Lecture 7

Semiconductors and optical properties

In this lecture we want to generalize the tight-binding model of Lecture 6 to the case of tetrahedral semiconductors (such as for instance Si, C, SiC, GaAs). The description will be very qualitative, with essentially no maths involved. Then we will discuss briefly the optical properties of semiconductors.

7.1 Tight-binding model for tetrahedral semiconductors

In the case of tetrahedral semiconductors each atom has 4 nearest neighbors and the bonds point to the directions $(111)$, $(\bar{1}1\bar{1})$, $(\bar{1}\bar{1}1)$, and $(1\bar{1}1)$. If our atom is sitting in the middle of a cube, these directions point to the 4 non-adjacent corners of the cube (Fig. 7.1). Tetrahedral semiconductors have not only $s$ electrons in the valence (as in the case of cubium), but also $p$ states. Instead of building a tight-binding model based on linear combinations of $s$ and $p$ orbitals, it is convenient to define hybrid orbitals. The

![Figure 7.1: Crystal structure of silicon, from http://en.wikipedia.org/wiki/Silicon. Each Si atom is coordinated to 4 nearest neighbors in a tetrahedral arrangement. To find the position of the neighbors we sit in the middle of a cube and we look at the 4 non-adjacent corners of the cube.](image-url)
concept of hybrid orbitals is most easily understood by considering the 1D case:

\[ h_1 = \frac{1}{\sqrt{2}} (s + p), \]
\[ h_2 = \frac{1}{\sqrt{2}} (s - p), \]

with \( s \) and \( p \) the initial orbitals and \( h_{1,2} \) their hybrids. While the \( s \) and \( p \) orbitals sit on top of an atom, hybrid orbitals concentrate the electronic charge on the bonds between nearest neighbor atoms (Fig. 7.2). In the 3D case the hybrid orbitals are obtained as follows:

\[ h_1 = \frac{1}{2} (s + p_x + p_y + p_z), \]
\[ h_2 = \frac{1}{2} (s + p_x - p_y - p_z), \]
\[ h_3 = \frac{1}{2} (s - p_x + p_y - p_z), \]
\[ h_4 = \frac{1}{2} (s - p_x - p_y + p_z), \]

with the signs determined according to Fig. 7.1. The formation of energy bands starting from hybrid orbitals is illustrated in Fig. 7.3. The magnitude of the band gap in a tetrahedral semiconductor within the tight-binding approximation is given by:

\[ E_g = 2|\beta| - \Delta E_{sp}, \]  

(7.1)

with \( \Delta E_{sp} = E_p - E_s \sim 7.5 \text{ eV} \) for C, Si, Ge, Sn. This result means that the larger the bond integral, the larger is the band gap. For example the band gap of diamond, Si,
Figure 7.3: Formation of energy bands starting from hybrid orbitals. The linear combination of \( s \) and \( p \) orbitals leads to hybrid orbitals sitting in the middle of each bond. Overlapping hybrids split in bonding and antibonding combinations, as in the case of the \( \text{H}_2 \) molecule. Then the bonding orbitals on each bond form bands due to the interaction with the bonding orbitals in nearest neighbor bonds, as in the case of cubium. The same happens for the antibonding orbitals. As a result we have hybrid bonding bands and hybrid antibonding bands. \( |\beta| \) is the bond orbitals between nearest neighbor hybrid orbitals.

Ge, and Sn are 5.5 eV, 1.1 eV, 0.7 eV, and 0.1 eV, respectively. This happens because, as we move down along the periodic table, the equilibrium bond length increases and the bond integral decreases accordingly.

The hybridization of \( s \) and \( p \) orbitals in tetrahedral semiconductors leads to the formation of bonding and antibonding hybrid bands. We call valence band the band which is filled with electrons at \( T = 0 \) K, and conduction band the first empty band immediately above. Semiconductors show electrical conductivity when electrons are thermally excited from the valence band to the conduction band. Extrinsic semiconductors are semiconductors doped with impurities, in such a way as to modify their electron concentration and move the fermi level across the band gap. Doped semiconductors exhibit very interesting electrical properties, which are the basis for the operation of field-effect devices.
It is now time to make a classification of materials in terms of their electrical properties. With reference to Fig. 7.4, when the Fermi level falls in the middle of a band we say that this material is a *metal*. In this situation the energy band is only partially filled and there exists a Fermi surface. Since above the Fermi level there is a continuum of empty electronic states, it is very easy for the electrons to change their momentum and energy under external perturbations. This is at the origin of the electrical properties of metals. There is a beautiful and extremely helpful definition of “metals” by Mackintosh reported in the book by Kittel: “a metal is a solid with a Fermi surface”. When the Fermi level is right at the top of a band, i.e. the band is fully occupied, and the highest occupied level is separated by the lowest empty level by an energy gap, then we say that the system is an *insulator*. In fact the electrons need a lot of energy (equal to the size of the gap) to jump into another quantum state with different energy and momentum, therefore the electrical conductivity is quenched. In those cases where the Fermi level is very close to the edge of a band we say that we have a *semiconductor*. Of course the separation between these three cases is not sharp and depends somewhat on what kind of measurements we are interested in. In Lecture 1 we also mentioned the existence of *half-metals*. In this class of materials the Fermi level falls in the middle of a band for spin-up electrons, and in the middle of a band gap for spin-down electrons. As a consequence spin-up electrons behave like in a metal, and spin-down electrons behave like in an insulator. These materials are interesting because they could be used as spin-filters in future spintronics applications.

