

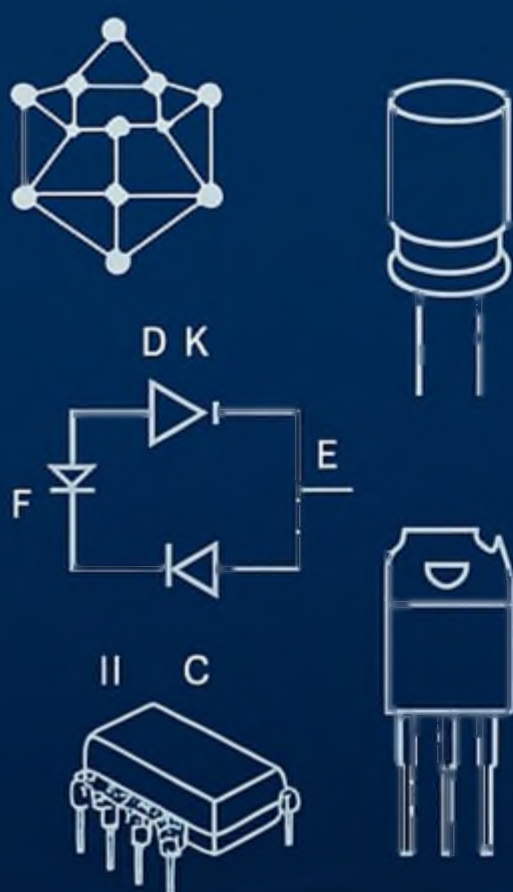


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K.A. Ismaylov, Kh.U. Kamalov, M.A. Askarov

ELECTRONIC TECHNICAL MATERIALS AND ELEMENTS





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**MINISTRY OF HIGHER EDUCATION, SCIENCE AND
INNOVATION OF THE REPUBLIC OF UZBEKISTAN**

**KARAKALPAK STATE UNIVERSITY
NAMED AFTER BERDAKH**



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ELECTRONIC TECHNICAL MATERIALS AND ELEMENTS

Textbook

Nukus – 2025

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This textbook has been developed within the framework of the European Union program – DEBSEUz project (101128871-ERASMUS-EDU-2023-CBHE) titled “*Development of the targeted Educational program for Bachelors in Solar Energy in Uzbekistan*”. It provides fundamental knowledge about electronic engineering materials and components used in modern instrumentation, electrical engineering, and radio electronics. The book presents an overview of the main groups of modern electrical engineering materials: conductors, dielectrics, semiconductors, and materials used in solar cells. For each group of materials, the crystal structure, electrophysical and optical properties, the physical nature of phenomena occurring within them, material production technologies, and applications in electronic devices and solar cells are covered.

The textbook is intended for undergraduate and graduate students specializing in “Renewable Energy Sources,” “Energy Engineering,” “Electrical Engineering,” and other related fields.

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INTRODUCTION

One of the inseparable elements of modern technological advancement is electronic technology and the materials that form its foundation. The importance of electronic engineering materials and components is increasing in the context of technological development and the transition to a digital economy. The rapid growth of areas such as electrical devices, microelectronics, automation systems, optoelectronics, and solar energy has further increased the demand for electronic materials. Therefore, it is essential for students to acquire deep theoretical and practical knowledge in this field, as it plays a crucial role in their future engineering careers.

This textbook presents systematic information on the physical properties, structures, and applications of electronic engineering materials and components in various devices. It is designed for undergraduate and graduate students, contributing to their knowledge in materials science, electronics, semiconductor technology, and energy.

Electronic engineering materials include semiconductors, dielectrics, magnetic materials, conductors, superconductors, and many other substances used in the creation of essential components of electronics.

The textbook includes the following main sections:

- **Basic Concepts on the Structure of Materials** – this chapter analyzes the particles forming materials, crystal lattices, interatomic bonds, and their impact on material properties.
- **Physical Processes and Phenomena in Conductive Materials** – addresses mechanisms of electrical conductivity, charge transport, and temperature dependence.
- **Main Properties and Applications of Conductive Materials** – discusses electrical and thermal conductivity, mechanical properties, and practical uses of metals like copper and aluminum.
- **Physical Processes and Phenomena in Semiconductor Materials** – focuses on charge carrier motion, intrinsic and extrinsic impurities, photoelectric and optical processes in semiconductors.
- **Main Properties, Technological Characteristics, and Applications of Semiconductor Materials** – explores electrical properties, production technology, and roles of silicon, germanium, and other semiconductors in integrated devices.
- **Electronic Engineering Materials for Solar Cells** – covers the photoelectric effect, selection of raw materials for solar cells, and factors affecting their efficiency.

The textbook not only provides students with theoretical knowledge but also helps develop skills to find practical solutions to scientific and technical problems. It serves as an essential methodological tool for modern education at the intersection of electronics and materials science.

This textbook is designed for professionals working in high-tech fields, students, and anyone interested in electronics and materials science. Theoretical concepts are supplemented with practical examples, diagrams, and formulas. Through this book, students will learn not only the operating principles of electronic materials but also how to optimize and apply them in new devices.

CHAPTER 1. BASIC INFORMATION ABOUT THE STRUCTURE OF MATERIALS

Studying the structure of substances is one of the fundamental scientific directions in modern materials science, physical chemistry, quantum physics, and many other natural sciences. The physical and chemical properties of any substance are directly related to the interactions and ordered structure of its constituent particles — atoms, molecules, ions, and electrons. Therefore, an in-depth analysis of the internal structure of matter enables a scientifically grounded understanding of its macroscopic properties and the creation of new materials.

This chapter presents the fundamental theoretical knowledge necessary to understand the nature of substances. It first provides general information about the classification of matter and the structure of its constituent atoms, including the atomic nucleus, electron shells, and energy levels. The main types of chemical bonds formed as a result of interatomic interactions — covalent, ionic, metallic, and hydrogen bonds — are examined. These bonds determine many parameters of a material, such as its stability, electrical and thermal conductivity, and mechanical properties.

In addition, the elements of band theory, which is widely used to explain the electronic structure of solids, are also discussed. Through band theory, the differences between conductors, semiconductors, and dielectrics are justified, and this theory serves as an important tool for explaining the distribution of electrons over energy bands and their movement.

Overall, the scientific foundations presented in this chapter provide a solid basis for understanding the nature of matter and the relationship between its structure and properties, creating a groundwork for a deeper comprehension of the physicochemical processes discussed in subsequent chapters.

1.1. Classification of Materials. Atomic Structure

There are thousands of materials available for use in engineering. Most materials fall into one of three categories based on atomic bonding forces: **metallic**, **ceramic**, and **polymeric**. In addition, different materials can be combined to create **composite materials**. Within each category, materials are commonly grouped based on their **chemical composition** or specific **physical or mechanical properties**. Composite materials are usually classified by the types of materials combined or by their internal arrangement. Below is a list of common classifications within these four broad material categories.

Metals

About two-thirds of all elements and approximately 24% of the Earth's mass consist of metals. Metals possess useful properties such as strength, ductility, high melting points, thermal and electrical conductivity, and toughness. As seen in the periodic table, a large number of elements are classified as metals.

- **Iron/Steel** – Steel alloys are used in applications requiring high strength.
- **Aluminum** – Aluminum and its alloys are widely used because they are easy to form, readily available, inexpensive, and recyclable.
- **Copper** – Copper and its alloys have several useful properties including high electrical and thermal conductivity, high ductility, and good corrosion resistance.
- **Titanium** – Titanium alloys are used in high-temperature ($\sim 1000^\circ\text{F}$) applications or where weight and corrosion resistance are critical.
- **Nickel** – Nickel alloys are suitable for even higher temperatures (~ 1500 – 2000°F) and offer excellent corrosion resistance.
- **Refractory metals** – These are used for the highest temperature applications ($>2000^\circ\text{F}$).



Fig. 1.1. Gold bars.



Fig. 1.2. Types of metals.

Metals are distinguished from nonmetals primarily by their metallic bonding. Free electrons in metallic materials move easily from one atom to another, contributing to properties such as high electrical conductivity. More details on the structure of metals will be discussed later.

Ceramics

Ceramics are traditionally defined as inorganic, non-metallic solid materials made from powdered substances and hardened by heating. They exhibit unique properties such as hardness, strength, low electrical conductivity, and brittleness. The term comes from the Greek word *keramikos*, meaning "pottery". Ceramics are typically crystalline compounds formed between metallic and non-metallic elements, such as:

- **Aluminum oxide (Al_2O_3);**
- **Calcium oxide (CaO);**
- **Silicon nitride (Si_3N_4).**

Depending on how they are processed, ceramics can be either dense or lightweight. They typically exhibit excellent strength and hardness, but are often brittle. Some ceramics can function as electrical conductors or insulators, while others (e.g., superconductors) display magnetic or superconducting behavior. Ceramics are more resistant to high temperatures and harsh environments than metals or polymers.



Fig. 1.3. Types of ceramics.

Major categories of ceramic products (Fig. 1.3):

- Structural clay products (bricks, sewer pipes, tiles, chimney liners)
- Whitewares (dinnerware, porcelain tiles, electrical insulators)
- Refractories (bricks for furnaces and kilns)
- Glasses (window glass, bottles, fiberglass insulation, optical fibers)
- Abrasives (natural and synthetic materials used for grinding, cutting, or polishing)
- Cements (used in roads, bridges, buildings, dams)
- Advanced ceramics (bioceramics, cutting tools, engine parts)

Atoms in ceramics are chemically bonded—most commonly through **covalent** and **ionic bonds**, which are much stronger than metallic bonds. These strong bonds explain the brittleness of ceramics and the ductility of metals.

Polymers

Polymers can be envisioned as solid materials made of many chemically bonded units, forming long molecular chains. The word "polymer" literally means "many parts". Two major classes of industrial polymers are:

- **Plastics** – A broad group of synthetic materials that can be shaped by molding or extrusion.

- **Elastomers (Rubbers)** – Materials that exhibit large elastic deformation under stress and return to their original shape when the stress is removed.

Key properties of many polymers (Fig. 1.4):

- Lower density than metals or ceramics;
- Good resistance to corrosion and atmospheric degradation;
- Biocompatibility with human tissue;
- Excellent electrical insulating properties.

Polymers are categorized into two classes based on their structure:

- **Thermoplastics** – Can be melted and reshaped (e.g., polyethylene, polypropylene, polystyrene, PVC)

- **Thermosets** – Cannot be re-melted after curing (e.g., epoxy, phenolics, polyurethanes)

Most polymers are derived from petroleum or natural gas, but renewable organic sources are becoming more common. Kevlar, a high-performance synthetic polymer, is used in bulletproof vests, strong lightweight frames, and underwater cables due to its strength, which is 20 times that of steel.

Composites

A composite is a combination of two or more materials that retain their individual properties but produce a material with superior performance that no single component could achieve alone. Examples include:

- **Concrete** – A mixture of Portland cement and aggregate

- **Fiberglass** – Glass fibers embedded in a polymer matrix

Composites consist of two phases:

- **Reinforcing phase** – fibers, particles, or sheets

- **Matrix phase** – surrounds and supports the reinforcement

Common classifications of composites (Fig. 1.5):

- Fiber-reinforced plastics
- Metal matrix composites
- Ceramic matrix composites
- Sandwich structures



Fig. 1.4. Types of polymers.



Fig. 1.5. Materials made from composite substances.

- Concrete

Composite materials can be classified by their reinforcement mechanism:

- Dispersion-strengthened
- Particle-reinforced
- Fiber-reinforced

For example, fiber-reinforced composites use the fiber to carry the primary load, with materials like carbon fiber or glass fiber. When properly designed and fabricated, composites can achieve a unique combination of properties — strength from the reinforcement and ductility or toughness from the matrix. However, composites tend to be more expensive than conventional materials.

Atomic structure

The bodies surrounding us are composed of the smallest particles - atoms. It is interesting to know what the structure of these "bricks" of the Universe is. Together with experts, we will consider modern scientific concepts of atomic structure.

Assumptions about the atomic structure of matter appeared even before our era. Even the thinkers of the Ancient East and Ancient Greece expressed ideas about the existence of extremely small, further indivisible material particles that make up the entire Universe.

The most famous is the theory of the ancient Greek philosopher Democritus. It was he who first introduced the term atomos, which means indivisible. Democritus believed that everything in the world consists of atoms and void, that atoms exist eternally, that no one created them, that they are material, that they have form, size, and weight. The combination of atoms into bodies occurs with the help of hooks and loops. The human soul is also composed of atoms that have a smooth shape. Atoms in a vacuum move only in a straight line, therefore a person has no freedom, everything is predetermined.

The student of Democritus, Epicurus, improved this doctrine and proposed that atoms can spontaneously deviate from the straight-line path, therefore humans still have freedom.

What is an atom?

Modern science defines an atom as an extremely small particle of matter in terms of size and mass, which is the smallest part of a chemical element and acts as the carrier of its chemical properties.

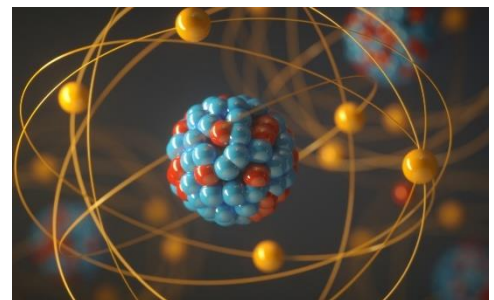


Fig. 1.6. Appearance of an atom.

A total of 118 atoms are known, of which 94 are found in nature, and the remaining 24 were synthesized artificially in nuclear reactors and laboratories.

Atoms have a certain mass, size, and structure. The masses of atoms are extremely small. For example, a hydrogen atom has a mass of only $1.67 \cdot 10^{-24}$ g. The weight of an atom is conventionally measured in atomic mass units (u). One such unit is equal to 1/12 of the mass of a carbon atom, the nucleus of which contains 6 neutrons and 6 protons. It turns out that $1 \text{ u} = 1 \text{ neutron} = 1 \text{ proton}$. For example, the nucleus of a hydrogen atom consists of 1 proton, therefore its mass is equal to 1 u.

The size of atoms is also small and ranges from 0.046-0.25 nm ($1 \text{ nm} = 10^{-9} \text{ m}$).

Information about atomic structure

Atomic nucleus

It is located in the center of the atom and constitutes almost its entire mass (99.9%). At the same time, the nucleus of an atom occupies only one trillionth of its volume. That is, the atom inside is practically empty.

Electron

The most active part of the atom, as it is constantly moving. It has an extremely small weight. Thus, the mass of an electron in a hydrogen atom is 0.0005 of the mass of the nucleus.

The lightest and heaviest atoms

If we talk about natural elements, the lightest is the hydrogen atom (its relative atomic mass is 1.00797), and the heaviest is the uranium atom (238.03).

Atomic composition

Atoms consist of a nucleus and electrons, which are sometimes called "electron clouds". The atomic nucleus consists of protons and neutrons.



The electron (derived from the Greek word "yantar", discovered in 1897) represents a negatively charged particle. Electrons move along electron shells.



A proton (from Greek - first, discovered in 1919) is a nuclear particle with a positive charge.



Neutron (from Latin "neither one nor the other", discovered in 1932) is an element of the nucleus that has no charge.



Protons and neutrons are also collectively called nucleons (nuclear particles).

Atoms differ in the number of protons and neutrons in the nucleus. Depending on the number of protons, an atom has a corresponding number in Mendeleev's periodic table and belongs to some chemical element.

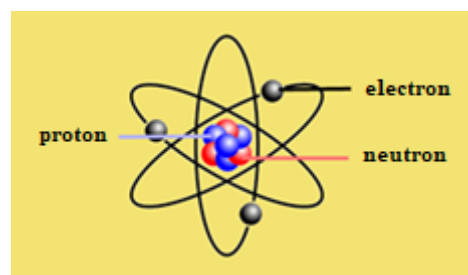


Fig. 1.7. Atomic structure.

The number of neutrons in the atomic nucleus indicates the isotope of the given element. Isotopes are varieties of atoms of the same chemical element that have the same atomic number but different masses.

Electronic scheme of atomic structure

The atom is electrically neutral because the positive charge of the nucleus is equal to the sum of the negative charges of the electrons rotating around the nucleus. Their movement occurs along electron shells. The number of electrons and electron shells depends on the magnitude of the atom's nuclear charge.

The structure of atoms is clearly represented in the Periodic Table of Chemical Elements. Let's take the chemical element sodium as an example. The element symbol is denoted by Latin letters (**Na**). The name is written in english letters - sodium.

Atomic number (**Z**) is the number of protons and electrons in an atom (for **Na** - 11).

The electron distribution across the layers for **Na** is 2, 8, 1.

The atomic mass of an element (atomic weight, relative atomic mass) is the total mass of neutrons, protons, and electrons in an atom, expressed in a.m.u. In **Na** it is 22.99.

The electron configuration of the Na atom is written as follows: $1s^2 2s^2 2p^6 3s^1$, where 1s is the first energy level where 2 electrons are located in the s-electron orbital; 2s and 2p are the second energy level, where there are 2 electrons in the s-electron orbital and 6 electrons in the p-electron orbital; 3s is the third energy level where there is 1 electron in the s-electron orbit.

Atomic structure models

In the history of science, various models of atomic structure have been developed. In 1803, John Dalton proposed a spherical model that depicted the atom as the smallest material sphere that cannot be destroyed.

In 1904, Joseph Thompson created a model called "Pudding with Raisins". In this model, the atom was considered as a certain positively charged body containing negatively charged electrons.

In 1911, Ernest Rutherford, based on his experiments, concluded that the atom resembles a small planetary system in which electrons orbit around the nucleus. However, the planetary model contradicted the principles of classical electrodynamics, according to which moving electrons must lose energy and fall on the nucleus.

Nils Bohr improved the planetary model of the atom by introducing the following additions:

- each electron can rotate around the nucleus only in strictly defined stationary orbits;

- in the process of such rotation, the atom does not emit energy;
- emission or absorption of energy occurs only when an atom transitions from one stationary state to another.

The modern model of the atom is called quantum mechanical. It uses Werner-Heisenberg's uncertainty and complementarity principles, according to which an electron is both a particle and a wave, there are no defined orbits, and electrons move around the nucleus, forming an electron cloud.

1.2. Main types of chemical bonds

The way different elements interact and bond to form molecules and solids is closely related to their electronic structure. Of course, for any type of molecule or solid to form, there must be a force of mutual attraction between atoms. However, there are also repulsive forces that prevent atoms from getting too close to each other. It is the equilibrium of the forces of attraction and repulsion that creates a balanced configuration between atoms in a solid, creating a three-dimensional spatial arrangement of atoms. For simplicity, we can consider two identical atoms that are gradually approaching each other. At large distances, the forces between atoms are very small (i.e., the potential energy of interaction can be said to be zero). As the atoms approach each other, the interaction potential increases, and the attractive forces that pull them together become active. Note that, from a mathematical point of view, this energy is negative, just like the binding energy of electrons in atoms, and to separate them, work must be done on the atoms. When the splitting of atoms is on the order of several atomic diameters, short-range repulsive forces are activated, preventing the crystals from collapsing into themselves. Here, potential energy has a positive meaning that work must be done to bring the atoms closer together. It is precisely the balance between these opposing forces that leads to the final equilibrium. Indeed, the attractive forces between atoms attract them until the electron clouds begin to overlap, and then strong repulsive forces arise, which corresponds to the Pauli exclusion principle. Equilibrium separation between atoms occurs where the two forces r_0 have the same value, giving a stable configuration of minimal potential energy. We can express this situation mathematically as a simple sum of the forces of attraction and repulsion, expressed by the following relation:

$$U(r) = -\frac{A}{r^n} + \frac{B}{r^m}, \quad (1.1)$$

where r is the distance between atomic centers, and A , B , n , and m are the constants specific to these atoms. The form of this equation is called the *Mi potential*. The force of interaction between atoms can be derived from:

$$F = -\frac{dU(r)}{dr} = -\frac{nA}{r^{n+1}} + \frac{mB}{r^{m+1}}. \quad (1.2)$$

This situation is illustrated in Figure 1.8. Note that equilibrium is established at the point where the potential energy is at a minimum and the interatomic force passes through zero. Moreover, at equilibrium ($r = r_0$) $F = 0$ and $U(r) = \min$, we can take the equilibrium separation of atoms as follows:

$$r_0 = \left(\frac{mB}{nA} \right)^{\frac{1}{m-n}}. \quad (1.3)$$

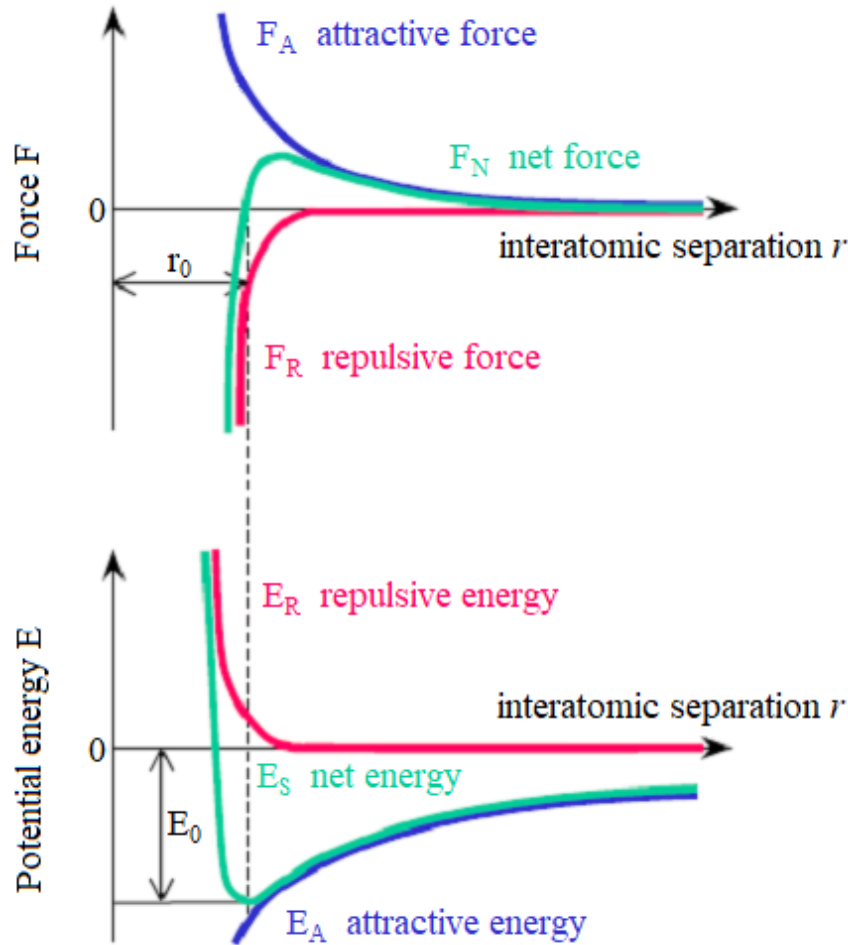


Fig. 1.8. Interatomic splitting, attraction, and repulsion regions are shown as a function of (a) potential energy and (b) force. The minimum depth of potential energy corresponds to the total bond energy between atoms. The separation of equilibrium is indicated by r_0 .

