Extrinsic Semiconductors. Doping

For practically all applications, the conductivity of semiconductors such as GaAs, Ge, and Si is dominated by **extrinsic carriers** provided by **doping** the semiconductor with **low concentrations** of impurities

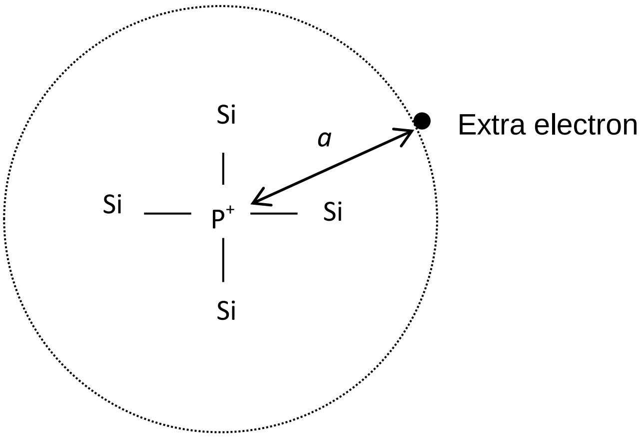
Two types of impurity (or **dopant**):

DONORS and ACEPTORS

Substitutional donors and acceptors have an excess or a deficit electron in their outer electron shell, respectively, as compared to the replaced lattice atom. ***Donors*** have one excess electron which can be *donated* to the conduction band. ***Acceptors*** have deficit of a one electron than the replaced lattice atom and can *accept* an electron from the filled valence band of the semiconductor, thereby creating a *hole*. We shall look into the effect of donors on conductivity in a semiconductor. The donor concentration is assumed to be N_D.

Impurity of valence ν+1 in semiconductor of valence ν, e.g. P or As in Si or Ge

3A	4A	5A
B	C	N
Al	Si	P
Ga	Ge	As



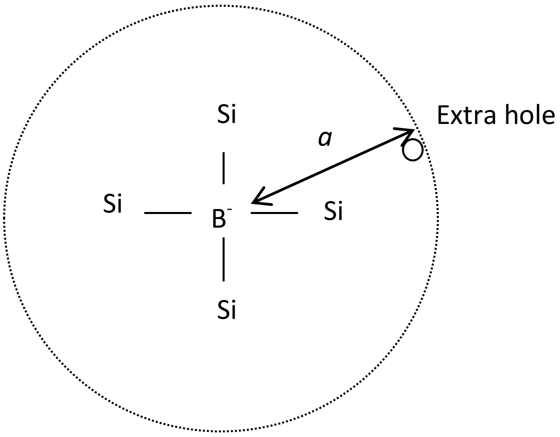
P^+ ion **donates** one electron to the semiconductor, *n* increases relative to *p*, material is said to be **n-type and** the electron the **majority carrier**

$m^*_c \approx 0.07\, m_e$ in GaAs $\Rightarrow \varepsilon_D \approx 5$ meV   i.e. very low binding energy

ACCEPTORS

Impurity of valence ν-1 in semiconductor of valence ν, e.g. B or Al in Si or Ge

3A	4A	5A
B	C	N
Al	Si	P
Ga	Ge	As



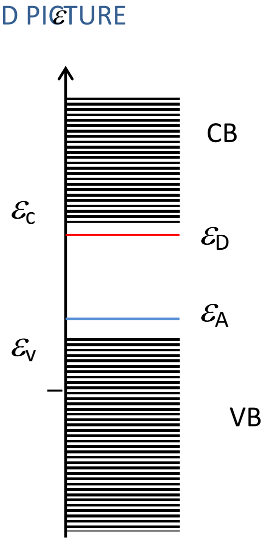
B^- ion **accepts** one electron from the semiconductor, *p* increases relative to *n*, material is said to be **p-type and** the hole the **majority carrier**

N_A=acceptor density

$\varepsilon_A \approx 5$ meV

Low binding energies mean donors and acceptors will be fully ionised at RT

BAND PICTURE



EXTRINSIC CARRIER DENSITY

Recall that for an intrinsic semiconductor the carrier density can be calculated as:

$$n = p$$

$$N_c f(\varepsilon_F) = N_V f(\varepsilon_F)$$

Since ε_F is many *kT* below conduction band and many *kT* above valence band we can approximate to:

$$N_c \exp\left(-\frac{\varepsilon_C - \varepsilon_F}{kT}\right) = N_V \exp\left(-\frac{\varepsilon_F - \varepsilon_V}{kT}\right)$$

and

$$n_i = \sqrt{N_C N_V} \exp\left(-\frac{\varepsilon_g}{2kT}\right)$$

where $N_{C,V} \sim T^{3/2}$

In case of the extrinsic semiconductors the law of mass action still applies

$$np \approx W \times T^3 \times e^{-\frac{\varepsilon_g}{k_B T}}$$

Charge neutrality condition:

