# "Complementi di Fisica" Lecture 21

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## In this lecture

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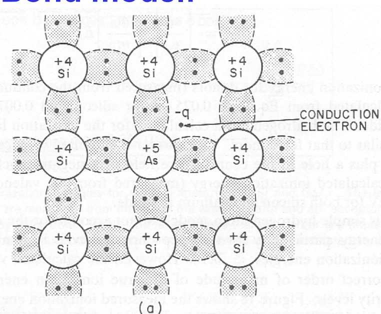
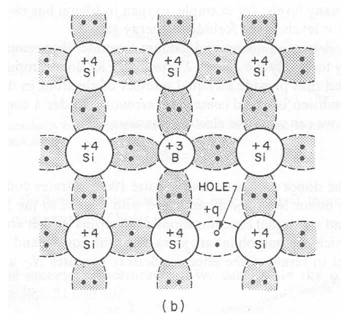
  - Doped ("*extrinsic*") semiconductors *at equilibrium*
    - Concentrations of charge carriers (electrons and holes)
    - Fermi level
- Reference textbooks
  - D.A. Neamen, Semiconductor Physics and Devices, McGraw-Hill, 3rd ed., 2003, p.83-96 (Density of states, Fermi-Dirac), p. 115-145 (4.2 Dopant atoms and energy levels, 4.3 extrinsic semiconductor, 4.4 Statistics of donors and acceptors, 4.5 Charge neutrality, 4.6 Position of the Fermi level)
  - R.F.Pierret, Advanced Semiconductor Fundamentals, Prentice Hall, 2003, 2nd ed., p. 96-128.
  - S.M.Sze, Semiconductor Devices - Physics and Technology, J.Wiley & Sons, 2nd ed., 1985, p. 21-28.

# "extrinsic" (doped) semiconductors

# Donors and acceptors

- **Bond model:**



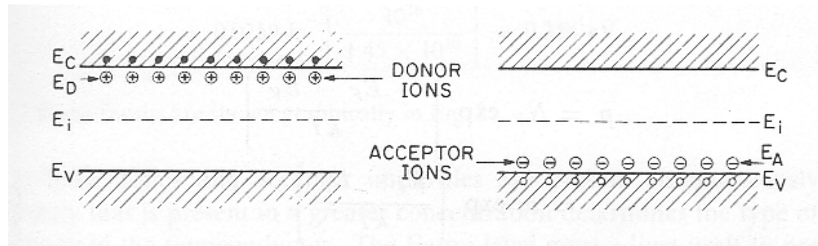




***n*-type**
Si with "***donor***" impurities
(As: 5 valence electrons)
The fifth electron is "***donated***"
to the conduction band;
the remaining positive ion is ***fixed***

***p*-type**
Si with "***acceptor***" impurities
(B: 3 valence electrons)
An additional electron is "***accepted***"
from the valence band, creating a hole
The resulting negative ion is ***fixed***

# Donors and acceptors

- **Energy band model**




**n-type**
Si with "***donor***" energy levels very close to the conduction band; ionization energy is very small, most donor atoms are ionized already at room temperature !

**p-type**
Si with "***acceptor***" energy levels very close to the valence band; most acceptor atoms capture an electron, leaving a free hole already at room temperature !

# Impurities and ionization energies - 1

A = Acceptor
D = Donor

- **Measured ionization energies (eV)**

**Si**
**energy gap**
$E_g$ = **1.12eV**

Sb P As Ti C Pt Au O
Si
0.039 0.045 0.054 0.21 0.25 0.25 A 0.16 0.38 A 0.54 A 0.51 0.41
1.12
0.34 0.35 D 0.36 D 0.29 D 0.3
0.045 0.067 0.072 0.16
B Al Ga In Pd

