band gap E_g determines the concentration of electrons in the conduction band and of holes in the valence band.

At a given temperature, the number of electrons and holes in the respective bands is equal:

MASS ACTION LAW

$$n = p = n_i$$
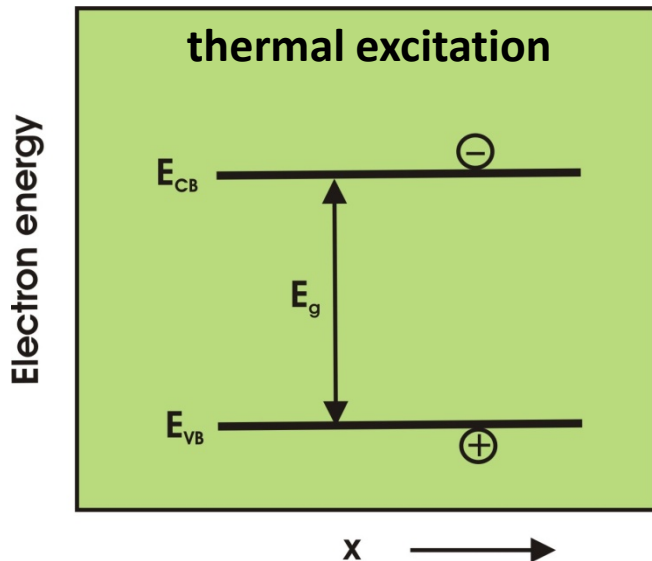
n – electron concentration

p – hole concentration

n_i – intrinsic carrier concentration

thermal excitation

Intrinsic semiconductors
Fermi level (E_F)
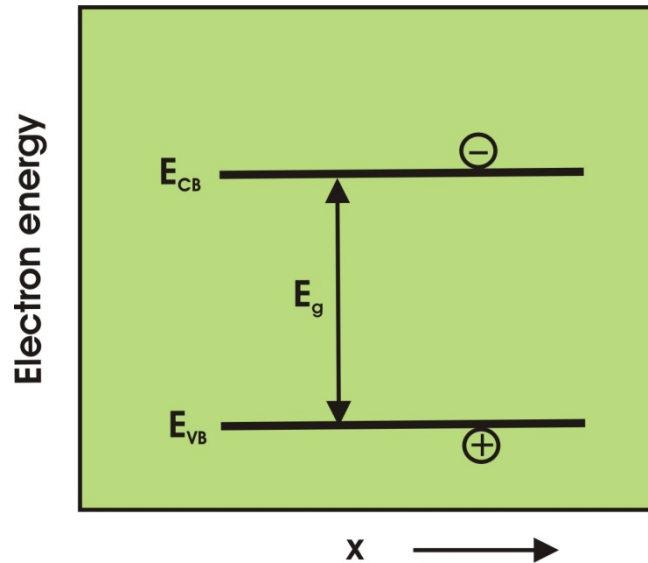
The concept of Fermi level for Fermions

Pauli exclusion principle for Fermions:
electrons can not be in the same place with all their quantum numbers being equal

