Lecture 2: Semiconductors: Introduction

Contents

1 Introduction

Metals have electrical conductivity. This is related to the fact that the energy band of the metal consists of *continuous* filled and empty states. This is related to either a half full orbtial (alkali metals) or due to overlap between filled and empty orbitals (alkali earth metals). At $0\ K$ the highest filled state is called the **Fermi energy** (E_F). Because the energy difference between the states in the outer band is non-existent, at room temperature, electrons can easily move in the metal during application of an external field. The electrons in the outer band of a metal are said to be *delocalized*, i.e. they belong to the entire solid rather than being tied down to a specific atom. These delocalized electrons are responsible for the high conductivity. A schematic for electrical conduction in metals is shown in figure 1.

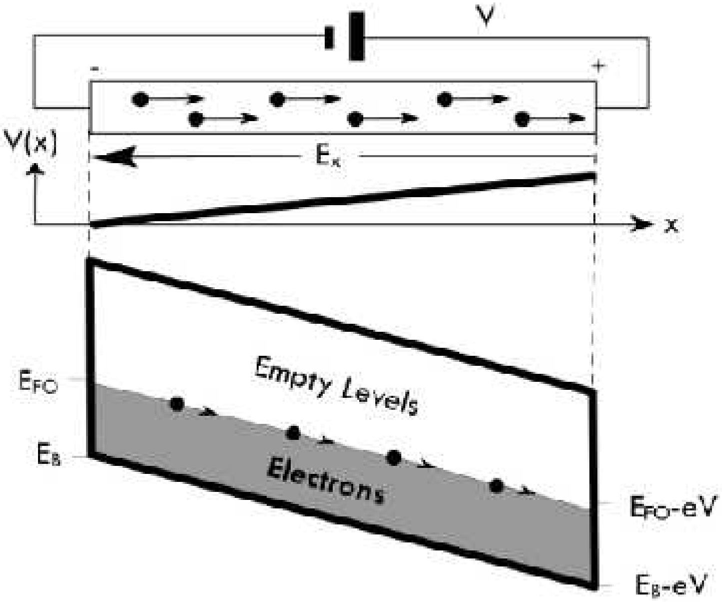


Figure 1: Electrical conduction in metals due to presence of empty electron states in close proximity to filled states. Upon application of an external field electrons move opposite to the field.

The formation of energy bands in semiconductors and by extension insulators can be explained in an analogous manner to metals. The difference being that in semiconductors (insulators) there is an energy gap between the filled valence band and the empty conduction band.

2 Band formation in semiconductors

Consider the example of energy band formation in Si (the most dominant in today microelectronics industry). Si has an atomic number of 14 and the electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^2$ shown schematically in figure 2. The $3s^2 3p^2$ forms the outer shell and we can ignore the inner shells as far as electrical conductivity is considered. The $3s$ and $3p$ orbitals in Si are close in energy and can hybridize to form sp^3 orbitals. Given that there are 4 electrons a total of 4 sp^3 hybrid orbtials are formed. These form 4 bonds that are directed along the corners of a tetrahedron, as shown in figure 3.

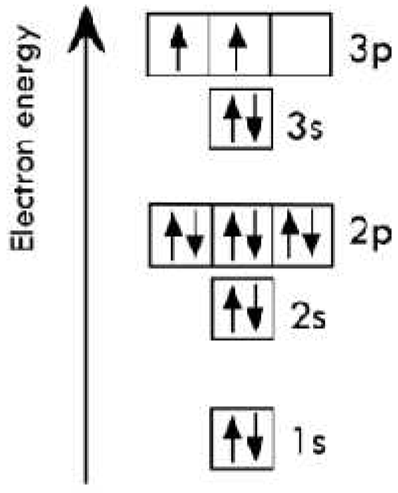
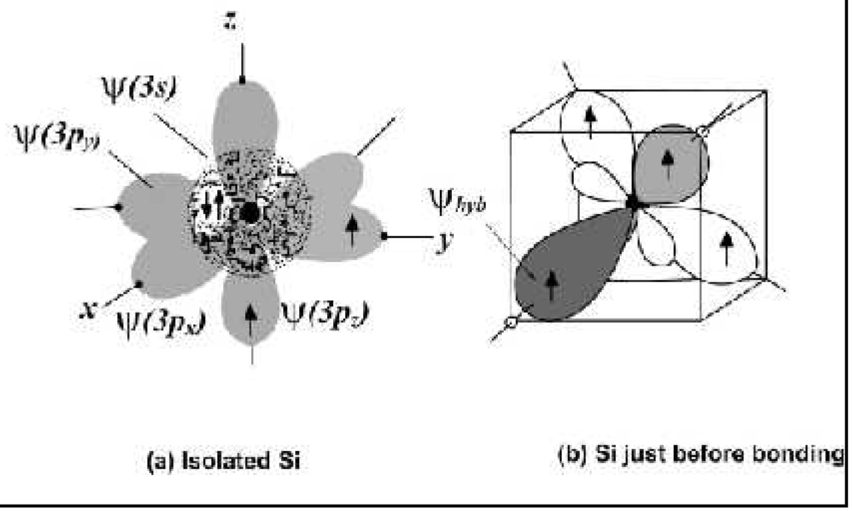


Figure 2: Electronic configuration of Si atom. The 3s and 3p together forms the outer shell while the others form the inner shells.



