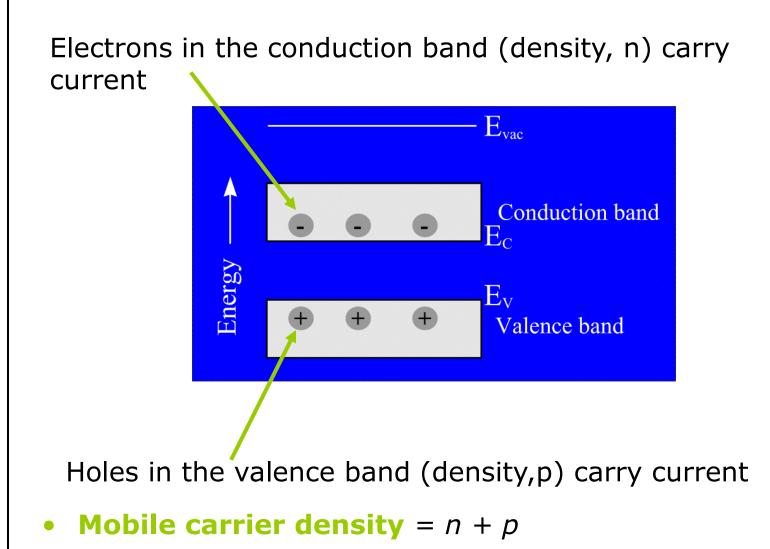
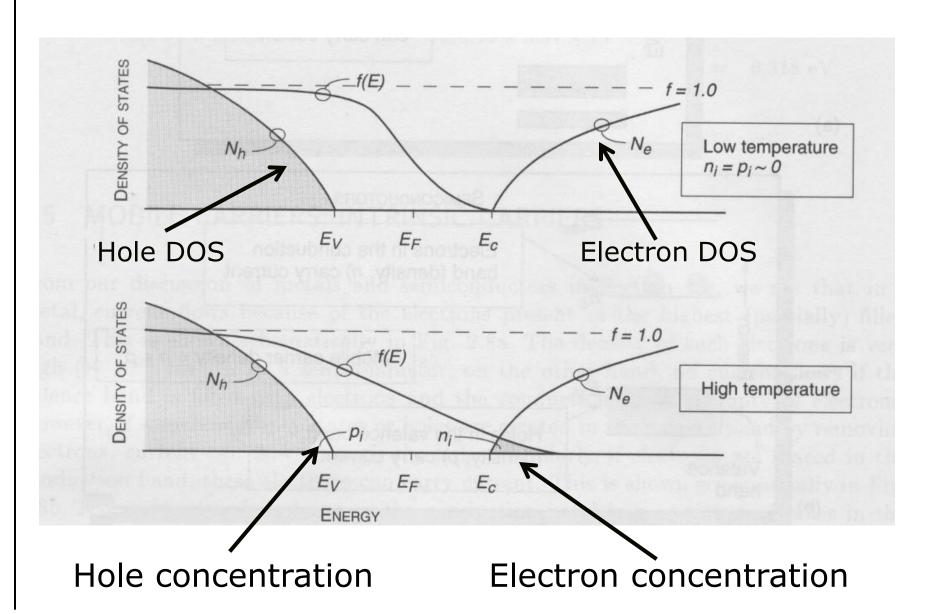
- Mobile charge carriers
 - Density of states
 - Law of mass action
 - Intrinsic Fermi level
 - Intrinsic carrier concentration
- Doping of semiconductors

- In **intrinsic semiconductors** the electron density is equal to the hole density (*n_i* and *p_i*).
- An intrinsic semiconductor is one that contains a relatively small amount of impurities compared with thermally generated electrons and holes.
- An extrinsic semiconductor, conversely, is a material which contains large amounts of impurities.



Density of states and Fermi function



- The intrinsic carrier concentration refers to the electrons (holes) present in the conduction (valence) band of a pure semiconductor.
- It is dependent on the magnitude of the bandgap and the temperature as well as the effective masses.
- The concentration of electrons in the conduction band is:

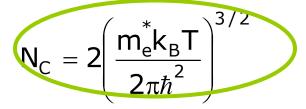
$$n = \int_{E_{C}}^{\infty} N_{e}(E)f(e)dE$$

• $N_e(E)$ is the electron density near the conduction band edge, f(E) is the Fermi function

• The concentration of electrons in the conduction band can hence be written:

$$n = \frac{1}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2} \right)^{3/2} \exp\left(\frac{E_F}{k_B T}\right)_{E_C}^{\infty} (E - E_C)^{1/2} \exp(-E/k_B T) dE$$
$$= 2 \left(\frac{m_e^* k_B T}{2\pi \hbar^2} \right)^{3/2} \exp[(E_F - E_C)/k_B T]$$
$$= N_C \exp[(E_F - E_C)/k_B T]$$
Effective density of

