Semiconductors, doping

1. Molecular orbital bands

(a) Band formation by orbital overlap

The overlap of a large number of atomic orbitals leads to molecular orbitals that are closely spaced in energy and so form a virtually continuous band. Bands are separated by band gaps, which are values of the energy for which there are no molecular orbitals.

Simply Band model: (for instance s band) The formation of bands can be understood by considering a line of atoms, and supposing that each atom has an s orbital that overlaps the s orbitals on its immediate neighbors. When there are N atoms in the line, there are N molecular orbitals. The total width of the band, which remains finite even as N approaches infinity, depends on the strength of the interaction between neighboring atoms. The band from s orbitals is called an s-band. If there are p orbitals available, a p-band can be constructed from their overlap. Because p orbitals lie higher in energy, there is often an energy gap between the s band and p band.

(b) The Fermi-Dirac distribution

For excited states of particles in gas phase usually the Boltzmann distribution is used. Yet for applying statistics to electrons this theory has to be modified for two reasons:

i) Pauling exclusion principle (1 electron per state)

ii) Electrons are indistinguishable (exchange of electrons between occupied states does not lead to a different arrangement)

Fermi-Dirac distribution gives the fraction of allowed levels with energy E which are occupied.

$P = 1 / [e^{(E-\mu)/kT} + 1]$, at high energies ($E >> \mu$), $P \approx e^{-(E-\mu)/kT}$

At 0 K there is a sharp cut-off between occupied and unoccupied states (Fermi energy E_f) while at higher temperatures this distribution is smeared out. In metallic solids E_f lies in the top filled band.

2. Semiconductor

The characteristic physical property of a semiconductor is that its **electrical conductivity increases with increasing temperature**. At room temperature, the conductivities of semiconductors are typically intermediate between those of metals and insulators (in the region of 10^3 Scm^{-1}). The dividing line between insulators and semiconductors is a matter of the size of the band gap.

typical band gaps of semiconductors: 1-3 eV

(a) Intrinsic semiconductors

In an intrinsic semiconductor, the band gap is so small that the Fermi-Dirac distribution results in some electrons populating the empty upper band. This occupation of the conduction band introduces negative carriers into the upper level and positive holes into the lower, and as a result the solid is conducting.

The conductivity of a semiconductor can be expected to be Arrhenius-like with an activation energy equal to half the band gap, $E_a \approx 0.5E_g$. This is found to be the case in practice. An Arrhenius-like temperature dependence follows the expression:

$\sigma = \sigma_0 e^{-E_a/kT}$

(b) Extrinsic semiconductors

The number of electron carriers can be increased if atoms with more electrons than the parent element can be introduced by the process called **doping**. This process gives rise to **n-type semiconductivity**, the “n” indicating that the charge carriers are negative electrons **(e.g. Si doped with As).**

p-type semiconductors are doped with atoms that remove electrons from the valence band. Because the charge carriers are positive holes in the lower band, this type of semiconductivity is so called p-type semiconductivity **(e.g. Si doped with In).**