Consequence:
the number of electrons results in quantum state's occupation limit – the FERMI LEVEL
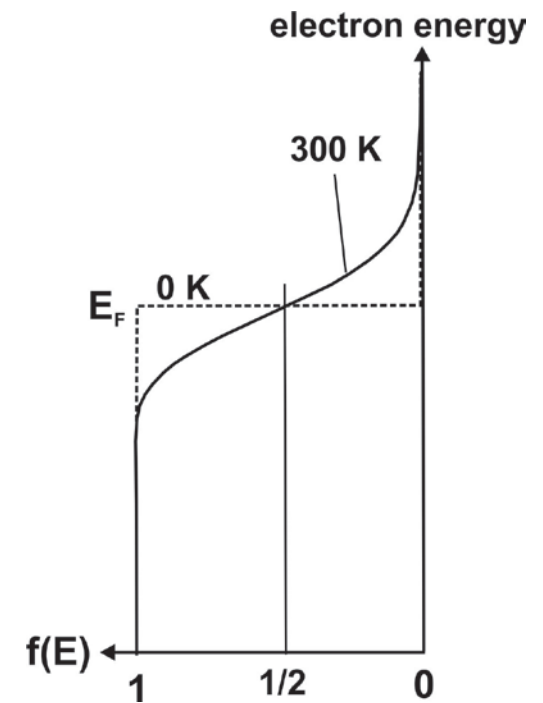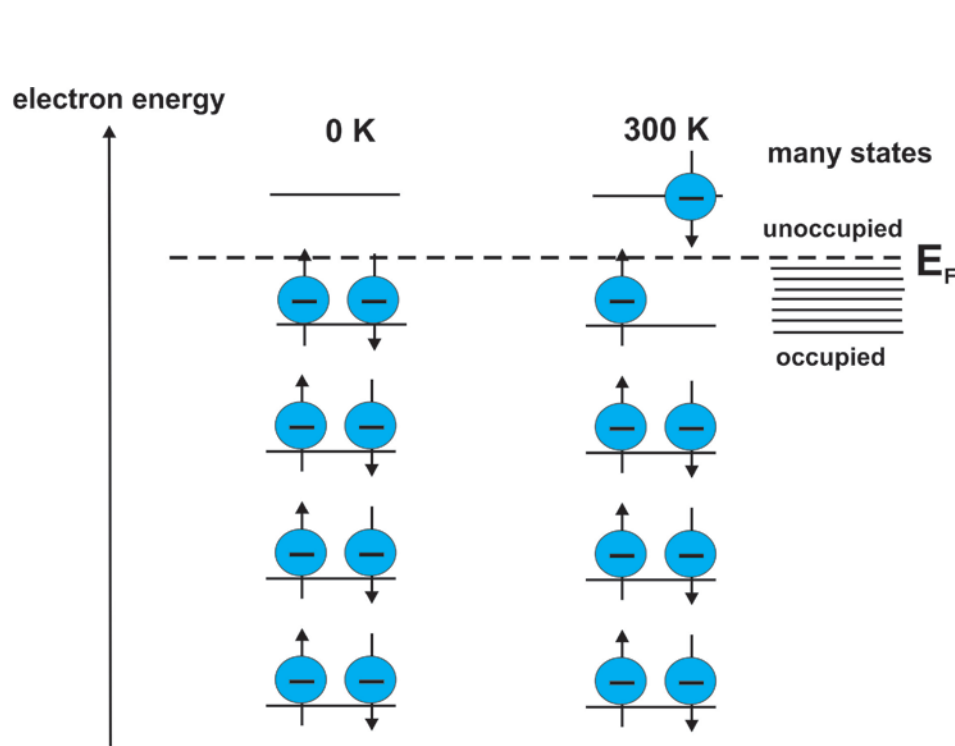
an example for Si:

n	1	2		3		
l	0	0	1	0	1	2
m	0	0	-1 | 0 | +1	0	-1 | 0 | +1	-2 | -1 | 0 | +1 | +2
s	$+\frac{1}{2}-\frac{1}{2}$	$+\frac{1}{2}-\frac{1}{2}$	$+\frac{1}{2}-\frac{1}{2}$ $+\frac{1}{2}-\frac{1}{2}$ $+\frac{1}{2}-\frac{1}{2}$	$+\frac{1}{2}-\frac{1}{2}$	$+\frac{1}{2}-\frac{1}{2}$ $+\frac{1}{2}-\frac{1}{2}$ $+\frac{1}{2}-\frac{1}{2}$	$+\frac{1}{2}-\frac{1}{2}$ $+\frac{1}{2}-\frac{1}{2}$ $+\frac{1}{2}-\frac{1}{2}$ $+\frac{1}{2}-\frac{1}{2}$ $+\frac{1}{2}-\frac{1}{2}$
	↑↓ 1s	↑↓ 2s	↑↓ ↑↓ ↑↓ 2p	↑↓ 3s	↑↓ ☐ ☐ 3p	☐ ☐ ☐ ☐ ☐ 3d

n- principal quantum number
l- azimuthal quantum number
m- magnetic quantum number
s- spin projection quantum number

Carrier concentration:

obtained by approximating the Fermi-Dirac integral by a Boltzmann distribution

for electrons

$$n = N_{CB} \exp\left(-\frac{E_{CB} - E_F}{kT}\right)$$

for holes

$$p = N_{VB} \exp\left(-\frac{E_F - E_{VB}}{kT}\right)$$

N_{CB}, N_{VB} : so-called effective density of states (trick to include the band structured by maintaining the free-carrier picture for electrons/holes in the solid).

The **carrier concentration for electrons in the conduction band** is given by the integration of
- the **probability distribution for Fermions**, f(E), multiplied with
- the **density of states for free particles**, N(E),
- over the energy

$$n = \int_{CB}^{\infty} N(E) f(E) \, dE$$

n- number of electrons
f(E)- Fermi distribution function
N(E)- density of states DOS

The energy state at energy E has define probability to be occupied by an electron.
f(E)- probability of occupancy (main conclusion of Fermi-Dirac statistic)

$$N(E) = \sqrt{E - E_{CB}} \qquad f(E) = \frac{1}{1 + e^{\frac{E - E_F}{kT}}}$$

N(E) dE- the number of electrons energy states per unit volume over energy interval

