

“Complementi di Fisica”

Lecture 27



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In this lecture

- **Contents**

- 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.



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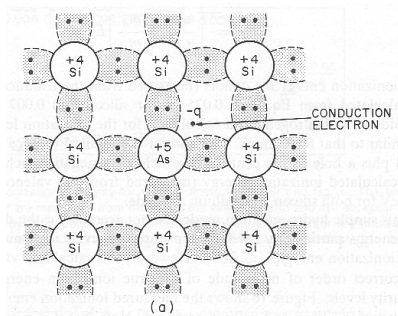
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“extrinsic” (doped) semiconductors

Donors and acceptors

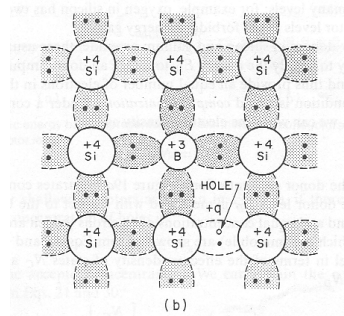
- Bond model:**



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**



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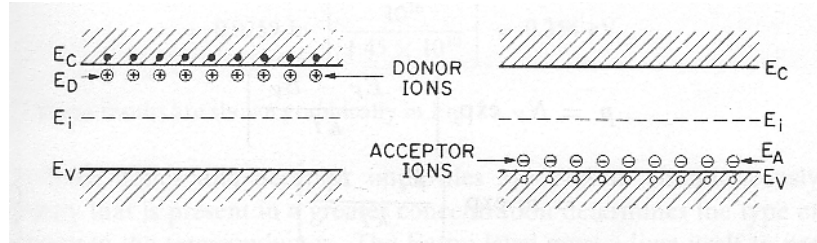
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Donors and acceptors

• 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 !



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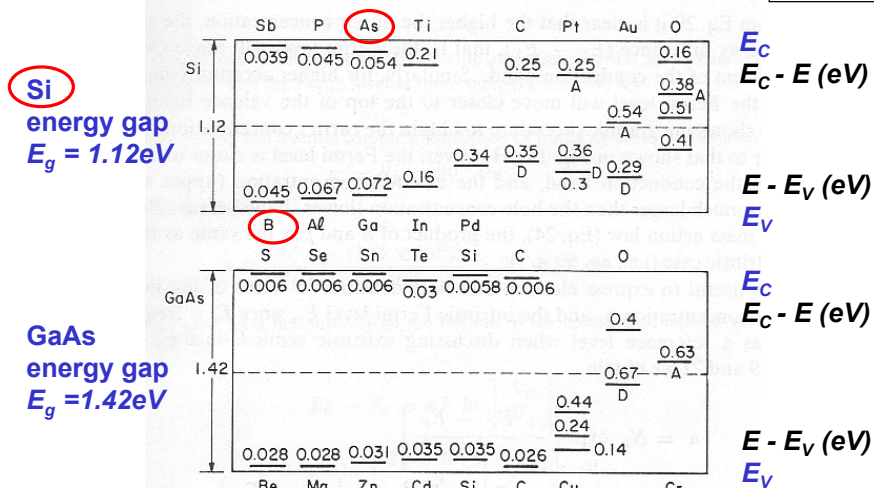
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Impurities and ionization energies - 1

• Measured ionization energies (eV)

A = Acceptor
D = Donor



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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)



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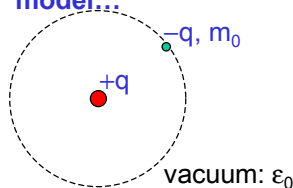
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Impurities and ionization energies - 3

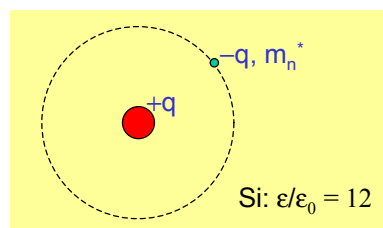
- **Donor ionization energies (eV): can we understand or at least guess the order of magnitude in simple terms? Bohr model...**



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

$$E_n = -\frac{m_0 q^4}{8\epsilon_0^2 h^2} \frac{1}{n^2} = -13.6 \frac{1}{n^2} \text{ eV}$$