Effective density of states at the conduction bandedge



- The carrier concentration is known when E_F is calculated.
- To find the intrinsic carrier concentration required finding the hole concentration *p* as well.
- Then hole distribution function is:

$$f_h = 1 - f_e$$

• Then:

$$p = 2 \left(\frac{m_h^* k_B T}{2\pi\hbar^2} \right)^{3/2} exp[(E_v - E_F)/k_B T]$$
$$= N_v exp[(E_v - E_F)/k_B T]$$

 In intrinsic semiconductors the electron concentration is equal to the hole concentration, an electron in the conduction band leaves a hole in the valence band.

$$np = 4 \left(\frac{k_{B}T}{2\pi\hbar^{2}}\right)^{3} (m_{e}^{*}m_{h}^{*})^{3/2} \exp(-E_{g}/k_{B}T)$$

- The product *np* is independent of the position of the Fermi level and is dependent only on the temperature and intrinsic properties of the semiconductor.
- This is known as the Law of mass action
- If *n* increases, *p* must decrease. $\rightarrow np=n_i^2$
- For the intrinsic case n=n_i=p=p_i, we take the square root of the above equation:

$$n_i = p_i = 2 \left(\frac{k_B T}{2\pi\hbar^2}\right)^{3/2} (m_e^* m_h^*)^{3/4} \exp(-E_g / 2k_B T)$$

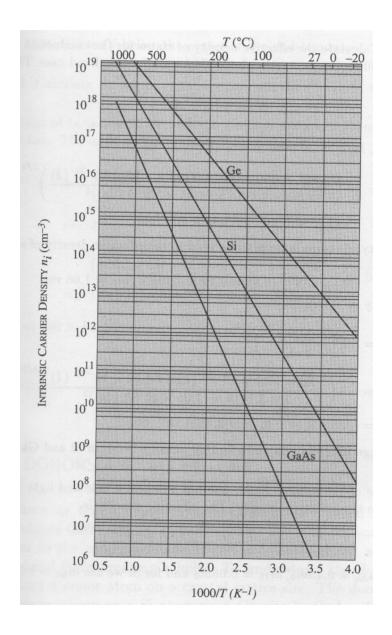
 Setting n=p we can obtain the Fermi level position. The intrinsic Fermi level denoted by E_{fi}

$$exp(2E_{Fi}/k_{B}T) = (m_{h}^{*}/m_{e}^{*})^{3/2} exp((E_{C} + E_{v})/k_{B}T)$$
$$E_{Fi} = \frac{E_{C} + E_{v}}{2} + \frac{3}{4}k_{B}T\ln(m_{h}^{*}/m_{e}^{*})$$

- The Fermi level of an intrinsic material lies close to the midgap.
- In calculating m_h* and m_e* the number of valleys and the sum of heavy and light hole states have to be included.

Material	Conduction band	Valence band	Intrinsic carrier
(300K)	effective density (N_C)	effective density (Nv)	concentration (n;=p;)
Si	2.78x10 ¹⁹	9.84x10 ¹⁸	1.5x10 ¹⁰
Ge	1.04x10 ¹⁹	6.0x10 ¹⁸	2.33x10 ¹³
GaAs	4.45x10 ¹⁷	7.72x10 ¹⁷	1.84x10 ⁶

- The carrier concentration increases exponentially as the bandgap decreases.
- Notice the strong dependence on temperature.
- In electronic devices where current has to be modulated, the concentration of intrinsic carriers is fixed by the temperature and this therefore detrimental to device performance.



- Once the intrinsic carrier concentration increases to ~10¹⁵cm⁻³, the material becomes unsuitable for electronic devices due to the high leakage current arising from the intrinsic carriers.
- High bandgap semiconductors such as diamond (C), and SiC have attracted growing interest.
- They can be used in high temperature applications.
- Pure semiconductors have a low concentration of mobile carriers:
 - Typically $\sim 10^{11}$ cm⁻³ for intrinsic semiconductors
 - And ~ 10^{21} cm⁻³ for metals.
- The addition of impurities doping can be used to change the conductivity of semiconductors.

- Calculate the position of the intrinsic Fermi level in Si at 300K.
- The density of states effective mass of the combined six valleys of silicon is:

$$m_{dos}^{*} = (6)^{2/3} (m_{l}^{*} m_{t}^{*})^{1/3} = 1.08 m_{0}$$

• The density of states mass for the valence band is $0.55m_0$. Hence the intrinsic Fermi level is given by:

$$E_{Fi} = \frac{E_g}{2} + \frac{3}{4}k_BT \ln\left(\frac{m_h^*}{m_e^*}\right) = \frac{E_g}{2} + \frac{3}{4}(0.026)\ln\left(\frac{0.55}{1.08}\right)$$
$$= \frac{E_g}{2} - (0.0132eV)$$

• The Fermi level is then 13.2meV below the centre of the mid-bandgap.