Fermi-Dirac integral

$$n = \int_{E_{CB}}^{\infty} \frac{\sqrt{E - E_{CB}}}{e^{\frac{E - E_F}{kT}} + 1} \, dE$$

very difficult to solve analytical; Boltzmann approximation where the denominator is purely exponential has to be used

$$e^{\frac{E - E_F}{kT}} \gg 1$$

$$E_{CB} - E_F \geq 4kT \ (4 \cdot 26meV = 104meV = 0.1eV)$$

$$for \ E - E_F = 3kT, \ e^{\frac{E - E_F}{kT}}, e^3 = 1.09$$

$$for \ E - E_F = 4kT, \ e^{\frac{E - E_F}{kT}}, e^4 = 54.6$$

$$for \ E - E_F = 5kT, \ e^{\frac{E - E_F}{kT}}, e^5 = 148.4$$

The Fermi Dirac integral can be numerically solved when the Fermi distribution function can be replaced by a Boltzmann distribution.
this can be done for:

$$\frac{E - E_F}{kT} >> 1$$

$$E_{CB} - E_F \geq 4kT(0.1eV)$$

The energetic distance between the conduction band (E_{CB}) minimum and the Fermi level (E_F) should not be much smaller than 0.1eV at room temperature. (non degenerate semiconductor)

The Fermi Dirac integral for electrons then becomes:

$$n = \frac{1}{2}\pi^2\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2}\exp\left(-\frac{E_{CB}-E_F}{kT}\right)(kT)^{3/2}\frac{1}{2}\pi\,{}^{1}\!/\!_{2}$$

Where:

$$N_{CB} = 2\left(\frac{m_e^*kT}{2\pi\hbar^2}\right)^{3/2}$$

Effective density of states at conduction band minimum

In consequence we get the **electron concentration in the conduction band** of semiconductor

$$n = N_{CB}\exp\left(-\frac{(E_{CB}-E_F)}{kT}\right)$$

In analogy the **concentration of holes at the valence band**:

$$N_{VB} = 2\left(\frac{m_h^* kT}{2\pi\hbar^2}\right)^{2/3} \qquad\qquad p = N_{VB}\exp\left(-\frac{\left(E_F - E_{VB}\right)}{kT}\right)$$

N_{VB}- effective density od states at valence band maximum

Carrier concentration

$$n = N_{CB} \exp\left(-\frac{(E_{CB} - E_F)}{kT}\right)$$

$$p = N_{VB} \exp\left(-\frac{(E_F - E_{VB})}{kT}\right)$$

Effective density of states DOS

at conduction band minimum:

$$N_{CB} = 2\left(\frac{m_e^* kT}{2\pi\hbar^2}\right)^{3/2}$$

at valence band maximum:

$$N_{VB} = 2\left(\frac{m_h^* kT}{2\pi\hbar^2}\right)^{2/3}$$

N_{CB}, N_{VB} - so-called **effective density of states** (trick to include the band structure by maintaining the free-carrier picture for electrons/holes in the solid).

m$_{e,h}$* denote the effective mass of electrons or holes; deviation of from free particles behaviour - to describe the energy band structure of solid within free electron picture.
it is a construct to work with quasi free particles where the crystal potential variation is expressed by a energy band structure directional dependence of the effective mass tensor.

The intrinsic carrier concentration

$$n \cdot p = n_i^2$$

n – electron concentration

p – hole concentration

n_i – intrinsic carrier concentration

$$n = N_{CB} \exp\left(-\frac{(E_{CB} - E_F)}{kT}\right)$$

$$p = N_{VB} \exp\left(-\frac{(E_F - E_{VB})}{kT}\right)$$

$$n_i = \left(N_{CB} N_{VB}\right)^{1/2} \exp\left(-\frac{(E_{CB} - E_{VB})}{2kT}\right) =$$

$$= \left(N_{CB} N_{VB}\right)^{1/2} \exp\left(-\frac{E_g}{2kT}\right)$$

MASS ACTION LAW

$$n \cdot p = n_i^2$$

| Semiconductor T=300K	Effective DOS N_{CB} / cm^{-3}	Effective DOS N_{VB} / cm^{-3}	Band gap E_g / eV	Intrinsic carrier concentration n_i / cm^{-3}
Ge	$1 \cdot 10^{19}$	$5 \cdot 10^{18}$	0.66	$2.4 \cdot 10^{13}$
Si	$3.2 \cdot 10^{19}$	$1.8 \cdot 10^{19}$	1.12	$1.45 \cdot 10^{10}$
GaAs	$4.7 \cdot 10^{17}$	$9 \cdot 10^{18}$	1.42	$1.79 \cdot 10^{6}$

- Exponential dependence of carrier concentration on the energy gap
  - large change in n_i at moderate differences in E_g
  - isolating for large band gaps

n_i- intrinsic carrier density which depends on the semiconductor bandgap (E_g) and temperature