$E_C$
$E_C$ - $E$ (eV)
$E$ - $E_V$ (eV)
$E_V$

**GaAs**
**energy gap**
$E_g$ =**1.42eV**

S Se Sn Te Si C O
GaAs
0.006 0.006 0.006 0.03 0.0058 0.006
0.4 0.63 A
1.42
0.67 D
0.44 0.24 0.14
0.028 0.028 0.031 0.035 0.035 0.026
Be Mg Zn Cd Si C Cu Cr

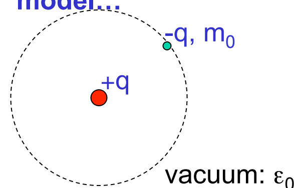
$E_C$
$E_C$ - $E$ (eV)
$E$ - $E_V$ (eV)
$E_V$

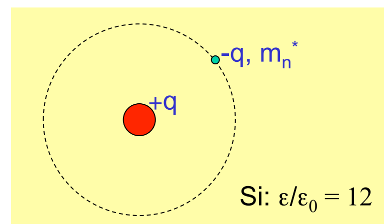
# Impurities and ionization energies - 2

- **Doping with donors (n-type)**
  - **For instance: P or As in Si**
  - **Level close to $E_C$**
- **Doping with acceptors (p-type)**
  - **For instance: B in Si**
  - **Level close to $E_V$**
- **Unwanted impurities**
  - **Many impurities (unavoidable, to some extent) contribute levels close to the center of the gap**
  - **Also these levels are important, as "traps" or "recombination-generation centers" (more on this later)**

# Impurities and ionization energies - 3

- **Donor ionization energies (eV): can we understand or at least guess the order of magnitude in simple terms? Bohr model…**




isolated H atom, lowest level: Bohr model, n=1

$$E_n = -\frac{m_0 q^4}{8\varepsilon_0^2 h^2}\frac{1}{n^2} = -13.6\frac{1}{n^2}\,\mathrm{eV}$$

$E_1 = -13.6\,\mathrm{eV}$ ionization energy

Donor atom in Si crystal: Lowest level for the external electron

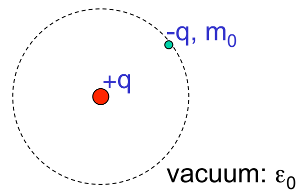
$$E_{D,n} = -\frac{m_n^* q^4}{8\varepsilon^2 h^2}\frac{1}{n^2} = \left(\frac{\varepsilon_0}{\varepsilon}\right)^2\left(\frac{m_n^*}{m_0}\right)E_{H,n}$$

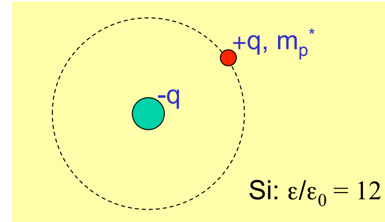
$$E_{D,1} \approx 13.6\,\mathrm{eV}\times\frac{1}{12^2}\times 0.9 \approx 0.085\,\mathrm{eV}$$

ionization energy

# Impurities and ionization energies - 4

- Acceptor ionization energies (eV): similar reasoning




isolated H atom, lowest level:
Bohr model, n=1

$$E_n = -\frac{m_0 q^4}{8\varepsilon_0^2 h^2}\frac{1}{n^2} = -13.6\frac{1}{n^2}\,\text{eV}$$

$E_1 = -13.6\,\text{eV}$ ionization energy

Acceptor atom in Si crystal:
Lowest level for the hole

$$E_{D,n} = -\frac{m_p^* q^4}{8\varepsilon^2 h^2}\frac{1}{n^2} = \left(\frac{\varepsilon_0}{\varepsilon}\right)^2\left(\frac{m_p^*}{m_0}\right)E_{H,n}$$