(a) Isolated Si

(b) Si just before bonding

Figure 3: (a) Isolated Si atoms showing the outer shell orbitals. (b) In a solid, these orbitals hybridize to form 4 sp^3 orbitals, just before bonding.

Hybridization is a common property of elements of Group IV of the periodic table to which Si belongs to. C which is in top of the group can form a variety of hybrid orbitals (sp^3, sp^2, sp). Both Si and the element below it, Ge, can form sp^3 hybrid orbitals. Sn and Pb (below Ge) are metals with low melting points. In the case of Si, the hybrid orbitals interact the same way that atomic orbitals interact in metals. Consider a bond formed between 2 sp^3 hybrid orbitals (1 from each Si atom). The two orbitals can interact to form a bonding (σ) and anti-bonding (σ^*) orbital. Since each Si atom will contribute one electron to the bond there will be a total of 2 electrons which will both go to the bonding orbital. Thus, each Si atom can form a bond with 4 other Si atoms and in all cases the bonding orbital (σ) will be full. A solid will be formed from a large number of these orbitals. When the bonding orbitals interact they will form an energy band, called **valence band**. This valence band will be completely full since the bonding orbital is full. Similarly, the anti-bonding orbitals can interact to form an energy band, called **conduction band**. This will be completely empty. Unlike metals, the valence and conduction band in a semiconductor is separated by a forbidden energy gap, this is called **band gap**. The formation of bands in Si crystal is show in figure 4.

