Appendix A

Theory of semiconductors

The understanding of semiconductors is essential to the understanding of TCOs. The main characteristics have been detailed in the body of this dissertation, but the basic theory is presented here.

This appendix has been written using Refs. [43, 44].

A.1 Band structure of a semiconductor

In a solid, electrons can have energies which are quantified and grouped in bands containing allowed energy levels and separated by forbidden bands in which there are no energy levels available. When $T = 0$ K and if the solid is at equilibrium, the system tends to minimize its total energy and the electrons fulfill energy levels from the lowest level to a level depending on the solid (due to Pauli exclusion principle, only two electrons can have the same level of energy). The valence band is the band containing the highest energy levels and in which all these levels are occupied. The band directly above the valence band in called the conduction band.

The difference between the band structure at $T = 0$ K for a metal, an insulator and a semiconductor is represented in Fig. A.1. It shows that for an insulator, the valence band is completely full with electrons while the conduction band is completely empty. The only difference between an insulator and a semiconductor is their band gap E_g : for an insulator, $E_g \sim 5$ eV and for a semiconductor, $E_g \sim 1 - 2$ eV.

The band structure is not exactly what is depicted in Fig. A.1 because it does not take into account the momentum of the electrons. Fig. A.2 represents the band structure for silicon and gallium arsenide. This shows that the top of the band valence does not always correspond to the bottom of the conduction band : they may differ by a given wave vector. If there is no difference, the semiconductor is said to have a direct band gap. If there is a difference, then it is said to have an indirect band gap. For example, silicon has an indirect band gap and gallium arsenide has a direct one.

The electronic properties of semiconductors are mostly determined by the density of electrons in the conduction band n and the density of holes in the valence band p. In the rest of this chapter, the developments will be given for electrons only (the developments for the holes being essentially the same).

A.2 Intrinsic concentration of charge carriers

The Fermi-Dirac distribution gives the probability for an electron to be in a certain energy state. The expression depends on the Fermi energy E_f and on the temperature :

$$f_e(E,T) = \frac{1}{\exp\left(\frac{E-E_f}{kT}\right)+1}. \tag{A.1}$$

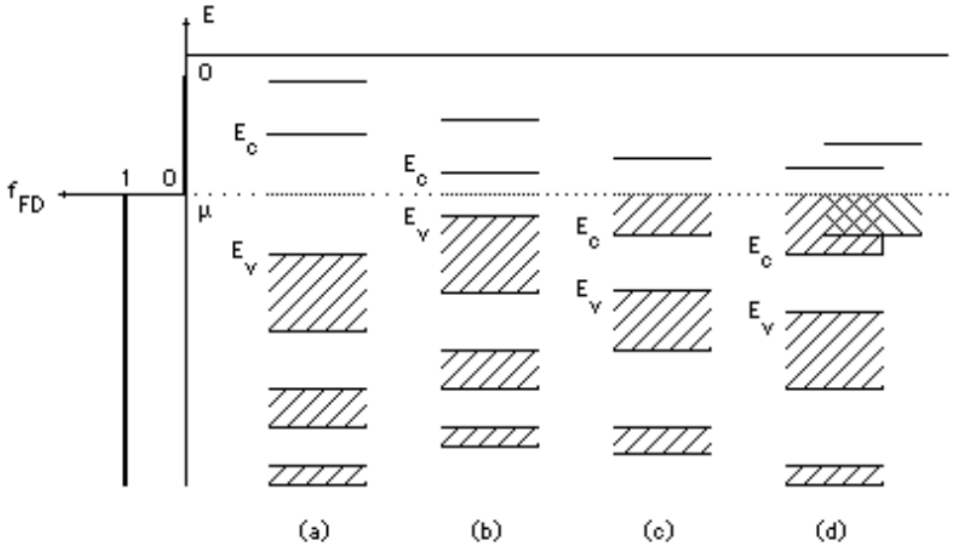


Figure A.1: Energy bands of (a) an insulator, (b) a semiconductor, (c) a metal and (d) a semi-metal for $T = 0$ K [44]. μ represents the Fermi level, E_v the energy level corresponding to the top of the valence band and E_c the energy level corresponding to the bottom of the conduction band.