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



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

$$E_{D,n} = -\frac{m_n^* q^4}{8\epsilon^2 h^2} \frac{1}{n^2} = \left(\frac{\epsilon_0}{\epsilon}\right)^2 \left(\frac{m_n^*}{m_0}\right) E_{H,n}$$

$$E_{D,1} \approx 13.6 \text{ eV} \times \frac{1}{12^2} \times 0.9 \approx 0.085 \text{ eV} \quad \text{ionization energy}$$



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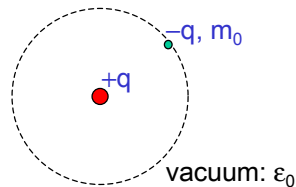
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Impurities and ionization energies - 4

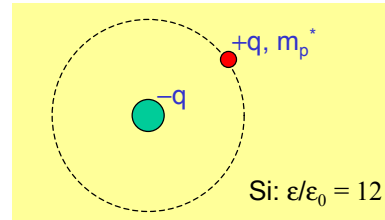
- **Acceptor ionization energies (eV): similar reasoning**



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

$$E_n = -\frac{m_0 q^4}{8\epsilon_0^2 h^2} \frac{1}{n^2} = -13.6 \frac{1}{n^2} \text{ eV}$$

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



Acceptor atom in Si crystal:
Lowest level for the hole

$$E_{D,n} = -\frac{m_p^* q^4}{8\epsilon^2 h^2} \frac{1}{n^2} = \left(\frac{\epsilon_0}{\epsilon}\right)^2 \left(\frac{m_p^*}{m_0}\right) E_{H,n}$$

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



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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 ϵ
 - Gives the correct orders of magnitude for ionization energies ($E_i < 0.1 \text{ eV}$): 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 $\Rightarrow$ most donor/acceptor atoms are ionized at room temperature**



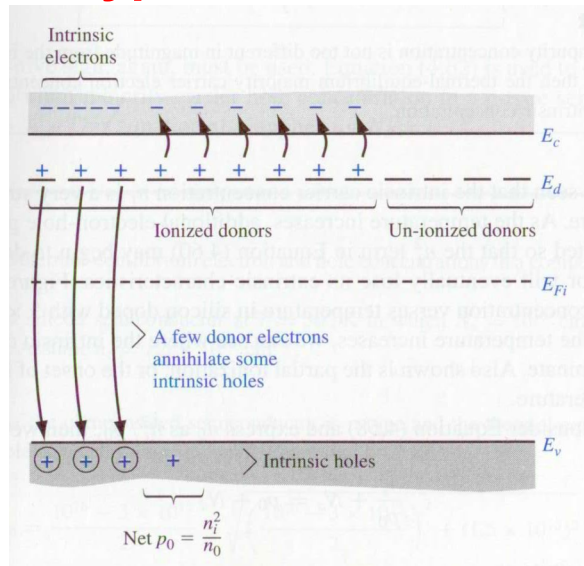
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n-type in more detail



Expect:

$$n > n_i$$

mobile electrons

$$N_D^+$$

fixed positive ions
(out of N_D donors)

$$p < n_i$$

mobile holes



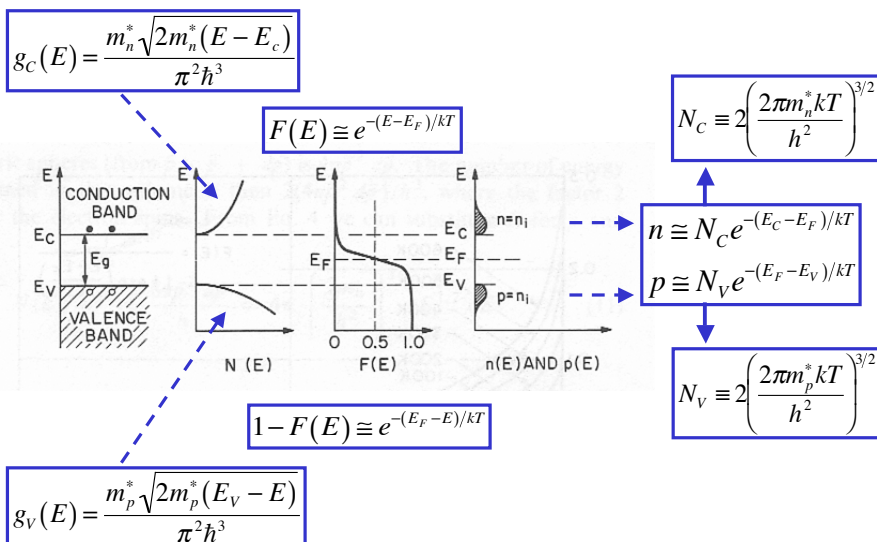
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Intrinsic carrier concentration



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Extrinsic carrier concentration

The same ingredients...