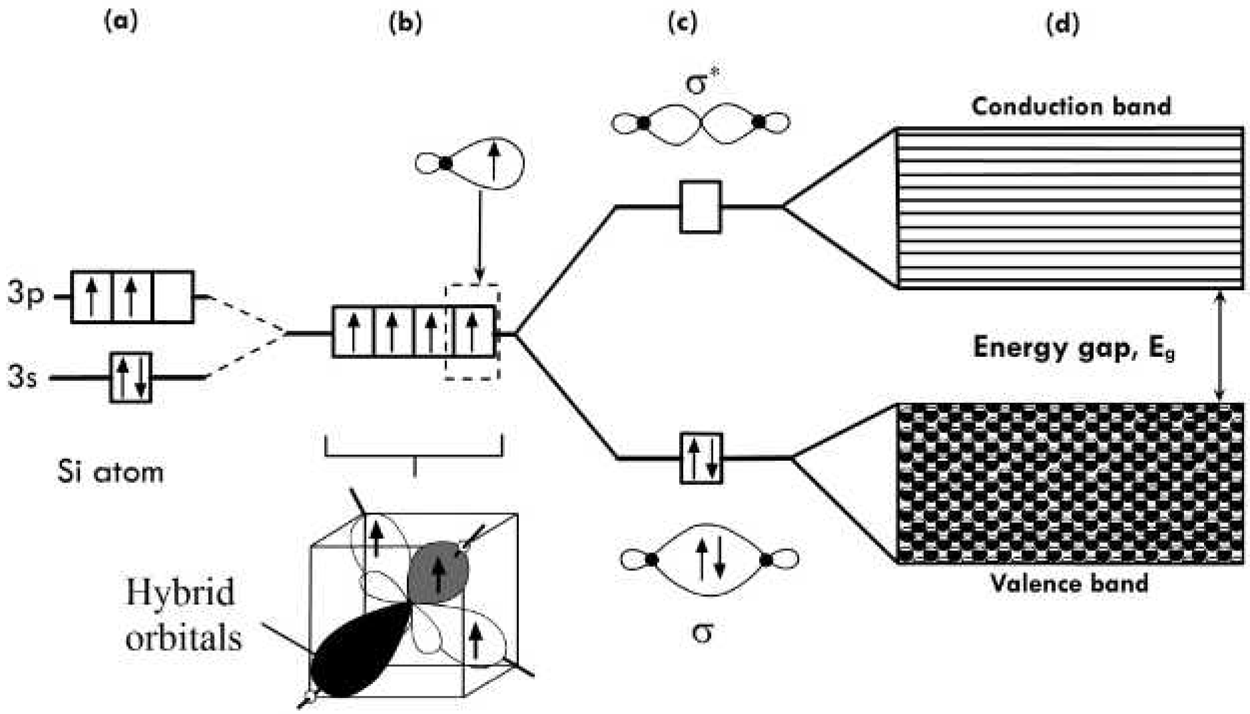
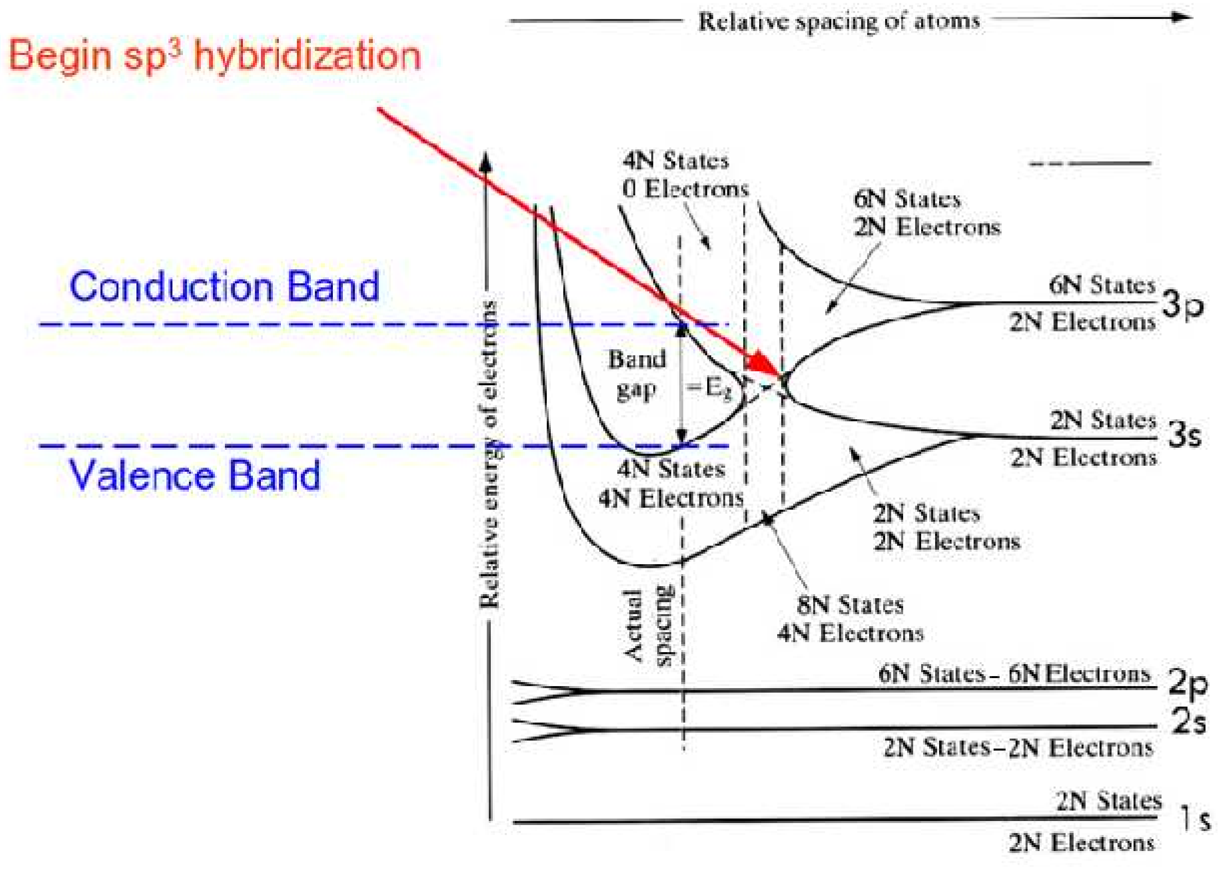


Figure 4: Formation of energy bands in Si. (a) Si atom with 4 electrons in outer shell form (b) 4 sp^3 hybrid orbitals. (c) The hybrid orbitals form σ and σ^* orbitals. (d) These orbitals overlap in a solid to form the valence and conduction band.

1st sp^3 orbital in a given Si atom interacts with sp^3 orbital from other Si atom. 2nd sp^3 orbital the given Si atom will interact with other sp^3 orbital from other second Si atom, and so on with other sp^3 orbitals in the given Si atom→ the 4 sp^3 orbitals in a given Si atoms need 4 other Si atom to form a bonded Si solid → in a solid of N Si atoms, each atom is bonded to four other Si atoms. This interaction will create a band (V. B) from σ orbitals full of electrons, and other band (C.B) from σ^* orbitals empty from electrons. These bands are separated by an energy gap (E_g)