At room temperature, the product $kT \simeq 0.0259$ eV so that if the Fermi level is far enough from the conduction and valence bands, the Fermi-Dirac distribution can be approximated by a Maxwell-Boltzmann one :

$$f_e(E) \simeq \exp\left(\frac{-(E - E_f)}{kT}\right). \tag{A.2}$$

The density of electrons in the conduction band at a given temperature is

$$n = \int_{E_c}^{\infty} g_c(E) f_e(E) dE \tag{A.3}$$

where $g_c(E)$ is the density of states (DOS) in the conduction band. If the effective mass of electrons is isotropic, then the DOS is given by (without demonstration)

$$g_c(E) = \frac{(2m_e^*)^{3/2}\sqrt{E - E_c}}{2\pi^2\hbar^3} \tag{A.4}$$

so that the density of electrons is

$$n = N_c \exp\left(\frac{E_f - E_c}{kT}\right) \tag{A.5}$$

with

$$N_c = 2\left(\frac{2\pi m_e^* kT}{h^2}\right)^{3/2}. \tag{A.6}$$

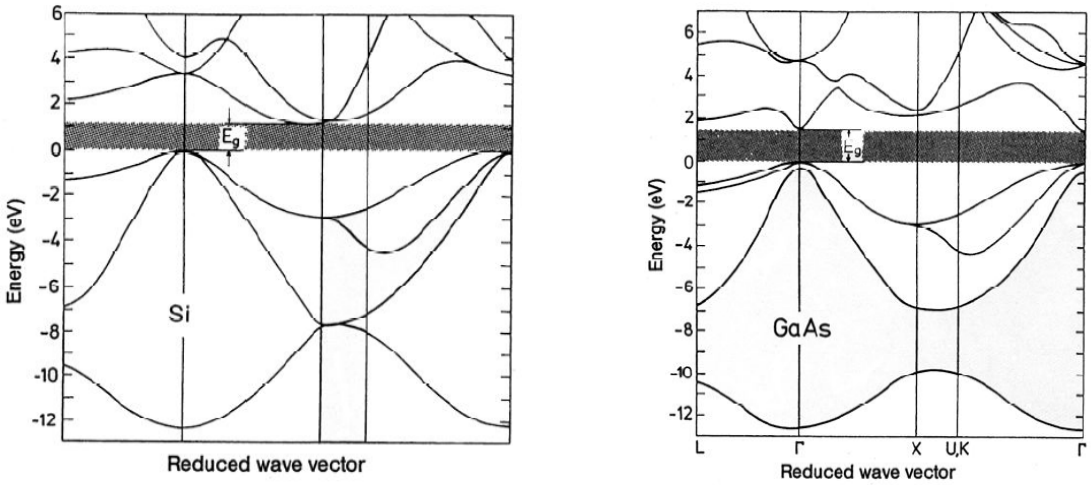
The results for the density of holes in the valence band can be derived by the exact same way and is given by

$$p = N_v \exp\left(\frac{E_v - E_f}{kT}\right) \tag{A.7}$$

$$N_v = 2\left(\frac{2\pi m_h^* kT}{h^2}\right)^{3/2}. \tag{A.8}$$

The product np can be determined :

$$np = 4\left(\frac{kT}{2\pi\hbar^2}\right)^3 (m_e^* m_h^*)^{3/2} \exp\left(-\frac{E_g}{kT}\right) \equiv n_i^2(T) \tag{A.9}$$



(a) (b)

Figure A.2: Band structure of (a) silicon and (b) gallium arsenide [43].

where n_i is called the intrinsic concentration. This shows that for a given temperature and for a given semiconductor, the product np is a constant. This relation is really useful even for doped semiconductors, as it will be shown in the next section.

For an intrinsic semiconductor, the density of holes in the valence band is equal to the density of electrons in the conduction band. Indeed, the only contributions to the densities come from the excitation of electrons from the valence band to the conduction band. As every excited electron leaves a hole in the valence band, the densities have to be the same. This gives

