

Part Two

Basic Functional Principles of Photovoltaics

2.1

Semiconductor Materials and their Properties

Angèle Reinders

University of Twente, Enschede, The Netherlands

2.1.1 Semiconductor Materials

Semiconductor materials are the basic materials which are used in photovoltaic (PV) devices. Though often semiconductors are not fully explained in text books about PV technologies (Archer and Hill, 2001; Chen, 2011), it would be helpful for most readers to have a basic knowledge in order to be able to understand important topics in photovoltaics such as doping, photogeneration, and carrier transport, which are discussed later in this book.

The aim of this chapter is to provide an introduction to solid-state physics and semiconductor properties that are relevant to photovoltaics without spending too much time on unnecessary information. Readers wishing a deeper understanding after reading this Part are referred to extensive handbooks such as those edited by Luque and Hegedus (2010) on PV science and engineering, the handbook by Sze and Lee (2012) on semiconductor devices, and even more fundamental works, such as those written by Kittel (2004) on solid-state physics.

A semiconductor material has a conductivity σ (in S/cm) that is used to distinguish conducting materials from insulating materials. This conductivity is particularly sensitive to temperature, impurities in the material, and light. Therefore, the conductivity and therefore also the resistivity, ρ (in Ω cm) can be tuned to the desired values by changing the amount of impurities, called donor and acceptor dopants.

Typical conducting materials, conductors, are the metals, among which are found silver and copper, with conductivity, σ , greater than 10^3 S/cm. Their conductivity can be modified only in a narrow range of values. Insulators have a conductivity, σ , smaller than 10^{-8} S/cm; an example is glass. Between these two extremes, semiconductors have a broad range of conductivity and therefore, depending on the condition, they can also behave as an insulator or a conductor.

Photovoltaic Solar Energy: From Fundamentals to Applications, First Edition.

Edited by Angèle Reinders, Pierre Verlinden, Wilfried van Sark, and Alexandre Freundlich.

© 2017 John Wiley & Sons, Ltd. Published 2017 by John Wiley & Sons, Ltd.

Companion website: www.wiley.com/go/reinders/photovoltaic_solar_energy

Table 2.1.1 Part of the Periodic Table of Elements related to semiconductors used in photovoltaic devices

Period	Column II	Column III	Column IV	Column V	Column VI
2		B	C	N	O
3	Mg	Al	Si	P	S
4	Zn	Ga	Ge	As	Se
5	Cd	In	Sn	Sb	Te
6	Hg		Pb		

Since this change in conductivity is controllable, by voltage, electric field, injection, doping, light, temperature, etc., these semiconductor materials can be used in electronic applications.

There are two groups of semiconductors: elemental materials and compound materials. Examples of elemental materials are germanium (Ge) and silicon (Si), also called Group IV materials because they can be found in column IV of the Periodic Table of Elements. Typical compound materials are gallium arsenide (GaAs), which is a III-V compound because it is a combination of gallium from column III and arsenic from column V in the Periodic Table of Elements. Compound materials can also be made from a combination of column II and column VI elements, for instance, cadmium telluride (CdTe), which is then called a II-VI compound made from cadmium and tellurium. In Table 2.1.1, a section of the Periodic Table of Elements is shown, with relevance to a large share of the established semiconductors which are used for photovoltaic devices as presented in this book. In recent years, new semiconductor compounds have been found and applied in research for photovoltaic application. For example, recent progress in the field of perovskite materials is presented in Chapter 6.3 of this book. The inverse design approach (Zakutayev *et al.*, 2013) to semiconductor materials is a generic quest to discover new materials which theoretically could be created for use in different applications, including photovoltaic technology.

2.1.2 Crystalline Structures of Semiconductors

Usually atoms in the group of semiconductor materials form crystalline structures in solid-state conditions. Ideally these structures consist of an infinite repetition of identical groups of atoms. The set of points to which groups of atoms are attached is called the lattice (Kittel, 2004); the group of atoms is called the basis, or the unit cell (Sze and Lee, 2012), that is, by repetition of the unit cell, the entire lattice can be formed.

The bonds between atoms in a semiconductor crystal are single covalent bonds. Covalent bonding is the sharing of valence electrons which are the electrons in the outer electron shell (orbit) of the atom. Due to the fact that, for instance, silicon has four valence electrons in its outer orbit – because it is a Group IV element, see Table 2.1.1 – each silicon atom in a crystalline structure is bound to four neighbouring silicon atoms at an equal distance to the central atom. This tetrahedron organization of the atoms forms the unit cell in the silicon crystal in a diamond lattice structure, see Figure 2.1.1. The same is true for germanium, another Group IV element. The number of valence electrons for a neutral atom is equal to the main group number. Therefore, III-V compound conductors have another lattice than silicon: they have a zincblende lattice. Another crystalline structure is the cubic crystal. In particular, Part 4 of this book will discuss typical crystalline structures of chalcogenide materials, such as Cu(InGa)Se₂ and CdTe.