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

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

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

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

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

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

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

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

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

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Carrier concentrations: *intrinsic*

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

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

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

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

$$N_V = n_i e^{(E_i - E_V)/kT}$$
- Intrinsic case ($E_F \equiv E_i$)

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

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

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

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Carrier concentrations: *extrinsic*

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

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

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

- 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

$$np = n_i^2$$

$$\begin{array}{ll} n\text{-type:} & n \approx N_D \quad p \approx n_i^2 / N_D \\ p\text{-type:} & p \approx N_A \quad n \approx n_i^2 / N_A \end{array}$$

approximate
for
complete
ionization



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Fermi level E_F for complete ionization

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

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

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

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

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

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



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E_F : dependence on n, p at fixed T

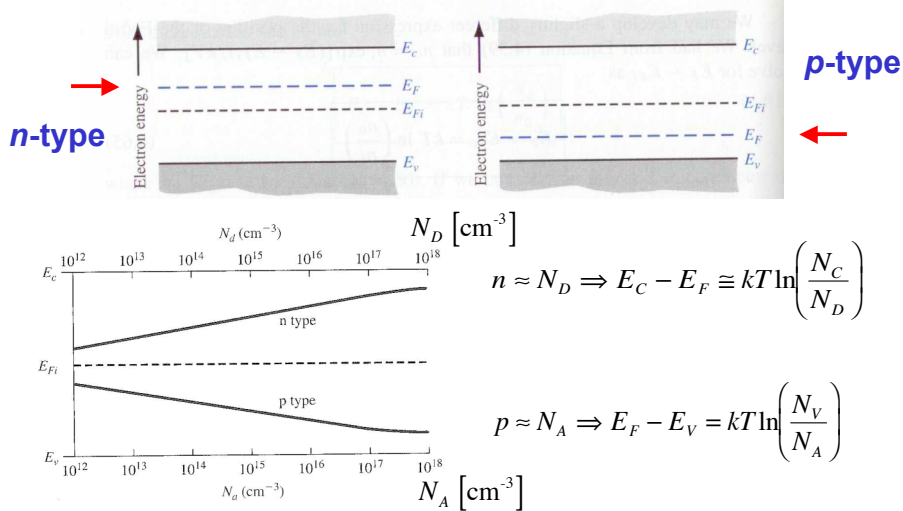


Figure 4.18 | Position of Fermi level as a function of donor concentration (n type) and acceptor concentration (p type).



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Concentrations and E_F : an example

- A silicon ingot is doped with As ($N_D \approx 10^{16}$ atoms/cm³). Find the carrier concentration and the Fermi level at room temperature ($T=300\text{K}$)

Assuming complete ionization of donors:

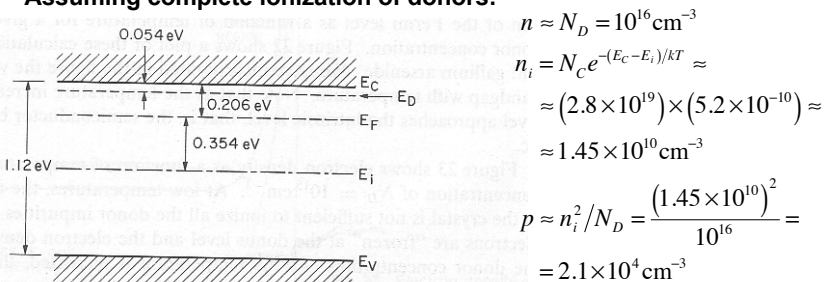


Fig. 21 Band diagram showing Fermi level E_F and intrinsic Fermi level E_i .

$$E_C - E_F = kT \ln \left(\frac{N_C}{N_D} \right) = 0.0259 \ln \left(\frac{2.8 \times 10^{19}}{10^{16}} \right) = 0.206 \text{ eV}$$