Substituting this into the potential energy, we can find the equilibrium potential as follows:

$$U(r_0) = -\frac{A}{r_0^n} \left(1 - \frac{n}{m} \right). \quad (1.4)$$

This value is considered negative, corresponding to the bound state. This will be the energy required to separate the two atoms. We see that in the equilibrium state, the forces of attraction and repulsion must be equal, but their corresponding energies are not equal; $m \neq n$. Indeed, stable compounds of atoms can arise only under the condition that $m > n$. This is another way of saying that repulsive forces should be at shorter distances than gravitational forces. We can show this by applying the condition:

$$\left[\frac{d^2U(r)}{dr^2} \right]_{r=r_0} > 0. \quad (1.5)$$

This condition directly leads to $m > n$. Of course, this should be evident from equation (1.4), because only then will $U(r_0)$ become negative for the bound state condition. The above is very precise and uses, for example, $m = 12$ and $n = 6$ and is defined as the Lennard-Jones potential (6 - 12).

Chemists are interested in how a small number of atoms bond to form a molecule, and in solid-state physics, we mainly deal with the same problem, although more atoms are involved. In the remainder of this section, we will describe the basic physical mechanism that does this. Here we rely on our knowledge of physical forces and the periodic table. Before discussing these mechanisms, let's note an important difference in the types of bonds: a strong bond occurs when electrons are exchanged in some form (such as ionic, covalent, and metallic bonds), while a weak bond occurs when electrons are unevenly distributed across atoms to create a dipole moment that interacts through electrostatic forces (hydrogen and Van der Waals bonds). The first is called a chemical bond, and the second is called a physical bond. The same difference exists for atoms on the surface, which can either chemisorb or physisorb, depending on whether there is an electron exchange or not.

Ionic bonding

This is probably the simplest form of connection. This occurs in compounds where elements easily form ions, which is an excess or shortage of electrons from their normal neutral state. An example of this is table salt NaCl. As can be seen from their position in the periodic table, Na and Cl lack one electron in the outer shell (Na) or one electron in the outer shell (Cl). Once these atoms are sufficiently close, the excess electron in Na becomes energetically favorable to fill the outer shell of Cl, and thus both remain in the ionic state; In Na^+ , Cl^- and more stable configurations, since both of them have filled their outer electron shells. The outer shell of a pair of atoms has the same number of redundant/deficient electrons, so pure ionic bonding occurs only in these states. Examples of such pairs are NaF, KCl, CsCl. Therefore, such a bond cannot be formed between atoms of the same type. The result of electron exchange is that the atoms become non-neutral and are

attracted to each other through Coulomb interaction. In other words, this process of electron transfer can be considered as the influence of the low ionization potential of the alkali metal (Na) and the high electron affinity of the halogen (Cl). The Coulomb potential looks like this:

$$U_{Coulomb}(r) = -\frac{ve^2}{4\pi\epsilon_0 r}, \quad (1.6)$$

where $v = 1$ for single-ionized species, as for NaCl. The energy associated with repulsion is often given exponentially, which is an alternative form of the repulsion energy mentioned above. This can be written as follows: $B \cdot \exp\left(-\frac{r}{\rho}\right)$. Here ρ acts as an indicator of repulsion (has units of length) and determines the distance at which repulsive forces are significant. The total energy per molecule of an ionic crystal can be written as:

$$U_{ion}(r) = -\frac{\alpha ve^2}{4\pi\epsilon_0 r} + B \exp\left(-\frac{r}{\rho}\right). \quad (1.7)$$

The additional constant a here is called the Madelung constant and depends on the geometric arrangement of the ions. (Here we note that for the NaCl structure this value is 1.74756, for the zinc sphalerite this value is 1.63805, and for the CsCl type structure we get 1.76267). We can eliminate one of the unknowns in equation (1.7) by acknowledging that the first derivative with respect to p is equal to zero at the equilibrium separation. From this, we find:

$$B = \frac{\alpha ve^2}{4\pi\epsilon_0 r_0^2} \exp\left(-\frac{r_0}{\rho}\right). \quad (1.8)$$

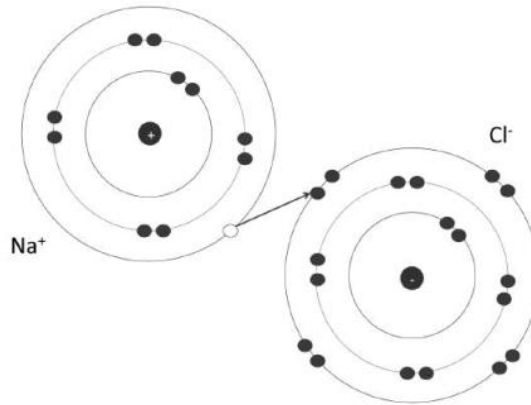


Fig. 1.9. Ionic bonding: The Na^+ cation (left) and the Cl^- anion (right) are formed by the transfer of an electron from the Na atom to the Cl atom, and they are held by Coulomb forces.

Now we can write energy as:

$$U_{ion}(r) = -\frac{\alpha ve^2}{4\pi\epsilon_0 r_0} \left[1 - \frac{r\rho}{r_0^2} \exp\left(-\frac{r-r_0}{\rho}\right) \right]. \quad (1.9)$$

It follows that estimating the binding energy (equilibrium potential energy) is a simple task:

$$U_{ion}(r_0) = -\frac{\alpha v e^2}{4\pi\epsilon_0 r_0} \left[1 - \frac{\rho}{r_0} \right]. \quad (1.10)$$

Usually, ρ constitutes a small percentage of r_0 and the Madelung term dominates in the binding energy. The mechanism of ionic bonding can be represented schematically in Figure 1.9.

Covalent bond

Elements in the central part of the periodic table do not easily transform into closed electron shell structures because transferring electrons between species requires extra energy, and therefore an ionic type bond is unlikely. Instead, bonding can occur by sharing valence electrons, in which each atom gives up one more electron to contribute. The mechanism of electron distribution is called covalent bonding. For the simplest hydrogen molecule H_2 , each of the two hydrogen atoms gives an $1s^1$ electron to form a covalent bond with an electron pair.

The proximity of two H atoms causes an interaction between their corresponding electrons, which is divided into two states with different energies. One of them is called the bond state and has an even (symmetrical) orbital wave function, the total energy of which is less than the energy of the isolated electron, and thus the bond is formed. A symmetrical solution requires the concentration of the electron charge density in the region between the nuclei $-e|\psi|^2$. The requirement of the Pauli principle is that the total wave function is antisymmetric and is satisfied for the $1s$ state when the electrons coincide with antiparallel spins. In the second state, called the antibonding state, there are two electrons with parallel spins, which is a pure repulsive state.



Fig. 1.10. The simplest form of covalent bonding between a pair of H atoms to form a H_2 molecule.

Since this latter state has high energy and two electrons can be placed in the $1s$ state, it is a generated, bonding state, which is carried out and a strong bond is formed. Note that such a case is impossible, for example, for two He atoms, since all s -positions are occupied, which leads to an increase in the total energy.

Obviously, for a covalent bond to exist, the valence electron shell cannot be fully occupied, as in He. Higher orbitals are occupied for heavier atoms. These

orbitals, unlike s-orbitals, have a very directed character, as shown in Figure 1.11. The nature of this orientation of orbitals stems from energy considerations and the Pauli principle, i.e., electrons try to escape each other, forming symmetrically distributed orbitals in space. The result of this is that the covalent bonds formed by the overlap of partially vacant orbitals are also highly directed. For example, the covalent bonds of carbon atoms form the tetrahedral unit of the diamond structure, which will be discussed in Chapter 2. The electron configuration for C is $1s^2 2s^1 2p^1 x 2p^1 y 2p^1 z$.

In this ground state configuration, we have four unpaired electrons, which hybridize to form four equal-distance segments (tetrahedra) of sp^3 hybrid orbitals, with angles between them equal to 109.5° (see Figure 1.12). Note here that hybridization of states (in this case, we are considering states *s* and *p*) involves the mixing of electronic states between more than one atom. This produces different energy levels that are more available to electrons and bind the atoms together. A compound has less total energy than isolated atoms. The covalent mechanism is responsible for the bonds in most organic compounds. It is also the dominant pair for halogen atoms. In most semiconductor materials, covalent bonding is also very important. sp hybridization (regardless of type 2 or 3) is important not only in the formation of diamond (sp^3), but also in the more common allotropic form of graphite, which forms an atomic thin carbon layer (graphene) as a result of sp^2 type bonds.

This structure is essentially a 2D hexagonal formation, where the Van der Waals interaction between graphene sides in graphite forms a 3D structure. The difference between diamond and graphite forms of carbon indicates the importance of the physical properties of the structure: diamond is an electrical insulator, while graphite is a good conductor. Weak interlayer bonds in graphite allow it to decompose or even produce graphene sides using adhesive tape. A covalent bond can be very strong and is responsible, for example, for the legendary hardness of a diamond.

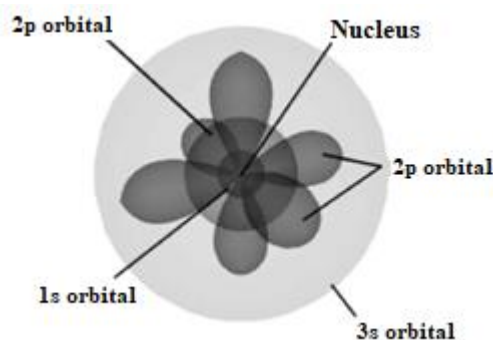


Fig. 1.11. Low-level orbitals showing the orientation character of p -orbitals and the symmetrical distribution of s -orbitals.

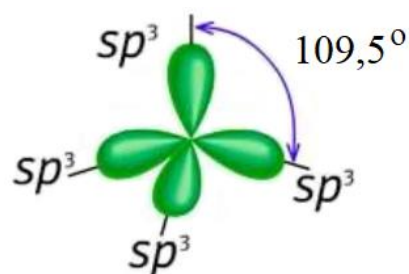
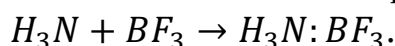


Fig. 1.12. Spatial distribution of sp^3 -orbitals, which form the basis of a tetrahedron.

Intermolecular and intramolecular interactions. Hydrogen bonding

The above-mentioned ionic, covalent, metallic, donor-acceptor bonds are the main types of chemical bonds. In addition to these types of bonds between atoms and molecules, there are also secondary types of bonds - hydrogen bonds and intermolecular attraction forces (Vander-Whals forces). These include orientational, dispersion, and induction forces. Hydrogen bonding is a specific type of chemical bond. It can be intermolecular and intramolecular. Intermolecular hydrogen bonds are formed between molecules containing hydrogen and atoms of a strong electronegative element - fluorine, oxygen, nitrogen, chlorine, and sulfur. In such molecules, the shared electron pair is shifted from the hydrogen atom towards the atom of the electronegative element. Since the positive hydrogen ion is small, it interacts with an unshared electron pair of another atom or ion, forming a weaker bond. This bond is called a hydrogen bond. For example: a donor-acceptor bond can also occur between two different molecules. For example,



Here, NH_3 is the electron pair donor, and BF_3 is the acceptor for this electron pair. The CO molecule also has an internal donor-acceptor bond. In this case, carbon acts as an acceptor, and oxygen as a donor. Usually, hydrogen bonds are marked with dots, indicating that they are much weaker than covalent bonds. Nevertheless, the association of molecules occurs due to this connection.

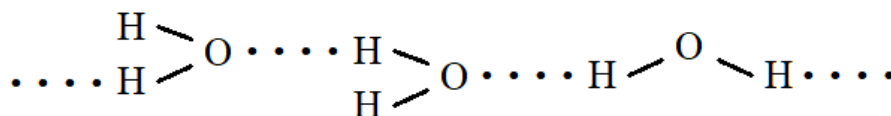


Fig. 1.13. Hydrogen bonding.

However, the energy of this connection is not very large. For example, the bond strength of the main types of chemical bonds is 84-1042 kJ/mol, while that of hydrogen bonds is 21-42 kJ/mol.

Valence of chemical elements. Valence and oxidation state of element atoms in compounds. The valency of an atom (element) is also among the basic concepts of chemistry. It shows the ability of atoms of elements to form chemical bonds. Atomic mass is either equal to the equivalent or several times greater than the equivalent. The number indicating how many times the atomic mass is greater than the equivalent is valence, denoted by the letter B.

$$V = \frac{A}{E}. \quad (2.11)$$

Valence is defined as follows: *The number indicating how many atoms of hydrogen are added or replaced to one atom of an element is called the valence of that element.*

One atom of oxygen combines with two atoms of hydrogen; therefore, oxygen is divalent. The valencies of elements can be determined not only by hydrogen, but

also by oxygen. Hydrogen and alkali metals are always monovalent, oxygen and alkaline earth metals are always divalent, aluminum is always trivalent. These elements are called elements with constant valency. However, there are some elements whose valencies change depending on the nature of the reacting elements and reaction conditions. For example: When copper is heated, depending on the conditions, it sometimes forms monovalent Cu_2O , and sometimes it forms divalent CuO . Thus, copper can be both monovalent and divalent, and N, P, As, halogens, and many other metals are elements with variable valency. Nitrogen can be 1, 2, 3, 4, 5 valent in its compounds. The valencies of inert gases of group VIII of the periodic table are equal to zero. That is, they do not combine with each other and with other elements. The number of bonds that an atom can form is equal to the number of its unpaired electrons. In the simplest cases, the valence of an element's atom is also determined by the number of unpaired electrons required to form a common pair of electrons. In this case, the polarity of the formed bonds is not considered, therefore there is no sign of valency. Valence, defined as the number of bonds, cannot be negative or equal to zero. Let us consider this using the example of nitrogen - N_2 , hydrazine - N_2H_2 , nitric acid - HNO_3 , ammonia - NH_3 . The arrangement of electrons in the nitrogen atom's quantum cells is shown in Fig. 1.14.

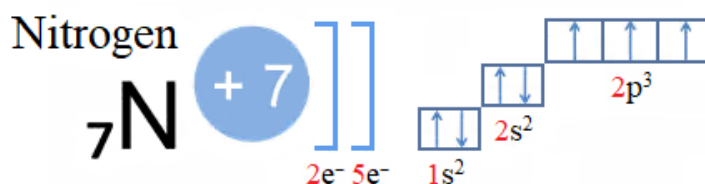


Fig. 1.14. Electron configuration of the nitrogen atom.

Since nitrogen has three unpaired electrons, it can form three chemical bonds and has a valence of 3. By denoting each pair of electrons of the covalent bond with a dash, we obtain the structural formulas: In all these compounds, nitrogen is trivalent. However, the oxidation state of nitrogen is equal to 0, -2, -3. In NH_4^+ , nitrogen is 4-valent, but the oxidation state of nitrogen is -3. In the HNO_3 molecule, the valency of nitrogen is equal to 4. The oxidation state is +5. When a given compound is assumed to have a completely ionic structure, the conditional charge of any element in its composition is called its oxidation state. When determining the oxidation state of elements, the oxidation state of oxygen is always taken as -2 and hydrogen as +1. The oxidation state of metal ions is assumed to be equal to their charge. For example, in H_2O , the oxidation state of hydrogen is +1, and oxygen is -2. In C, potassium is +1, iodine is -1. In most cases, the oxidation state of an element's atom does not correspond to the number of bonds it forms, i.e., it is not equal to the valence of this element. This is especially evident in the example of organic compounds. It is known that in organic compounds, the valency of carbon is equal to 4 (forms 4 bonds), but the oxidation state of carbon in methane CH_4 is -

4, in methanol CH_3OH -2, in formal CH_2O -0, in formic acid HCOOH +2, in carbon dioxide CO_2 +4. In compounds without covalent bonds, it is impossible to talk about the valence of atoms; in this case, it is necessary to speak about the degree of oxidation. Therefore, it is advisable to use the concept of oxidation state in inorganic chemistry and the concept of valency in organic chemistry. This is due to the fact that most inorganic compounds have a non-molecular structure, while most organic compounds have a molecular structure.

1.3. Elements of Band Theory of Solids

Brillouin Zone

To explain Brillouin zones, let us consider a two-dimensional crystal lattice. We connect an atom located at lattice with its neighboring atoms. Each connecting line between neighboring atoms is bisected perpendicularly. The resulting shaded shape is called the Wigner-Seitz primitive cell (Fig. 1.15). By translating this cell in the plane along the lattice translation vectors, we can reconstruct the crystal lattice structure. In other words, the Wigner-Seitz cell is one method of selecting a primitive cell.

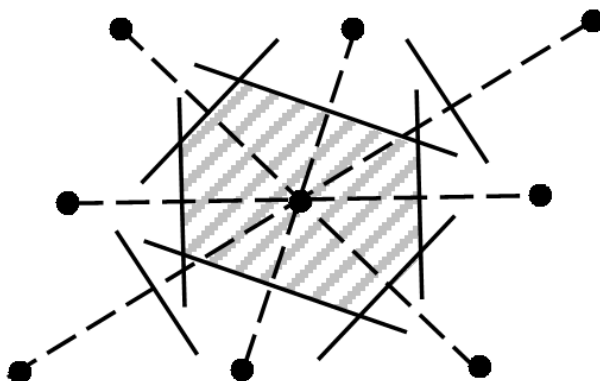


Fig. 1.15. The Wigner-Seitz unit cell in a two-dimensional crystal is a region bounded by perpendiculars drawn to the centers of the segments connecting the nearest nodes.

Now, let us construct the reciprocal lattice corresponding to this crystal lattice and similarly identify a primitive cell in this lattice. The primitive cell of the reciprocal lattice obtained in this way is called the first Brillouin zone. The physical significance of the Brillouin zone lies in the fact that all X-ray beams with wave vectors k lying inside the Brillouin zone can be reflected from the crystal according to the Bragg-Wolf condition. Although Brillouin zones are not commonly used in modern crystallography, they play a crucial role in the band theory of crystals. Electrons located within the Brillouin zone can continuously change their energy and momentum. However, for an electron to leave the Brillouin zone, its energy must change in a discontinuous (quantum) jump.

Energy Level Splitting

An electron interacting with the nucleus of an atom resides in a potential well, so the electron's energy spectrum in the atom is discrete. This statement is true not only for an isolated atom but also for a system consisting of non-interacting atoms, such as a rarefied gas. In this case, the electron energy levels simply repeat. If the system contains N atoms, then each energy level is degenerate by a factor of N .

During the formation of a crystal lattice, the atoms approach each other and begin to interact. The electron wave functions partially overlap. As a result, the degenerate energy levels are split (Fig. 1.16). The split levels form an energy band.

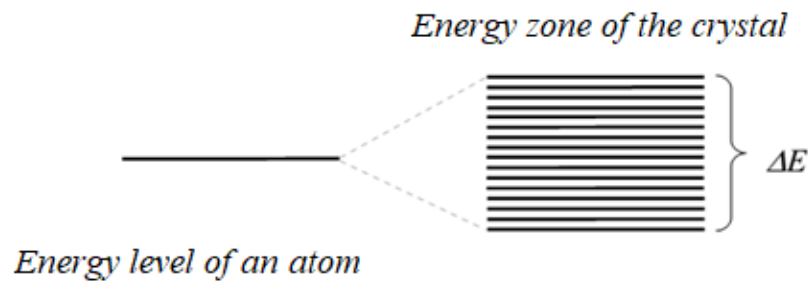


Fig. 1.16. Splitting the energy level of an atom into energy bands.

Since the splitting is determined by the degree of overlap of electron shells, the energy levels of the inner shells localized near the nucleus are split less than those of the valence electrons. The width of the energy bands increases with distance from the nucleus. Therefore, the band corresponding to the valence electrons is wide.

Let's consider these general principles using lithium atoms as an example. The electron configuration of a lithium atom is $1s^2 2s^1$. Two electrons with different spin orientations are in the $1s$ state and one electron is in the $2s$ state.



Fig. 1.17. Spectra of two non-interacting lithium atoms.

Figure 1.17 shows the spectra of two non-interacting (distant) lithium atoms. The energy levels are degenerate.

Bringing the atoms closer together will result in overlapping wave functions. The Pauli principle prohibits two fermions from having the same set of quantum numbers. Therefore, the $1s$ and $2s$ energy levels will split into two sublevels. The $1s$ state is weaker, while the $2s$ state is stronger, since the wave functions of the $2s$ state

will overlap more significantly. The energy spectrum of a system consisting of two atoms is shown on the left in Figure 1.18.

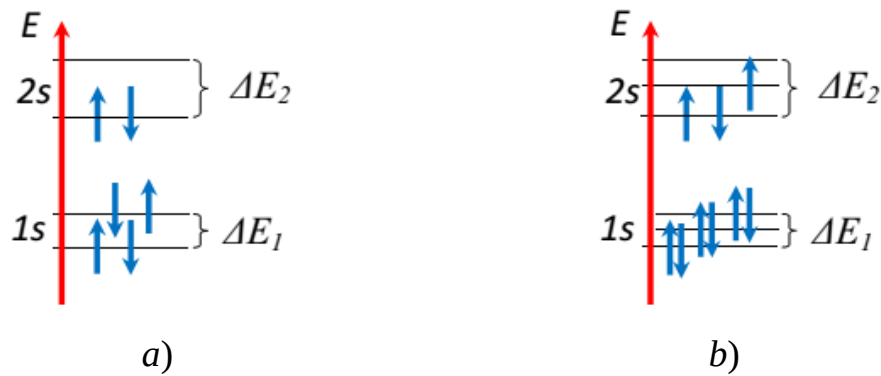


Fig. 1.18. Energy spectrum of a system consisting of two (a) and three (b) atoms.

The energy spectrum of a system consisting of three atoms is shown on the right. The magnitude of the splitting, determined by the interatomic distance, remains the same. The third level is located between the two existing ones. According to this logic, increasing the number of atoms will lead to a decrease in the distance between the sublevels.