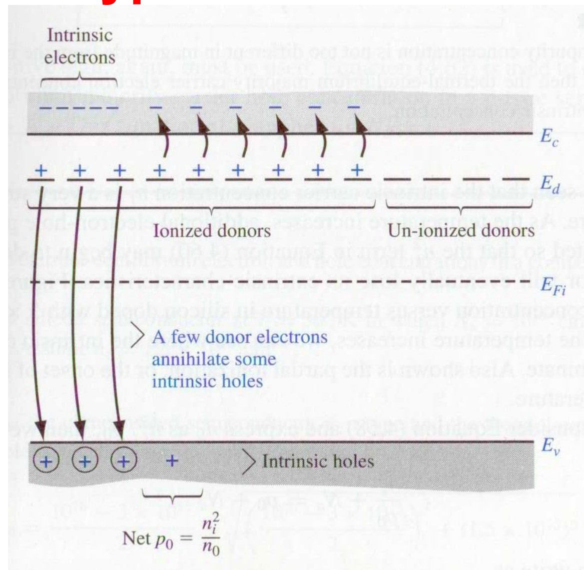
$$E_{D,1} \approx 13.6\,\text{eV} \times \frac{1}{12^2} \times 0.19 \approx 0.018\,\text{eV}$$

ionization energy

# Impurities and ionization energies - 5

- **The simple Bohr model for donor and acceptor ionization energies:**
  - **Describes the impurities in an oversimplified way (pseudo-hydrogen atoms with outer electron or hole orbiting through the semiconductor material):**
    - **Effective mass $m_n^*$, $m_p^*$**
    - **Dielectric constant $\varepsilon$**
  - **Gives the correct orders of magnitude for ionization energies ($E_I < 0.1eV$): OK because many semiconductor atoms are included in the Bohr orbit corresponding to the lowest level (Exercise: easily checked by computing the Bohr radius)**
  - **Is not supposed to be able to reproduce the details !**
- **Small ionization energy ⇒ most donor/acceptor atoms are ionized at room temperature**

# *n*-type in more detail




Expect:

$n > n_i$
mobile electrons

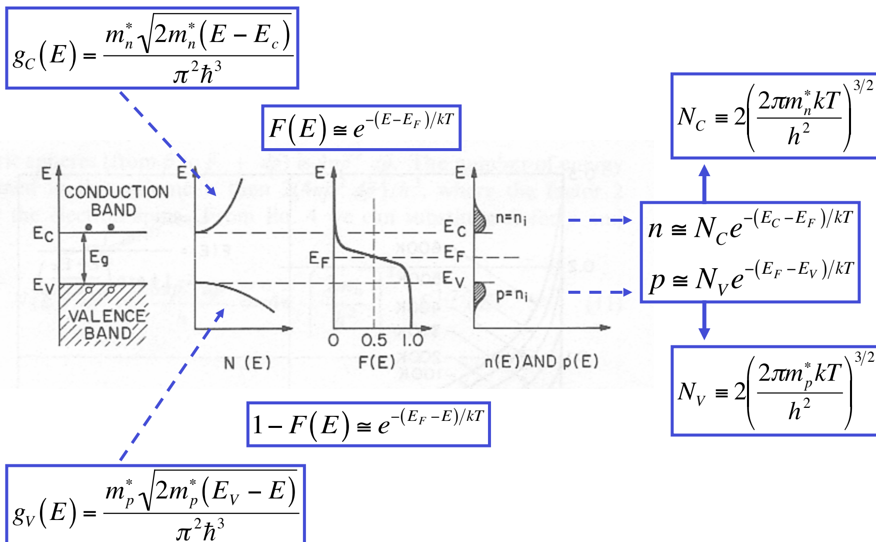
$N_D^+$
fixed positive ions (out of $N_D$ donors)