Intrinsic carrier concentration: T-dependence for Ge, Si and GaAs

T-dependence according for three semiconductors
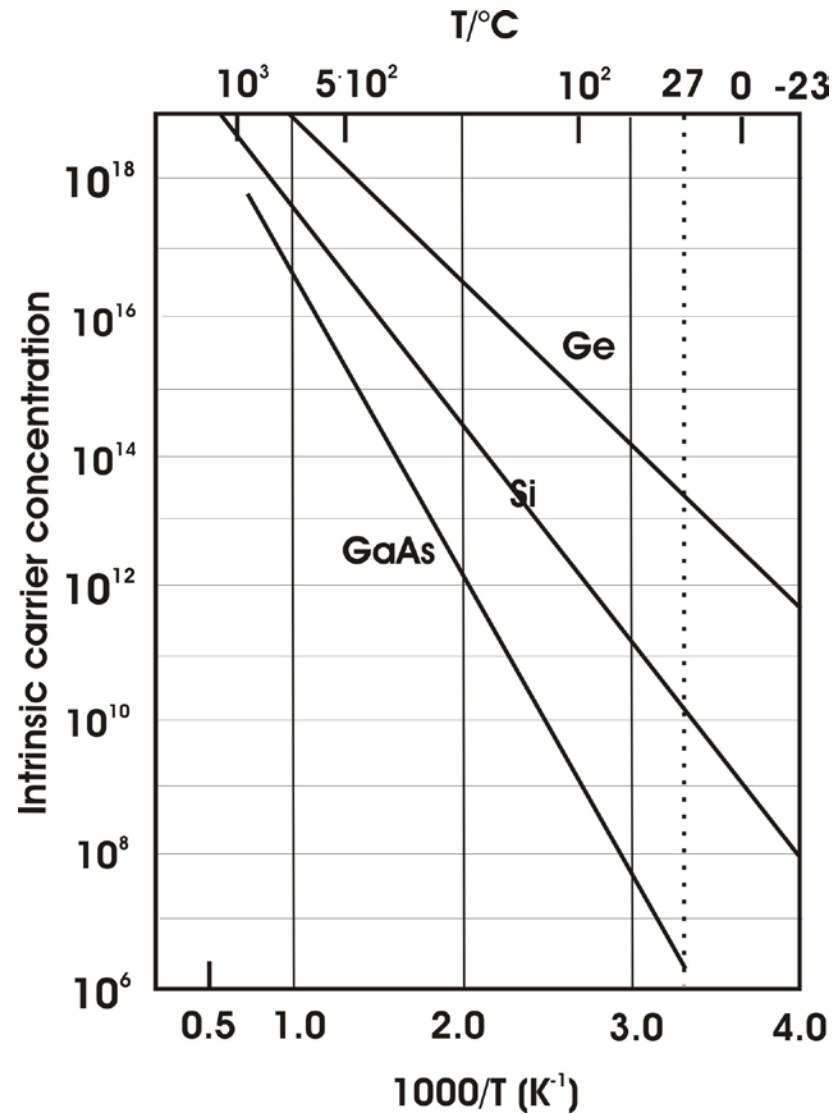
With increase of temperature the number of exited carriers increases exponentially

Intrinsic semiconductor Fermi level
from charge neutrality condition p=n

MASS ACTION LAW

$$n = N_{CB} \exp\left(-\frac{(E_{CB} - E_F)}{kT}\right)$$

$$n = p = n_i$$

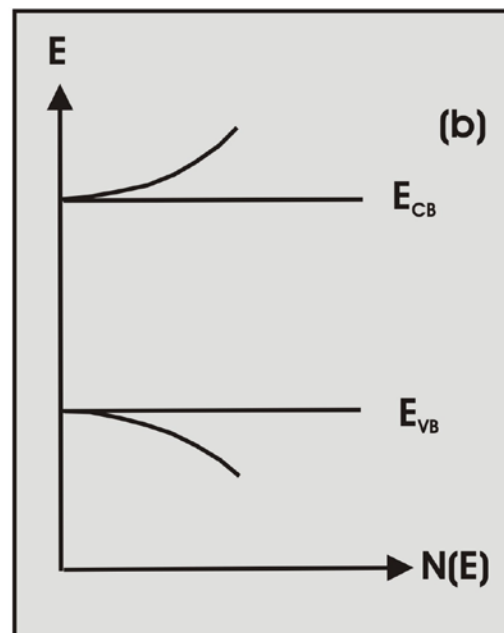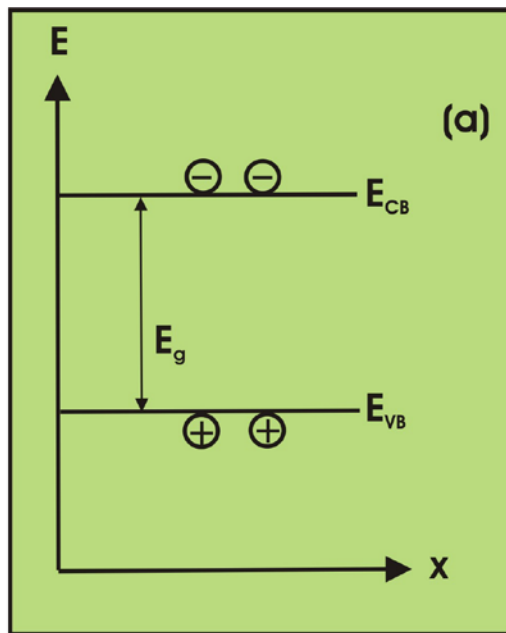$$p = N_{VB} \exp\left(-\frac{(E_F - E_{VB})}{kT}\right)$$