Figure 1.19 shows the splitting of the energy levels of a lithium atom during crystal formation. The fully filled $1s^2$ electron shell splits to form a narrow band. The second, valence, half-filled $2s^1$ shell splits to form a much wider band. Both filled and unfilled levels are split. The energy bands of allowed energy values corresponding to the $1s^2$ and $2s^1$ electron shells are separated from each other by a band of forbidden energy values. Accordingly, these bands are called allowed and forbidden bands.

The band of highest electron energies in a crystal is called the conduction band, while the band below it in the energy spectrum is called the valence band.

The uncertainty principle $\Delta E \cdot \tau > h$ allows us to estimate the band width. In an atom, the excited-state lifetime is $\tau \approx 10^{-8}$ s, so the natural energy level width is $\Delta E \approx h / \tau \approx 10^{-7}$ eV. In a crystal, the lifetime is $\tau \approx 10^{-15}$ s, and the energy band width is $\Delta E \approx h / \tau \approx 1$ eV.

The energy band width does not depend on the crystal size but is determined by the nature of the atoms that make up the solid. The energy levels fill the band very densely. For example, if the number of atoms in a crystal is $N \approx 10^{23}$, then the energy levels in the

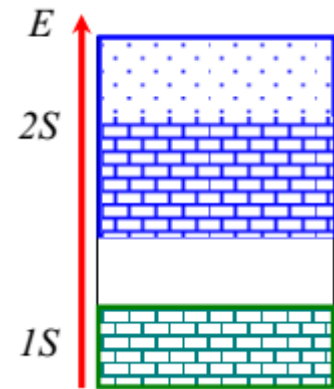


Fig. 1.19. Diagram of the splitting of the energy levels of a lithium atom during crystal formation.

band are spaced at $\sim 1 \text{ eV} / N \approx 10^{-23} \text{ eV}$. If we compare the obtained value with the energy of thermal motion at room temperature, $kT \approx 10^{-2} \text{ eV}$, we can assume that the energy in the band is distributed continuously.

Let's consider the formation of a sodium crystal. The electron configuration of the sodium atom is $1s^2 2s^2 2p^6 3s^1$. The energy spectrum of the sodium atom is shown in Figure 1.20. The first and second electron shells of the sodium atom are completely filled, the 5-shell in the third is partially filled, and the p - and d -shells are empty.

The spectrum of the second sodium atom is also shown there. The distance between atoms, r , significantly exceeds the interatomic distance in the crystal lattice, denoted as a . For a sodium crystal, $a \sim 0.5 \text{ nm}$. The atoms do not interact, so their energy spectra simply repeat each other.

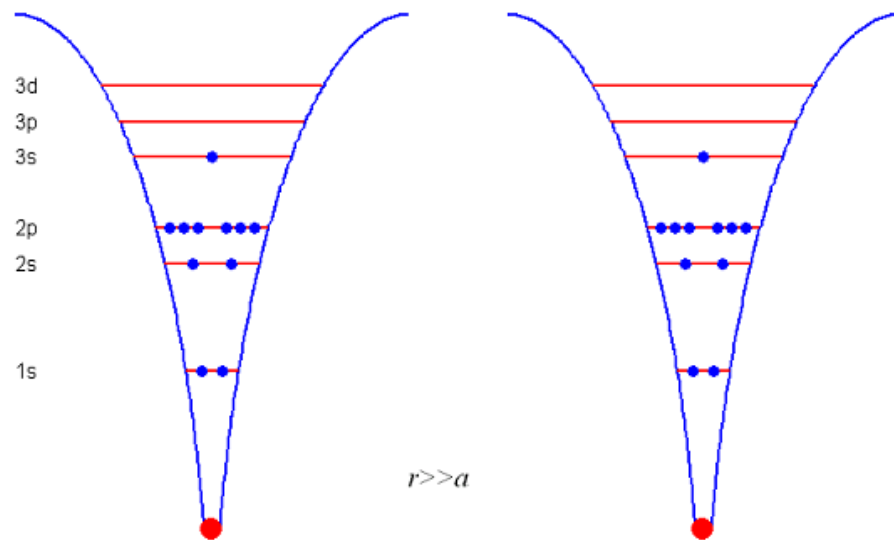


Fig. 1.20. Energy spectrum of the sodium atom.

During crystallization, interatomic distances decrease. Atoms begin to interact. The superposition of the wave functions of different atoms alters the energy spectrum of the system.

The energy spectrum of a sodium crystal is shown in Figure 1.21. The energy levels are split, with the widest band forming around the valence electrons. The potential energy curves of isolated atoms (dashed line) partially overlap, and the resulting curve (solid line) descends. The width and height of the potential barrier between adjacent atoms decrease. For the valence electrons of the third layer, this barrier disappears completely.

In this case, electrons are able to easily move from one atom to another. These electrons are collectivized (socialized) by the crystal. In effect, they become free particles, and their aggregate — an electron gas.

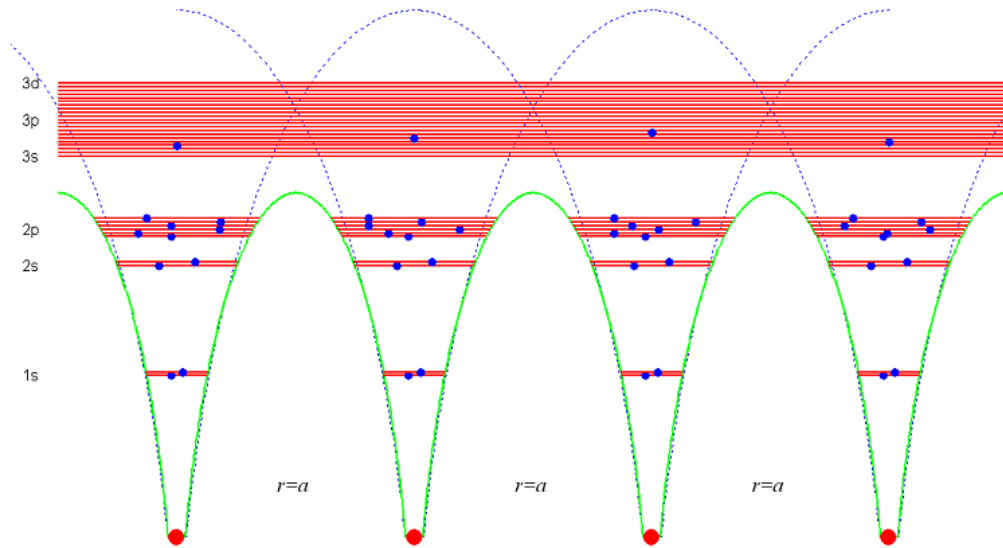


Fig. 1.21. Energy spectrum of a sodium crystal.

Crystal Classification

Crystalline solids are divided into metals, semiconductors, and dielectrics. The band theory of crystals provides a unified explanation of their fundamental properties. For example, the existence of broad energy bands explains the continuous spectrum of thermal radiation from solids. The classification of electrical properties based on band theory is the most consistent.

The most important factors are the band structure, their width, and the nature of their electron occupation. Possible variations are shown in Figure 1.22. To exclude the influence of thermal motion, the case at $T = 0$ is considered.

Metals. At a temperature equal to absolute zero, electrons partially fill the valence band. However, free quantum states unoccupied by electrons remain in the band. Even slight heating leads to thermal motion. The energy of thermal motion is sufficient to elevate some electrons to higher energy levels. The electrons then become free states. When an electric field is applied, these electrons change their quantum state and undergo ordered spatial motion against the field. An electric current is generated.

It should be noted that electrons in filled energy levels cannot participate in spatial motion. Any movement of an electron means a change in its quantum state. The Pauli principle, according to which a system cannot have two or more electrons with the same set of quantum numbers, prohibits them from moving into already occupied states and, therefore, from undergoing spatial motion.

A crystal with a completely filled valence band and a zero band gap also turns out to be a metal. The conduction band is adjacent to the valence band or even partially overlaps it. This case is fundamentally no different from the one considered previously. The energy of thermal motion is sufficient to transfer electrons from filled states to unoccupied ones.

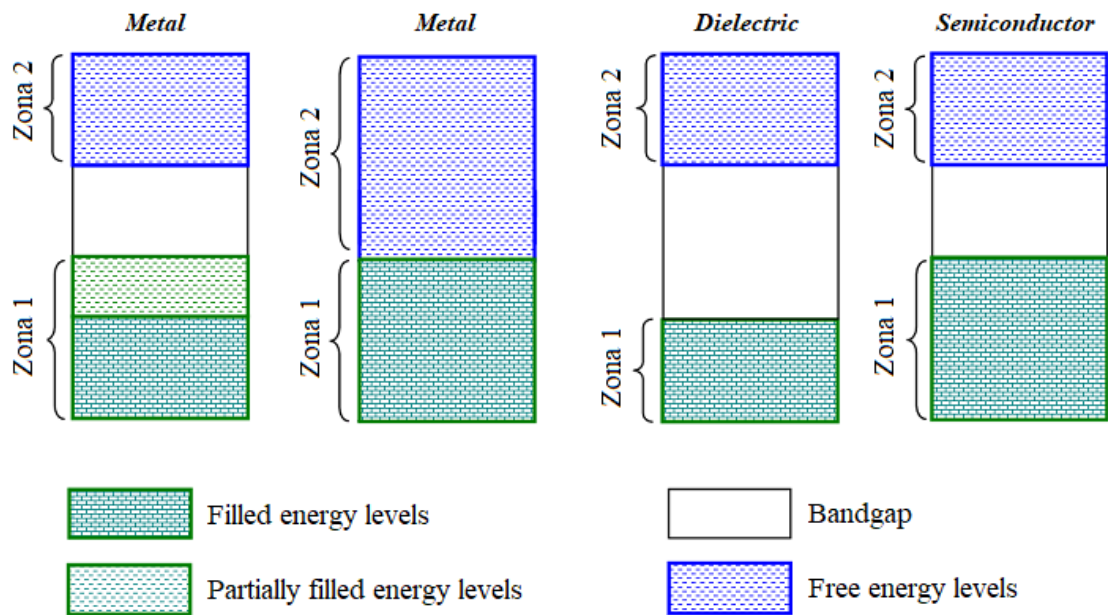


Fig. 1.22. Type of energy zones according to the classification of crystals.

Dielectrics. Electrons at a temperature equal to absolute zero completely fill the valence band. The band gap is significant, at least 5 eV. The energy of thermal motion is insufficient to transfer a significant number of electrons to the band of unoccupied states, the conduction band. Such crystals do not conduct electric current.

Semiconductors. Fundamentally, semiconductors are no different from insulators at absolute zero. Electrons completely fill the valence band, but the band gap is narrow, less than 3 eV. The energy of thermal motion or absorbed photons from external radiation is sufficient to transfer electrons to the conduction band. The higher the temperature, the greater the electron concentration in the conduction band, and the better the crystal conducts electric current.

The quantum-mechanical solution to the interaction of the vast number of electrons and ions in a crystal lattice is impossible. However, it is quite productive to consider the self-consistent field approximation: an electron moves in the averaged and consistent field of all electrons and nuclei. Conduction electrons form a gas of free particles. Their interaction with the crystal lattice is taken into account by introducing the so-called effective mass for electrons instead of the real mass.

Quantum Statistics

Systems consisting of a huge number of particles are described by probabilistic (statistical) characteristics and regularities. The statistical characteristics of a system are not inherent to an individual particle. This is how the concepts of pressure and temperature are formulated for an ideal gas. This approach is valid not only for classical systems but also for quantum systems.

Quantum statistics is a branch of statistical physics that studies systems consisting of a huge number of particles that obey the laws of quantum mechanics.

In a classical system, even if it is represented by an ideal gas consisting of identical molecules, the particles are distinguishable. They can be simply numbered, and if this is not possible, then knowledge of the coordinates and momenta at the initial moment of time always allows one to calculate the position of the particle at subsequent moments of time. And if two identical particles in different states exchange places, the state of the system changes.

In quantum systems, statistics change significantly, primarily because the principle of indistinguishability of identical particles applies. If two identical particles in different quantum states swap, the state of the system remains unchanged.

In quantum theory, all particles are divided into fermions and bosons. Bosons are particles with integer spin, while fermions are particles with half-integer spin. The Pauli principle prohibits two or more fermions from sharing the same quantum numbers (the same state). These restrictions do not apply to bosons. Therefore, the statistics of fermions and bosons differ. Fermions are described by Fermi-Dirac statistics, while bosons are described by Bose-Einstein statistics.

<i>Classical particles</i>	<i>Bosons</i>	<i>Fermions</i>																																																						
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Fig. 1.23.

Let's illustrate the difference in statistics with the following example. Suppose there are two particles, *A* and *B*, each of which can be in one of three states. If the particles are considered classical and the quantum state is represented by a cell, then the system has nine possible states, as shown in Figure 1.23. These states are equally probable. The probability of each is 1/9.

Bosons are distributed among quantum states differently. The permutation of particles $A \leftrightarrow B$ does not change the state of the system. The particles are identical,

so they are depicted identically in the figure. There are six possible states, with the probability of each being 1/6. Fermions cannot exist in a single quantum state, so the system is left with only three states, and the probability of each is 1/3.

The most important object of study in quantum statistics is a system of non-interacting particles (an ideal gas). A particle can be in the i -th quantum state, possessing energy E_i . The state of the quantum system is then determined by the degree of occupation of the quantum states. The degree of occupation of the i -th quantum state, or occupation number, is the number of particles in this state – n_i .

The task of statistical physics is to determine the most probable distribution of the system's particles among quantum states with energies E . It is the most probable distribution that realizes the system's state of thermodynamic equilibrium. The most probable distribution is the one that can be realized in the greatest number of ways. The probability of a state, in turn, determines the entropy of the system. Therefore, the problem of finding the equilibrium distribution of particles is reduced to finding the extremum (maximum) of the system's entropy, assuming a constant number of particles and energy.

$$\begin{aligned} n_1 + n_2 + n_3 + \dots &= N, \\ n_1 E_1 + n_2 E_2 + n_3 E_3 + \dots &= E. \end{aligned}$$

Maxwell-Boltzmann Distribution. The state of thermodynamic equilibrium of a classical ideal gas is described by the Maxwell-Boltzmann distribution:

$$\bar{n}_i = n_0 \exp\left(-\frac{E_i}{kT}\right),$$

$\bar{n}_i$ – is the average occupation number of the i -th level.

Chemical potential. Heat exchange dQ and work performed dA change the internal energy dU of a thermodynamic system, where $dU = dQ - dA$. However, in systems with a variable number of particles, the internal energy can be changed by adding (removing) one of them, then $dU = dQ - dA + \mu dN$.

If the system is isolated and does no work, then $dQ = dA = 0$. Then, for the thermodynamic parameter μ , called the chemical potential, we obtain

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{v,Q}.$$

Chemical potential is a thermodynamic parameter of a system that determines how its internal energy will change if another particle is added to the system, provided that the other parameters affecting the internal energy remain unchanged.

Bose-Einstein distribution. A system of quantum particles — identical bosons — obeys Bose-Einstein statistics. The average occupation numbers of energy levels n are determined by the function

$$\bar{n}_i = \frac{1}{\exp\left(\frac{E_i - \mu}{kT}\right) - 1}.$$

Let's assume that the chemical potential of a boson system is positive. In this case, for energy levels $E_i < \mu$, the exponent in the denominator will be less than unity, and the occupation numbers will become negative, which is impossible. Therefore, the chemical potential of a boson system is negative, $\mu \leq 0$. Note that for Bose systems with a variable number of particles, $\mu = 0$.

The average occupation numbers in Bose-Einstein statistics are $\bar{n}_i \geq 0$ and are not bounded by anything. For small values of the exponent argument, the population of low-energy levels can be very large, which leads to the emergence of unique physical properties in systems consisting of Bose particles.

Fermi-Dirac distribution. A system of identical fermions obeys Fermi-Dirac statistics. The average occupation numbers of energy levels n are determined by the function

$$\bar{n}_i = \frac{1}{\exp\left(\frac{E_i - \mu}{kT}\right) + 1}.$$

Suppose the chemical potential of fermions is negative. Then, at temperature $T \rightarrow 0$, the exponent in the denominator would become infinite, and the occupation numbers would vanish, which is impossible. Consequently, the chemical potential of fermions is positive, $\mu > 0$.

Fermions are subject to the Pauli exclusion principle, so without taking spin into account, the average occupation numbers of the energy levels of fermion systems are $0 \leq \bar{n}_i \leq 1$.

Degenerate systems. Let the average occupation numbers be small, $\bar{n}_i \ll 1$. In both boson and fermion statistics, small occupation numbers are achieved at values of $E_i - \mu \gg kT$, since the unity in the denominator can be neglected at this point. Both statistics then transition to classical Maxwell-Boltzmann statistics.

$$\bar{n}_i = n_0 \exp\left(-\frac{E_i}{kT}\right), \quad n_0 = \exp\left(\frac{\mu}{kT}\right).$$

Quantum systems that obey Maxwell-Boltzmann statistics are called non-degenerate; they are essentially dilute quantum gases.

Otherwise, when $E_i - \mu \ll kT$, the system is called degenerate. The properties of degenerate systems differ significantly from classical ones. Both the quantum properties of particles and the quantum properties of systems as a whole come to the fore.

Chapter Review Questions

1. Into what main groups are materials divided? Give examples for each.
2. What is an atom and what are its main components?
3. What are the masses and charges of protons, neutrons, and electrons?
4. What particles make up the atomic nucleus?
5. What do the s, p, d, and f orbitals in the electron shell represent?
6. What are quantum numbers and what do they describe?
7. What are the shapes of atomic orbitals?
8. What is the Pauli principle and how does it affect the arrangement of electrons?
9. What is Heisenberg's uncertainty principle?
10. What energy levels do electrons in an atom possess?
11. What is a chemical bond and how is it formed?
12. Between which atoms does an ionic bond occur? Give an example.
13. How is a covalent bond formed? For what types of substances is it typical?
14. What characterizes a metallic bond, and in what materials does it occur?
15. Under what conditions does a hydrogen bond form?
16. What kinds of interactions are dipole–dipole and van der Waals forces considered to be?
17. How are electron pairs distributed in a covalent bond?
18. What determines the energy of chemical bonds?
19. What are the properties of ionic crystals?
20. How does chemical bonding affect material properties such as hardness, melting point, and electrical conductivity?
21. What does band theory explain?
22. In a solid, what are the valence band and the conduction band?
23. What is meant by the forbidden band (band gap)?
24. What kind of energy bands do metals, semiconductors, and dielectrics have?
25. How does the band structure affect the electrical conductivity of a solid?
26. How does electrical conductivity arise in semiconductors?
27. In band theory, what is meant by “delocalized electrons”?
28. What do curved (nonlinear) bands represent, and how are they determined?
29. How is the relationship between direct current and conduction electrons explained?
30. How does temperature affect the regions between energy bands?
31. What is chemical potential?
32. Explain the meaning of the Bose–Einstein and Fermi–Dirac distributions.

CHAPTER 2. PHYSICAL PROCESSES AND PHENOMENA IN CONDUCTIVE MATERIALS

The phenomenon of electrical conductivity is closely related to the microscopic structure of matter and occurs through the motion of free charge carriers — typically electrons — within a material. Conductive materials, particularly metals, are distinguished by their high electrical conductivity and constitute an essential component of modern electrical and electronic devices. Their electrical properties, especially electrical resistance, are directly influenced by factors such as temperature, the structure of the crystal lattice, and various structural defects.

In this chapter, the physical nature of electrical conductivity in conductive materials — specifically metals — is examined on the basis of quantum mechanics and the statistics of charge carriers. First, the electrical conductivity of metals is explained using the free-electron model, and the dependence of electrical resistance on temperature is analyzed in connection with crystal lattice vibrations (phonons) and electron–electron collisions.

The subsequent section explores the influence of the real structure of metals — that is, defects such as impurities, dislocations, and grain boundaries — on their electrical properties. Particular attention is given to the processes of diffuse electron scattering observed in various alloys, which lead to an increase in resistance and the emergence of its temperature-independent component (alloy resistance). The electrical properties of metallic alloys depend on their composition and structural characteristics, making them of great importance in technical applications.

The theoretical principles discussed in this chapter serve as a scientific and methodological foundation for the physical analysis of electrical materials, the prediction of their performance characteristics, and the development of new, high-efficiency materials.

2.1. General information about conductors. The physical nature of electrical conductivity in metals. Temperature dependence of metal conductors' resistance

Solids, liquids, and under certain conditions, even gases, can serve as conductors of electric current. Metals, metal alloys, and certain modifications of carbon are classified as solid conductors. Metals are characterized by their distinct luster and high electrical and thermal conductivity, as well as plasticity. Among materials used in electronic engineering, metals occupy one of the most important positions.

Liquid conductors include molten metals and various electrolytes. Typically, metals have high melting points; only mercury has a melting point of -39°C , which allows it to be used as a liquid conductor under normal temperature conditions. Gallium, with a melting point close to normal conditions (29.8°C), is another example. Other metals act as liquid conductors only at elevated or high temperatures.

The mechanism of electric current conduction through metals in solid and liquid states is determined by the movement of free electrons. Such materials are referred to as electronic conductors or first-type conductors.

Electrolytes, or second-type conductors, include aqueous solutions of acids, bases, and salts, as well as melts of ionic compounds. In these conductors, current flow is associated with the movement of both electric charges and a portion of molecules (ions), resulting in gradual changes in the composition of the electrolyte and the appearance of electrolysis products at the electrodes.

All gases and vapors, including metal vapors, are non-conductive when exposed to a low electric field strength. However, if the field strength exceeds a critical value sufficient to initiate impact ionization or photoionization, the gas can become a conductor with both electronic and ionic conductivity.

A strongly ionized gas, in which the number of electrons and positive ions per unit volume is equal, constitutes a special, balanced conducting medium known as plasma.

The Physical Nature of Electrical Conductivity in Metals

Experimental Laws and the Electron Theory. The classical electron theory of metals, developed by P. Drude and H.A. Lorentz, is based on the concept of a gas of free (delocalized) electrons, often referred to as the electron gas. This theory models the behavior of free electrons in a metal similarly to the behavior of molecules in an ideal gas. Accordingly, the motion of electrons follows the laws of classical statistics.

If the atoms in a metal are assumed to be singly ionized, then the concentration of free electrons is approximately equal to the concentration of atoms. This can be calculated using the following formula:

$$n = \frac{\rho}{A} \cdot N_A,$$

here,

- ρ denotes the density of the material,
- A is the atomic mass,
- N_A represents Avogadro's number.