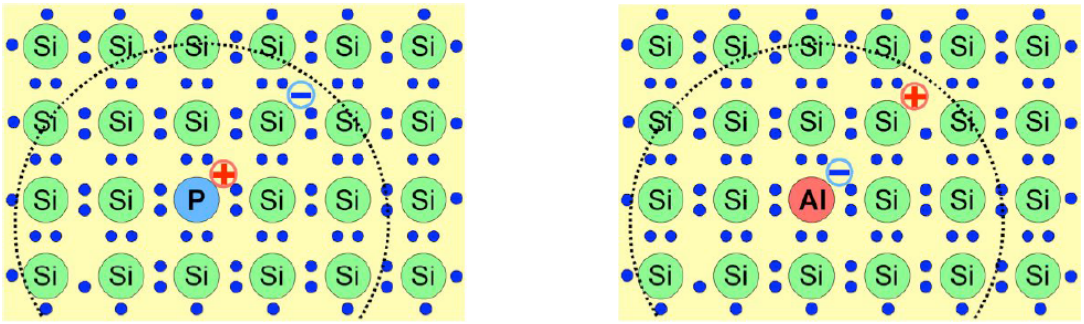
$$n = p = n_i = p_i = 2\left(\frac{kT}{2\pi\hbar^2}\right)^{3/2}(m_e^* m_h^*)^{3/4}\exp\left(-\frac{E_g}{2kT}\right). \tag{A.10}$$

A.3 Doping a semiconductor : change in concentrations

The intrinsic densities of electrons and holes in a semiconductor are really small at room temperature. For example, at 300 K the intrinsic density for silicon is $n = 1.5 \cdot 10^{10}$ cm^{-3}, and for gallium arsenide the density is $n = 5 \cdot 10^{7}$ cm^{-3} while the atomic concentration is around 10^{23} cm^{-3}. The introduction of impurities in a semiconductor leads to the introduction of free charges (no polaronic effects are taken into account here). This is called the doping of a semiconductor. In a lattice composed of silicon (for example), which is of valence 4, the replacement of a silicon atom by a donor element like phosphorus (valence 5) is easy because the sizes of the atoms are nearly the same. 4 of the electrons of valence from the phosphorus are used in order to satisfy the covalent bonds with other silicon atoms. The last electron is the one which will be useful for the electronic properties. The impurities are easily ionized (the thermal energy at room temperature is high enough to ionize the atoms) once they are in the lattice, so the delocalization of free charges is way easier in this case than in the intrinsic case.

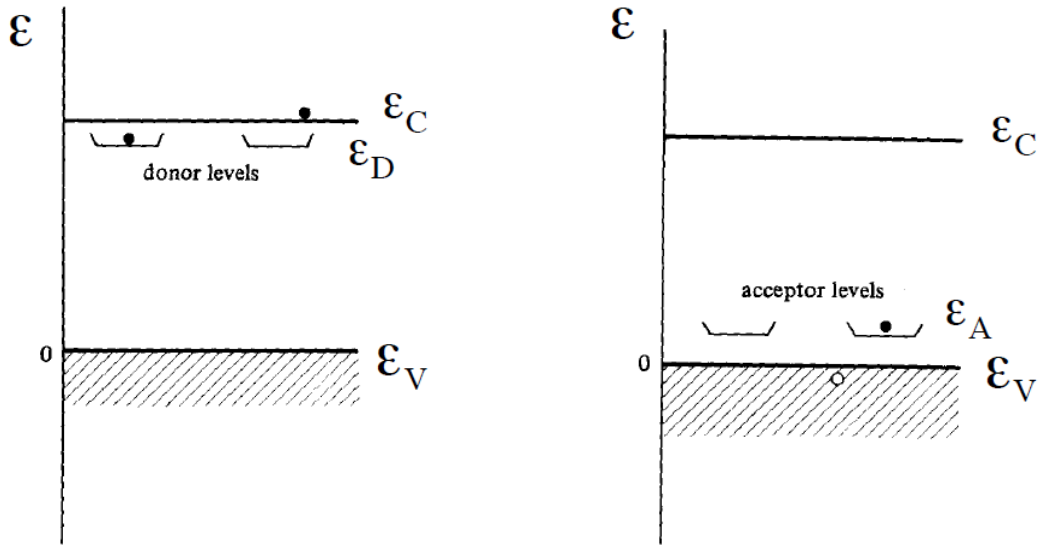
The same reasoning can be done for an acceptor of electrons like boron (valence 3). Here, an electron of the lattice will be taken by the acceptor in order to satisfy the covalent bonds. A positive charge will thus be delocalized while the negative ion is staying around its equilibrium position. Fig. A.3 shows the effect of the addition of a donor and of an acceptor of electron.

The introduction of impurities in a semiconductor also leads to the introduction of energy levels inside the forbidden band. The donors introduce a level E_D which is really close to the conduction band (the donor is easily ionized) and the acceptors introduce a level E_A which is really close to the valence band. Fig. A.4 represents both different situations.



(a) (b)

Figure A.3: Effect of (a) donor and (b) acceptor species in a semiconductor [43].