$p < n_i$
mobile holes

# *Intrinsic* carrier concentration

$$g_C(E) = \frac{m_n^* \sqrt{2m_n^*(E - E_c)}}{\pi^2 \hbar^3}$$

$$F(E) \cong e^{-(E-E_F)/kT}$$




$$1 - F(E) \cong e^{-(E_F-E)/kT}$$

$$g_V(E) = \frac{m_p^* \sqrt{2m_p^*(E_V - E)}}{\pi^2 \hbar^3}$$

$$N_C \equiv 2\left(\frac{2\pi m_n^* kT}{h^2}\right)^{3/2}$$

$$n \cong N_C e^{-(E_C-E_F)/kT}$$

$$p \cong N_V e^{-(E_F-E_V)/kT}$$

$$N_V \equiv 2\left(\frac{2\pi m_p^* kT}{h^2}\right)^{3/2}$$

## *Extrinsic* carrier concentration

The same ingredients…

$$g_C(E) = \frac{m_n^* \sqrt{2m_n^*(E - E_c)}}{\pi^2 \hbar^3}$$

$$F(E) \cong e^{-(E-E_F)/kT}$$

$$N_C \equiv 2\left(\frac{2\pi m_n^* kT}{h^2}\right)^{3/2}$$

$$n \cong N_C e^{-(E_C - E_F)/kT}$$

$$p \cong N_V e^{-(E_F - E_V)/kT}$$

$$N_V \equiv 2\left(\frac{2\pi m_p^* kT}{h^2}\right)^{3/2}$$

$$1 - F(E) \cong e^{-(E_F - E)/kT}$$

$$g_V(E) = \frac{m_p^* \sqrt{2m_p^*(E_V - E)}}{\pi^2 \hbar^3}$$



…the same (formal) results !
But now $n \neq p$ : why ??

## Carrier concentrations: *intrinsic*

- (approximate) equations valid for both intrinsic and extrinsic:

$$n \cong N_C e^{-(E_C - E_F)/kT} \qquad N_C \equiv 2\left(\frac{2\pi m_n^* kT}{h^2}\right)^{3/2}$$

$$p \cong N_V e^{-(E_F - E_V)/kT} \qquad N_V \equiv 2\left(\frac{2\pi m_p^* kT}{h^2}\right)^{3/2}$$

$$N_C = n_i e^{(E_C - E_i)/kT}$$

$$N_V = n_i e^{(E_i - E_V)/kT}$$

- Intrinsic case ($E_F \equiv E_i$)

$$n = p = n_i = N_C e^{-(E_C - E_i)/kT} = N_V e^{-(E_i - E_V)/kT}$$

$$E_F = E_i = \ldots \approx \frac{E_C + E_V}{2}$$

$$np = n_i^2 = N_C N_V e^{-(E_C - E_V)/kT} \quad \Rightarrow n_i = \sqrt{N_C N_V}\, e^{-E_g/2kT}$$

# Carrier concentrations: *extrinsic*

- (approximate) equations valid for both intrinsic and extrinsic:

$$n \cong N_C e^{-(E_C - E_F)/kT} \qquad N_C \equiv 2\left(\frac{2\pi m_n^* kT}{h^2}\right)^{3/2} \qquad N_C = n_i e^{(E_C - E_i)/kT}$$

$$p \cong N_V e^{-(E_F - E_V)/kT} \qquad N_V \equiv 2\left(\frac{2\pi m_p^* kT}{h^2}\right)^{3/2} \qquad N_V = n_i e^{(E_i - E_V)/kT}$$

- Extrinsic case: $n \neq p \Leftrightarrow E_F \neq E_i$

$$n = n_i e^{(E_C - E_i)/kT} e^{-(E_C - E_F)/kT} = n_i e^{(E_F - E_i)/kT}$$

$$p = n_i e^{(E_i - E_V)/kT} e^{-(E_F - E_V)/kT} = n_i e^{(E_i - E_F)/kT}$$

$E_F$ moves away from $E_i$

$$np = n_i^2$$

$$n\text{-type}: \quad n \approx N_D \quad p \approx n_i^2 / N_D$$

$$p\text{-type}: \quad p \approx N_A \quad n \approx n_i^2 / N_A$$

approximate for complete ionization

# Fermi level $E_F$ for complete ionization

- Complete ionization of donors (*n*-type):

$$n = N_C e^{-(E_C - E_F)/kT} \approx N_D \quad \Rightarrow \frac{N_C}{N_D} = e^{(E_C - E_F)/kT}$$

$$\Rightarrow E_C - E_F = kT \ln\left(\frac{N_C}{N_D}\right)$$

- Complete ionization of acceptors (*p*-type):