According to the kinetic theory of ideal gases, the average kinetic energy of electrons, which are in a state of continuous chaotic motion, increases linearly with temperature:

$$\langle E_k \rangle = \frac{3}{2} kT ,$$

where

- $\langle E_k \rangle$ is the average kinetic energy of an electron,
- k is Boltzmann's constant,
- T is the absolute temperature (in Kelvin).

$$\frac{m_0 \bar{u}^2}{2} = \frac{3}{2} kT , \quad (2.1)$$

here, $\bar{u}$ represents the average thermal velocity of electrons.

At a temperature of 300 K, the average thermal velocity corresponds approximately to 10^5 m/s.

The application of an external voltage causes the electrons to drift in the direction of the force exerted by the electric field. In other words, the electrons acquire an additional velocity associated with their directed motion, superimposed on their random thermal movement. This directed motion results in the generation of electric current.

The current density in the conductor is expressed by the following equation:

$$\vec{j} = ne\vec{v} , \quad (2.2)$$

where:

- n is the free electron concentration,
- e is the elementary charge (electron charge),
- $\vec{v}$ is the drift velocity of electrons.

In a copper conductor with a current density of 10^6 A/m², the drift velocity of electrons is on the order of 10^{-4} m/s. This means that under real conditions, the inequality $\bar{v} \ll \bar{u}$ is always satisfied, where $\bar{v}$ is the drift velocity and $\bar{u}$ is the average thermal velocity.

Between collisions with the lattice nodes, electrons accelerate under the influence of the electric field with the following acceleration:

$$a = \frac{eE}{m_0} .$$

The maximum drift velocity attained by an electron at the end of its free path is given by:

$$v_{\max} = a\tau_0 ,$$

where:

- a is the acceleration due to the electric field,
- τ_0 is the mean free time (time interval between successive collisions, i.e., the free-flight time).

After a collision, the directed velocity of most electrons drops to zero, meaning that the accumulated kinetic energy is transferred to the lattice atoms.

Therefore, the average drift velocity during the free-flight time is equal to half of the maximum value:

$$\bar{v} = \frac{eE}{2m_0} \tau_0 .$$

Since $\bar{v} \ll \bar{u}$ the drift velocity is much smaller than the average thermal velocity. Therefore, when calculating the mean free time, the contribution of $\mathfrak{V}_d$ can be neglected i.e., the influence of the directed (drift) motion is negligible compared to random thermal motion:

$$\tau_0 = \frac{\bar{l}}{\bar{u}} ,$$

here, $\bar{l}$ - denotes the mean free path of electrons.

Substituting the obtained relationships into the current density expression (equation 2.2) yields the following result:

$$\bar{j} = \frac{e^2 n \bar{l}}{2m_0 \bar{u}} E = \gamma E , \quad (2.3)$$

$$\gamma = \frac{e^2 n \bar{l}}{m_0 \bar{u}} . \quad (2.4)$$

This expression shows that the electrical conductivity of a metal depends on:

- the concentration of free electrons n ,
- the charge of the electron e ,
- the mean free path $\bar{l}$,
- the mass of the electron m ,
- and the average thermal velocity $\bar{u}$.

Since the average thermal velocity $\bar{u}$ increases with temperature, the overall conductivity σ decreases as temperature rises. This explains why the resistance of metals increases with temperature — a key experimental fact.

The concept of free electrons easily leads to the Wiedemann–Franz experimental law, which establishes the relationship between the electrical conductivity and thermal conductivity of metals. Electrons in a metal not only carry electric charge, but also distribute heat, thereby ensuring high thermal conductivity. Due to the high concentration of free electrons, the electronic component of thermal conductivity dominates over other mechanisms of heat transfer. In this case, according to the kinetic theory of ideal gases, the specific thermal conductivity can be expressed as:

$$\lambda_T = \frac{1}{2} k n \bar{u} \bar{l} . \quad (2.5)$$

By dividing expression (2.5) by the specific conductivity obtained from formula (2.4), and considering formula (2.1), we obtain the following:

$$\frac{\lambda_T}{\gamma} = 3k^2 e^{-2} T = L_0 T ,$$

That is, the ratio of the specific thermal conductivity to the specific electrical conductivity of a metal at a given temperature is a constant that does not depend on the nature of the conductor. From this, in particular, it follows that good electrical conductors are also good thermal conductors.

The quantity $L_0 = 3k^2 e^{-2}$ is called the *semi-empirical Lorenz number*. A more rigorous analysis based on the quantum statistics of electrons provides a slightly different expression for the Lorenz number, although its numerical value does not change significantly:

$$L_0 = \frac{\lambda_T}{\gamma T} = \frac{\pi^2}{3} k^2 e^{-2} = 2,45 \cdot 10^{-8} B^2 K^{-2}. \quad (2.6)$$

For most metals, the experimental values of the Lorenz number at room temperature are in good agreement with the theoretical value. However, aside from the problems successfully explained from the viewpoint of classical electron theory of metals, certain discrepancies with experimental data have also emerged. In particular, classical theory failed to explain the small heat capacity of the electron gas.

The molar heat capacity of any solid body — which can be considered as a system of harmonically vibrating oscillators — is equal to $3R$ (where R is the universal gas constant). This result is known in physics as the Dulong–Petit law, which holds true for solids at high temperatures.

In metals, not only vibrating atoms but also free electrons should participate in the process of energy absorption. From this point of view, the heat capacity of a metal should be significantly greater than that of dielectrics, which contain no free electrons.

Assuming that the number of free electrons in a metal is equal to the number of atoms, and that the electrons behave as particles of an ideal gas with an average energy of $(3/2)kT$, we obtain the following expression (2.7) for the molar heat capacity of metals:

$$C = C_{\text{lattice}} + C_e = 3R + \frac{3}{2} k N_A = \frac{9}{2} R, \quad (2.7)$$

here, C_{lattice} denotes the heat capacity of the crystal lattice, and C_e represents the heat capacity of the electron gas.

However, in reality, the heat capacity of metals at high temperatures differs only slightly from that of crystalline dielectrics. This indicates that the electron gas does not, in practice, absorb significant heat when the metal conductor is heated — contradicting the predictions of classical electron theory.

The mentioned contradiction is one of the main, though not the only, criticisms against classical theory. In metals with high conductivity, the mean free path of electrons is approximately 10^2 to 10^3 angstroms under normal conditions, and significantly larger at low temperatures. When this value is compared to the interatomic distances in the crystal lattice (also measured in angstroms), it must be acknowledged that electrons can travel across hundreds of lattice periods without collision. These difficulties were successfully overcome with the help of the quantum theory of metals, developed by Soviet physicist Ya. I. Frenkel and German physicist Arnold Sommerfeld.

Temperature Dependence of the Specific Resistance of Metallic Conductors. It is known from physics that elementary particles, including electrons, exhibit wave-particle duality. Therefore, the motion of free electrons in a metal can be considered as the propagation of plane electron waves, whose wavelength is determined by the de Broglie relation:

$$\lambda = \frac{h}{m_0 u} = \frac{h}{\sqrt{2m_0 E_p}}. \quad (2.8)$$

Such plane electron waves can propagate in a perfectly periodic potential field without energy scattering (i.e., without attenuation). In other words, the ideal, defect-free crystal lattice of a solid does not cause scattering of the electron flow. This implies that in an ideal crystal, the mean free path of electrons tends to infinity, and the electrical resistance approaches zero. The fact that the resistance of pure, annealed metals approaches zero as the temperature approaches absolute zero confirms this idea. The free motion of an electron in an ideal crystal lattice has no classical mechanical analog. Scattering that leads to resistance arises when the regular structure of the lattice is disturbed or disordered in some way.

As previously noted, structural defects can be both dynamic and static, as well as atomic (point-like) or large-scale defects. It has been theoretically proven that effective wave scattering occurs when the size of the scattering centers (defects) exceeds one-fourth of the wavelength.

In metals, the energy of conduction electrons ranges from 3 to 15 eV, which corresponds to wavelengths of approximately 3 to 7 Å (see formula (2.8)). Therefore, any microscopic inhomogeneity in the structure impedes the propagation of electron waves and increases the specific resistance of the material.

In perfectly structured pure metals, the only factor limiting the mean free path of electrons is the thermal vibrations of atoms at the crystal lattice sites. The temperature-dependent component of the metal's specific resistance, caused by thermal effects, is denoted as ρ_T .

It is evident that as temperature increases, the amplitudes of atomic thermal vibrations and the associated fluctuations in the periodic crystal potential field also

increase. This, in turn, enhances the scattering of electrons and leads to an increase in specific resistance.

To qualitatively determine the character of the temperature dependence of specific resistance, we use the following simplified model: We assume that the scattering intensity is directly proportional to the cross-sectional area of the spherical volume occupied by a vibrating atom.

If the electron flow falls on a flat surface with area F_0 , then the probability S_0 of one electron being scattered by one vibrating center is given by the following expression:

$$F_0 = \frac{\pi \cdot \Delta a^2}{S_0},$$

here, Δa – is the amplitude of the thermal vibrations of atoms. As the electron beam penetrates to a depth L_0 , the probability of electron scattering increases proportionally with the number of atoms contained within the considered volume:

$$F_L = F_0 \cdot N \cdot S_0 \cdot L_0,$$

here, N denotes the number of atoms per unit volume of the scattering medium. The average free path length of electrons, l_T is inversely proportional to the probability of their scattering per unit path length F_1 , which gives the following expression:

$$\bar{l}_T = \frac{1}{F_l} = \frac{1}{F_0 N S_0} = \frac{1}{\pi \Delta a^2 N}. \quad (2.9)$$

The potential energy of an atom displaced by Δa from its lattice site is given by the following expression:

$$E_p = \frac{1}{2} k_0 \Delta a^2,$$

here, k_0 is the elastic force constant that tends to restore the atom to its equilibrium position. According to classical statistics, the average energy of a one-dimensional harmonic oscillator (i.e., a vibrating atom) is equal to kT .

On this basis, the following relation can be written:

$$\frac{1}{2} k_0 \Delta a^2 = kT. \quad (2.10)$$

Using formulas (2.9) and (2.10), it is easy to show that the mean free path of electrons is inversely proportional to the temperature:

$$\bar{l}_T = \frac{k_0}{2\pi N k T}. \quad (2.11)$$

It should be noted that the obtained relation does not hold at low temperatures. This is because, as the temperature decreases, not only the amplitude of atomic thermal vibrations decreases, but their vibration frequency may also decrease.

Therefore, in the low-temperature region, the scattering of electrons by thermal vibrations of the lattice atoms becomes ineffective. The interaction between an electron and a vibrating atom only causes a very slight change in the electron's momentum. In the theory of lattice vibrations, temperature is evaluated relative to a characteristic temperature known as the Debye temperature. The Debye temperature Θ_D determines the maximum frequency of thermal vibrations that can occur in the crystal:

$$\Theta_D = \frac{h\nu_{\max}}{k}.$$

This temperature depends on the strength of the interatomic bonds in the crystal lattice and is considered an important parameter of a solid.

By substituting (2.11) into the expression

$$\gamma = \frac{e^2 n \bar{l}}{m_n u_F}$$

we can conclude that when $T > \Theta_D$, the specific resistance of metals changes linearly with temperature:

$$\rho_T = \frac{1}{\gamma} = \frac{2\pi k m_n u_F}{e^2 k_0} T = BT, \quad (2.12)$$

here

$$B = \frac{2\pi k m_n u_F}{e^2 k_0}.$$

Experimental data show that the linear approximation of the temperature dependence $\rho_T(T)$ remains valid up to temperatures near $2/3\Theta_D$, with an error not exceeding 10%. For most metals, the characteristic Debye temperature lies between 400 and 450 K. Therefore, the linear approximation is generally valid at room temperature and above.

At low temperatures ($T \ll \Theta_D$), where the specific resistance decreases, theory predicts a power-law dependence $\rho_T \sim T^5$, which is related to the gradual suppression of new phonon vibration frequencies. This relation is known in physics as the Bloch–Grüneisen law. The temperature range in which this steep power-law dependence of $\rho_T(T)$ is observed is usually not very broad, and the experimental values of the exponent typically fall between 4 and 6.

A typical curve of the temperature dependence of the specific resistance of a metallic conductor is shown in Figure 2.1. In the narrow region I near absolute zero, some metals can transition into the superconducting state (this will be discussed in more detail later). In Figure 2.1, a sharp drop in specific resistance is observed at the critical temperature T_{sc} .

In perfectly structured pure metals, as the temperature approaches 0 K, the specific resistance tends to zero (see the dashed curve), and the mean free path of

electrons tends to infinity. Even at ordinary temperatures, the mean free path of electrons in metals is hundreds of times greater than the interatomic distances (see Table 2.1).

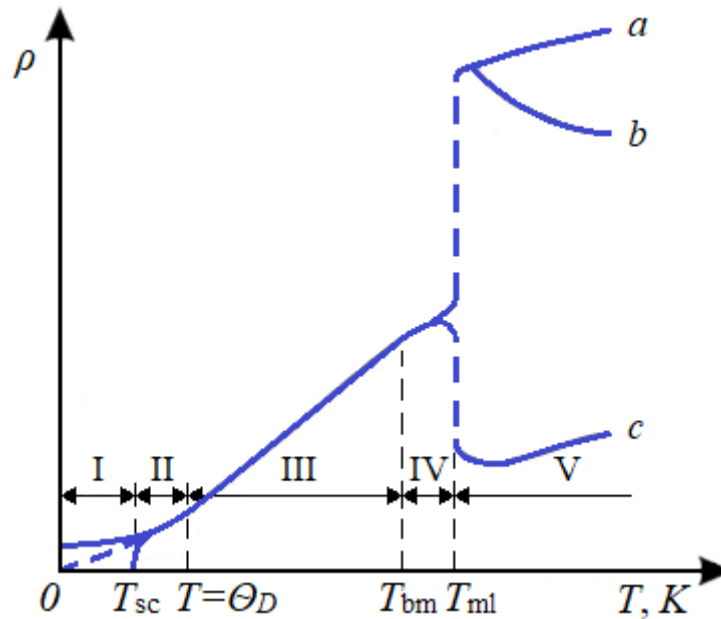


Fig. 2.1. Temperature dependence of the specific resistance of a metallic conductor over a wide temperature range: *a, b, c* – different variation patterns of specific resistance for various molten metals.

In region II, at the boundary of the transition zone, a rapid increase in the specific resistance ρ with temperature T is observed, where the exponent n can be as high as 5. However, with increasing temperature, n gradually decreases, and at $T=\Theta_D$ it approaches values close to 1.

The linear region of the temperature dependence $\rho(T)$ (region III) extends up to temperatures near the melting point for most metals. An exception to this behavior is found in ferromagnetic metals, where additional electron scattering occurs due to the disordering of spin alignment.

In region IV, near the melting point (marked by temperature T_{bm} in Figure 2.1), and for typical metals, deviation from linearity can occur. During the solid-to-liquid phase transition, the specific resistance of most metals increases by approximately 1.5 to 2 times. However, there are unusual cases as well: for example, in substances with complex crystal structures such as bismuth and gallium, the specific resistance decreases upon melting.

Experimental results reveal the following pattern: if the melting process is accompanied by an increase in volume, then a jump-like increase in specific resistance ρ is observed; Conversely, when melting is accompanied by volume contraction, the resistance decreases.

During melting, neither the number of free electrons nor the nature of their interaction with ions changes significantly. Instead, it is the disordering of atomic positions and the breakdown of long-range order that have a decisive effect on the change in ρ .

The anomalies observed in the properties of certain metals (such as Ga and Bi) can be explained by an increase in the bulk modulus upon melting, which should be accompanied by a decrease in the amplitude of atomic thermal vibrations.

Table 2.1

Mean Free Path of Electrons in Various Metals at 0 °C

metal	Li	Na	K	Ni	Cu	Ag	Au	Fe
$\bar{l} \cdot 10^{-10}, m$	110	350	370	133	420	570	410	220

The relative change in specific resistance when the temperature changes by one kelvin is called the temperature coefficient of specific resistance:

$$\alpha_{\rho} = \frac{1}{\rho} \frac{d\rho}{dT}. \quad (2.13)$$

A positive sign of α_{ρ} corresponds to a situation in which the specific resistance increases with rising temperature around a given point.

The coefficient α_{ρ} is also a function of temperature. In the region of linear dependence of $\rho(T)$, the following relation is valid:

$$\rho = \rho_0 [1 + \alpha_{\rho} (T - T_0)],$$

here:

- ρ – specific resistance at temperature T ,
- ρ_0 – specific resistance at reference temperature T_0 ,
- α_{ρ} – temperature coefficient of specific resistance, referenced to the starting point of the temperature range T_0 .

The total temperature coefficient can be written as:

$$\alpha_{\rho} = \alpha_R + \alpha_l,$$

where:

- α_R – temperature coefficient of the conductor's electrical resistance,
- α_l – temperature coefficient of the material's linear thermal expansion.

In pure metals, $\alpha_l \ll \alpha_{\rho}$, so it is commonly approximated that $\alpha_{\rho} \approx \alpha_R$. However, for thermally stable metallic alloys, such an approximation is not valid.

2.2. The Influence of Impurities and Other Structural Defects on the Electrical Resistivity of Metals. Electrical Properties of Metal Alloys

In metals, the scattering of electron waves is caused not only by the thermal vibrations of lattice atoms but also by static structural defects that disturb the

periodicity of the crystal potential field. Scattering on static defects is not temperature-dependent. Therefore, as the temperature approaches absolute zero, the resistivity of real metals tends to a constant value known as the residual resistivity (see Figure 2.1). This leads to the Matthiessen's rule of the additivity of resistivity:

$$\rho = \rho_T + \rho_{\text{res}}$$

where:

- ρ_T is the resistivity associated with electron scattering by thermal lattice vibrations,
- ρ_{res} is the residual resistivity associated with electron scattering by static structural defects.

This rule does not apply to superconducting metals whose resistance disappears below a certain critical temperature.

In real conductors, scattering on impurities — either unintentional contaminants or deliberately introduced alloying elements — makes a major contribution to residual resistivity. It should be emphasized that any impurity, even one with higher electrical conductivity than the base metal, increases ρ . For example, adding 0.01 parts of silver to a copper conductor increases its resistivity by $0.002\mu\Omega\cdot\text{m}$. Experiments show that at low impurity concentrations, the resistivity increases proportionally with the concentration of impurity atoms. This empirical regularity can be explained as follows: impurity scattering limits the free path of electrons, which in a real conductor is defined by the relation:

$$\frac{1}{\bar{l}} = \frac{1}{\bar{l}_T} + \frac{1}{\bar{l}_p}, \quad (2.14)$$

where the two terms $\bar{l}_T$ and $\bar{l}_p$ — represent scattering due to thermal vibrations and impurity atoms, respectively.

Assuming the impurity atom to be a sphere with cross-sectional area S_p , the free path limited only by impurity scattering can be written (similar to formula 2.9) as:

$$\frac{1}{\bar{l}_p} = N_p S_p,$$

where N_p is the number of impurity atoms per unit volume.

Considering both types of scattering, the total resistivity of the conductor is expressed as:

$$\rho = \frac{m_p u_F}{e^2 n \bar{l}} = \rho_T + \frac{m_p u_F}{e^2 n} N_p S_p. \quad (2.15)$$

Matthiessen's rule is illustrated in Figure 2.2. It shows that the temperature dependence of the specific resistivity of pure copper and its alloys (with up to ~4 atomic percent of indium, antimony, tin, and arsenic) follows parallel trends.

However, for alloys with transition metals, certain deviations from this rule are observed.

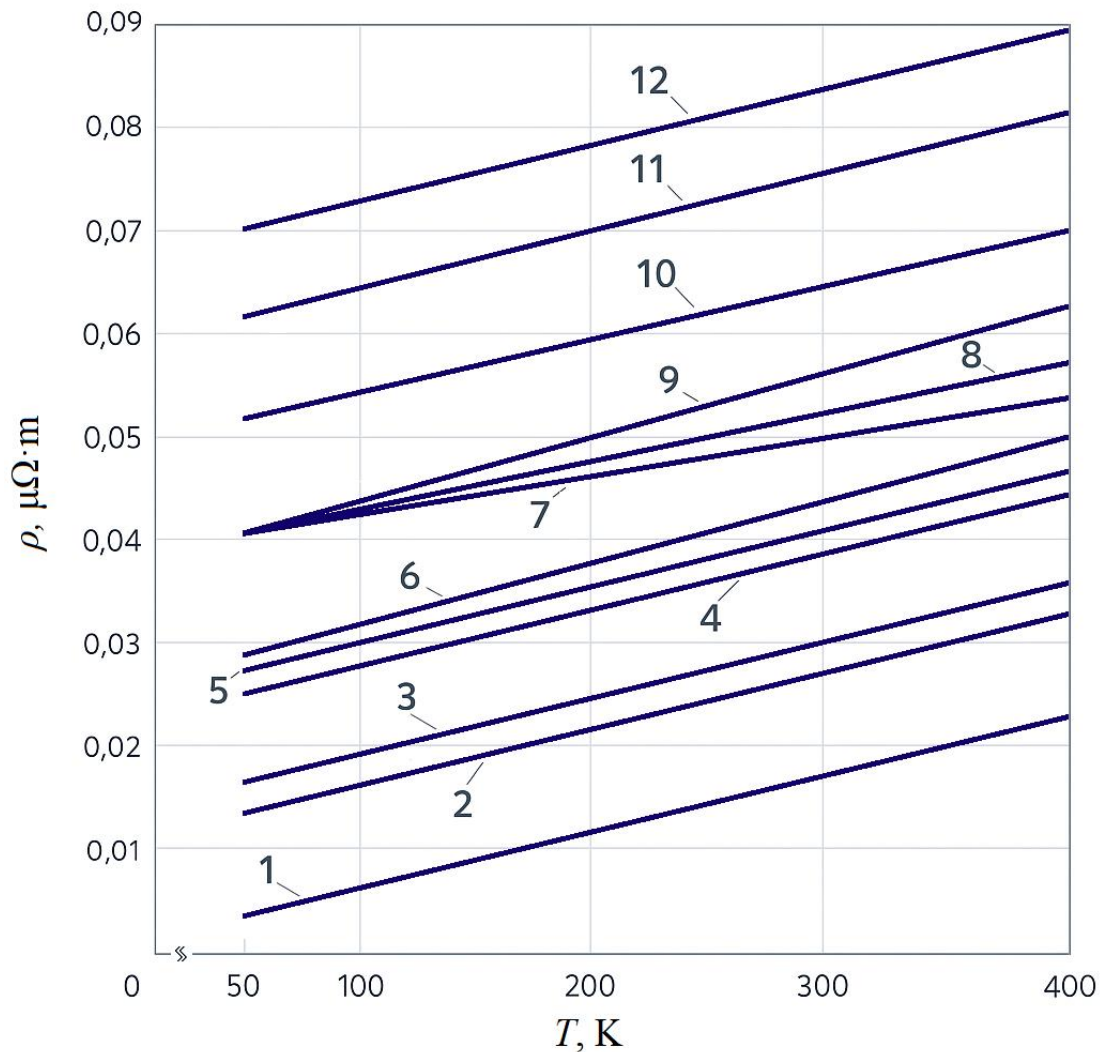


Fig. 2.2. Temperature dependence of the specific resistivity for solid solution type copper alloys:

1 — pure Cu; 2 — Cu–In (1.03 at.%); 3 — Cu–Ni (1.12 at.%); 4 — Cu–Sb (0.40 at.%); 5 — Cu–Sn (0.89 at.%); 6 — Cu–Ni (2.16 at.%); 7 — Cu–Mn (1.20 at.%); 8 — Cu–Fe (0.61 at.%); 9 — Cu–Ni (3.32 at.%); 10 — Cu–Fe (0.87 at.%); 11 — Cu–Sb (1.13 at.%); 12 — Cu–As (1.01 at.%)

One reason for deviations from Matthiessen's rule may be related to the effect of impurities on the elastic properties of the metal. These changes influence the vibrational spectrum of the crystal lattice. Different impurities affect the residual resistivity of metallic conductors to varying degrees. The efficiency of impurity scattering is determined by the disturbing potential in the lattice, which increases with the difference in valency between the impurity atom and the host metal atom.