$$N_{CB} \exp\left(-\frac{(E_{CB} - E_F)}{kT}\right) = N_{VB} \exp\left(-\frac{(E_F - E_{VB})}{kT}\right)$$

$$-E_{CB} + E_F + E_F - E_{VB} = kT \ln\frac{N_{VB}}{N_{CB}}$$

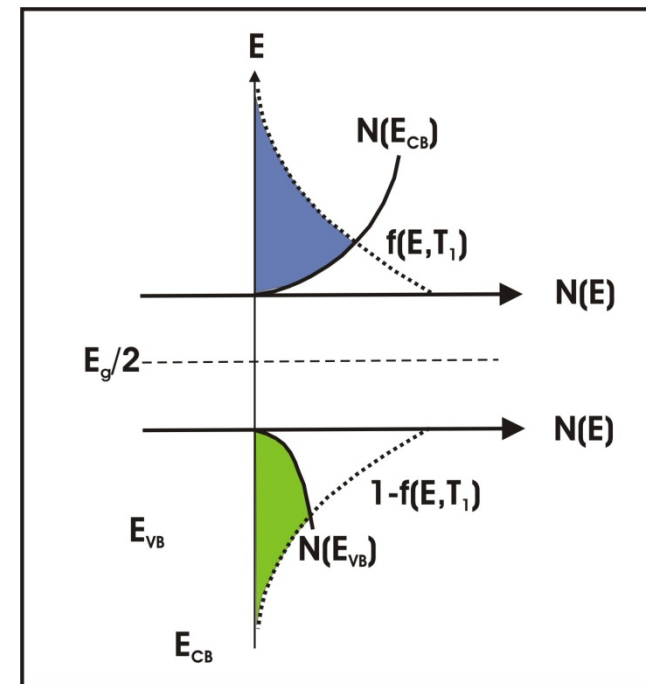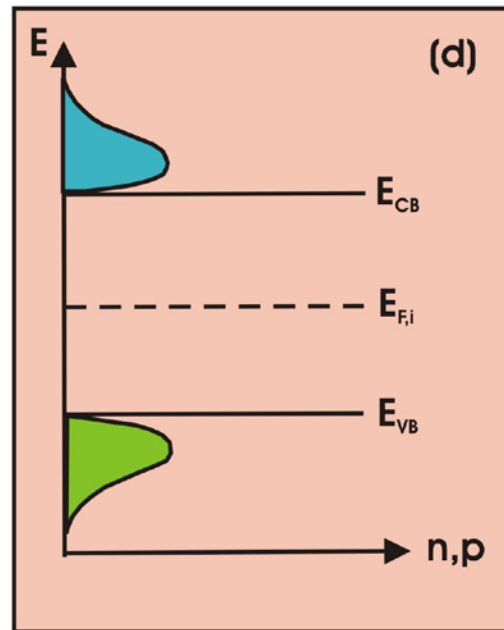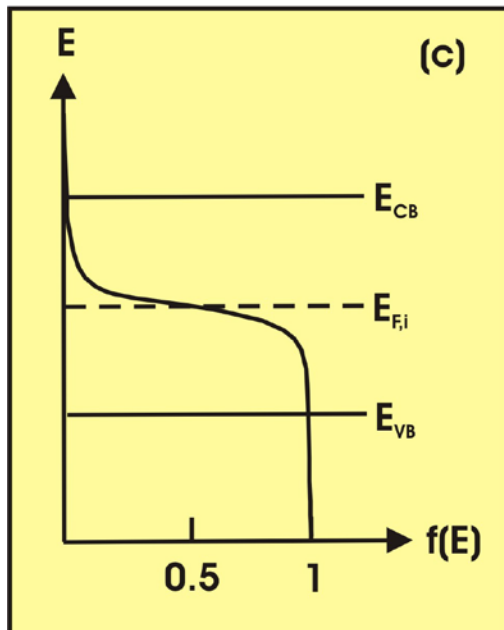$$E_F = \frac{(E_{VB} + E_{CB})}{2} + \frac{kT}{2}\ln\frac{N_{VB}}{N_{CB}}$$
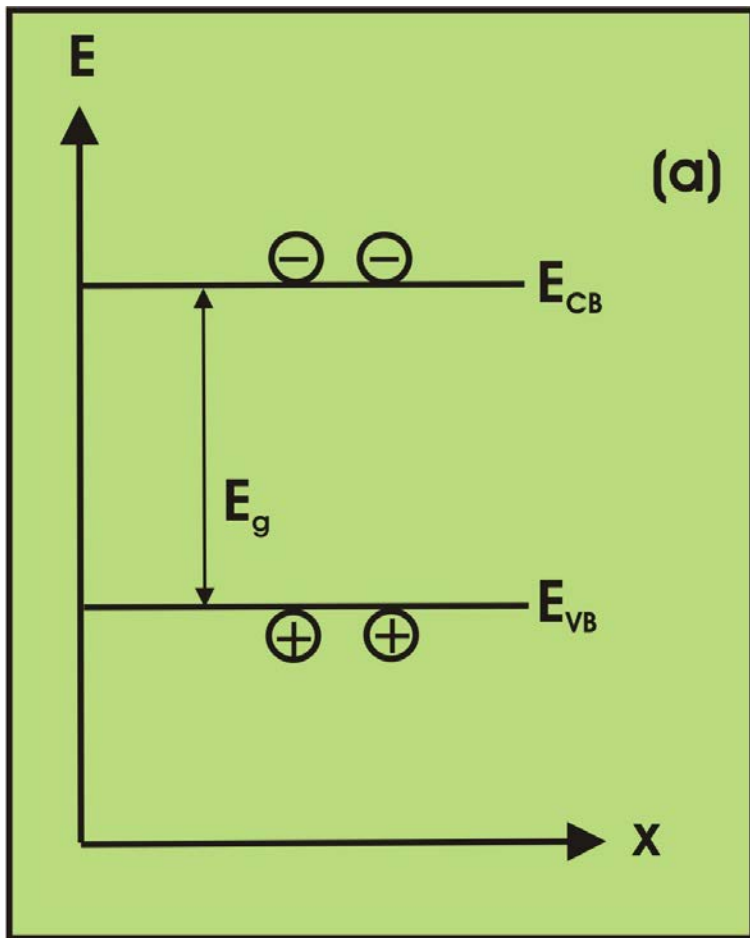
middle of energy band gap