Bands formation in Si

Formation of Energy Bands in Si

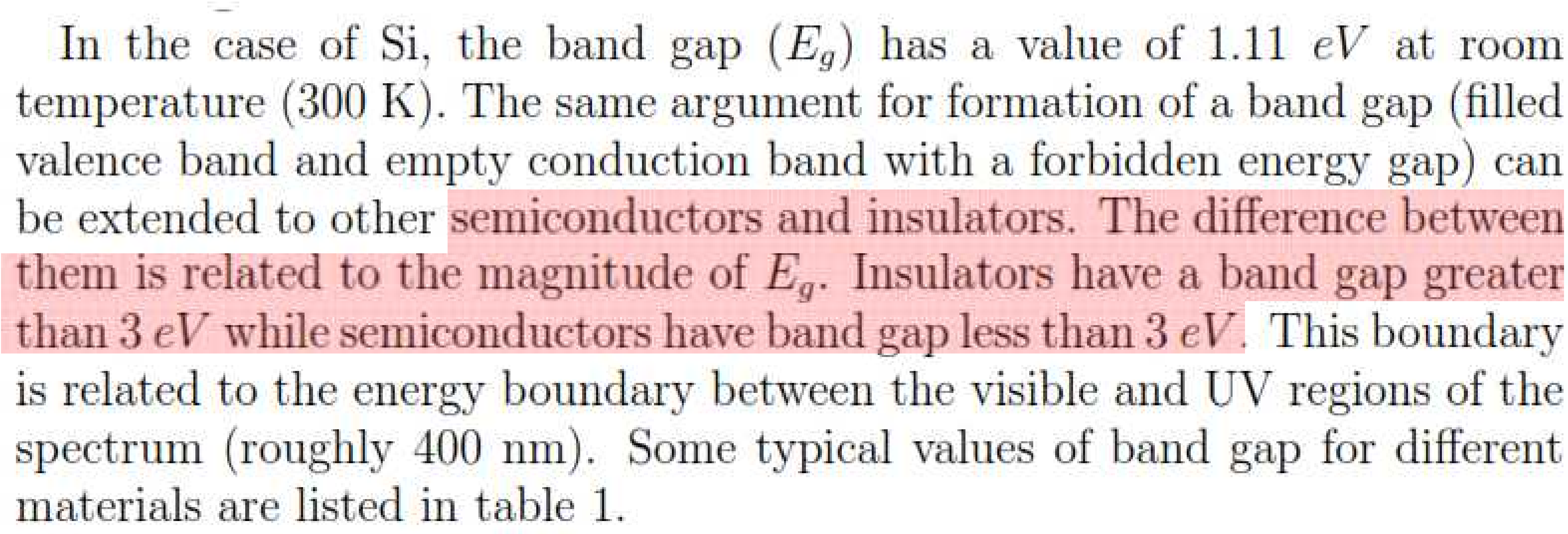


1) For N Si atoms, we have 14 N electrons distributed over 18 N states as shown

2) When atoms becomes close together → hybridization of outer shell to sp3 orbitals

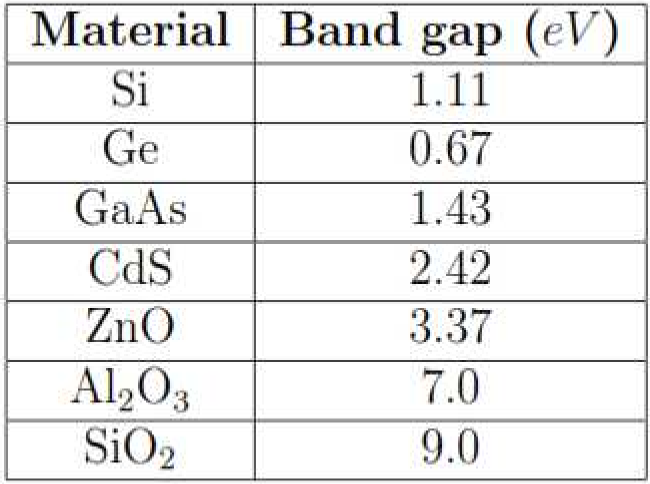
3) splitting of orbitals into valence band (4 N lower states full of electrons) and conduction band (4 N upper states empty)

As distance reduces the bands first mix among themselves, then hybridize (mix), and then for even lower distance splits into conduction and valence bands



In the case of Si, the band gap (E_g) has a value of 1.11 eV at room temperature (300 K). The same argument for formation of a band gap (filled valence band and empty conduction band with a forbidden energy gap) can be extended to other semiconductors and insulators. The difference between them is related to the magnitude of E_g. Insulators have a band gap greater than 3 eV while semiconductors have band gap less than 3 eV. This boundary is related to the energy boundary between the visible and UV regions of the spectrum (roughly 400 nm). Some typical values of band gap for different materials are listed in table 1.

Table 1: Room temperature band gap of typical semiconductors and insulators. Materials with band gap less than 3 eV are semiconductors while greater than 3 eV are insulators. ZnO is usually considered a wider band gap semiconductor rather than an insulator.