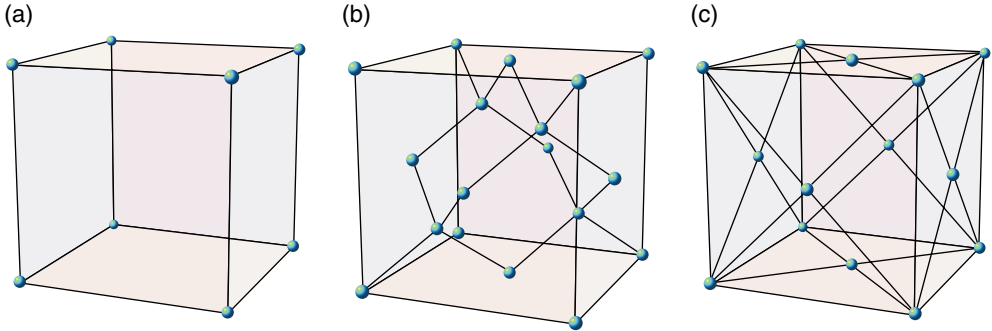


Figure 2.1.1 (a) Simple cubic lattice; (b) Diamond lattice with tetrahedron bonds; (c) Face centered cubic lattice. Source: Courtesy of Boudewijn Elsinga (2015)

2.1.3 Energy Bands in Semiconductors

When individual atoms are brought together in a crystalline lattice, energy bands are formed in a semiconductor material (Kittel, 2004; Sze and Lee, 2012). These energy bands indicate the allowed states of energy of electrons under respective bound conditions and conductive conditions according to the following mechanisms.

At zero Kelvin, electrons in a semiconductor are all bound to their atoms in their lowest energy states; they stay in what is called the valence band. By gaining a discrete amount of energy, an electron can move from the top of the valence band E_v to the bottom of the conduction band E_c where it is free to move to other empty states under the forces of an electric field or diffusion. The discrete amount of energy to move an electron from the valence band to the conduction band must therefore be higher than $(E_c - E_v)$. This energy difference is called the bandgap energy E_g , indicated in Figure 2.1.2. The bandgap energy depends among other things on the composition of the material and the temperature. For semiconductor materials used in photovoltaic devices, E_g is in the range of ~ 1.1 eV for silicon up to values of ~ 2.5 eV for III-V compounds.

When an electron leaves the valence band, a ‘void’ remains in the crystal, which is called a hole. This hole is in principle a deficient electron, for which reason it can be considered an electron with a positive charge. The creation of what are called electron-hole pairs in pure semiconductor materials – also called intrinsic semiconductors – happens at temperatures above zero Kelvin. This process is called thermal excitation.

The density of electrons and holes in intrinsic semiconductors is mainly determined by thermal excitation and therefore by temperature. The density of electrons and holes is equal and is called the intrinsic carrier concentration. For instance, the value of the intrinsic carrier concentration, n_i (in cm^{-3}), in silicon as a function of temperature T (in Kelvin) is given by Equation (2.1.1) (Misiakos and Tsamakis, 1993):

$$n_i(T) = 5.29 \times 10^{19} \times (T / 300)^{2.54} \times e^{(-6726/T)} \quad (2.1.1)$$

The energy band representation of materials can visually explain the difference between insulators, semiconductors and conductors, see Figure 2.1.3. In Figure 2.1.3, it is shown that in, for instance, a conducting material, the conduction and valence band can overlap so that a bandgap does not exist (another option is that the conduction band is partially