$$E_F = \frac{E_g}{2} + \frac{kT}{2}\ln\frac{N_{VB}}{N_{CB}}$$

Summarizing of properties of intrinsic semiconductors
a) energy band diagram in space
b) energy dependence of the density of states
c) Fermi distribution function
d) carrier occupation density

(a)

the valence- and conduction band of an intrinsic semiconductor in real space (coordinate x) where the number of thermally excited electrons in the conduction band equals the number of excited defect electrons (holes) in the valence band

(b)
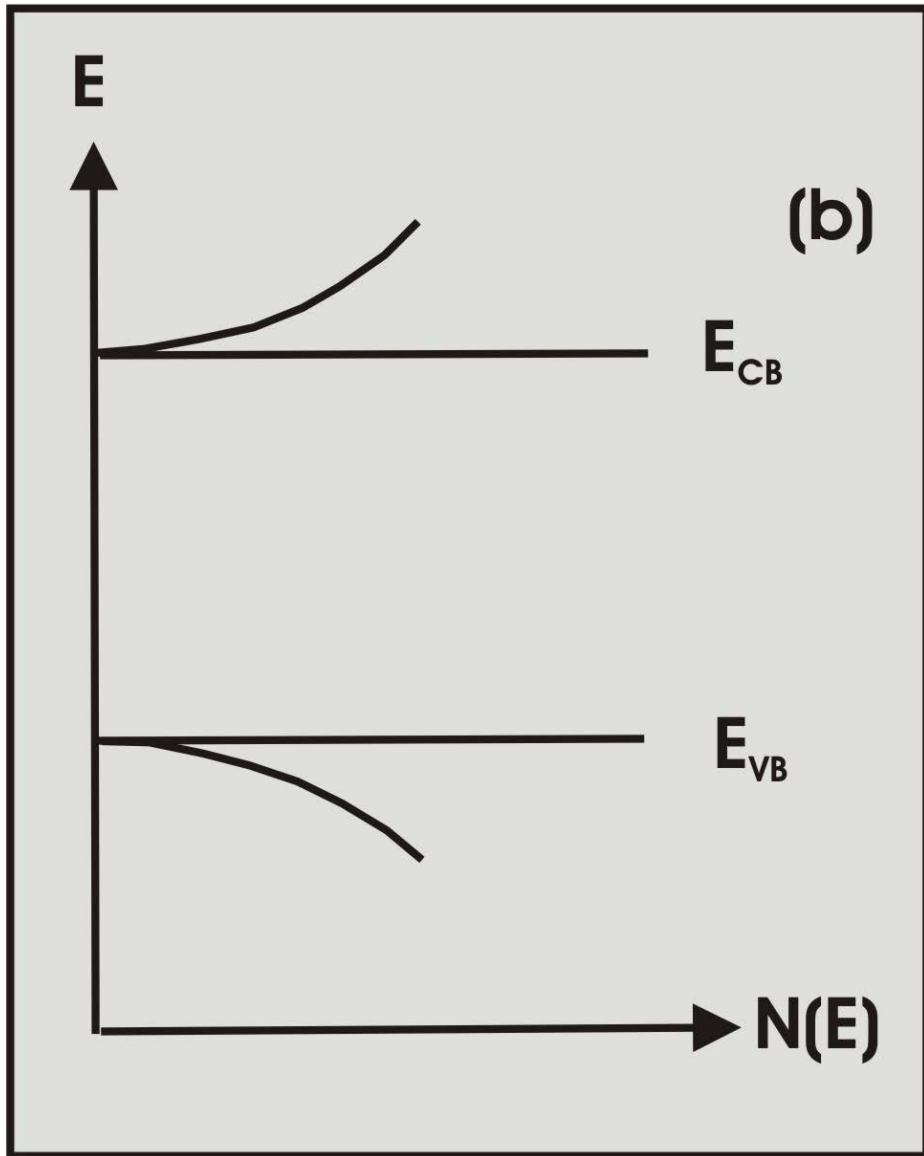
The energetic dependence of the density of states N(E);