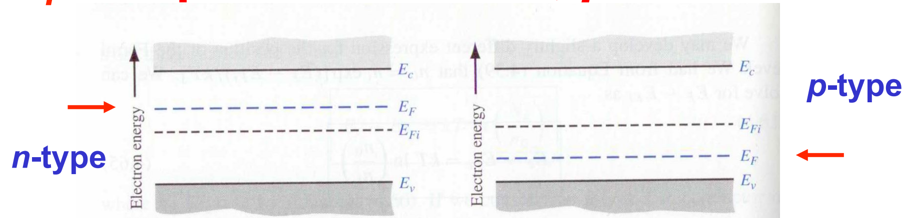
$$p = N_V e^{-(E_F - E_V)/kT} \approx N_A \quad \Rightarrow \frac{N_V}{N_A} = e^{(E_C - E_F)/kT}$$

$$\Rightarrow E_F - E_V = kT \ln\left(\frac{N_V}{N_A}\right)$$

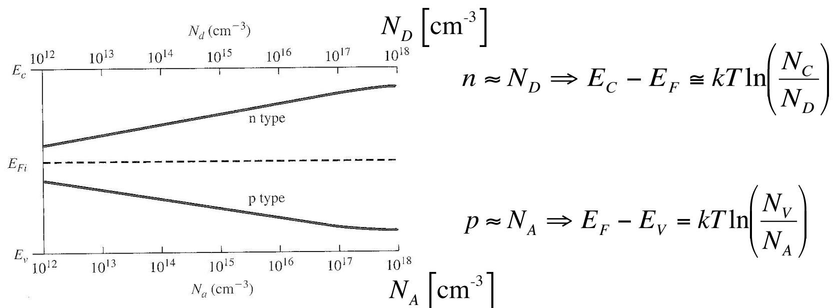
# $E_F$ : dependence on *n*, *p* at fixed *T*

*n*-type

*p*-type




$N_D\ [\text{cm}^{-3}]$




$N_A\ [\text{cm}^{-3}]$

**Figure 4.18** | Position of Fermi level as a function of donor concentration (n type) and acceptor concentration (p type).

$$n \approx N_D \Rightarrow E_C - E_F \cong kT \ln\left(\frac{N_C}{N_D}\right)$$

$$p \approx N_A \Rightarrow E_F - E_V = kT \ln\left(\frac{N_V}{N_A}\right)$$

# Concentrations and $E_F$ : an example

- A silicon ingot is doped with As ($N_D \approx 10^{16}$ atoms/cm$^3$). Find the carrier concentration and the Fermi level at room temperature (T=300K)

**Assuming complete ionization of donors:**

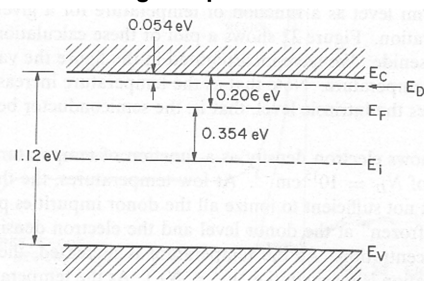



**Fig. 21** Band diagram showing Fermi level $E_F$ and intrinsic Fermi level $E_i$.

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

$$n_i = N_C e^{-(E_C - E_i)/kT} \approx$$

$$\approx \left(2.8 \times 10^{19}\right) \times \left(5.2 \times 10^{-10}\right) \approx$$

$$\approx 1.45 \times 10^{10}\,\text{cm}^{-3}$$

$$p \approx n_i^2 / N_D = \frac{\left(1.45 \times 10^{10}\right)^2}{10^{16}} =$$

$$= 2.1 \times 10^4\,\text{cm}^{-3}$$

$$E_C - E_F = kT \ln\left(\frac{N_C}{N_D}\right) = 0.0259 \ln\left(\frac{2.8 \times 10^{19}}{10^{16}}\right) =$$

$$= 0.206\ \text{eV}$$

$$n = n_i e^{(E_F - E_i)/kT} \Rightarrow E_F - E_i = kT \ln\left(\frac{n}{n_i}\right)$$

$$E_F - E_i = 0.0259 \ln\left(\frac{10^{16}}{1.45 \times 10^{10}}\right) = 0.354\ \text{eV}$$