$n - p = N_D - N_A$

The charge state of donors is *neutral* when occupied by an electron and positively charged if the electron is excited to the conduction band. The total concentration of donors is the sum of neutral donor concentration and ionized donor concentration:

$$N_D = N_D^0 + N_D^+$$

The probability of occupation of an acceptor or donor level follows Fermi – Dirac statistics, hence:

$$N_D^0 = N_D f(\varepsilon_D)$$

It then follows from the above that the concentration of ionised donors N_D^+ is:

$$N_D^+ = N_D[1 - f(\varepsilon_D)] = N_D\left[1 - \left(1 + \frac{1}{g} exp\left(\frac{\varepsilon_D - \varepsilon_F}{kT}\right)\right)^{-1}\right] = N_D\left(1 + g \times exp\left(\frac{\varepsilon_F - \varepsilon_D}{kT}\right)\right)^{-1}$$

where *g* is the ground-state degeneracy of the donor. The value of the ground-state degeneracy in GaAs is *g* = 2 for hydrogen-like donors (see below) since the donor can donate one electron of either spin.

At low T most electrons occupy donor states. Then Boltzmann statistics can be used for the occupation of conduction band states:

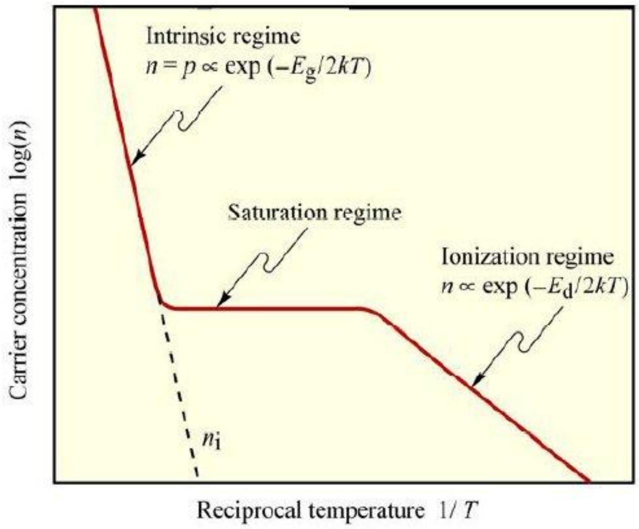
$$n = N_C exp\left(-\frac{\varepsilon_C - \varepsilon_F}{kT}\right)$$

For the free carrier concentration in n-type semiconductor ($n = N_D^+$) we shall obtain using Fermi-Dirac statistics:

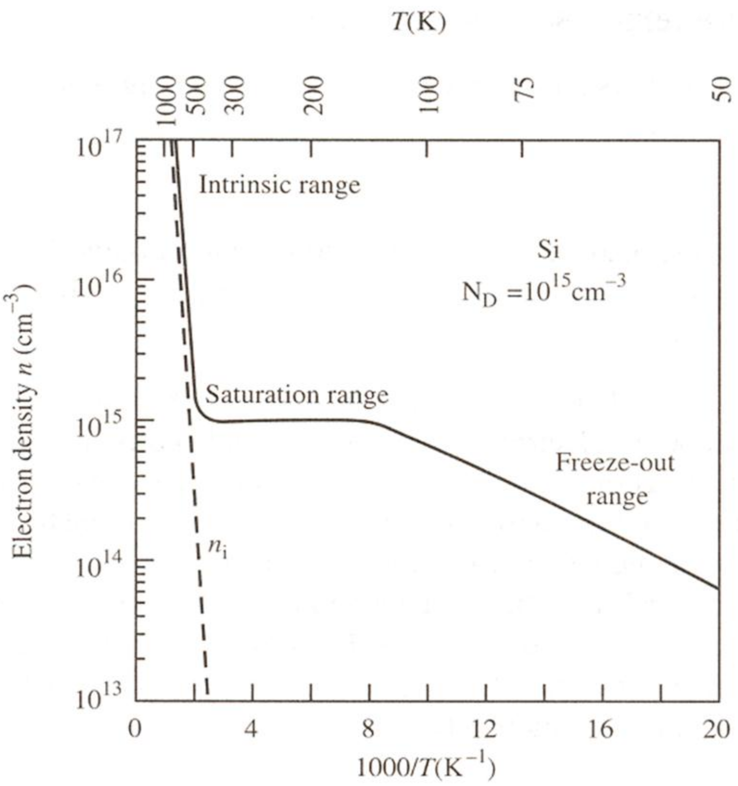
$$n^2 - \frac{1}{g} N_D N_C exp\left(-\frac{\varepsilon_D}{kT}\right) + \frac{1}{g} n N_C exp\left(-\frac{\varepsilon_D}{kT}\right) = 0$$