In monovalent metals, the change in residual resistivity per 1 at. % impurity follows the empirical rule:

$$\Delta\rho_{qol} = a + b \cdot \Delta Z^2, \quad (2.16)$$

where:

- a and b are constants dependent on the nature of the metals and the period of the impurity element in the periodic table,
- ΔZ is the difference in valency between the host metal and the impurity atom.

This relationship is known in physics as the Linde rule. It suggests that metalloids typically have a stronger effect on reducing conductivity than metallic impurities. Experimental confirmation of this rule is illustrated in Figure 2.3.

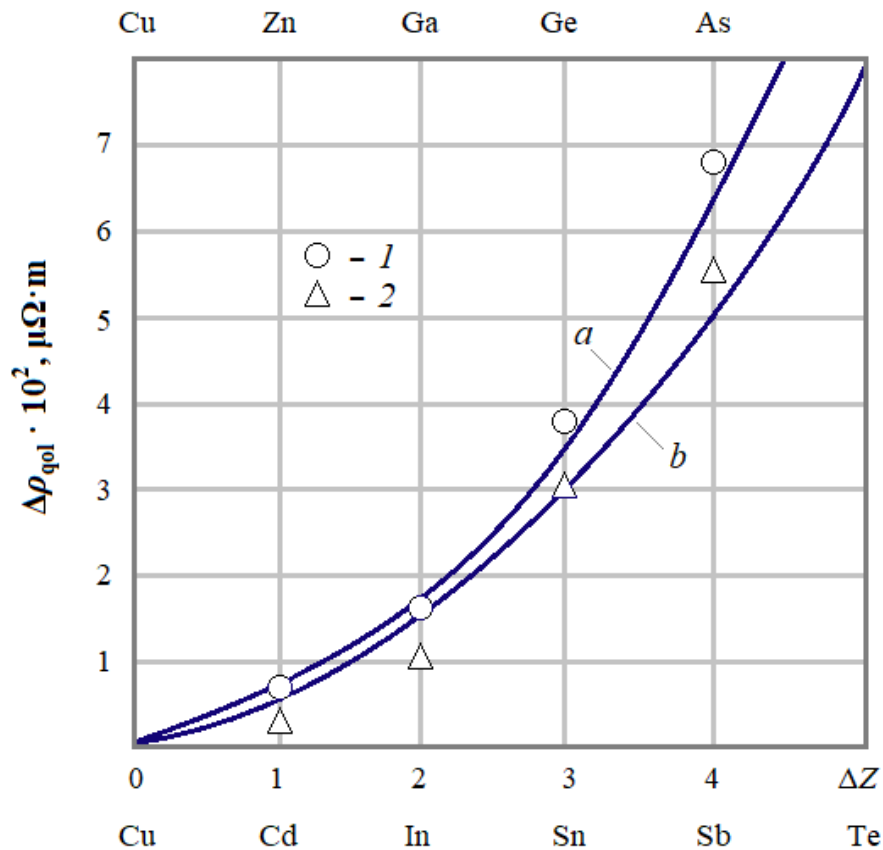


Fig. 2.3. Residual resistivity of copper at 1 atomic percent. Impurity concentration %: 1 – upper row of elements; 2 – lower row of elements.

$$a - \Delta\rho_{res} = 0,4\Delta Z^2; \quad b - \Delta\rho_{res} = 0,32\Delta Z^2.$$

In addition to impurity atoms, residual resistivity is also affected by structural point defects such as vacancies, dislocations, grain boundaries, and interstitials. The concentration of point defects increases exponentially with temperature and can reach high levels near the melting point. Moreover, exposure to high-energy particles (e.g., neutrons in a reactor or ions in an accelerator) can induce vacancies and interstitial atoms. By measuring the resulting resistivity, it is possible to evaluate the level of radiation damage to the crystal lattice. Likewise, this method can monitor the recovery (annealing) of irradiated samples.

For copper, the contribution to residual resistivity per 1 at. % of point defects is approximately:

- Vacancies: 0.010–0.015 $\mu\Omega\cdot\text{m}$
- Impurity atoms: 0.005–0.010 $\mu\Omega\cdot\text{m}$

The residual resistivity is an extremely sensitive indicator of both the chemical purity and the structural perfection of metals. In practice, when working with ultra-pure metals, the amount of impurities is evaluated by measuring the ratio of resistivity at room temperature to that at the temperature of liquid helium:

$$\beta = \frac{\rho_{300}}{\rho_{4,2}}.$$

The purer the metal, the greater the value of β . In modern ultra-pure metals (with a purity of 99.99999%), the β parameter can reach values on the order of 10^5 .

Mechanical stresses that because structural deformation have a significant effect on the specific resistivity of metals and alloys. However, the extent of this effect depends on the nature of the deformation.

For instance, hydrostatic compression tends to decrease the resistivity of most metals. This is due to the compression of atomic spacing and a reduction in the amplitude of thermal vibrations. In contrast, elastic tension or torsion increases interatomic distances, which increases electron scattering and hence resistivity. This effect can be quantified as:

$$\rho = \rho_0 (1 \pm \varphi \sigma), \quad (2.17)$$

where:

- φ is the coefficient of resistivity change with pressure,
- σ is the mechanical stress in the sample cross-section.

The “+” sign corresponds to tension, and the “–” sign corresponds to compression. The coefficient φ typically ranges from 1×10^{-11} to 5×10^{-11} .

Plastic deformation and densification (strain hardening) always increase the specific resistivity of metals and alloys. This is due to an increase in dislocation density and other structural defects. However, even in highly strained pure metals, the increase is usually only a few percent.

Thermal aging (stress relaxation) leads to an increase in ρ , which is associated with structural damage and the development of internal stresses. Through annealing, the material can undergo recrystallization, which restores resistivity to its original value, as defects are healed and internal stresses are eliminated.

Electrical Properties of Metal Alloys

In engineering applications, metal alloys with a random solid solution structure are widely used. When a solid solution is formed, the crystal lattice of the

solvent metal is preserved, although its periodicity may change slightly. Many metals with similar crystal structures can form continuous solid solution series.

However, there are also many binary metal systems in which components are only partially soluble or completely insoluble in the solid state. The random distribution of dissimilar atoms within the lattice nodes causes fluctuations in the periodic potential, leading to strong electron scattering.

As in pure metals, the total resistivity of a metal alloy can be expressed as:

$$\rho_{\text{alloy}} = \rho_T + \rho_{\text{res}}, \quad (2.18)$$

here, ρ_T refers to the resistivity associated with the scattering of electrons due to thermal vibrations of the lattice, and ρ_{res} (residual resistivity) is the additional resistance caused by the scattering of electrons at inhomogeneous regions in the alloy structure.

A distinctive feature of solid solutions is that the increase (in resistivity) can significantly (by multiple times) exceed the thermal component of the resistivity.

For many binary alloys, the variation of resistivity with composition is well characterized by a parabolic relationship.

$$\rho_{\text{alloy}} = Cx_Ax_B = Cx_B(1-x_B), \quad (2.19)$$

where:

- C is a constant depending on the nature of the alloy,
- x_A, x_B are the atomic fractions of components A and B, respectively.

This relationship is known as the Nordheim rule. According to this law, in A–B binary solid solutions, the residual resistivity increases regardless of whether A atoms are added to B or vice versa. The graph of this relationship forms a symmetric curve, peaking when the components are present in equal amounts ($x_A = x_B = 0.5$).

In a continuous series of solid solutions, the farther the composition is from the pure components, the higher the residual resistivity becomes. The maximum value of resistivity is reached at 50/50 atomic composition.

The Nordheim rule holds well as long as no phase transitions occur with changing composition and neither component is a rare-earth or transitional element. Examples of systems that obey this rule include: Au–Ag, Si–Ag, Si–Au, W–Mo, and others.

In contrast, solid solutions composed of intermediate group metals may behave differently (see Figure 2.4). In such cases, at high concentrations, a significantly larger residual resistivity is observed. This phenomenon is attributed to the transfer of conduction electrons into the unfilled inner d -orbitals of intermediate metal atoms. Moreover, the maximum resistivity ρ often occurs at compositions not equal to 50%, but rather at offset values.

A key trend in such alloys is that the higher the residual resistivity, the lower the temperature coefficient of resistivity α_p . This is because $\rho_{\text{res}} \gg \rho_T$ and thus dominates the temperature behavior.

The temperature coefficient can be expressed approximately as:

$$\alpha_{\rho}^{\text{qot}} = \frac{1}{\rho_{\text{qot}}} \frac{d\rho_{\text{qot}}}{dT} = \frac{1}{\rho_{\text{qol}} + \rho_T} \frac{d\rho_T}{dT}. \quad (2.20)$$

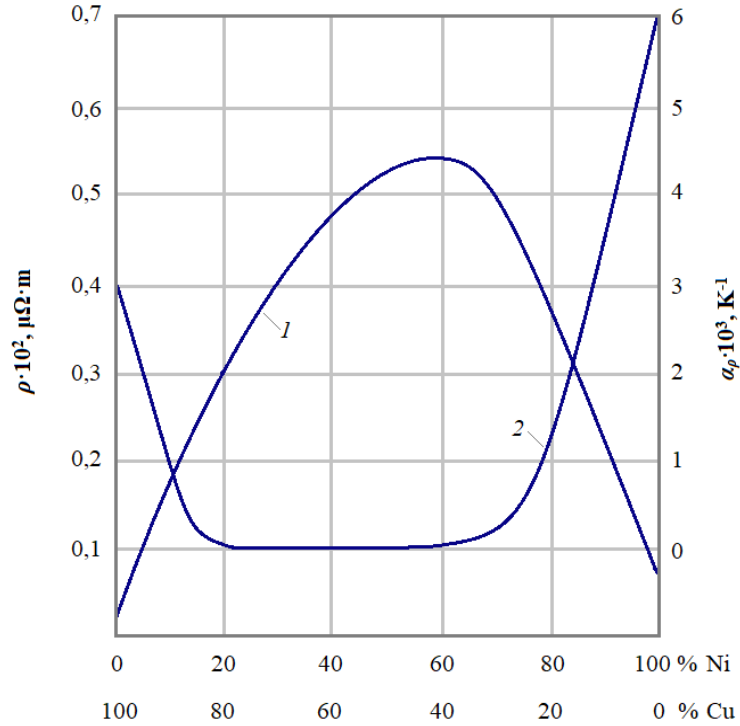


Fig. 2.4. Dependence of the specific resistivity (1) and the temperature coefficient of specific resistivity (2) of copper-nickel alloys on the composition of components.

Since the α_R values of pure metals are generally similar, equation (2.20) simplifies to:

$$\alpha_{\rho}^{\text{qot}} = \frac{1}{1 + \frac{\rho_{\text{qol}}}{\rho_T}} \frac{1}{\rho_T} \frac{d\rho_T}{dT} \approx \frac{\alpha_{\rho}^{\text{met}}}{1 + \frac{\rho_{\text{qol}}}{\rho_T}}. \quad (2.21)$$

In concentrated solid solutions, the residual resistivity ρ_{res} is often one order of magnitude — or more — greater than the thermal component ρ_T . Consequently, the overall temperature coefficient α_p can be significantly lower than that of pure metals. This is the principle behind the design of thermostatic conducting materials.

In many cases, the temperature dependence of the specific resistivity in alloys is more complex than the simple additive relationship in equation (2.18). The actual temperature coefficient α_p of alloys can be much smaller than predicted by Equation (2.21). These anomalies are most clearly observed in copper-nickel alloys (see Figure 2.4).

In certain alloys, for specific compositional ratios, the temperature coefficient α_p may even become negative. Such behavior indicates that these complex alloys should not be considered classical metals, as their conductivity depends not only on the electron free path but also on other factors.

For example, in some cases, as temperature increases, the carrier concentration behind the Fermi level may also increase, which compensates for the reduction in mean free path. In such alloys, the temperature coefficient of resistivity may approach zero — a very useful property for precision resistors and thermal compensation applications.

In dilute solutions, where one component (say, B) is present in very low concentrations and acts as an impurity, equation (2.19) can be simplified. Assuming $(1-x_B) \approx 1$, we obtain a linear relationship between residual resistivity and impurity concentration:

$$\rho_{qol} = C \cdot x_B,$$

here, the constant C represents the increment in residual resistivity per 1 atomic percent of impurity.

Electrical Properties of Two-Phase Alloys

In binary systems where the components are completely insoluble in the solid state, the solidified alloy structure consists of a mixture of two phases. In such heterogeneous alloys, the resistivity changes linearly with composition as a first approximation — it increases proportionally with the content of the higher-resistance metal.

However, because the electrical properties of non-uniform materials are highly sensitive to structure, significant deviations from simple additivity can occur. These deviations depend on:

- Particle size
- Particle shape
- Distribution of phases within the matrix

For example, if one phase forms a continuous matrix, and the second phase exists as dispersed, non-contacting inclusions, then the effective conductivity of the mixture should be calculated using the following relation:

$$\gamma = \frac{1}{\rho} = \gamma_0 \frac{\Theta_v}{\frac{1-\Theta_v}{3} + \frac{\gamma_0}{\gamma_1 - \gamma_0}},$$

where:

- γ_0 is the conductivity of the matrix phase
- γ_1 is the conductivity of the inclusion phase
- Θ_v is the volume fraction of the inclusions

Chapter Review Questions

1. What is an electrical conductor?
2. Into what types are conductive materials divided?
3. How are materials classified according to their ability to conduct electric current?
4. Why do metal atoms conduct electricity well?
5. What are the main industrial applications of conductive materials?
6. What are the differences between conductors and semiconductors?
7. How can the conductivity of metal and graphite be compared?
8. What are free electrons in metals?
9. Through which particles is electrical conductivity in metals achieved?
10. How is the electrical conductivity of metals explained on a quantum-mechanical basis?
11. How does the Drude model explain electrical conductivity?
12. What is the difference between the free-electron theory and the quantum model?
13. Compare the conductivity properties of copper and iron.
14. How does the electrical resistance of metals change with increasing temperature?
15. Under what conditions does the conductivity of a metal decrease?
16. How does an increase in temperature affect the lattice vibrations of a metal?
17. Why does the motion of electrons slow down as temperature rises?
18. Compare the temperature-dependent conductivity of a superconductor and an ordinary metal.
19. In which metals is the sensitivity to temperature low?
20. What role do impurities play in the structure of metals?
21. Into what types are structural defects classified?
22. How do impurities interfere with the passage of electric current?
23. How do dislocations and grain boundaries affect electrical conductivity?
24. Compare the electrical properties of pure metals and alloyed metals.
25. Compare a perfect crystal structure with a defective metal structure.
26. What is meant by metallic alloys?
27. What well-known electrical alloys do you know?
28. How is the conductivity of alloys determined?
29. In what cases does an alloy have lower conductivity than a pure metal?
30. Compare the conductivity of nichrome and copper.
31. Compare alloys and pure metals in terms of their electrical properties.

CHAPTER 3. MAIN PROPERTIES AND APPLICATIONS OF CONDUCTIVE MATERIALS

The progress of modern engineering and technology is unimaginable without high-quality conductive materials that ensure the transmission, distribution, and efficient use of electrical energy. The rapid development of electrical and electronic industries, the emergence of new-generation information systems, energy-saving technologies, and quantum devices require an in-depth study of the properties of conductive materials and their purposeful improvement. Therefore, the scientific analysis of the physical, chemical, and structural characteristics of conductive materials, along with their areas of application, is one of today's most pressing issues.

Conductive materials are substances that allow the flow of electric current. Their electrical conductivity depends on the number of free electrons in the crystal lattice and the degree of their mobility. Metals with high electrical conductivity — such as copper, silver, gold, and aluminum — are used in almost all fields of electrical engineering. At the same time, superconducting materials, whose conductivity can change dramatically under the influence of temperature, magnetic field, pressure, and other external factors, play a special role in modern physics and technology. Their resistance becomes absolutely zero, and their ability to completely expel a magnetic field (the Meissner effect) allows for wide applications in high-efficiency energy systems, magnetic levitation, medical tomography, and quantum computing technologies.

In recent decades, various carbon modifications — graphite, fullerenes, nanotubes, graphene, and their derivatives — have opened a new chapter in the chemistry of conductive materials. Due to their unique electrical, mechanical, and thermal properties, these modifications are used in nanocomposite materials, sensors, electrochemical energy sources, high-frequency electronics, and supercapacitors. In particular, the π -electron systems in fullerenes and fullerides enable their use as semiconductors, metals, or superconductors.

In addition, composite and oxide conductive materials — with their complex phase structures — are created on metallic, ceramic, or polymer bases. These materials provide stable electrical conductivity while offering mechanical strength, corrosion resistance, and favorable dielectric properties. Such materials are widely applied in aerospace, nuclear energy, electronics, and micro- and nanoelectronic devices.

This chapter provides a detailed analysis of the classification of conductive materials, the nature of their conductivity, their physical, mechanical, and thermal properties, as well as the scientific and technical foundations and practical

applications of advanced types of conductive materials — including highly conductive, superconducting, composite, and carbon-based materials.

3.1. Classification of Conductive Materials. High-Conductivity Materials, Superconducting Metals and Alloys

Currently, there is no universally accepted classification of conductive materials. In physics, chemistry, and engineering, conductive materials are classified based on different criteria. A possible scheme based on composition, properties, and technical applications of conductors is presented in Figure 3.1.

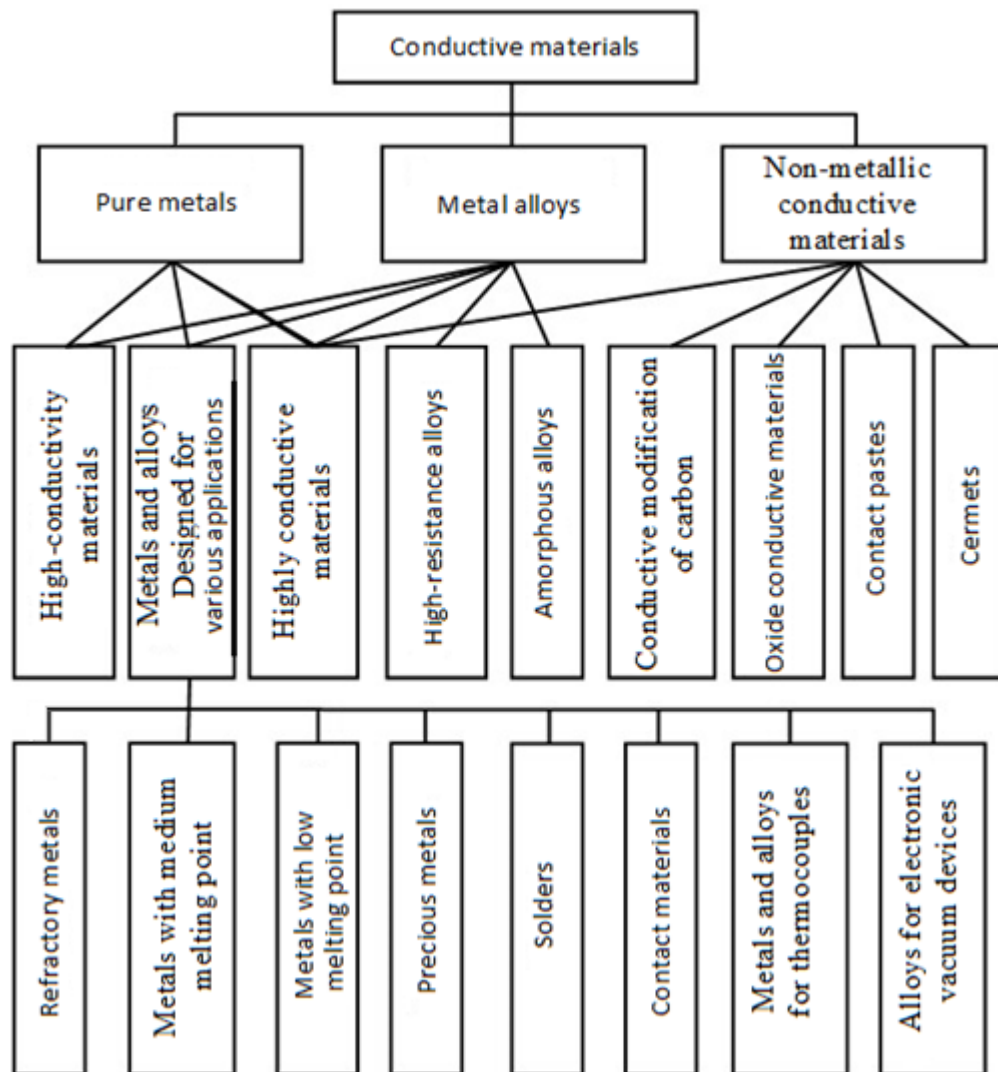


Fig. 3.1. Classification of Conductive Materials.