![Figure 7.4: Schematic classification of metals, insulators, and semiconductors based on the location of the Fermi level in the band structure.](image-url)
7.2 Optical properties of semiconductors

The band structures of two important semiconductors, GaAs and Si, are shown in Fig. 7.5. We note that in GaAs the top of the valence band and the bottom of the conduction band both have the same wavevector $k = \Gamma$. In this case we say that the semiconductor has a *direct gap*. On the other hand, in Si the top of the valence band is at $\Gamma$, while the bottom of the conduction band is at $\sim 0.8 \Gamma X$. In this case we say that Si has an *indirect gap*. The nature of the band gap (direct or indirect) bears important implications on the optical properties of a semiconductor. In fact, when we shine light on a semiconductor in the frequency range between the infrared and the visible (1 eV to 4 eV, i.e. wavelengths from 1200 nm to 300 nm), light absorption can take place only if the energy of the photons can be transferred to the electrons. This happens if the electrons can be promoted from the valence band to the conduction band by overcoming the band gap. It is possible to use “perturbation theory” in order to calculate the absorption spectra of semiconductors (see for instance Yu and Cardona, Fundamentals of Semiconductors). The derivation is rather difficult, therefore we only discuss the qualitative results.

In the absorption process energy and momentum (wavevector) are conserved:

$$\hbar k^i + \hbar q = \hbar k^f \quad \text{conservation of momentum}$$
$$E^i + \hbar \omega = E^f \quad \text{conservation of energy},$$

Figure 7.5: Band structures of GaAs and Si calculated using the Empirical Pseudopotential Method by T.K. Bergstrasser and M. L. Cohen [taken from Physical Review B 141, 798, (1966)]. The Brillouin zone is the one in Fig. 5.3 because both GaAs and Si take the fcc structure. GaAs is a direct-gap semiconductor, while Si is an indirect-gap semiconductor.
where $\hbar k^i$ and $\hbar k^f$ are the initial and final electron momenta, respectively, and $E^i$, $E^f$ the associated energies. $\hbar q$ is the photon momentum and $\hbar \omega$ the associated quantum of energy. The initial electron can be transferred to another quantum state only if the final state is unoccupied, therefore the minimum photon energy required to promote a transition equals the band gap:

$$\hbar \omega_{\text{min}} = E^f - E^i = E_g.$$  \hspace{1cm} (7.2)

The typical momentum of a visible photon is very small compared to the size of the Brillouin zone:

$$q = \frac{2\pi}{\lambda} \ll \frac{2\pi}{a},$$  \hspace{1cm} (7.3)

since $\lambda \sim 500$ nm and $a \sim 0.5$ nm. For practical purposes it is reasonable to take $\hbar q = 0$. The fact that optical absorption is accompanied by a negligible momentum transfer implies that the initial and final electronic states have the same wavevector:

$$k^i = k^f.$$  \hspace{1cm} (7.4)

If we apply these considerations to the band structure of GaAs displayed in Fig. 7.5 we find that optical absorption in this material takes place by promoting electrons from the top of the valence band at $\Gamma$ to the bottom of the conduction band at $\Gamma$, and for photons with a minimum energy of 1.4 eV (Fig. 7.6). This optical process is called direct absorption because it takes place by overcoming a direct band gap.

If we now consider the band structure of Si in Fig. 7.5, we realize that the condition of momentum conservation given by Eq. (7.4) cannot be satisfied for photons with energy $\hbar \omega = E_g = 1.1$ eV. In fact the bottom of the conduction band in Si is found close to the $X$ point of the Brillouin zone. In this case the process described for GaAs still takes place, but we need a much higher photon energy (about 3 eV) to promote the electrons up to the $\Gamma_{15}$ state of Fig. 7.5. Therefore the energy threshold for direct absorption in silicon is about 3 eV. For photon energies around the band gap $E_g = 1.1$ eV we can still have absorption of photons, but in order to conserve momentum this process has to involve additional particles. The most important mechanism in this case is the absorption mediated by phonons, called indirect absorption. If we call the phonon momentum $\hbar Q$ and the phonon energy $\hbar \Omega$, the conservation equations can be rewritten as:

$$\hbar k^i + \hbar q + \hbar Q = \hbar k^f \quad \text{conservation of momentum},$$

$$E^i + \hbar \omega + \hbar \Omega = E^f \quad \text{conservation of energy}.$$  \hspace{1cm} (7.4)

Taking into account that $\hbar q \sim 0$ and that the phonon energy ($\sim 10 - 100$ meV) can be neglected, we have:

$$\hbar k^i + \hbar Q = \hbar k^f \quad \text{conservation of momentum},$$

$$E^i + \hbar \omega = E^f \quad \text{conservation of energy}.$$
Figure 7.6: Schematic representation of direct (GaAs) and indirect (Si) optical absorption. The wiggly black line is the incoming photon, the red arrows represent the electrons, the blue arrow represents the phonon. Optical absorption near the band gap in indirect semiconductors is very weak because it takes place through a second order process involving phonons.

This process is schematically illustrated in Fig. 7.6. Since we have two particles involved (a photon and a phonon) we say that this is a second order process and we can calculate the absorption coefficient using second order perturbation theory. Indirect absorption is much weaker that the direct absorption because second order processes have a much smaller probability to take place than first order processes. For practical applications we can say that direct-gap semiconductors such as GaAs are good for optoelectronics, while indirect-gap semiconductors such as Si are not very good (at least in their bulk crystalline forms, things may change in nanostructures).