# Carrier concentrations: general case

- **Both donor and acceptor impurities present simultaneously**
  - **Concentrations: $N_D$ and $N_A$ respectively**
  - **$N_D^+$ and $N_A^-$ : concentrations of *ionized* donors and acceptors**

$$N_D^+ = N_D - n_D$$

***$n_D$ electrons in donor states***
**(non-ionized donors)**

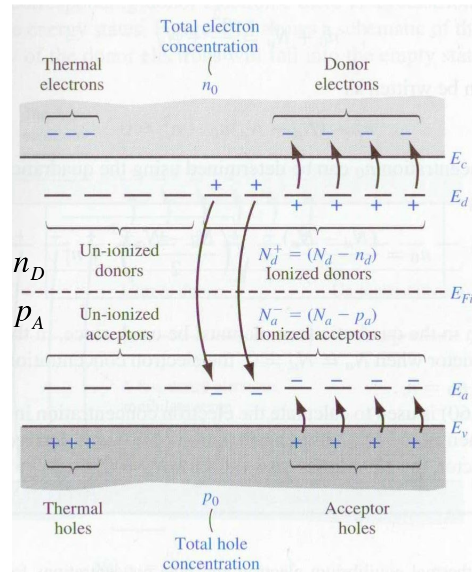
$$N_A^- = N_A - p_A$$

***$p_A$ holes in acceptor states***
**(non-ionized acceptors)**

- **Starting point: overall *charge neutrality* (only "unbalanced" charges appear explicitely), and *mass action law***

$$n + N_A^- = p + N_D^+ \qquad np = n_i^2$$

# Carrier concentrations: general case




$$N_D^+ = N_D - n_D$$

$$N_A^- = N_A - p_A$$

# Carrier concentrations

- **Assuming complete ionization of donors and acceptors**

$$N_A^- \approx N_A \qquad N_D^+ \approx N_D$$

$$n + N_A = p + N_D \qquad np = n_i^2$$

# Carrier concentrations

- **Solving for *n, p*:**

$$n + N_A = p + N_D \qquad np = n_i^2$$

**n-type: $N_D > N_A$**

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

$$p_n = n_i^2 / n_n$$

$$\text{if} \quad |N_D - N_A| >> n_i$$

$$n_n \approx N_D - N_A$$

**p-type: $N_A > N_D$**

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

$$n_p = n_i^2 / p_p$$

$$\text{if} \quad |N_D - N_A| >> n_i$$

$$p_p \approx N_A - N_D$$

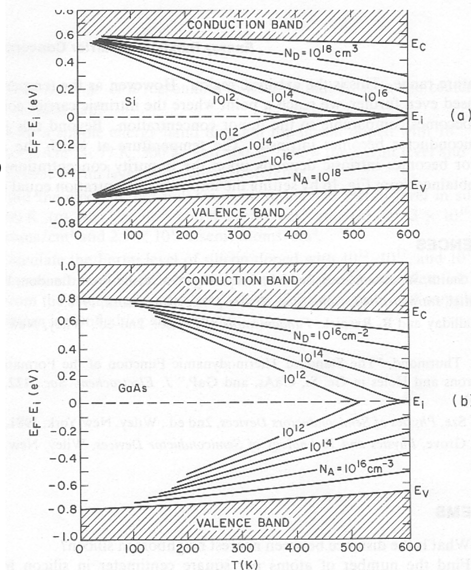
# Extrinsic Fermi level vs temperature

- **Fermi level computation in the general case, taking *T* into account:**
  - from $N_D$ and $N_A$ compute n, p
  - from n, p extract $E_F$

$$n = n_i e^{(E_F - E_i)/kT} \Rightarrow E_F - E_i = kT \ln\left(\frac{n}{n_i}\right)$$