As shown in the classification scheme, all conductive materials are divided into metals and non-metals according to their chemical composition. In terms of specific resistivity, metal alloys are positioned between pure metals and non-metallic conductive media. Among metals and alloys, materials are distinguished for general and special purposes.

Materials for general purposes include:

- High-conductivity metals
- Alloys with high electrical resistance

In electronics, specific applications are served by:

- Refractory metals
- Electrovacuum alloys
- Soldering and contact materials
- Ordered magnetic metals
- Alloys for thermocouples

Superconductors represent a distinct group of materials that exhibit anomalous electrical behavior at low temperatures. Not only metals and alloys, but also a wide range of oxide compounds can transition into a superconducting state. Under normal conditions, some oxide compounds, which are otherwise good conductors of electricity, can retain superconducting properties at temperatures significantly higher than the boiling point of liquid nitrogen, a widely used coolant.

High-Conductivity Materials

This group includes materials with specific electrical resistivity of no more than $0.1 \mu\Omega \cdot \text{m}$ under normal conditions. Among these, the most widely used materials are copper and aluminum.

Advantages of Copper as a Conductive Material

Copper is widely used as a conductive material due to the following advantages:

- Low specific electrical resistivity (among metals, only silver has slightly lower resistivity than copper);
- Sufficiently high mechanical strength;
- Good corrosion resistance in most environments — even in high humidity conditions, copper oxidizes more slowly in air than iron. Significant oxidation of copper occurs only at elevated temperatures (see Figure 3.2);
- Excellent workability — copper can be processed into sheets, strips, and wires, with thicknesses reduced to fractions of a millimeter;
- Relatively easy to solder and braze.

Copper Production

Copper is extracted from sulfide ores, which are commonly found in nature. For electrical engineering purposes, the ore undergoes intensive roasting, followed by several stages of smelting and heating, and then undergoes electrolytic purification.

After electrolysis, the copper cathode plates obtained weigh 80–90 kg, depending on the production method. The copper may be hard or soft.

Soft copper is produced by annealing, i.e., heating the metal to several hundred degrees Celsius followed by slow cooling. Compared to hard copper, soft copper is more flexible and has lower electrical resistance.

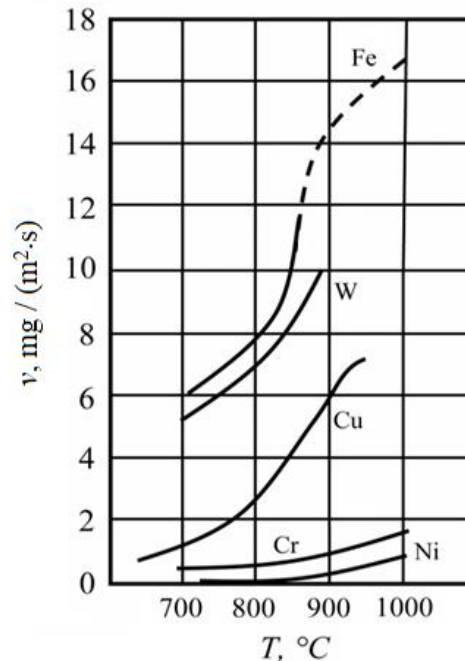


Fig. 3.2. Temperature dependence of oxidation rate for iron, tungsten, copper, nickel, and chromium (in air).

Oxygen-Free Copper and Its Alloys in Electrical and Electronic Engineering

In electrovacuum technology, oxygen-free types of copper are used. Oxygen in copper is considered one of the most harmful impurities, as it degrades mechanical properties and makes brazing difficult. The purest copper is obtained by melting in a vacuum under low residual gas pressure, which prevents oxygen from entering the metal. In electrical engineering, copper is used for manufacturing conductors, cables, transformer and electric motor windings, as well as foiled getinax and textolite. In microelectronics, copper is applied as deposited layers on substrates in the production of hybrid microcircuits. As structural materials, copper-based alloys such as brass and bronze are widely used.

Brass

Brass is an alloy of copper and zinc. Zinc improves the mechanical properties of copper and reduces its cost. Brass is corrosion-resistant in atmospheric, potable, and seawater environments, but only if it does not come into contact with steel.

Brass:

- Is well deformable
- Is easily machined by cutting
- Can be brazed and spot welded

- Wears out quickly under dry friction

To obtain specific properties, additional elements such as aluminum, iron, silicon, manganese, nickel, tin, and lead are added.

Brass is used for:

- Bushings, washers, tool frames, and fasteners
- Springs and components operating at 80–100°C

Bronze

Bronze is an alloy of copper with elements like tin, phosphorus, aluminum, manganese, and others. Many types of bronze combine:

- High mechanical strength
- High electrical and thermal conductivity (e.g., beryllium, cadmium, silicon-manganese, chromium bronzes)

Bronzes with tin, aluminum, and silicon (with other alloying elements) are used as structural, non-magnetic, corrosion-resistant materials.

They are:

- Easily welded and brazed
- Have good antifriction properties
- Used in fittings, springs, contacts, and holders

Aluminum

Aluminum is more abundant in nature than copper and therefore cheaper. Its specific resistivity is 1.6 times higher than copper's, but it is 3.5 times lighter.

Drawbacks of aluminum include:

- Low mechanical strength
- Difficult brazing and welding

The surface of aluminum oxidizes actively, forming a layer of Al_2O_3 , which — unlike copper oxide — is a good dielectric, strong, and heat-resistant.

Aluminum is widely used in electrical engineering for:

- Conductors
- Electrolytic capacitors

In microelectronics, it is used to create contacts and interconnections in integrated circuits.

High-Resistance Alloys

These are conductive materials with specific resistivity of not less than $0.3 \mu\Omega \cdot \text{m}$. They are used for manufacturing:

- Electrical measuring instruments
- Resistors
- Electric heating devices

Each application has different material requirements.

For example:

- In heating devices, the conductor must operate at temperatures around 1000°C for extended periods.
- In measuring devices and resistors, a low temperature coefficient of resistivity (α_p) and a low thermoelectric EMF relative to copper are important.

The most commonly used alloys for these purposes include:

- Manganin (86% Cu, 12% Mn, 2% Ni)
- Constantan (60% Cu, 40% Ni)
- Nichrome (various compositions of nickel and chromium)

Table 3.1

Main Properties of High-Resistance Alloys

Alloy	ρ (Resistivity), $\mu\Omega \cdot m$	Temperature Coefficient of Resistivity ($\alpha_p \times 10^{-6}$ K^{-1})	Thermo-EMF relative to copper, $\mu V/K$	Operating Temperature, $^{\circ}C$
Manganin	0.42-0.48	5 – 30	1 – 2	Up to 100
Constantan	0.48-0.52	–(5 – 25)	40 – 50	Up to 450
Nichrome	1.0	~ 100	–	Up to 1000

Alloys and Solders for Thermocouples

Alloys used for thermocouples are intended for temperature measurement. The most widely used thermocouple alloys include:

- Chromel (90% Ni, 10% Cr)
- Copel (56% Cu, 44% Ni)
- Alumel (95% Ni with additions of Al, Si, Mn)
- Platinum-rhodium (90% Pt, 10% Rh)
- Constantan (60% Cu, 40% Ni)

Materials for thermocouples are selected based on their ability to provide a maximum thermoelectric EMF (thermo-EMF) and the required temperature measurement range.

Thermocouples made of platinum–platinum-rhodium (Pt-Rh) alloys provide the highest stability, excellent workability, and are suitable for wide temperature ranges up to 1600°C.

The maximum specific thermo-EMF is found in chromel–copel (CH-C) pairs (see Figure 3.3).

Solders

Solders are special alloys used for soldering, which is the process of forming mechanical or electrical contact between parts. During soldering, the joint is heated, the solder melts and flows, filling the gaps between the joined parts.

Solders are classified into:

- Soft solders (melting point up to 300°C)
- Hard solders (melting point above 300°C)

Soft solders include tin-lead solders (Sn-Pb). Hard solders include:

- Copper-zinc solders (Cu-Zn)
- Silver-based solders (Ag-based)

In addition to solders, fluxes are used in the soldering process. The functions of fluxes are to:

- Remove oxides and contaminants from the surface of the parts to be joined
- Improve solder flow over the surface
- Protect the molten solder from oxidation

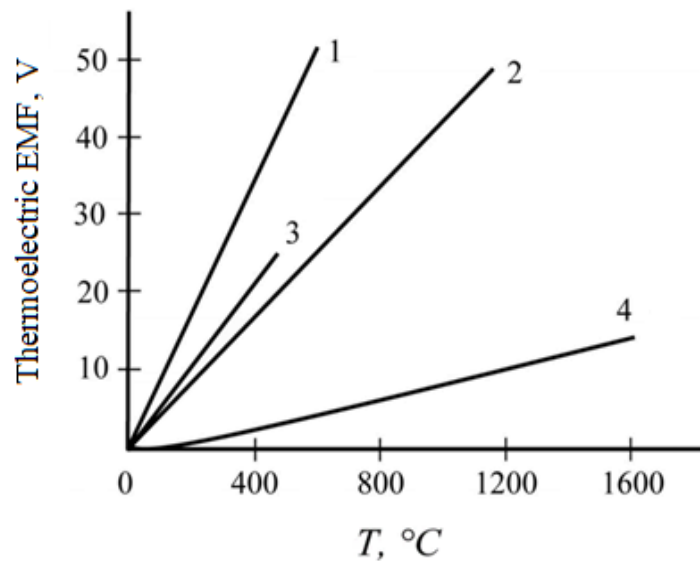


Fig. 3.3. Dependence of thermoelectric EMF on the temperature difference at thermocouple junctions: 1 – Chromel–Copel, 2 – Copper–Constantan, 3 – Chromel–Alumel, 4 – Platinum–Platinum-Rhodium.

Refractory Metals

Refractory metals are those with a melting point above 1700°C. The main refractory metals include tungsten, molybdenum, tantalum, niobium, chromium, vanadium, titanium, zirconium, and rhenium.

All refractory metals remain chemically active at elevated temperatures and tend to oxidize rapidly, forming instantaneous chemical bonds. Therefore, they are typically used only in vacuum or protected atmospheres, especially for heating elements. One example is evaporators, used in vacuum systems for depositing thin films.

Refractory metals are generally produced by powder metallurgy methods, including pressing powders followed by sintering.

Among all metals, tungsten has the highest melting point (3400°C). It is a gray, heavy, and hard metal with a fine-grained structure, high internal crystal

strength, and weak intergranular bonding. To improve the properties of pure tungsten, various additives such as thorium, silicon, and aluminum oxides are introduced.

Tungsten is one of the most important materials in electrovacuum technology, used in electrodes and heating elements of electron tubes.

Molybdenum has similar appearance and properties to tungsten but is more ductile, making it easier to machine into complex components.

Tantalum is a rare and expensive metal due to its low natural abundance. It has good ductility and shape stability, making it suitable for electrovacuum device components, similar to molybdenum.

Tantalum is especially important for capacitor manufacturing, as its surface can readily form a layer of Ta_2O_5 , a dense dielectric with high permittivity ($\epsilon \approx 25$). Tantalum nitride (Ta_2N) is used in the fabrication of thin-film resistors.

Chromium is highly resistant to oxidation, even at elevated temperatures, making it ideal for protective coatings. In microelectronics, thin chromium layers are used in thin-film resistors and as adhesion layers to improve bonding between substrates and other layers.

Chromium is also widely used in:

- Heating devices
- Thermocouples
- Stainless steels
- Magnetic material alloys

Medium-Melting-Point Metals

Among medium-melting-point metals, iron, nickel, and cobalt are the most commonly used in electronic technology.

These metals are ferromagnetic, meaning they can become magnetized under an external magnetic field. As a result, a distinctive feature of these metals is their nonlinear temperature dependence of specific resistivity.

This is explained by the alignment of magnetic moments of atoms at higher temperatures. Any disorder in the crystal structure, as described by quantum mechanics, leads to an increase in specific resistivity.

According to Matthiessen's Rule, different scattering mechanisms contribute additively to the total electrical resistivity:

$$\rho_{\text{total}} = \rho_{\text{thermal}} + \rho_{\text{defect}} + \rho_{\text{magnetic}}.$$

In this context:

- ρ_{th} and ρ_{imp} represent the components of resistivity due to thermal lattice vibrations and electron scattering by impurities, respectively.
- ρ_{m} is the magnetic contribution to electrical resistivity, caused by disorder in the orientation of atomic magnetic moments.

Above the Curie temperature (T_k), ρ_m remains constant, and thus the temperature dependence of specific resistivity becomes linear in character (see Figure 3.4).

The specific resistivity of iron depends on the composition of its alloys. Among the alloying elements, silicon has the most significant effect. It is added during the production of electrotechnical steels to increase specific resistivity, thereby reducing eddy current losses compared to pure iron.

Due to iron and steel's high magnetic permeability (μ), the skin effect becomes significant — at high frequencies, the current density near the surface of a conductor is much greater than that in its interior.

Nickel is a silver-white metal widely used as a structural component in electrovacuum devices. It is easily machinable and chemically stable.

An alloy based on iron, nickel, and cobalt known as Covar is commonly used. Covar has a very low coefficient of linear expansion, making it suitable for soldering to glass, serving as a replacement for tungsten and molybdenum.

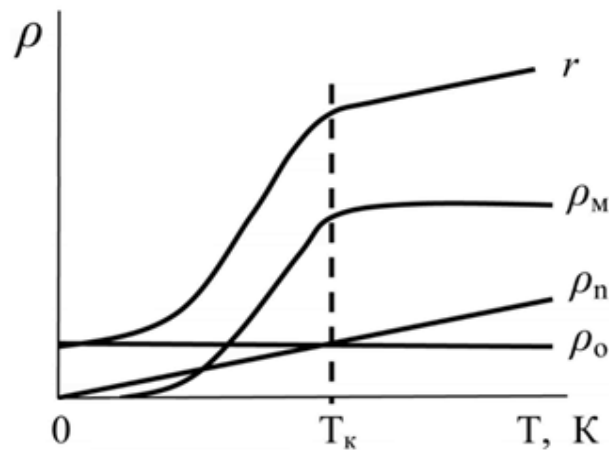


Fig. 3.4. Temperature dependence of the specific resistivity of ferromagnetic materials.

Nonmetallic Conductive Materials

In addition to metals and metallic alloys, various composite materials and conductive modifications of carbon are used as resistors, contacts, and current-carrying elements. Common carbon-based materials include graphite, soot, pyrolytic carbon, and anthracite.

These materials are used to produce:

- Brushes for electric motors
- Electrodes for projectors
- Electrodes for arc furnaces

To form the final products, ground powder is mixed with a binder (e.g., coal tar pitch or liquid glass), pressed into molds, and then heat-treated at high temperatures to soften and consolidate the structure.

To reduce the electrical resistance of carbon-based materials, metal powder additives may be introduced.

Carbon powder is used in the production of high-resistance resistors, and in microphones to generate pressure-dependent variable resistance.

Graphite is the most widely used in electrical engineering due to its:

- High chemical and thermal stability (melting point around 3900°C)
- Ease of machining

It is used to manufacture various heating elements, crucibles, and other components. Graphite is a semiconductor, and its specific resistivity decreases with increasing temperature (see Figure 3.5).

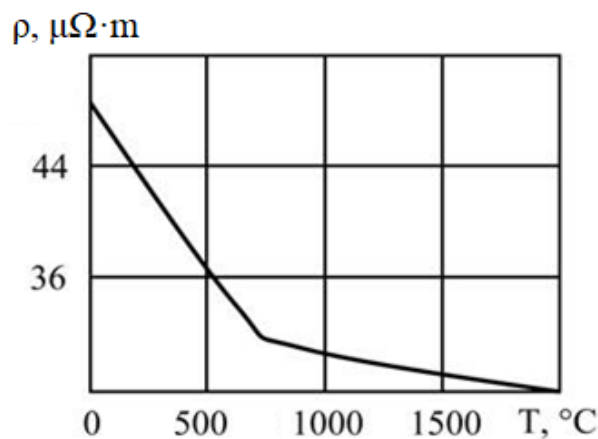


Fig. 3.5. Temperature dependence of the specific resistivity of carbon (coal).

Composite Conductive Materials

Composite conductive materials are mechanical mixtures of a conductive filler and a dielectric binder. The electrical properties of these materials can be adjusted by modifying the composition of the components.

Typical conductive phase components include:

- Metals
- Graphite
- Soot

The binder can be organic or inorganic dielectrics, such as glass or synthetic resins.

Conductive Polymers and Oxides

Contact pastes — electrically conductive adhesives and paints based on organic resins — are used to create electrical contacts between metals, or between metals and semiconductors, and to form electrodes on dielectric surfaces, among other applications.

Cermets

Cermets are composite materials with inorganic binders, often based on glass or silicon monoxide (SiO). They are designed for use in thin-film resistors.

The resistance of such resistors depends on:

- The percentage of the conductive component
- The thermal processing conditions during manufacturing

As the conductive phase, fine-dispersed chromium powder or chromium disilicide (CrSi_2) is typically used.

To reduce the electrical resistance of carbon-based materials, metal powder additives are applied.

Conductive Oxides

While most metal oxides are dielectric, under partial oxidation, some can exhibit significant electrical conductivity. Notable examples include:

- Tin dioxide (SnO_2)
- Indium oxide (In_2O_3)

Their specific resistivity depends on the degree of deviation from stoichiometric composition and can reach as low as $10 \mu\Omega \cdot \text{m}$.

The combination of high optical transparency and enhanced electrical conductivity allows these oxides to be used in:

- Transparent conductive coatings on the inner walls of glass electrovacuum devices
- Liquid crystal displays (LCDs)
- Image intensifier electrodes
- And other optoelectronic applications.

3.2. Fullerenes, fullerides, graphite, and other modifications of carbon.

Composite and oxide conductive materials

Fullerenes are artificially obtained carbon-like modifications, its clusters, and spatial materials with a multi-faceted structure. In 1985, American scientist H.Kroto, in collaboration with his colleagues, discovered a beautiful spatial 32-faceted C_{60} molecule by evaporating graphite with the help of a laser. The molecular weight of C_{60} is 720.669, and its density is $2.5\text{--}3.0 \text{ g/cm}^3$. The authors proposed the name fullerene for this new carbon cluster (C_{60}) in honor of their compatriot, architect, engineer, and inventor R. B. Fuller. This name was suggested because the structure of the new substance resembled an enlarged model of the geodesic dome used as a pavilion in the 1967 World Expo in Montreal, similar in appearance to a soccer ball.

Soon after, it was discovered that carbon clusters exist in the spectra of stars, meteorites, cosmic particles, and even in common soot. In 1988, several representatives of carbon clusters — C_{28} , C_{32} , C_{50} , and C_{70} — were synthesized. In 1990, the crystalline forms of fullerene were obtained and named fullerites. When various elements, including alkali metals, were introduced into fullerites, substances

with unique properties called fullerides were synthesized. For example, K_3C_{60} demonstrated superconductivity at 18 K. The C_{60} structure consists of 20 hexagons, 12 regular pentagons, and has 32 faces, and can withstand temperatures up to 1000°C.

Fullerenes are materials with a bright future. They can be used as construction materials in chemical industries, mechanical engineering, shipbuilding, aviation, underground structures, buildings, and the construction of spherical and geodesic domes.

Production of Carbon-Based Fullerenes and Powders

Nowadays, powder metallurgy and the devices created on its basis are being developed extensively. Using solid carbon, powder production methods based on reduction processes can generally be divided into two main groups:

- Dispersion method – obtaining powders by grinding materials. This is the simplest method of powder production, where the material is ground into powder form.
- Condensation method – obtaining powders by “growing” atoms during the synthesis process. This method involves forming powders by combining individual atoms.

Both methods play an important role in studying the physical properties of powders. According to the definition of condensation, it is the transition of a substance from a gaseous state to a condensed (solid or liquid) state through cooling. Various physical phenomena occur during this process. Based on this method, the initial materials are first evaporated, then the resulting vapor condenses until powders of the required size are formed. As a result, the compact material transforms into an ultradispersed substance.

All powder production methods require a strong energy flow from an external source. As the system cools, particles begin to form and grow. These particles arrange and merge into granules. In the study of powder physics, this process continues until the system regenerates its initial monocrystal. When the number of powder particles in the vapor increases significantly and their size reaches about 100 nm, the system is said to be in a nanostate. When the system reaches equilibrium, the particles transition into powder form.

Today, methods for producing carbon-based powder materials with various sizes and properties have been developed. According to the technology, carbon powders and fullerenes are obtained through chemical transformations of carbon materials at high temperatures.

Scientists Methods for Obtaining Fullerenes and Powders

Scientists have proposed a method based on creating an electric discharge between graphite electrodes in a chamber filled with inert gas, where gas atoms are

ionized. At high temperatures in the chamber, the surface of graphite evaporates. When the evaporated carbon atoms move from the hot region of the plasma to a cooler region, they suddenly cool and settle on the chamber walls and the cathode surface. It has been found that such structures consist of fullerenes and powders. A portion of the material — graphite, soot, and fullerenes — settles on the cool walls of the chamber, while graphite and powders accumulate on the cathode.

In addition, there is also a laser-based method. In this method, graphite is evaporated using a laser and then condenses on a cooled collector. The graphite is placed in a special quartz powder furnace. The products formed from the thermal vaporization of graphite are carried from the hot zone and deposit on the surface of the cooled collector. The resulting deposit contains not only graphite powders but also fullerenes and fine powders.

The main advantage of this method is that the characteristics of the powders obtained are highly sensitive to the parameters of the laser radiation. Specifically, the diameter of the powder particles depends on the power of the laser beam. This makes it possible to obtain powders with a predefined and desired structure. However, a drawback of this method is its relatively low productivity and the difficulty of applying it on a large scale.

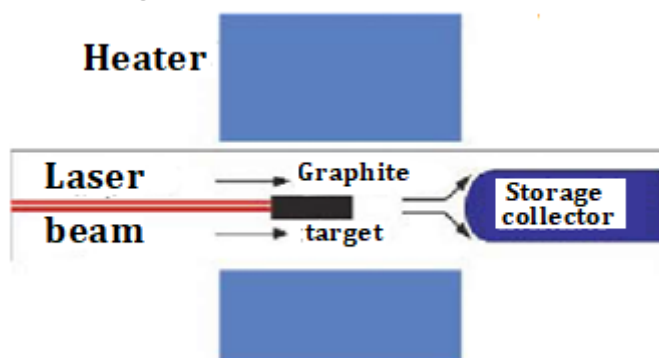


Fig. 3.6. Schematic diagram of a device for obtaining powder from solid carbon using the laser evaporation method.