(a) (b)

Figure A.4: Introduction of energy levels due to the presence of (a) donor and (b) acceptor species [43].

The energy needed in order to ionize the impurities is either $E_c - E_D$ or $E_A - E_v$. In the case of an n-type semiconductor (doped with donor impurities) with a concentration N_D of impurities, the variation of n with the temperature is the following.

- For really low temperatures, the thermal energy kT is not high enough to ionize the impurities. The electrons are localized in the valence band and on the energy levels introduced by the donors.
- If the temperatures get a little higher, the donors will slowly become ionized. In this case,

$$n \propto \exp\left(-\frac{E_d}{2kT}\right) \tag{A.11}$$

  with $E_d = E_c - E_D$.
- If the temperature is such that all the donors are ionized ($kT \gg E_d$), then

$$n \simeq N_D \quad \text{and} \quad p \ll n. \tag{A.12}$$

- If the temperature gets even higher, the intrinsic ionization cannot be ignored :

$$n = p + N_D \tag{A.13}$$

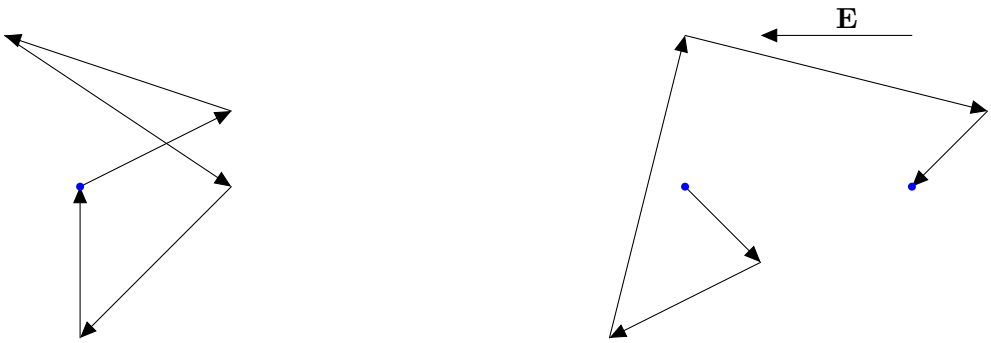


Figure A.5: Movement of an electron in a solid. On the left, there is no external electric field and the net movement is equal to 0. On the right, the electric field leads to a global movement in the direction of the electric field. Inspired from [44].

In the intrinsic regime, the electrons in the conduction band come from both the valence band and the ionized impurities, but the number of electrons excited from the valence band stays really small compared to the number of impurities introduced. The relation $np = n_i^2$ is still satisfied for such a semiconductor and leads to the conclusion that $p \ll n$. The electrons are then called the majority carriers and the holes the minority carriers.

For temperatures around 300 K, the situation considered is the one where all impurities are ionized and the intrinsic regime is not reached yet.

A.4 Current in a semiconductor due to an electric field

The motion of a charge carrier in a solid is random and changes constantly of direction due to collisions with impurities, lattice defaults or phonons (quanta of energy stored in lattice vibrations). When there is no external force applied to the carriers, the net motion of each one of them is zero, so that there is no spontaneous current in the material. But when an electric field is applied, the net motion of the carriers is different from 0 and tends to be aligned with the electric field. Fig. A.5 depicts both scenarios.

If τ_n is the mean time between two collisions for an electron, the drift velocity of electrons is[1]

$$\mathbf{v}_D = -\frac{q\tau_m}{m_e^*}\mathbf{E} \tag{A.14}$$

so that the current density is

$$\mathbf{J_n} = -nq\mathbf{v}_D = \frac{nq^2\tau_n}{m_e^*}\mathbf{E}. \tag{A.15}$$

The mobility of the electron μ_n is then defined as

$$\mu_n = \frac{q\tau_n}{m_e^*}. \tag{A.16}$$

The same kind of expressions can be obtained for holes :

$$\mathbf{J_p} = \frac{nq^2\tau_p}{m_h^*}\mathbf{E} \tag{A.17}$$

$$\mu_p = \frac{q\tau_p}{m_h^*}. \tag{A.18}$$

The total current density is then

$$\mathbf{J} = \mathbf{J_n} + \mathbf{J_p} = q(n\mu_n + p\mu_p)\mathbf{E}. \tag{A.19}$$

[1]Both classical and quantum considerations lead to this result.