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:

\[ \sigma = e n \mu \]

\(\sigma\)- conductivity
\(n\)- carrier concentration
\(\mu\)- 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 determines its 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.

Acceptor levels are B and Al, characterized by the smallest energetic distance to the valence band maximum.

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**Diagram:**

- Si
- $E_g = 1.12 \text{eV}$
- $E_{cb}$
- $E_{vb}$
- Donor levels (Li, Sb, P, As) at $E_g$ with distances 33, 39, 45, 54 meV
- Acceptor levels (B, Al, Ga, In, Cu, V) at $E_{vb}$ with distances 45, 67, 72, 160, 240, 400, 530, 490 meV
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**

\[
t = t_0 \exp \left( \frac{E_{CB} - E_T}{kT} \right)
\]

For so called deep traps \((E_{CB} - E_T) \gg kT\) 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

\[ \Delta E = E_{CB} - E_D \approx E_A^- - E_{VB} \leq kT \]
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

\[ N_D >> N_A \text{ so } |N_D - N_A| >> n_i \]

Effective doping concentration is much higher than the intrinsic carrier concentration

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

\[ n = N_{CB} \exp \left( -\frac{(E_{CB} - E_F)}{kT} \right) = N_D \approx N_D^I \]
Doping and Fermi level cont’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
\( n_i = 1.45 \times 10^{10} \text{cm}^{-3} \)

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

\( N_D \gg n_i \) 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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Formation of band structure and energy

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 $0.3eV < E_g < 3eV$

- $T \uparrow \rightarrow$ resistivity $\downarrow$ (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
Insulators: $E_g > 3$ 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

4.05 eV

0.2-0.3 eV

1.12 eV
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:

\[ n = p = n_i \]

- $n$ – electron concentration
- $p$ – hole concentration
- $n_i$ – intrinsic carrier concentration
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:

<table>
<thead>
<tr>
<th>n</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>l</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>m</td>
<td>0</td>
<td>0</td>
<td>-1 0 1</td>
</tr>
<tr>
<td>s</td>
<td>+1/2, -1/2</td>
<td>+1/2, -1/2</td>
<td>+1/2, -1/2</td>
</tr>
</tbody>
</table>

\[
\begin{array}{c}
1s \\
\begin{array}{c}
\uparrow \\
\downarrow
\end{array}
\end{array}
\begin{array}{c}
2s \\
\begin{array}{c}
\uparrow \\
\downarrow
\end{array}
\end{array}
\begin{array}{c}
2p \\
\begin{array}{c}
\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow
\end{array}
\end{array}
\begin{array}{c}
3s \\
\begin{array}{c}
\uparrow \downarrow
\end{array}
\end{array}
\begin{array}{c}
3p \\
\begin{array}{c}
\uparrow \downarrow
\end{array}
\end{array}
\begin{array}{c}
3d \\
\begin{array}{c}
\hline \hline \hline \hline
\end{array}
\end{array}
\end{array}

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

\[
\int_{CB} N(E) f(E) \, dE
\]

\( n \) - 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)

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

\( N(E) \, dE \) - the number of electrons energy states per unit volume over energy interval
Fermi-Dirac integral

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

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

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

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

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:

\[
\frac{E - E_F}{kT} \gg 1
\]

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

The energetic distance between the conduction band (E_{CB}) minimum and the Fermi level (E_F) should not be much smaller than \textbf{0.1eV} at room temperature. (non degenerate semiconductor)
The Fermi Dirac integral for electrons then becomes:

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

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:

\[ N_{VB} = 2 \left( \frac{m^*_h kT}{2 \pi \hbar^2} \right)^{2/3} \]

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

\( N_{VB} \) - effective density of states at valence band maximum
Carrier concentration

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

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

MASS ACTION LAW

\[ n \cdot p = n_i^2 \]

- \( n \) – 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

\[ n \cdot p = n_i^2 \]

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>Effective DOS N(_{\text{CB}}) / cm(^{-3})</th>
<th>Effective DOS N(_{\text{VB}}) / cm(^{-3})</th>
<th>Band gap E(_g) / eV</th>
<th>Intrinsic carrier concentration n(_i) / cm(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>1 \cdot 10^{19}</td>
<td>5 \cdot 10^{18}</td>
<td>0.66</td>
<td>2.4 \cdot 10^{13}</td>
</tr>
<tr>
<td>Si</td>
<td>3.2 \cdot 10^{19}</td>
<td>1.8 \cdot 10^{19}</td>
<td>1.12</td>
<td>1.45 \cdot 10^{10}</td>
</tr>
<tr>
<td>GaAs</td>
<td>4.7 \cdot 10^{17}</td>
<td>9 \cdot 10^{18}</td>
<td>1.42</td>
<td>1.79 \cdot 10^{6}</td>
</tr>
</tbody>
</table>

- 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 \( p = n \)

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

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

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

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

\[
E_F = \frac{(E_{VB} + E_{CB})}{2} + \frac{kT}{2} \ln \frac{N_{VB}}{N_{CB}}
\]

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

middle of energy band gap
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
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.
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 \( T = 0\text{K} \) defines the Fermi level. At \( T = 0\text{K} \), 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.
The dependence of the carrier concentration for the respective energy obtained from the product \( f(E) \cdot N(E) \).

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.