The DOS for a given energy describes the number of quantum mechanically possible energy states per cm^3 within a small energy interval dE around E.

In the forbidden energy gap, N(E) is zero.

In the nearly free particle approximation, N(E) increases in the conduction band with increasing energy with a parabolic dependence, i.e. N(E).

In the valence band, N(E) increases accordingly with decreasing energy since defect electrons are considered.
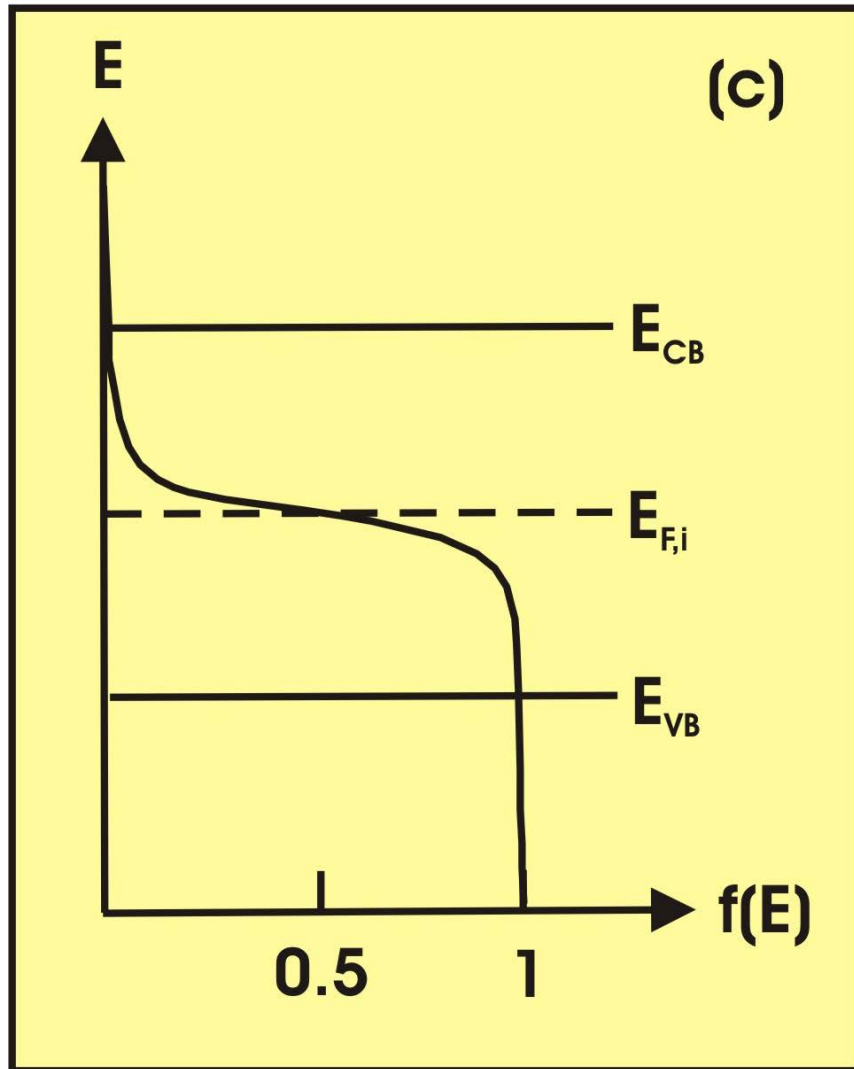
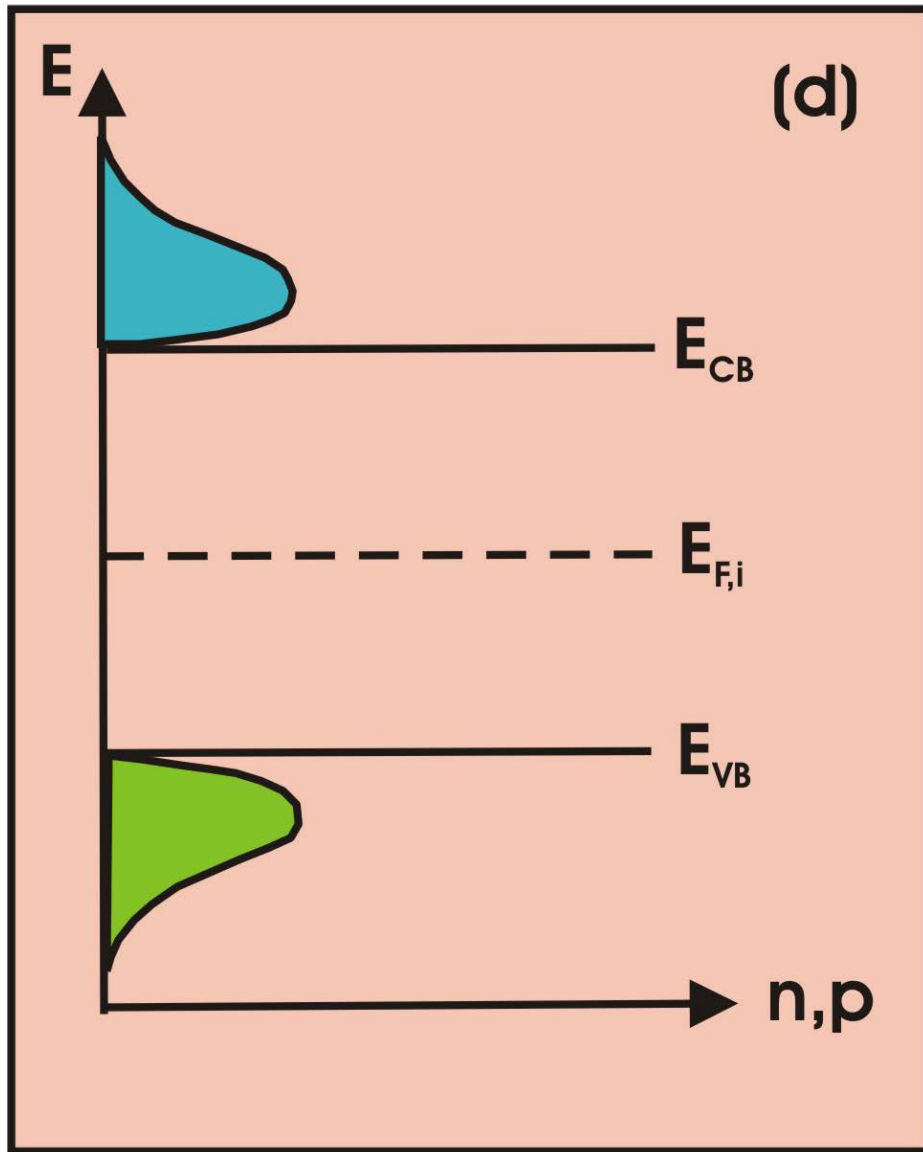The energy dependence of f(E), the Fermi distribution function.

It represents the probability of the occupation of a state for a given temperature. Electrons, particles with spin +/- 1/2, are Fermions and are described by Fermi statistics where the Pauli exclusion principle demands that each quantum mechanical state can be occupied at most by two electrons which differ in their spin quantum number.

The highest occupied level for T = 0K defines the Fermi level. At T = 0K, all states up to the Fermi energy are occupied each by two electrons ($f(E) = 1$).

Energetically higher lying levels are empty ($f(E) = 0$).

At increased temperatures, an increasing number of states above E_F can be thermally occupied. Accordingly, the occupation probability below E_F decrease and become smaller than 1.

Since it is only probability of occupation the $f(E) \neq 0$ in the forbidden gap of semiconductor.

(d)

density of states N(E)
Fermi distribution function f(E)

The dependence of the carrier concentration for the respective energy obtained from the product f(E) . N(E).

The drop of n and p (= n_i) for higher (electrons) and lower (holes) energy results from the governing role of the exponential decay of f(E) compared to the square root increase of N(E). Energy integration yields the absolute number of carriers in each band. This concentration is equal for electrons and holes.