The products formed from the thermal vaporization of graphite are carried away from the hot zone and settle on the surface of a cooled collector. The resulting deposit may contain not only graphite powders but also fullerenes and other particles. The great benefit of this method is the sensitivity of the powder characteristics to laser radiation parameters. In particular, powder size depends on laser beam power, allowing for the production of powders with desired structural features.

The disadvantage of the method is its relatively low productivity and the difficulty of applying it on a large scale.

- There is also a method of chemical vapor deposition (CVD) for producing carbon-based powders. This is a convenient and widely used method based on the

thermochemical deposition of carbon gas onto the surface of a hot metal catalyst. This method is also known as the catalytic decomposition of hydrocarbons.

- A carbon-containing gas mixture (typically acetylene C_2H_2 or methane CH_4 mixed with nitrogen) is passed through quartz powder in a furnace at a temperature of 700–1000°C.

Inside the quartz powder, there is a ceramic container that holds a metal powder catalyst. The geometric dimensions of the powder are largely dependent on process conditions such as time, temperature, pressure, type of gas, etc., as well as on the degree of dispersion and type of the catalyst.

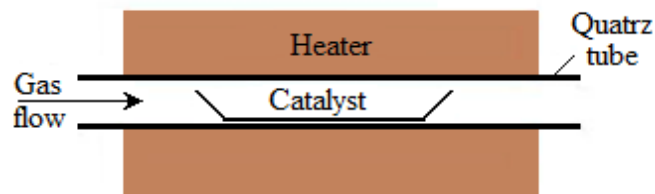


Fig. 3.7. Schematic diagram of a device for obtaining fullerenes and powders via chemical vapor deposition (CVD)

Composite Materials

Composite materials (CMs) are complex materials composed of two or more components, bonded together in various ways and possessing distinct properties.

The first composite material was patented in 1867 by the French gardener J. Monier, who used wire and cement to reinforce garden pots. In 1942, a composite material made of polyester resin reinforced with glass fiber (known as fiberglass) was used in aircraft construction.

Composite materials are widely used in mechanical engineering and apparatus design because they meet the following requirements:

- Lightweight
- Maximum strength and rigidity
- High durability and performance during operation

For these reasons, composite materials are extensively used in aerospace engineering. For example, the Soviet aircraft “Ruslan” incorporated 5.5 tons of structural composite materials, resulting in a weight saving of 15 tons.

Modern aircraft structures consist of:

- 15–20% composite materials in civil transport airplanes
- 25–30% in military aircraft
- 45–55% in military helicopters
- 75–80% in strategic missiles

Composite materials are characterized by the following properties:

- a) The composition, shape, and distribution of the components are predefined;

- b) They consist of two or more chemically distinct materials that remain separable;
- c) The properties of the composite are defined by the properties of its individual components;
- d) The composite's properties differ from those of its individual constituents;
- e) At the macroscale, the composite appears homogeneous, while at the microscale, it is heterogeneous;
- f) These materials do not occur naturally and are human inventions.

According to their geometrical characteristics, the components differ. The continuously distributed phase throughout the volume that maintains the integrity of the composite is called the matrix. The discontinuous or segmented material that provides reinforcement or strengthening is known as the reinforcing agent or armature.

Zero-Dimensional Filler Composite Materials

In this type of composite material, the matrix is mainly composed of metals or alloys. Metal-based composites are uniformly reinforced with dispersed particles. These dispersed particles are:

- a) Microscopic ($d = 0.01\text{--}0.1\ \mu\text{m}$)
- b) Fine particles ($d = 1\text{--}50\ \mu\text{m}$)

The properties of such materials are isotropic.

Composites reinforced with dispersed particles are often produced by the powder metallurgy method. The main stages of this process include:

1. Preparation of a mixture of matrix metal and reinforcing powders (the powders are obtained using specialized methods and then mixed in special machines).

2. Pressing the powder into steel matrices and converting it into a compact blank. This is followed by thermal processing (sintering). During pressing, deformation, and thermal treatment, the product acquires an optimal and stable dislocation structure.

Chapter Review Questions

1. Into what groups are conductive materials divided?
2. What is the main difference between metals and semiconductors?
3. How are conductors evaluated in terms of electrical conductivity?
4. Why are copper and aluminum the most widely used conductive materials in industry?
5. How does a change in temperature affect the conductivity of metals?
6. Explain the differences between metallic conductors and ionic conductors.
7. Compare conductors and dielectric materials in terms of their physical properties.
8. Give examples of metals with high electrical conductivity.
9. What is a superconductor?
10. Under what conditions does the phenomenon of superconductivity occur?
11. Describe the practical applications of superconductors.
12. What is the difference between ordinary metals and superconductors?
13. What is the difference between temperature-dependent conductivity and superconductivity?
14. What is a fullerene and what is its structure?
15. What is the electrical conductivity of graphite?
16. Why is graphite a conductor, but diamond is not?
17. What are the structural and property differences between fullerene and graphene?
18. Compare the various carbon modifications in terms of their electrical conductivity.
19. What is the main difference between graphite and graphene?
20. What are composite materials?
21. Give examples of oxide conductors.
22. Why can ceramic oxide conductors sometimes outperform metals?
23. How does the structure of composite materials affect their electrical properties?
24. Compare the advantages and disadvantages of oxide and metallic conductors.
25. Explain the differences between composite conductors and conventional metallic conductors.

CHAPTER 4. PHYSICAL PROCESSES AND PHENOMENA IN SEMICONDUCTOR MATERIALS

Semiconductors are materials whose specific conductivity is intermediate between that of conductors and dielectrics. Their specific conductivity strongly depends on the concentration of impurities, temperature, and the influence of various types of radiation. The main property of semiconductors is that their electrical conductivity increases with increasing temperature.

Semiconductors are crystalline materials with a band gap in the electron-volt (eV) range. For example, diamond is classified as a wide-bandgap semiconductor (approximately 5.47 eV), while indium arsenide is a narrow-bandgap semiconductor (0.35 eV). Semiconductors include many elemental substances — such as silicon, germanium, selenium, tellurium, and arsenic — as well as a large number of compounds, including gallium arsenide, gallium nitride, cadmium mercury telluride alloys, cadmium telluride, and bismuth.

An atom of a different chemical element embedded in a pure crystalline lattice (for example, a phosphorus or boron atom in a silicon crystal) is referred to as an impurity. Depending on whether the impurity atom donates an electron to the crystal (as phosphorus does in the example above) or accepts one (as boron does), such atoms are classified as donors or acceptors, respectively. The nature of the impurities can vary depending on which atom in the crystal lattice they replace and on which crystallographic plane they are located.

4.1. General information about semiconductors. Intrinsic and extrinsic semiconductors. Majority and minority charge carriers

Semiconductors are a unique class of materials that differ significantly from others due to their distinctive properties. In general, materials are classified into three broad categories based on their electrical conductivity:

Conductors – electrical conductivity greater than $10^6 \Omega^{-1} \cdot \text{cm}^{-1}$,

Semiconductors – electrical conductivity in the range of 10^{-8} to $10^6 \Omega^{-1} \cdot \text{cm}^{-1}$,

Dielectrics (insulators) – electrical conductivity less than $10^{-8} \Omega^{-1} \cdot \text{cm}^{-1}$.

As demonstrated by the data presented above, semiconductor electrical conductivity covers a broad range of values.

One of the most important characteristic features of semiconductors is the extreme sensitivity of their electrical conductivity to the type and concentration of impurities. For example, introducing impurities in concentrations as low as $10^{-10} \div 10^{-7} \%$ into a pure semiconductor can drastically alter its conductivity.

Another key property of semiconductors is their exceptional sensitivity of electrical conductivity to temperature. This dependence can be expressed as follows:

$$\sigma = \sigma_0 \exp \frac{W_a}{kT}, \quad (4.1)$$

where σ is the electrical conductivity at a given temperature T , σ_0 is a constant, W_a is the activation energy of the charge carriers, and k is the Boltzmann constant. For example, a change in the semiconductor's temperature by just 1°C can result in a 5–6 % change in its electrical conductivity.

Exposure to light also causes a sharp change in the electrical conductivity of many semiconductors and the devices based on them. Such devices include various semiconductor detectors, light-emitting diodes (LEDs), photoresistors, and several other types of components.

It is worth noting that semiconductor properties are not exclusive to solid-state materials. There also exist glassy amorphous semiconductors composed of organic compounds in the liquid state that exhibit similar properties. However, due to a number of known limitations, they have not yet found widespread technical application.

A wide variety of solid-state materials exhibit semiconductor properties. These include elements such as silicon, germanium, boron, diamond, phosphorus, sulfur, selenium, and tellurium, as well as many natural minerals and compounds such as GaAs, GaP, InSb, SiC, ZnS, CdTe, GaSb, and others. These semiconductors differ significantly in their various properties, which is why different types are used for different applications.

However, in modern technology, only a few types of semiconductors are widely used. Among them, silicon (Si), germanium (Ge), and gallium arsenide (GaAs) hold leading positions. In particular, silicon dominates contemporary microelectronics due to its numerous properties that meet complex technological requirements.

Most semiconductor materials used in electronic engineering possess a crystalline structure. The degree of perfection of this crystal structure, the presence or absence of various defects, and their quantity are key factors that determine the fundamental properties of the semiconductor.

Semiconductor materials possess the following characteristic properties that distinguish them from other materials:

1. The specific (electrical) resistivity of a semiconductor material increases exponentially with rising temperature.
2. The specific resistivity of semiconductors can be controlled by doping with impurity atoms. For example, adding just 0.001 mg of boron (B), phosphorus (P), or

antimony (Sb) — which is about a billion times fewer atoms than in 1 kg of silicon — can change the resistivity of silicon by a factor of 10^3 .

Thus, at room temperature, the resistivity of silicon can be adjusted from approximately $\rho \sim 10^5 \Omega \cdot \text{cm}$ to $\rho \sim 10^{-3} \Omega \cdot \text{cm}$ simply by varying the concentration of dopant atoms within the range of 10^{11} to 10^{19} cm^{-3} . This sharp change in semiconductor properties due to the introduction of impurities highlights their unique characteristics.

3. Unlike metals, semiconductor materials possess two types of charge carriers — electrons and holes. This means that a single semiconductor material can be made into either an *n*-type material with electron conductivity, or a *p*-type material with hole conductivity. This property formed the basis for:

- the discovery of the *p–n* junction and transistors, which laid the foundation of solid-state physics,
- the emergence and advancement of modern microelectronics and nanoelectronics.

This unique feature of semiconductor materials initiated a true technological revolution that profoundly transformed the course of human technological development.

4. The concept of carrier lifetime — the average time electrons and holes exist before recombination — does not apply to metals but is fundamental in semiconductors. The ability to control carrier lifetime has enabled the development of entirely new classes of devices based on semiconductors, such as lasers, photodetectors, and other optoelectronic systems. In semiconductors, carrier lifetime can vary over an extremely wide range (from 10^{-11} to 10^{-3} seconds), which has become a key factor in the design of modern high-speed computing systems.

5. Compared to metals, semiconductors exhibit exceptional sensitivity of their electrical, optical, and magnetic properties to external influences such as magnetic fields, radiation, pressure, and light. This characteristic has led to the development of detectors, photovoltaic cells, photoresistors, and other devices that have driven revolutionary advances in computing technology, robotics, and diagnostic systems.

6. Semiconductors differ from metals not only in having significantly higher charge carrier mobility, but also in the strong dependence of this mobility on temperature and crystal lattice defects. This property enables precise control of the electronic characteristics of materials in both microelectronics and nanoelectronics.

Semiconductor materials are classified into six groups based on their elemental composition and crystal structure:

1. Elementary (simple) semiconductors: Si (silicon), Ge (germanium), Sn (tin in the α -phase).

2. Compound semiconductors of the $A^{III}B^V$ type: AlAs (aluminum arsenide), AlP (aluminum phosphide), GaAs (gallium arsenide), GaP (gallium phosphide), InAs (indium arsenide), InP (indium phosphide).

3. Compound semiconductors of the $A^{II}B^{VI}$ type: CdS (cadmium sulfide), CdSe (cadmium selenide), CdTe (cadmium telluride), ZnS (zinc sulfide).

4. Compound semiconductors of the $A^{IV}B^{IV}$ type: SiC (silicon carbide), SiGe (silicon-germanium).

5. Compound semiconductors of the $A^{VI}B^{VI}$ type: PbS (lead sulfide), PbSe (lead selenide), PbTe (lead telluride).

6. Multicomponent (solid solution) semiconductor materials: $Zn_xGa_{1-x}As$ (zinc-gallium arsenide), $Zn_xHg_{1-x}Te$ (zinc-mercury telluride).

Crystal structure of semiconductors. All elementary semiconductors, most $A^{III}B^V$ and $A^{II}B^{VI}$ compounds, as well as certain other complex semiconductor materials, crystallize in a tetrahedral phase with a diamond-like or sphalerite (zinc blende) crystal structure, in which each atom is bonded to four neighboring atoms at equal distances.

The bonding between adjacent atoms is explained by electron pairs with oppositely oriented spins. Therefore, in elementary semiconductors, the chemical bond can be considered 100% covalent. In $A^{III}B^V$ compounds, the bonding is of an ionic-covalent nature. In $A^{II}B^{VI}$ compounds, part of the bonding is ionic.

The primary type of chemical bonding in semiconductor materials is covalent bonding. Since most atoms that form semiconductors have unfilled s - and p -electron shells, the formation of a crystal requires the completion of the outer electron shells of all atoms. As a result, each atom in the crystal obtains eight electrons in its outer shell, achieving the stable s^2p^6 configuration.

In such bonds, two electrons with opposite spins, shared between two atoms, form a bond that holds them together. For example, in a silicon (Si) crystal (Fig. 4.1), the valence electrons of the atoms are in the s^1p^3 state. Such an atom accepts one electron with opposite spin from each of its four neighboring atoms, transitioning to the s^2p^6 state. These types of bonds are therefore referred to as s^1p^3 hybrid bonds.

For covalent s^1p^3 bonding to exist in semiconductor materials, the crystal must be composed of atoms such that the sum of the valence electrons of any two neighboring atoms equals eight.

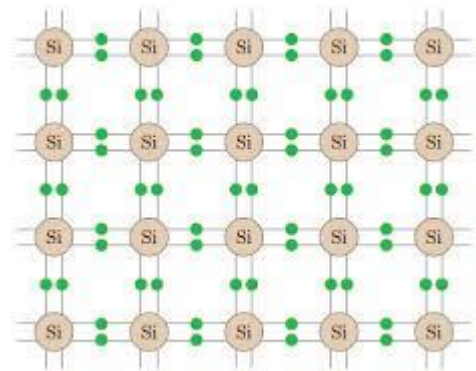


Fig. 4.1. Filling of electron shells in Si and covalent bonding of Si crystal.

Such crystals are formed from the following:

1. Group IV elements – Si (s^2p^2), Ge (s^2p^2), Sn (s^2p^2), C (s^2p^2)

2. III-V compounds – Elements from group III (e.g., Ga, In (s^2p^1)) and group V (e.g., As, Sb, P (s^2p^3)), where one electron from the group V atom is fully transferred to the group III atom. As a result, both atoms achieve an s^1p^3 configuration.

3. II-VI compounds – Elements from group II (e.g., Cd, Zn (s^2p^0)) and group VI (e.g., S, Se, Te (s^2p^4)), where two electrons are fully transferred from the group VI element to the group II element, resulting in both atoms attaining an s^1p^3 state and forming tetrahedral covalent bonds.

The crystal lattices of semiconductors are generally classified into four main types:

1. Diamond-like lattice,
2. Sphalerite (zinc blende) lattice,
3. Wurtzite lattice,
4. Rock salt-type lattice.

The diamond, sphalerite, and rock salt lattices are all based on a face-centered cubic (FCC) structure. The diamond lattice can be considered as two interpenetrating FCC lattices, displaced relative to one another. In elementary semiconductors, these two FCC lattices are offset by a distance equal to one-fourth the length of the unit cell along the body diagonal. If the coordinates of the origin of the first FCC lattice are taken as (0, 0, 0), the origin of the second lattice lies at ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) along the spatial diagonal from an atom of the first lattice.

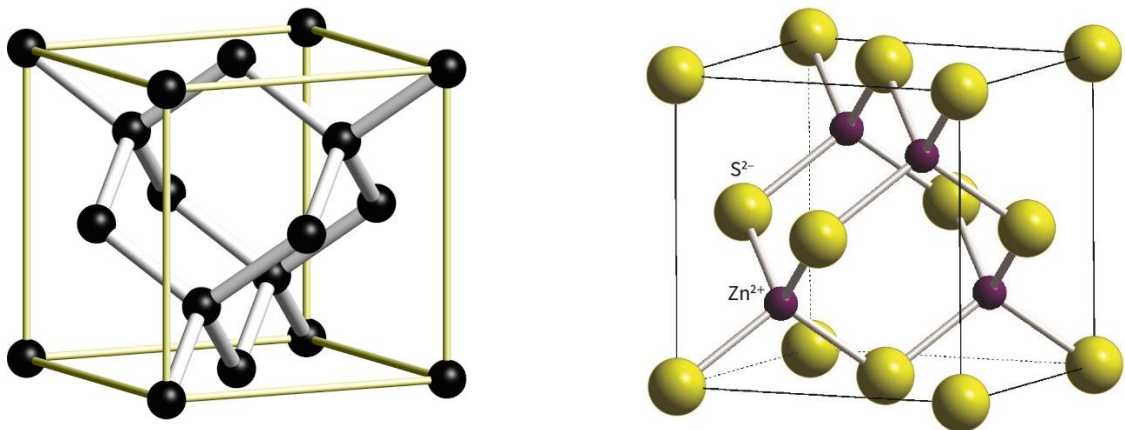


Fig. 4.2. Crystal lattice structure of diamond and sphalerite.

If the sequence of two different atoms positioned at the nodes of a body-centered cubic (BCC) lattice is preserved, a crystal structure with a sphalerite-type arrangement can be obtained, based on the diamond-like crystal lattice (Fig. 4.2). For example, in the first lattice site there is a Ga atom, and in the second site — an As atom. The Ga and As atoms occupy the lattice points (0, 0, 0) and ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$),

respectively. The rock salt-type crystal structure consists of two interpenetrating body-centered cubic lattices. The first cube contains a Na atom, and the second contains a Cl atom. In this structure, the atoms are located at coordinates (0, 0, 0) and ($\frac{1}{2}$, 0, 0).

The wurtzite structure represents a hexagonal lattice in which the atoms are spaced at ($\frac{1}{3}$, $\frac{1}{3}$, $\frac{1}{3}$) intervals.

In the diamond crystal lattice, each atom is covalently bonded — through its valence electrons — to four other atoms positioned at the vertices of a tetrahedron, forming a mutual interaction involving both attraction and repulsion (Fig. 4.2).

The crystal lattice of elemental semiconductors consists of identical atoms located at the lattice points. Elemental semiconductor materials such as Si, Ge, and Sn each have four valence electrons and, as shown, form bonds with four neighboring atoms in the crystal lattice. These properties indicate that they possess a diamond-type crystal structure.

The sphalerite crystal lattice can be viewed as consisting of two face-centered cubic (FCC) sublattices, whose unit cells are offset relative to each other by $\frac{1}{4}$ of the space diagonal.

The main difference between the sphalerite lattice and the diamond lattice, or other types of semiconductor crystal lattices, lies in the fact that one lattice site in the unit cell is occupied by an atom of one element, while the other is occupied by an atom of a different element. For example, the crystal lattice formed by Ga and As atoms can be considered (Fig. 4.3). Such lattices form the basis of the following semiconductor materials: AlAs, AlP, BN, BP, GaAs, GaP, GaSb, InAs, InP, and others. Semiconductor compounds of the $A^{III}B^V$ type are characterized by a tetrahedral structure and an ionic-covalent bond.

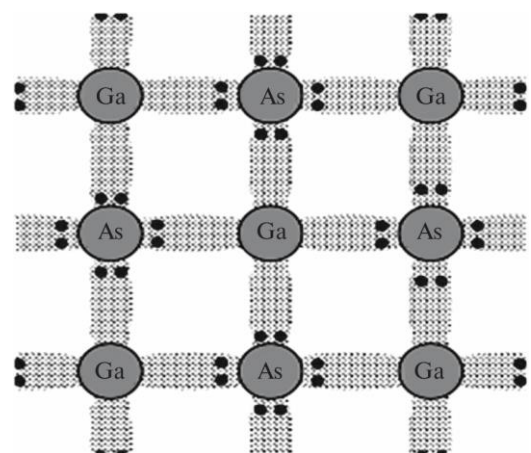


Fig. 4.3. Tetrahedral ionic-covalent bonding of $A^{III}B^V$ semiconductor materials.

The wurtzite crystal lattice can be represented as two hexagonal crystal lattices connected to each other (Fig. 4.4).

In the wurtzite crystal lattice, just like in the sphalerite lattice, two different atoms are positioned as nearest neighbors in tetrahedral lattice sites. This structure is formed by semiconductor materials such as CdS, CdSe, CdTe, and ZnS. Semiconductor materials based on $A^{II}B^{IV}$ compounds possess a tetrahedral ionic-covalent bond (Fig. 4.5).

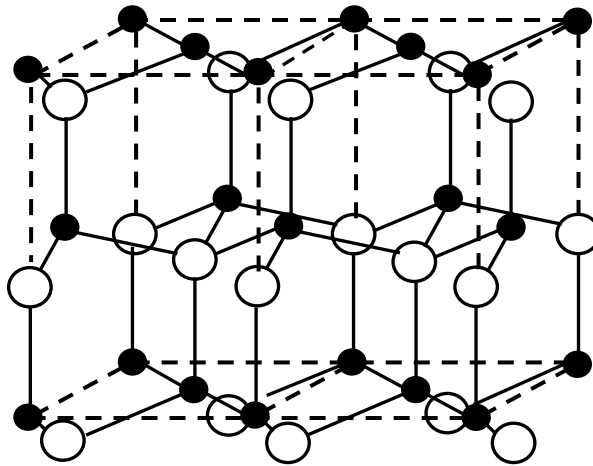


Fig. 4.4. Wurtzite crystal lattice.

The rock salt crystal lattice can be represented as two face-centered cubic sublattices with like-charged ions (either positive or negative) positioned adjacent to each other (Fig. 4.6). Such a crystal lattice is formed by the following semiconductor compounds: PbS, PbSe and PbTe.

