FoP3B Part II Lecture 4: Extrinsic Semiconductors

The electrical conductivity of a semiconductor depends on its electron and hole concentrations, which from the **law of mass action** can be controlled by varying the band gap and/or temperature. However, these two parameters are fixed according to the device application (e.g. a blue light emitting diode operating at room temperature). An alternative way of changing the charge carrier concentration is therefore required. This is achieved through the process of **doping**, i.e. *the <u>controlled</u> addition of 'impurities' or **dopants** to a pure **intrinsic** semiconductor*. A doped semiconductor is called an **extrinsic** semiconductor. Dopants generate either an excess of electrons or an excess of holes. *Dopants that provide excess electrons are called **n-type** dopants or **donors**. **p-type** dopants (or **acceptors**) provide excess holes.*

n-type doping (excess electrons)

Consider silicon as an example of an intrinsic semiconductor. **Silicon is a group IV element**. *In order to complete an octet of electrons and form a stable compound a single silicon atom must covalently bond with four neighbouring atoms* (Figure 1a). This results in the familiar **diamond cubic** crystal structure of silicon. Now assume a Group V element (e.g. nitrogen, phosphorous) is added to the silicon lattice. *The extra electron from the Group V element will orbit around the impurity atom (Figure 1b)*. The energy of this extra electron and the orbiting radius can be calculated approximately using Bohr's model of the atom. <u>*Due to the high*</u> **<u>dielectric constant ε_r</u>** <u>*for a semiconductor (e.g. $\varepsilon_r = 11.7$ for silicon) the energy is small (meV) and the orbit radius large (several nm)*</u>. **The extra electron is weakly bound compared to valence electrons, but not as free as conduction electrons, and so occupies an energy level slightly below the conduction band (Figure 1c)**. This is known as the **donor energy level**.
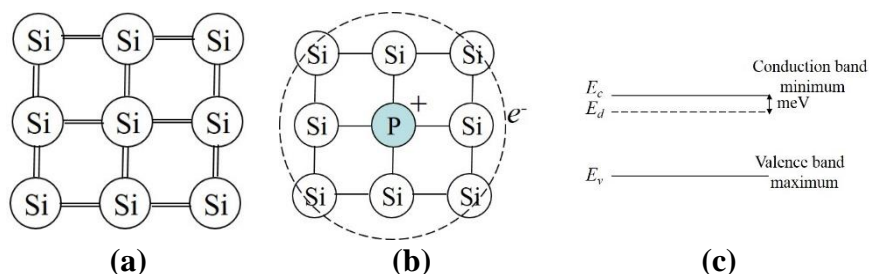

Fig 1: (a) 2D projection of a perfect Si crystal and (b) with a Group V impurity. The extra electron occupies the donor energy level E_d below the conduction band (c).

Let us examine the effect of temperature on Group V doped silicon. **The key point to bear in mind is that the binding energy of donor electrons is only meV and so can easily be promoted into the conduction band via thermal excitation[1].** At absolute zero all donor electrons occupy the donor energy level, i.e. they remain loosely bound to the Group V impurity. This is the so-called **freeze-out regime**. As the temperature is raised more and more donor electrons can be promoted to the conduction band leaving the Group V donor atoms **ionised** (i.e. they acquire positive charge due to the missing electron). Eventually all donor atoms are ionised and the material is in the **saturation regime**. *At room temperature most semiconductors are in the saturation regime, where the donor energy level is largely empty.* As the temperature is increased still further the only possible electronic transition is from the valence band to the conduction band. This process is comparatively inefficient since the

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[1] Recall *kT* at room temperature is ~25 meV.

electronic transition must take place across the (moderately large) 1-4 eV **band gap**. Nevertheless provided the temperature is sufficiently high (e.g. several 100ºC) the material enters the **intrinsic regime**, where the number of electrons generated by thermal excitation across the band gap far outnumber the excess electrons due to dopant atoms. *Due to the nature of excitation across the band gap the electron and hole concentrations are approximately equal in the intrinsic regime.* The different regimes for an *n*-type semiconductor are shown in Figure 2a.
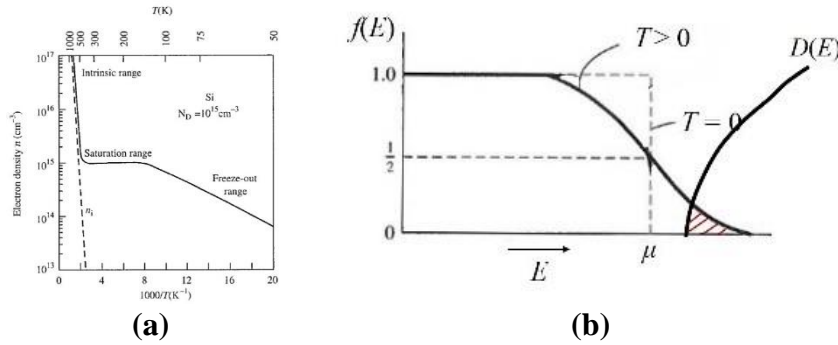

(a)   **(b)**

Fig 2: (a) Electron concentration as a function of temperature for a *n*-type semiconductor. (b) The Fermi-Dirac distribution function and conduction band density of states. The overlap region (shaded) determines the electron concentration.