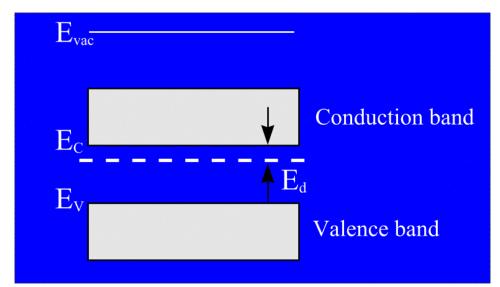
- There are two kinds of dopants:
 - Donors, which donate an electron to the conduction band. (n-type)
 - Acceptors, which accept an electron from the valence band – and therefore create a hole. (p-type)
- A donor atom should have one or more electrons in its outer shell than the atom it replaces.
- In silicon (a four valent atom) the addition of a pentavalent atom means the remaining fifth electron now sees a positively charged ion to which it is attracted.
- The attractive potential is simply:

$$U(r) = \frac{-e^2}{4\pi\epsilon r}$$

The lowest-energy solution for this problem is the ionisation energy:

$$E_{d} = E_{C} - \frac{e^{4}m_{e}^{*}}{2(4\pi\epsilon)^{2}\hbar^{2}}$$
$$= E_{C} - 13.6 \left(\frac{m^{*}}{m_{0}}\right) \left(\frac{\epsilon_{0}}{\epsilon}\right)^{2} eV$$

- Notice the effective mass m* is used.
- The energy level is measured from the bandedge.



Limitations of hydrogen formalism

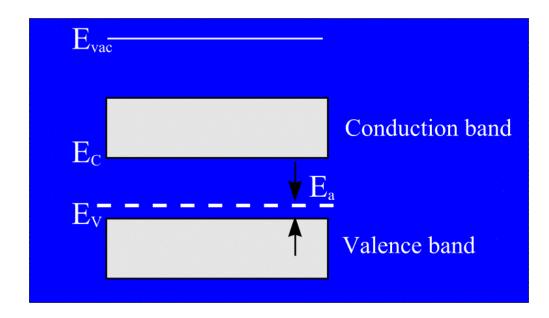
- The simple hydrogen model cannot account for the details of ionisation energy, particularly for the deep impurity levels in semiconductors (ionisation energies >3kT).
- Calculated values do predict the correct order of magnitude of the true ionisation energies for shallow impurity levels.
- For shallow impurities in Si and GaAs, there is usually enough thermal energy E_d to ionise all donor impurities, and thus provide an equal number of electrons in the conduction band.
- This condition is called **complete ionisation**.
- Under complete ionisation the electron density (n) equals the donor concentration (N_D) .
- Carrier freezeout occurs if donor (acceptor) electrons (holes) are tied to there respective lattice sites.

- Another effective mass m_σ*, the conductivity effective mass is introduced to describe how electrons respond to external potentials.
- This mass is used for donor energies as well as for charge transport in an electric field.
- For direct bandgap semiconductors, this is the effective mass.
- For indirect materials such as silicon the conductivity mass is:

$$m_{\sigma}^{*} = 3 \left(\frac{2}{m_{t}^{*}} + \frac{1}{m_{l}^{*}} \right)^{-1}$$

• Reminder: The density of states mass represents the properties of the electrons at a constant-energy surface in the band structure.

- The acceptor levels are produces when impurities that have a similar core potential as the atoms in the host lattice, but have one less electron in the outer shell, are introduced.
- Group III elements can act as acceptors in Si or Ge.
- Under complete ionisation the hole density (p) equals the acceptor concentration (N_A) .



Summary of donors and acceptors

Semiconductor	Impurity	Donor Energy	Impurity	Acceptor Energy
	(Donor)	(meV)	(Acceptor)	(meV)
GaAs	Si	5.8	С	26
	Ge	6	Be	28
	S	6	Mg	28
	Sn	6	Si	35
Si	Li	33	Be	45
	Sb	39	AI	67
	Р	45	Ga	72
	As	54	In	160
Ge	Li	9.3	В	10
	Sb	9.6	AI	10
	Р	12	Ga	11
	As	13	In	11

Doped semiconductors are referred to as **extrinsic** semiconductors.

• We can now write the Fermi level in terms of the effective density of states N_c and the donor concentration N_d :

• Recall:
$$n = N_C \exp \left[\frac{(E_F - E_C)}{k_B T}\right]$$
 and $n = N_d$

• Therefore:
$$E_F - E_C = k_B T ln \left[\frac{N_d}{N_C} \right]$$

• Similarly for shallow acceptors $p = N_A$ and:

$$E_{v} - E_{F} = k_{B}T ln \left[\frac{N_{a}}{N_{v}}\right]$$

• For higher donor concentration, the smaller the energy difference $(E_F - E_C)$, the Fermi level moves closer to the bottom of the conduction band.

- Considering material that have a dominance of donors (n-type) or acceptors (p-type).
- There is no longer equality between the electrons and holes: $n p \neq 0$
- The law of mass action still holds and only changes at high doping levels:

 $np = constant = n_i^2$

- As indicated, when the semiconductor is doped n-type (p-type), the Fermi level moves towards the conduction (valence) bandedge.
- When the Fermi level approaches the bandedge, the Boltzmann approximation is not very good and the simple expressions relating the carrier concentration and Fermi level are not very accurate.

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