and since $n \ll N_D$ at low T, the third term can be neglected resulting in:

$$n \approx C \times exp\left(-\frac{\varepsilon_D}{2kT}\right)$$



Exercise: can you explain this diagram for the temperature variation of n-type Si?

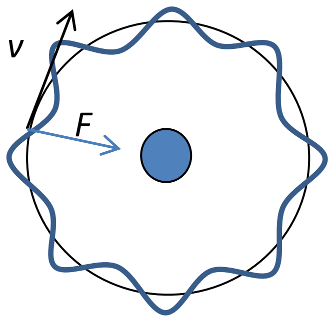


Impurities in semiconductors - Bohr's hydrogen atom model

Shallow impurities ($\varepsilon_D \ll 100meV$)are ionized at room temperature and therefore of great technological importance in semiconductors since they determine the conductivity and the carrier type of the semiconductor. Shallow impurities can be either acceptors or donors.

The hydrogen atom is used to calculate various properties of shallow impurities such as ionization energy and state wave functions.

$$F = \frac{e^2}{4\pi\varepsilon_0 r^2}$$ Coulomb force



Electron describes a circular orbit $\Rightarrow$ momentum, *p*, is constant $\Rightarrow$ $\lambda = h/p$

For the orbit to be a stationary state $2\pi r = n\lambda$, (*n*=integer)

$rp = nh/2\pi = n\hbar$

Since ,$p=m_e v$, $m_e v r = n\hbar$

Equation of motion, $F= m_e v^2/r = m_e \omega^2 r$

$$\Rightarrow \quad \frac{m_e v^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2} \quad \text{or} \quad m_e v^2 = \frac{e^2}{4\pi\varepsilon_0 r}$$

$$\Rightarrow \quad r = \frac{4\pi\hbar^2 \varepsilon_0 n^2}{m_e e^2}$$

For *n*=1, $a_B = \frac{4\pi\hbar^2 \varepsilon_0}{m_e e^2}$ = 5.3 x 10^{-11} m (or 0.53 Å), called **Bohr radius**

Energy of electron-nucleus system = kinetic + potential

$$\Rightarrow \ \varepsilon = \varepsilon_k + \varepsilon_p = \frac{1}{2} m_e v^2 - \frac{e^2}{4\pi\varepsilon_0 r} = -\frac{e^2}{4\pi\varepsilon_0 (2r)}$$

$\varepsilon = -\dfrac{m_e e^4}{2(4\pi\varepsilon_0 \hbar n)^2} = -\dfrac{13.6}{n^2}$ eV and for n=1 is called *Rydberg* energy $\varepsilon_{Ryd} = -13.6\ eV$

Applications to semiconductors

Using the effective-mass and the dielectric constant corrections the ***effective Bohr radius*** can be obtained as:

$$\boldsymbol{a^*_{B,n} = \frac{4\pi\varepsilon n^2 \hbar^2}{m^*_e e^2}}$$

and the radius of the donor ground state is then:

$$\boldsymbol{a^*_B = \frac{4\pi\varepsilon\ \ \hbar^2}{m^*_e e^2} = \frac{\varepsilon}{m^*_e / m_e} a_B}$$

For example, if we consider a donor in GaAs with ε = 13.1 and m_e* = 0.067 m_e we shall obtain for a_B* = 103 Å - *effective* Bohr radius of donors in GaAs.

By similarity with the Bohr's radius we can also consider an *effective Rydberg* energy to determine the donor ionisation energy (transition fron n=1 to n=∞):

$$\varepsilon_D \equiv \varepsilon^*_{Ryd} = \frac{m^*_e e^4}{2(4\pi\varepsilon\hbar)^2} = \frac{m^*_e / m_e}{\varepsilon^2} \varepsilon_{Ryd}$$

Thus we can see that this approach allows one to quickly determine some important macroscopic parameters in extrinsic semiconductors.