Material	**Band gap (eV)**
Si	1.11
Ge	0.67
GaAs	1.43
CdS	2.42
ZnO	3.37
Al_2O_3	7.0
SiO_2	9.0

insulators

3 Classification of semiconductors

There are different ways of classifying semiconductors depending on the property being measured. One classification that is fairly straightforward is

1. Elemental semiconductors
2. Compound semiconductors

Out of the elemental semiconductors Si and Ge are the most common. There are different type of compound semiconductors - II-VI and III-V are the most common and these can be understood by looking at the portion of the periodic table, shown in figure 5.

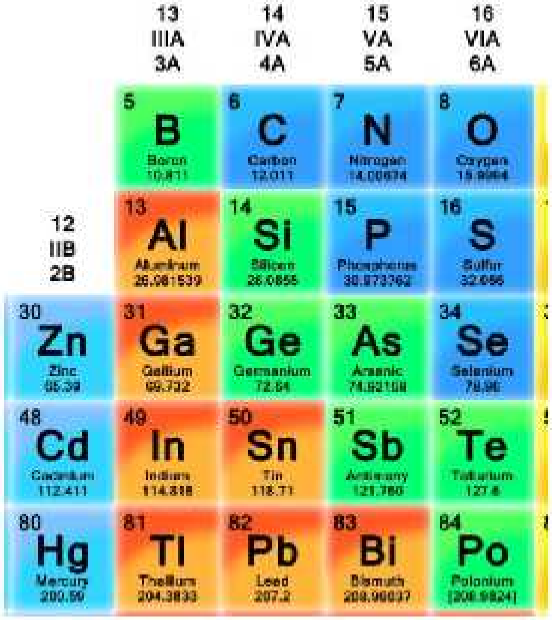


Figure 5: Portion of the periodic table showing the group IV elements and their common dopants.

Elemental semiconductors (Si and Ge) belong to group IVA of the periodic table. C which is on top of the group is an insulator (diamond) with E_g of 5.5 eV while Sn and Pb are metals. Compound semiconductors can be formed by combining elements of groups IIIA and VA - the III-Vs. Examples include GaAs, GaP, GaN, InSb. AlN is also a III-V but its band gap is around 6.2 eV making it an insulator. Similarly II-VI compound semiconductors can be formed, examples include ZnO, ZnS, CdSe, CdTe.

Another way of classifying semiconductors based on their band structure is

1. Direct band gap semiconductor
2. Indirect band gap semiconductor

This can be understood from the band picture of the semiconductor, as shown in figure 6. Semiconductors have a filled valence band and an empty conduction band. Electrons from the valence band can be excited to the conduction band by either thermal excitation or by optical absorption.

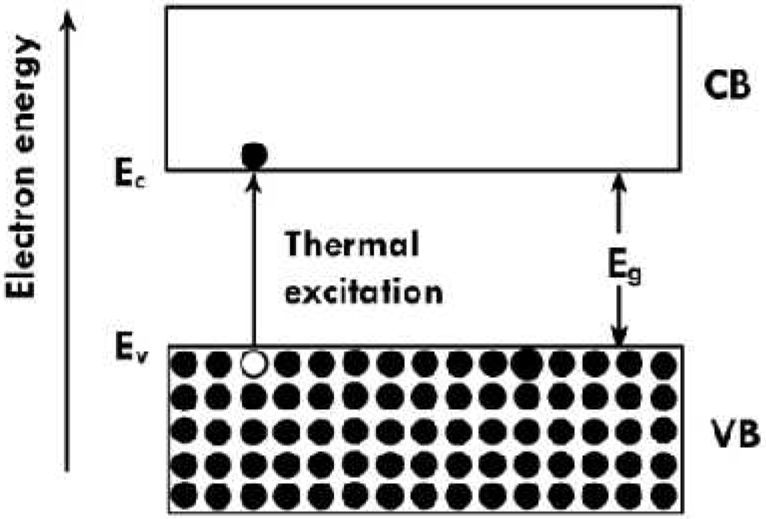
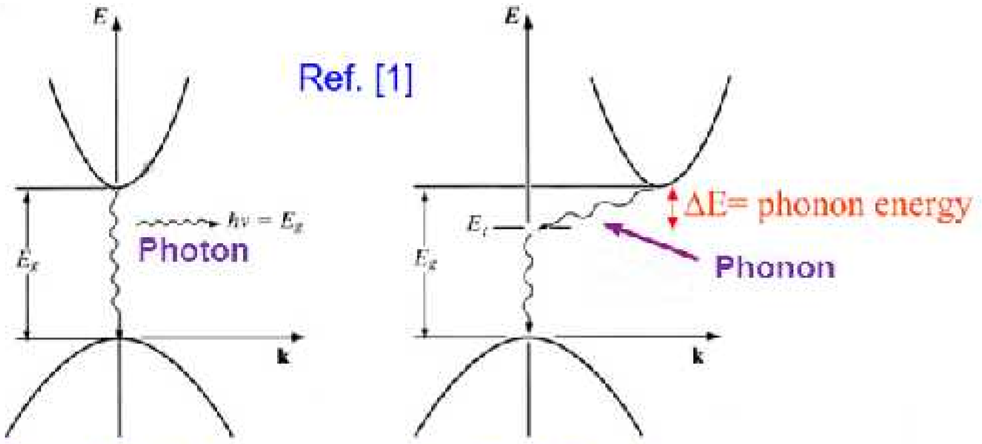