It is possible to calculate the electron and hole concentrations in the saturation regime due to *n*-type doping (we focus on the saturation regime since this corresponds to room temperature). From the law of mass action the electron (*n*) and hole (*p*) product *np* is given by:

$$np = N_c N_v \exp\left(-\frac{E_g}{kT}\right)$$

… (1)

(see Lecture 3 summary for a definition of terms). <u>*np* is therefore constant for a given semiconductor at fixed temperature.</u> *Equation (1) was derived from statistical physics and is valid irrespective of whether the semiconductor is pure (i.e. intrinsic) or doped (i.e. extrinsic).* If the semiconductor is intrinsic $n = p$, since electrons and holes are generated equally by thermally exciting a valence band electron into the conduction band. Let us denote by n_i the **intrinsic electron (or intrinsic hole) concentration** for the undoped semiconductor. Then for the doped, extrinsic semiconductor we can write:

$$np = n_i^2$$

… (2)

Comparing (1) and (2) it is clear that $n_i = \sqrt{N_c N_v}\exp(-\frac{E_g}{2kT})$.

The semiconductor must also be charge neutral. In an *n*-type semiconductor the positive charges are due to holes (*p*) and ionised donors. In the saturation regime the latter is equal to the Group V **donor atom concentration** N_D. The negative charge is due to conduction band electrons (*n*). Therefore:

$$n = p + N_D$$

… (3)

Using (2) and (3) to solve for n and assuming[2] $N_D \gg n_i$ gives $n \sim N_D$. Hence from (2) $p \sim n_i^2/N_D$. We have for an n-type semiconductor $n > n_i$ and $p = n_i(n_i/N_D) < n_i$, so that $n > p$. In an n-type extrinsic semiconductor electrons are **majority carriers** and holes are **minority carriers** (cf. an intrinsic semiconductor where $n = p$).

It is also possible to calculate the **chemical potential** μ for an n-type semiconductor in the saturation regime. The electron concentration n is given by:

$$n = N_c \exp\left[-\frac{(E_c - \mu)}{kT}\right]$$

$$\ldots (4)$$

(see Lecture 3 summary). Substituting $n = N_D$ and re-arranging for μ gives:

$$\mu = E_c - kT\ln\left(\frac{N_c}{N_D}\right)$$

$$\ldots (5)$$

This indicates that the chemical potential μ lies below the conduction band minimum E_c. In fact for an intrinsic semiconductor, where $n = p$, μ is located close to the mid-gap position. Therefore for an n-type extrinsic semiconductor, where $n > p$, μ must move closer to the conduction band, since from Figure 2b the electron concentration is determined over the energy range where the conduction band **density of states** and **Fermi-Dirac distribution function** overlap (see Lecture 3 summary). From Equation (5) the higher the doping concentration N_D the larger the value of n and consequently the closer μ is to E_c.

p-type doping (excess holes)

Consider adding a Group III element (e.g. boron, aluminium) to a silicon lattice. The Group III electron is now missing an electron in order to complete its full octet. This missing electron can be provided by a neighbouring silicon bond (Figure 3a). *However, this would result in the Group III atom being negatively charged (i.e. 'ionised') and hence the extra electron will be bound but higher in energy than a valence electron.* The electron therefore occupies an **acceptor energy level** that is above the valence band (Figure 3b).
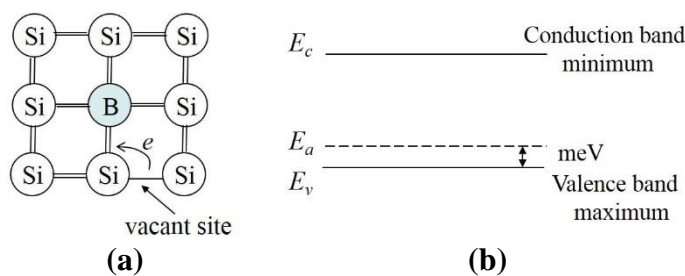

(a)   (b)

Fig 3: (a) 2D projection of a Si crystal with a Group III impurity. The extra electron required to complete the octet occupies the acceptor energy level E_a above the valence band.

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[2] This assumption is justified since n_i is relatively small (recall that thermal excitation across the band gap at room temperature is not an efficient process). Dopant concentrations even at parts per million is therefore sufficient to satisfy the condition $N_D \gg n_i$.

The effect of temperature on the hole concentration is similar to the arguments presented for an *n*-type semiconductor. *At absolute zero the valence band is completely full and there are no electrons in the acceptor energy level, i.e. the Group III impurities have not acquired an electron from neighbouring bonds.* This is the freeze-out regime. *As the temperature is raised first valence band electrons are promoted to the acceptor energy level*, i.e. the Group III impurities gain an electron and become 'ionised'. *The partially full valence band can now conduct electricity due to holes. With increasing temperature all acceptor energy states become occupied resulting in the saturation regime. Increasing the temperature still further results in the intrinsic regime where the electrons and holes are primarily due to thermal excitation across the band gap.*

The hole concentration for a *p*-type semiconductor in the saturation regime is derived using the same arguments of law of mass action and charge conservation. Assuming $N_A \gg n_i$ we find that $p \sim N_A$ and $n \sim n_i^2/N_A$, where N_A is the Group III **acceptor atom concentration**. *Thus for a p-type semiconductor holes are the majority carriers and electrons the minority carriers.*

From the equation for the hole concentration *p* the chemical potential μ is found to be:

$$\mu = E_v + kT\ln\left(\frac{N_v}{N_A}\right)$$

$$\dots (6)$$

Thus μ is above the valence band maximum E_v. This is easily understood by noting that $p > n$ and that the hole concentration is due to overlap of the valence band density of states and probability of *unoccupation* (i.e. [1-*f*(*E*)]) curves.