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

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



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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

$$N_D^+ = N_D - n_D \quad \leftarrow n_D \text{ electrons in donor states (non-ionized donors)}$$

$$N_A^- = N_A - p_A \quad \leftarrow p_A \text{ holes in acceptor states (non-ionized acceptors)}$$

- Starting point: overall *charge neutrality* (only “unbalanced” charges appear explicitly), and *mass action law*

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



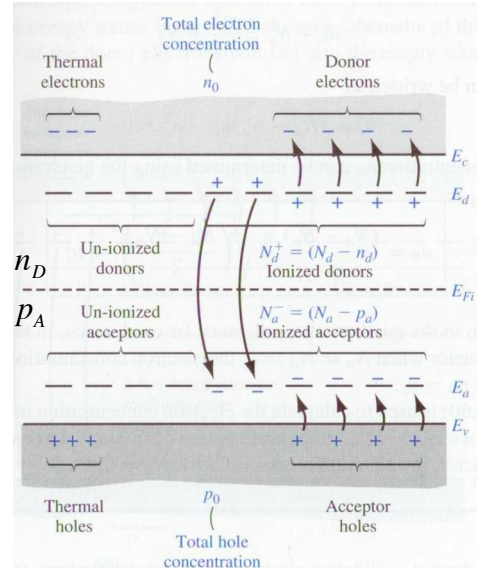
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Carrier concentrations: general case



$$N_D^+ = N_D - n_D$$

$$N_A^- = N_A - p_A$$



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Carrier concentrations

- Assuming complete ionization of donors and acceptors

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

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



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Carrier concentrations

- Solving for n, p :

$$\boxed{n + N_A = p + N_D \quad np = n_i^2}$$

n-type: $N_D > N_A$

p-type: $N_A > N_D$

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

$$p_n = n_i^2 / n_n$$

if $|N_D - N_A| \gg n_i$

$$n_n \approx N_D - N_A$$

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

$$n_p = n_i^2 / p_p$$

if $|N_D - N_A| \gg n_i$

$$p_p \approx N_A - N_D$$



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Extrinsic Fermi level vs temperature

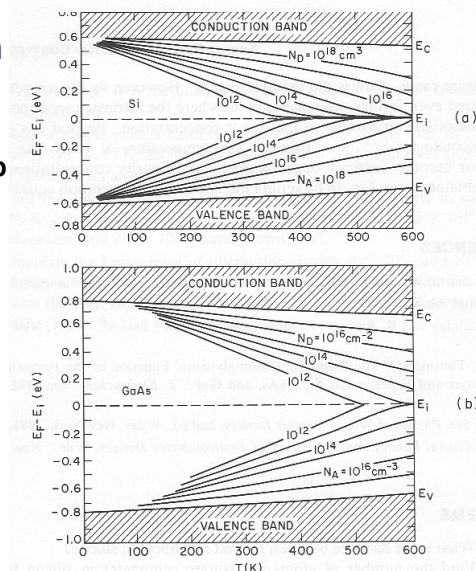
- Fermi level computation in the general case, taking T into account:

- 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



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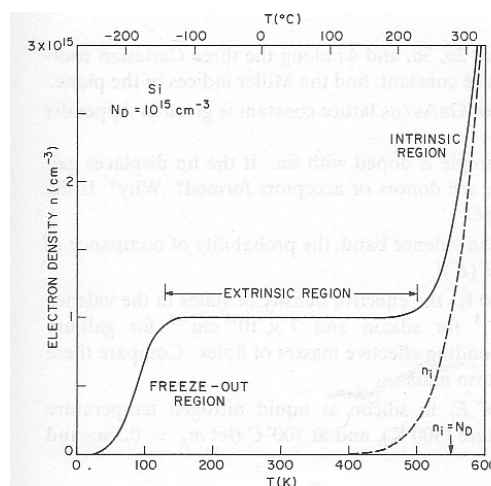
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Electron density vs temperature

- 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
 - $n \approx n_i$



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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



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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 !



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Lecture 27 - exercises

- **Exercise 1:** A silicon sample at $T=300\text{K}$ contains an acceptor impurity concentration of $N_A=10^{16}\text{ cm}^{-3}$. 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 1×10^{15} boron atoms/ cm^3 and (b) for 3×10^{16} boron atoms / cm^3 together with 2.9×10^{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 $N_D^+ = N_D(1-F(E_D))$.