Figure 6: Band picture of a semiconductor showing the full valence band and empty conduction band. The gap between these is called the band gap. At room temperature thermal excitation can cause some electrons to move from valence to conduction band. The exited electron will leave a hole in the valence band → creation of electron-hole pair

When the electron returns to the valence band the energy is released either as heat or as photons. In *direct band gap semiconductors* the *dominant mechanism* by which the energy is released (in the absence of defects) *is by photons*(electromagnetic radiation) while in *indirect band gap semiconductors* the energy *is released by phonons* (heat). Direct band gap semiconductors are useful for opto electronic devices like LEDs, and lasers.
The difference between direct and indirect band gap semiconductors is related to their band structure. Electrons in solids have a wave like character. An electron wave is characterized by a wave vector $\overrightarrow{k}$. Thus, for crystalline materials it possible to plot E vs. $\overrightarrow{k}$ diagrams. These are related to the simple band diagrams that show the valence and conduction band.

Direct and Indirect Semiconductors

In Energy - Momentum (E-k) Space:



Direct Bandgap

GaAs, GaN

(direct semiconductors)

Indirect Bandgap

Si, Ge

(indirect semiconductors)

The complete electronic band structure for Si (indirect band gap semiconductor) and GaAs (direct band gap semiconductor) are shown in figure 9.

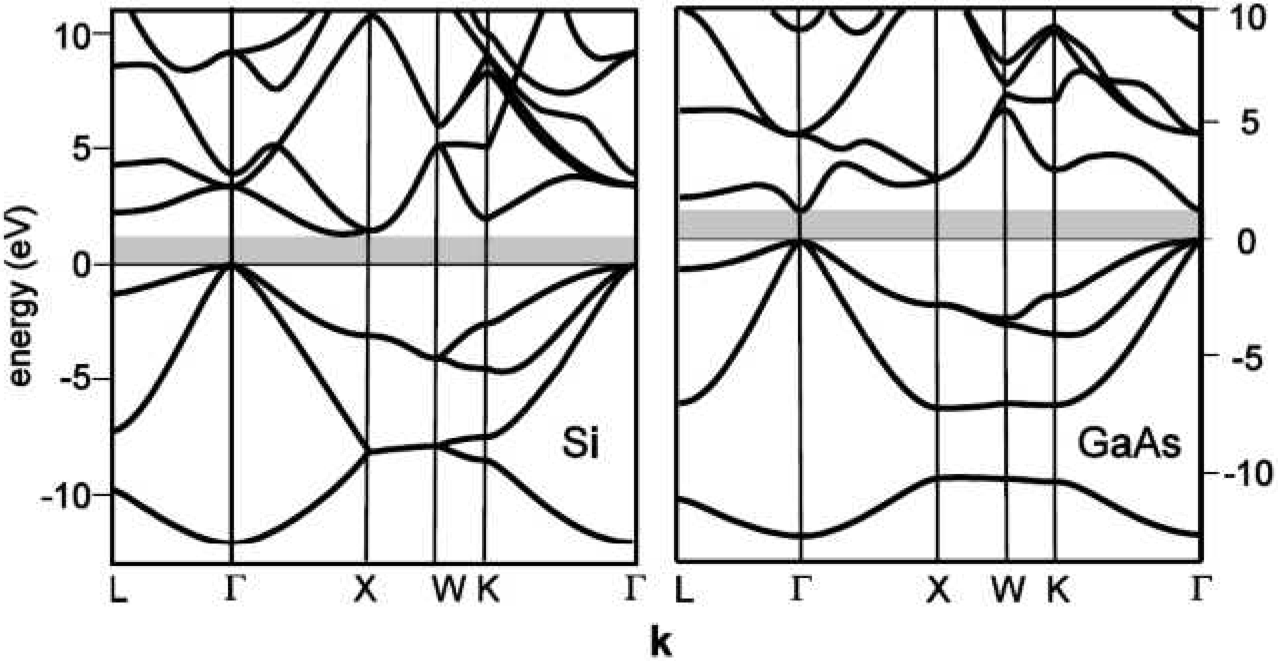


Figure 9: E vs. k diagram compared for GaAs and Si. GaAs is a direct band gap semiconductor while Si an indirect band gap semiconductor. The grey shaded region represents the band gap.