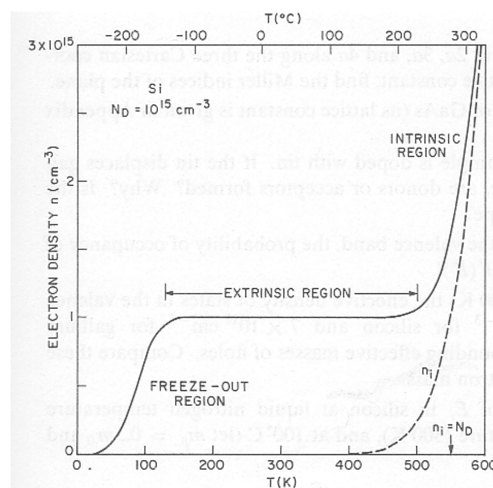
$$p = n_i e^{(E_i - E_F)/kT} \Rightarrow E_i - E_F = kT \ln\left(\frac{p}{n_i}\right)$$

- **$n_i$ increases with T !**
  - Low T: extrinsic behaviour
  - High T: intrinsic behaviour



# Electron density vs temperature

- **Another point of view: electron concentration in n-type semiconductor**
  - Very low *T*:
    - "freeze-out" region
    - donors not ionized
  - Medium *T*:
    - "extrinsic" region
    - $n \approx N_D$
  - High *T*:
    - "intrinsic" region
    - $n \approx n_i$



# Non-degenerate and degenerate s.c.

- All the results in this lecture assumed the Boltzmann approximation, that is $E_C - E_F > 3kT$, $E_F - E_V > 3kT$ *("non-degenerate" semiconductors)*
  - Relatively small doping concentrations: donor and acceptor atoms can be considered as "isolated" (energy levels)
- For very large doping concentrations ($N_D \approx N_C$ , $N_A \approx N_V$) (*"degenerate" semiconductors*)
  - Donor (acceptor) energy levels become bands, overlapping with the conduction (valence) band
  - The effective forbidden gap becomes smaller
  - The Fermi level is inside the enlarged conduction (valence) band, with a very large concentration of electrons (holes) available for conduction
  - The Boltzmann approximation is no longer valid in this case

# Lecture 27 - summary

- The "mass action law" ($np = n_i^2$) is valid also for extrinsic s.c.
- The intrinsic concentration $n_i$ increases with $T$
- We found relations between $n$, $p$, $n_i$ and $E_F$
- In the intrinsic case $n = p = n_i$
- We have learned how to compute $n$, $p$, and $E_F$ in the general extrinsic case (depending on $N_D$, $N_A$)
- Specifying $E_F$ is a very convenient way of parameterizing $n$, $p$
- Intrinsic/extrinsic behaviour depends on $T$ !

# Lecture 27 - exercises

- Exercise 1: **A silicon sample at T=300K contains an acceptor impurity concentration of $N_A=10^{16}$ cm$^{-3}$. Determine the concentration of donor impurity atoms that must be added so that the silicon is n-type and the Fermi energy is 0.20 eV below the conduction band edge.**
- Exercise 2: **Find the electron and hole concentrations and Fermi level in silicon at 300K (a) for $1\times10^{15}$ boron atoms/cm$^3$ and (b) for $3\times10^{16}$ boron atoms /cm$^3$ together with $2.9\times10^{16}$ arsenic atoms/cm$^3$.**
- Exercise 3: **Calculate the Fermi level of silicon doped with $10^{15}$, $10^{17}$ and $10^{19}$ phosphorus atoms/cm$^3$, assuming complete ionization. From the calculated Fermi level, check if the assumption of complete ionization is justified for each doping. Assume that the ionized donors density is given by $N_D^+ = N_D(1-F(E_D))$.**