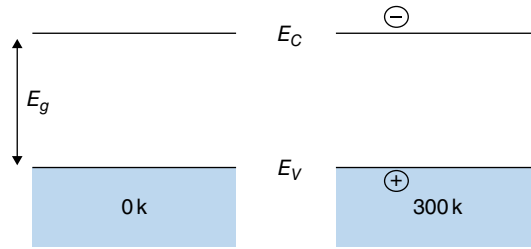


Figure 2.1.2 Energy band diagram at zero Kelvin and at 300 Kelvin

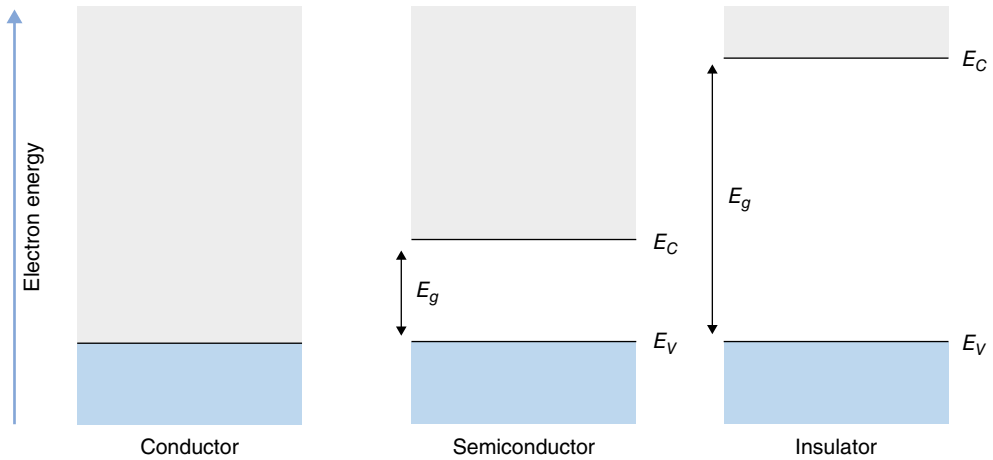


Figure 2.1.3 Energy band diagrams for a conductor, a semiconductor and an insulator

filled, however, this is not visually represented here). Therefore, electrons can freely move even at low temperatures, leading to good conductive properties of the material. In insulators, the valence electrons are very tightly bound to the atoms. Therefore, the thermal energy required to move a valence electron to the conduction band is too high to be achievable. Though a conduction band does exist in insulators, the probability that an electron will surpass the bandgap is therefore too low for good conductive properties. Hence, an insulator has a very high resistivity. On the other hand, a semiconductor's bandgap energy is low enough to achieve conductivity under specific circumstances. Chapter 2.3 will explain this further.

Besides energy band diagrams, other schemes such as energy-momentum diagrams are used to explain the optical-electrical functioning of semiconductor materials, see also Chapter 2.3. In principle, an energy-momentum diagram represents the energy of charge carriers – electrons or holes – E , in relation to their momentum, p , using Equation (2.1.2) for electrons:

$$E = p^2 / 2m_n \quad (2.1.2)$$

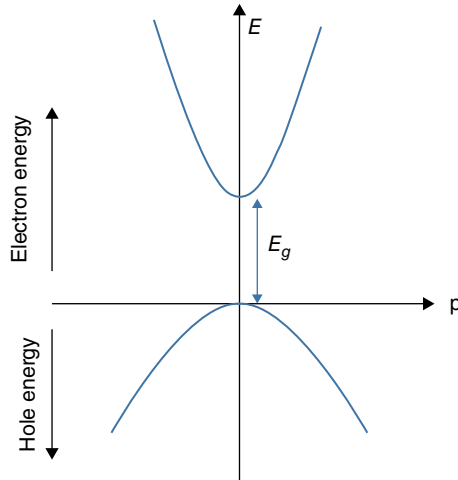


Figure 2.1.4 Energy-momentum diagrams for a semiconductor

where m_n (in g) is the effective mass of an electron and a similar equation for holes where m_n is replaced by m_p the effective mass of a hole. The effective mass depends on the semiconductor material and therefore also on the crystalline structure. Equation (2.1.2) can also be represented by the energy-momentum diagram shown in Figure 2.1.4.

List of Symbols

Symbol	Description	Unit
E	Energy	eV or 1.609×10^{-19} J
E_C	Conduction band	eV
E_g	Band gap energy	eV
E_v	Valence band	eV
m_n	Effective mass of an electron	g
m_p	Effective mass of a hole	g
n_i	Intrinsic carrier concentration	cm^{-3}
p	Momentum	g.m/s
ρ	Resistivity	$\Omega.\text{cm}$
T	Temperature	K
σ	Conductivity	S/cm

List of Acronyms

PV	Photovoltaic or Photovoltaics
----	-------------------------------

References

- Archer, M.D. and Hill, R. (eds) (2001) *Clean Electricity from Photovoltaics*, Series on Photoconversion of Solar Energy: vol. 1. Imperial College Press, London.
- Chen, C.J. (2011) *Physics of Solar Energy*. John Wiley & Sons, Inc., Hoboken, NJ.
- Kittel, C. (2004) *Introduction to Solid State Physics*, 8th edition. John Wiley & Sons, Ltd, Chichester.
- Luque, A. and Hegedus, S. (eds) (2010) *Handbook of Photovoltaic Science and Engineering*, 2nd edition. John Wiley & Sons, Ltd, Chichester.
- Misiakos, K. and Tsamakis, D. (1993) Accurate measurements of the silicon intrinsic carrier density from 78 to 340 K. *Journal of Applied Physics*, **74** (5), 3293–3297.
- Sze, S.M. and Lee, M.-K. (2012) *Semiconductor Devices: Physics and Technology, International Student Version*, 3rd edition. John Wiley & Sons, Inc., New York.
- Zakutayev, A., Zhang, X., Nagaraja, A. *et al.* (2013) Theoretical prediction and experimental realization of new stable V-IX-IV semiconductors using the Inverse Design approach. *Journal of the American Chemical Society*, **135** (27), 10048–10054.