Direct Semiconductors: Electrons can make a smallest-energy (bandgap) transition from the conduction band to the valence band without a change in *k* value, i.e. without change in momentum. Such direct transitions give rise to particles called Photons.

Indirect Semiconductors: Electrons cannot make the smallest-energy transition from the conduction band to the valence band without a change in *k* value . Electrons must undergo a change of *k* value first. The change of *k* value will result from either losing or gaining energy from the lattice vibrations or Phonons.

4 Electron effective mass

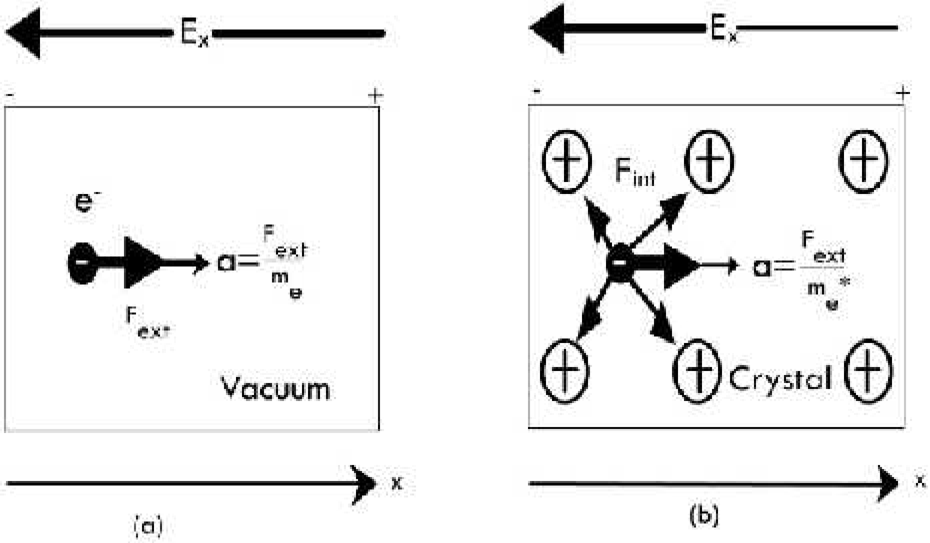
Electrons in the valence band of Si are bound to the covalent bond between the Si atoms. These electrons are not free to move in the solid. When the electron gets excited to the conduction band they are said to be *delocalized* and can move through the solid. This can be contrasted with metals where the electrons in the valence band are delocalized and are shared with all the atoms in the solid (metallic bond). When an electron in Si gets excited from the valence band to the conduction band it leaves behind a **hole** in the valence band. The hole is the absence of an electron and it is denoted by h or h^+. Hole formation is shown schematically in figure 6. The hole can move in the valence band by electron hopping from one bond to another and thus can be said to be delocalized.

When we apply an electric field these electron and holes can move. Consider the motion of free electron and electrons in a solid, in the presence of a field, as shown in figure 10. The electric field goes from positive to negative, so that the electrons travel in the direction opposite to the field. In vacuum the acceleration of the electrons (a_e) is given by

$$a_e = \frac{eE_x}{m_e} \tag{1}$$

where E_x is the electric field and m_e is the rest mass of the electron (ignoring relativistic effects).

Figure 10: Electron motion in (a) vacuum and (b) solid. In a solid the motion is affected by the interaction with the atoms. This is manifest as an effective mass of the electron.



(a)

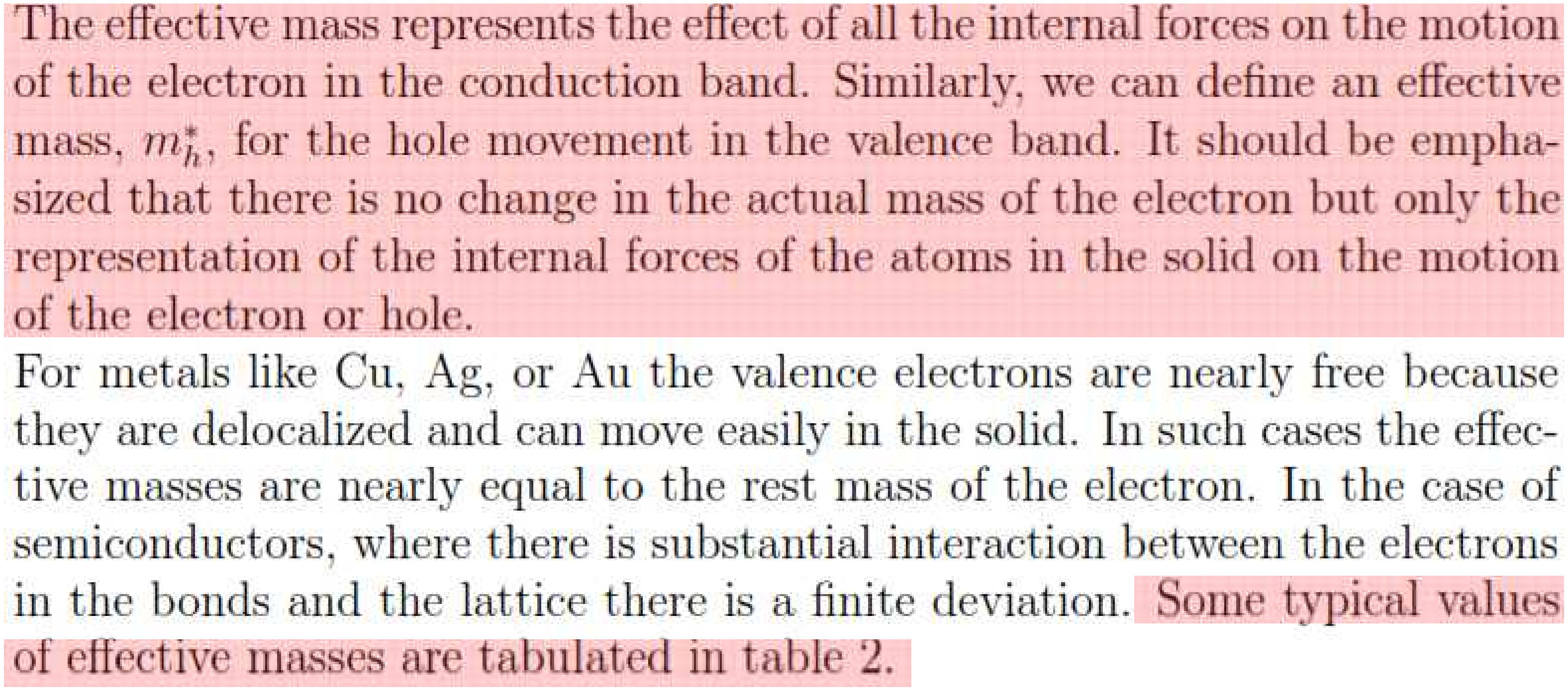
(b)

In the case of an electron in a solid, under an external field, the interaction with the solid atoms should also be taken into account. Let ΣF_{int} represent the sum of the interaction of the electron with the atoms in the solid. Then the acceleration of the electron, given by using equation 1, is

$$a_e = \frac{eE_x + \Sigma F_{int}}{m_e} \qquad (2)$$

The value of the internal forces depends on the location of the electron in the E vs. $\overrightarrow{k}$ landscape and hence equation 2 can be simplified by saying that the electron has an *effective mass*, m_e^*, so that we can rewrite equation 2 simply as

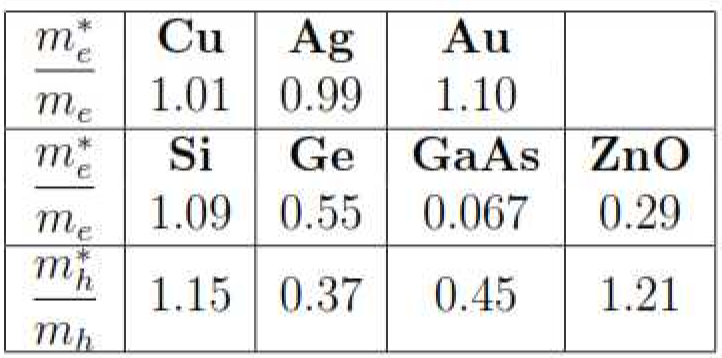
$$a_e = \frac{eE_x}{m_e^*} \qquad (3)$$



The effective mass represents the effect of all the internal forces on the motion of the electron in the conduction band. Similarly, we can define an effective mass, m_h^*, for the hole movement in the valence band. It should be emphasized that there is no change in the actual mass of the electron but only the representation of the internal forces of the atoms in the solid on the motion of the electron or hole.

For metals like Cu, Ag, or Au the valence electrons are nearly free because they are delocalized and can move easily in the solid. In such cases the effective masses are nearly equal to the rest mass of the electron. In the case of semiconductors, where there is substantial interaction between the electrons in the bonds and the lattice there is a finite deviation. Some typical values of effective masses are tabulated in table 2.

Table 2: Effective masses of electrons and holes in some selected materials. For metals, only electrons are listed since there are no explicit holes in them. For semiconductors. electron effective mass is for the conduction band and hole effective mass is for the valence band.



$\frac{m_e^*}{m_e}$	**Cu** 1.01	**Ag** 0.99	**Au** 1.10	
$\frac{m_e^*}{m_e}$	**Si** 1.09	**Ge** 0.55	**GaAs** 0.067	**ZnO** 0.29
$\frac{m_h^*}{m_h}$	1.15	0.37	0.45	1.21