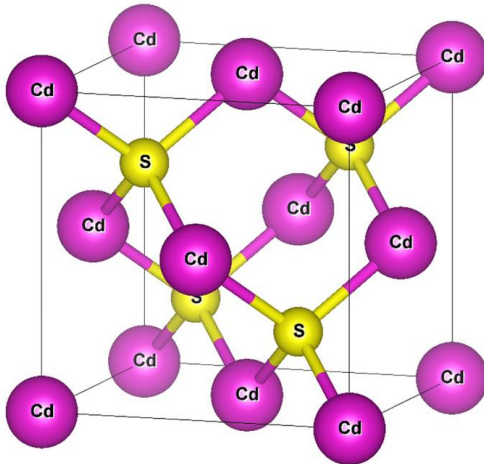


Fig. 4.5. Tetrahedral ionic-covalent bonding of semiconductor materials with the $A^{II}B^{VI}$ compound (in the case of CdS).

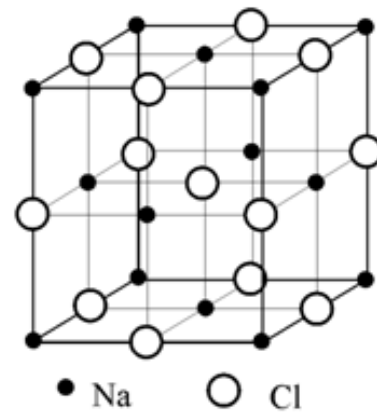


Fig. 4.6. Crystal lattice of rock salt.

Band structure of semiconductors. The electrical properties of crystals vary depending on the characteristics of the energy bands and the width of the band gap. In dielectrics, the valence band is completely filled, and the gap to the higher conduction band is large. In this case, electrons cannot transition from the valence band to the conduction band and therefore do not participate in electrical conductivity.

In order for electrical conductivity to occur, an electron must leave the valence band and enter the empty conduction band. Consequently, the greater the energy gap E_g between the bands, the more energy is required for the electron to make this transition.

So where can the electron obtain this energy?

It is known that at a given temperature, the atoms of a solid (just like the atoms of a gas) possess a certain amount of thermal energy. For example, the probability that an atom has thermal energy E_g is proportional to the expression $\exp\left(-\frac{E_g}{kT}\right)$.

Whereas gas molecules move freely throughout the volume they occupy, atoms in a solid continuously vibrate around their equilibrium positions and interact with one another.

As a result of this interaction, an atom can completely or partially transfer its thermal energy to an electron. If this energy is sufficient for the electron to transition from the valence band to the conduction band, then a free electron appears in the conduction band, and a vacancy is left in the valence band — this vacancy, left by the valence electron, is referred to as a hole (see Fig. 4.7).

Calculations show that in a semiconductor with a bandgap of width E_g , the probability that an electron from one of the atoms will acquire the necessary energy to transition from the valence band to the conduction band is given by the following expression:

$$p = \theta \cdot C_c \cdot C_v \cdot \exp\left(-\frac{E_g}{kT}\right), \quad (4.2)$$

where θ is a constant depending on the frequency of electron-atom "collisions", C_c is the number of available states near the bottom of the conduction band, C_v is the number of electrons near the top of the valence band, k is the Boltzmann constant, and T is the absolute temperature.

According to this relationship, the greater the band gap energy E_g , the lower the probability of electrons transitioning to the conduction band (and therefore, the lower the electrical conductivity of the given crystal).

Approximate calculations show that if the band gap width is greater than $E_g > 2$ eV, this probability becomes extremely small at any practically achievable temperature. Thus, substances with a band gap larger than 2 eV do not conduct electric current and are classified as dielectrics. Clearly, the value $E_g = 2$ eV serves as a conventional boundary, since there is no strict dividing line between dielectrics and semiconductors.

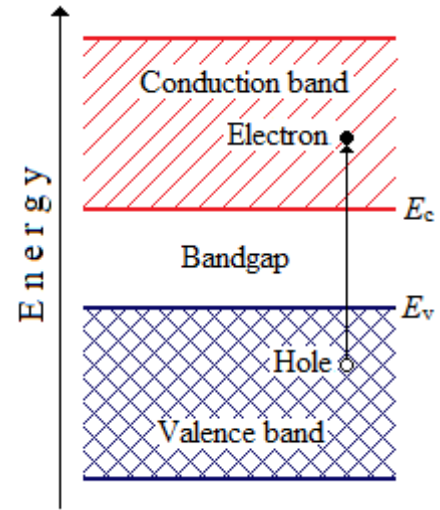


Fig. 4.7. Formation of a “hole” – a vacant place in the valence band.

In semiconductors, the valence band is completely filled, but the distance to the next available band — the conduction band — is relatively small (less than 2 eV). At absolute zero temperature, the valence band is fully occupied, and the conduction band is empty; therefore, the electrical conductivity is zero. As temperature increases, thermal energy causes more electrons to transition to the conduction band exponentially. Consequently, the number of “holes” in the valence band also increases, which in turn raises the electrical conductivity of the semiconductor. For intrinsic (undoped) semiconductors, the number of electrons n_0 in the conduction band and the number of holes p_0 in the valence band depend on temperature as follows:

$$n_0 = p_0 = Ae^{-\frac{E_g}{2kT}}, \quad (4.3)$$

where A is a constant associated with the semiconductor.

It is known that electrical conductivity is proportional to the concentration of free charge carriers:

$$\delta = \mu_n en_0 = \mu_p ep_0, \quad (4.4)$$

where μ_n and μ_p are the mobilities of electrons and holes, respectively, and e is the elementary charge. Thus, the electrical conductivity of semiconductors as a function of temperature follows the law:

$$\sigma \cong Be^{-\frac{E_g}{2kT}}, \quad (4.5)$$

here B is a constant value. Thus, the electrical conductivity of a semiconductor increases significantly with increasing temperature. This is one of the important and characteristic properties of semiconductors.

Intrinsic (pure) semiconductor. In a semiconductor, the valence band (filled) and the conduction band (empty) are separated by an energy gap E_g . This gap is small enough that, at room temperature, some electrons with sufficient thermal energy can overcome it. In this process, electrons transition from the top of the valence band to the bottom of the conduction band. The probability that any electron will leave the top levels of the valence band and move to the lower levels of the conduction band decreases sharply as the energy gap E_g increases.

As noted earlier, electrons in the valence band do not contribute to electrical conductivity. However, at room temperature, when a certain number of electrons move from the valence band to the conduction band, the valence band loses a corresponding number of electrons, resulting in a partially unfilled state. In other words, vacant bonds — positively charged holes — are formed in the valence band (see Fig. 8.8). Electrons can now jump from other bonds into these holes. As a result, the hole is filled by an electron and disappears, but a new hole appears elsewhere in

the lattice. In this way, it appears as though the hole moves randomly through the crystal from one position to another.

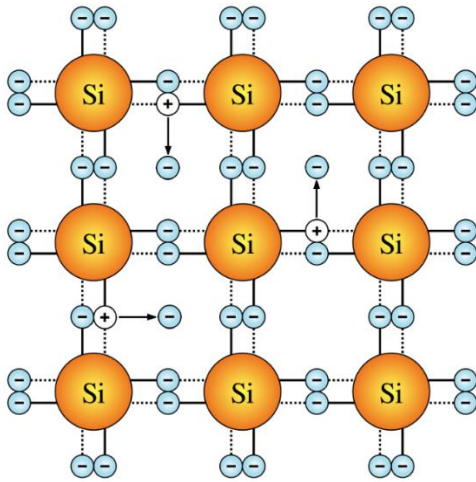


Fig. 4.8. The appearance of positively charged “holes” in the valence band.

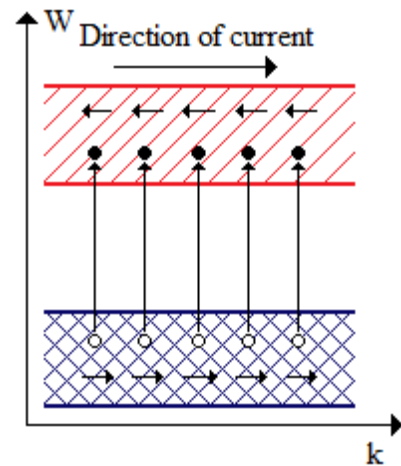


Fig. 4.9. Ordered motion of free electrons and holes in a semiconductor under the influence of an external electric field.

If an external electric field is applied to such a semiconductor, the valence electrons, which randomly jump between bonds in the valence band, will begin to move in an orderly fashion opposite to the direction of the field. Consequently, an orderly movement of holes will appear in the valence band in the direction opposite to that of the electrons — i.e., along the electric field — which constitutes a hole current. At the same time, in the conduction band, the free electrons will generate an electron current (see Fig. 4.9).

A pure semiconductor, consisting of atoms of a single type, in which the number of electrons is equal to the number of holes ($n_0=p_0$), is called an intrinsic semiconductor. For example, a semiconductor without any impurities can act as an intrinsic semiconductor. Naturally, the conductivity of such a semiconductor under given conditions is quite low compared to semiconductors of the same type that are not intrinsic. For instance, the specific resistivity of intrinsic silicon at room temperature is approximately $300 \text{ k}\Omega \cdot \text{cm}$.

It is important to always remember that in intrinsic semiconductors, both electrons and holes participate in the conduction of electric current.

***n*-type impurity semiconductor.** If some atoms in a semiconductor crystal are replaced by atoms of an element with a different valency, the strict order of the crystal lattice is disrupted. The presence of the impurity alters the energy band diagram. However, if the amount of impurity is small (for example, about one hundred-thousandth of the number of host atoms), the energy diagram of the ideal semiconductor crystal can be considered practically unchanged. This is because the

introduction of impurity atoms only leads to the formation of new quantum states between the existing bands (assuming only one type of impurity is introduced). Since the impurity atoms are generally spaced far apart, the quantum states they introduce can, in most cases, be treated as localized energy levels in specific regions within the forbidden band, while neglecting interactions between the impurity atoms themselves.

The position of these additional energy levels between the main energy bands of the crystal has a significant impact on its conductivity, even at extremely low impurity concentrations.

Atoms of pentavalent elements (such as phosphorus, arsenic, and antimony) form additional donor levels in germanium and silicon, located near the conduction band. At low temperatures, these impurity levels are filled with electrons; however, as the temperature increases, electrons can gain enough thermal energy to transition from these levels into the conduction band. In this case, they become free electrons and participate in the electrical conductivity of the crystal.

Under such conditions, the concentration of conduction electrons is approximately equal to the concentration of impurity atoms, and the conductivity of the crystal is directly proportional to the impurity concentration.

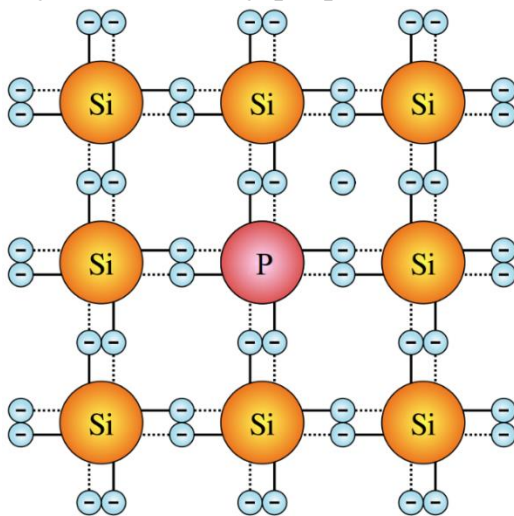


Fig. 4.10. Covalent bond of a pentavalent impurity atom in silicon.

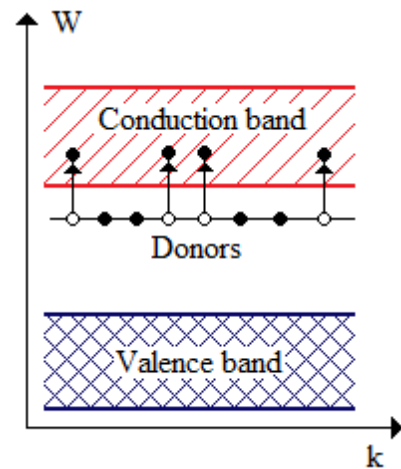


Fig. 4.11. Charge carriers in an *n*-type semiconductor.

The physico-chemical nature of the process by which a pentavalent impurity in a silicon crystal readily donates one electron to the conduction band is as follows: since silicon atoms are tetravalent, they form covalent bonds with four neighboring atoms using four electrons (Fig. 4.10).

If a silicon atom in a crystal lattice node is replaced by a pentavalent impurity atom, that atom uses four of its electrons to form covalent bonds with neighboring atoms. The fifth valence electron does not participate in chemical bonding and

remains weakly bound to the atom. Even a small amount of thermal energy is enough for this electron to detach from the atom and enter the conduction band, becoming a free electron (see Fig. 4.10).

Fig. 4.11 shows the charge carriers responsible for current in an *n*-type semiconductor.

***p*-type impurity semiconductor.** Atoms of trivalent elements (such as gallium or boron) in germanium and silicon crystals create impurity levels located near the valence band. At low temperatures, these impurity levels remain unoccupied. However, with increasing temperature, electrons can move from the valence band to the impurity levels due to thermal motion. As a result, they become immobile negative charges (since these levels are relatively deep, the return of electrons from them is difficult), and additional free holes are created in the valence band.

A hole behaves as a quasi-particle with a positive charge. In essence, it represents the absence of an electron in the crystal lattice (considering the valence bonds).

Let us consider, for example, a unit cell of the silicon crystal lattice consisting of five atoms. Eight electrons participate in the valence bonds of this cell: four from the central atom and one from each of the four surrounding atoms. Each surrounding atom, in turn, forms valence bonds with three other atoms using three valence electrons. Thus, all the valence electrons of the silicon atoms are shared in the covalent bonds. At the same time, the electrical neutrality of each atom is preserved: the positive charge of the nucleus is balanced by the total charge of the electrons.

If a valence electron leaves its bond (e.g., due to thermal energy or external influence) and moves into the conduction band, the atom that lost this electron becomes a positive ion — a hole is created. When another electron enters this bond, it fills the hole, and an electron-hole recombination occurs.

A trivalent impurity is called an acceptor because it accepts an electron from the valence band. But why does this impurity capture an electron? As mentioned earlier, a silicon atom is tetravalent and forms four covalent bonds in the crystal lattice. When a silicon atom is replaced by a trivalent atom, one electron is missing to form a complete covalent bond, which leads to the formation of a hole (see Fig. 4.12). As soon as an opportunity arises to capture an additional electron, the impurity atom takes it. Such electrons are constantly generated in the crystal due to thermal fluctuations at a given temperature. Therefore, in each unit volume of the crystal, there is a concentration of holes corresponding to the concentration of introduced acceptor atoms.

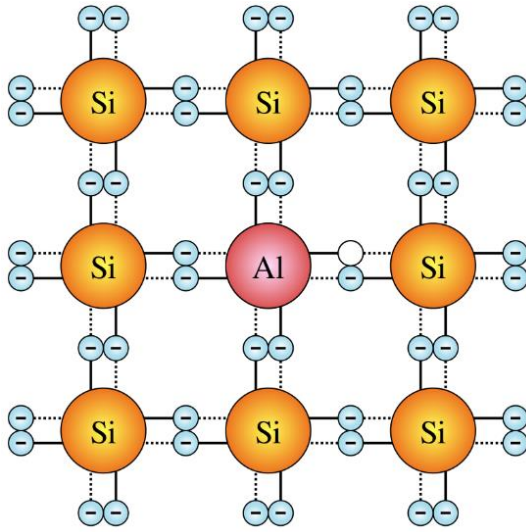


Fig. 4.12. Covalent bond of a trivalent impurity atom in silicon.

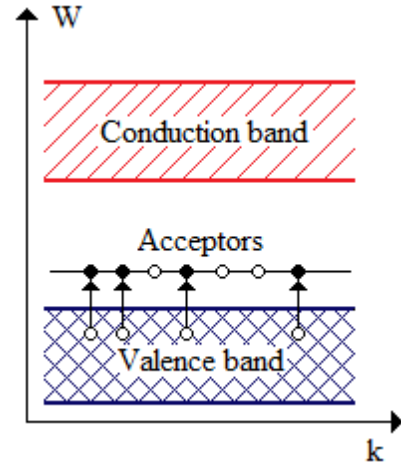


Fig. 4.13. Charge carriers in a *p*-type semiconductor.

Since the electrical conductivity of the crystal in this case is primarily determined by holes, such a semiconductor is called a *p*-type or hole-type semiconductor. In a *p*-type semiconductor, holes are the majority charge carriers, while electrons are the minority carriers.

Figure 4.13 shows the free charge carriers responsible for current in a *p*-type semiconductor.

One may mistakenly assume that minority carriers in *n*-type and *p*-type semiconductors can be neglected. This is absolutely incorrect. Minority carriers play a key role in the operation of most semiconductor devices.

4.2. Temperature dependence of charge carrier concentration

In a unit volume of a given semiconductor at a specific temperature, there is a certain number of free carriers, referred to as the carrier concentration. To determine the carrier concentration, one must take into account the number of available energy levels in the allowed bands (the conduction band for electrons and the valence band for holes), denoted as $N(\varepsilon)$, while considering the Pauli exclusion principle.

Solid-state theory demonstrates that the density of energy states N (i.e., the density of states), corresponding to a unit energy interval, depends on the energy level (see Fig. 4.14a):

$$N_c(\varepsilon) = \frac{4\pi}{h^3} (2m_n^*)^{3/2} \sqrt{\varepsilon - \varepsilon_c} \quad (4.6)$$

$$N_v(\varepsilon) = \frac{4\pi}{h^3} (2m_p^*)^{3/2} \sqrt{\varepsilon_v - \varepsilon} \quad (4.7)$$

In systems of particles described by antisymmetric wave functions, the Fermi-Dirac distribution applies. This statistical distribution characterizes the behavior of *fermion systems* (such as electrons, protons, and neutrons) — particles that obey the Pauli exclusion principle and possess half-integer spin ($\pm 1/2$). The probability that allowed energy levels are occupied is determined by the Fermi-Dirac distribution function (see Fig. 4.14b), which includes the temperature and the Fermi energy as state parameters:

$$f_n(\varepsilon) = \left[1 + \exp\left(\frac{\varepsilon - \varepsilon_F}{kT}\right) \right]^{-1} \quad (4.8)$$

$$f_p(\varepsilon) = \left[1 + \exp\left(\frac{\varepsilon_F - \varepsilon}{kT}\right) \right]^{-1} \quad (4.9)$$

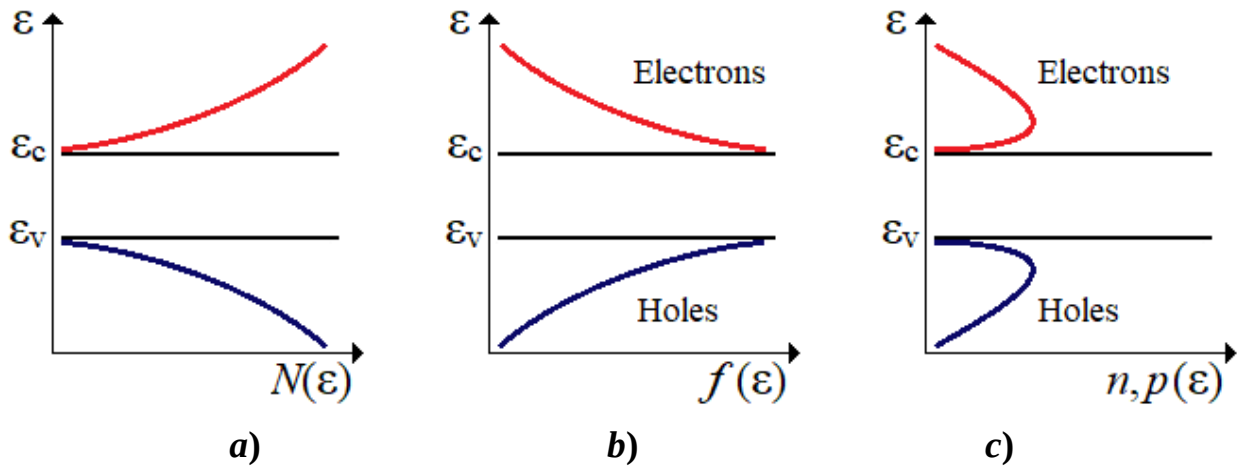


Fig. 4.14. Energy dependence of the density of states (a), the probability of occupancy of energy levels by free carriers (b), and the concentration of free carriers (c) in an intrinsic semiconductor.

If the number of electrons (or holes) per energy interval is less than the number of available states, the semiconductor is said to be *non-degenerate*. Intrinsic and lightly doped semiconductors are examples of non-degenerate semiconductors. Semiconductors become *degenerate* at high impurity concentrations, when the number of mobile carriers exceeds the number of available states. In non-degenerate semiconductors, electrons and holes have energies that differ significantly from the Fermi energy. The difference $\varepsilon - \varepsilon_F$ typically exceeds $3kT$.

Therefore, the unity in the denominators of equations (4.8) and (4.9) can be neglected. In this case, the probability of occupancy of energy levels in the conduction band follows the Maxwell-Boltzmann distribution of classical statistics

$$f_n(\varepsilon) \approx \exp\left(-\frac{\varepsilon - \varepsilon_F}{kT}\right). \quad (4.10)$$

And the probability of a hole occurring is given by

$$f_p(\varepsilon) \approx \exp\left(-\frac{\varepsilon_F - \varepsilon}{kT}\right). \quad (4.11)$$

The energy density of electrons and holes is equal to

$$n(\varepsilon) = N_c(\varepsilon) f_n(\varepsilon) \quad (4.12)$$

$$p(\varepsilon) = N_v(\varepsilon) f_p(\varepsilon). \quad (4.13)$$

To determine the concentration of electrons and holes in a semiconductor, the energy density of electrons and holes must be integrated over energy, respectively

$$n = \int_{\varepsilon_c}^{\infty} N_c(\varepsilon) f_n(\varepsilon) d\varepsilon = N_c \exp\left(-\frac{\varepsilon_c - \varepsilon_F}{kT}\right) \quad (4.14)$$

$$p = \int_0^{\varepsilon_v} N_v(\varepsilon) f_p(\varepsilon) d\varepsilon = N_v \exp\left(-\frac{\varepsilon_F - \varepsilon_v}{kT}\right). \quad (4.15)$$

Here, N_c is the effective density of states in the conduction band, and N_v is the effective density of states in the valence band:

$$N_c = 2 \left(\frac{2\pi m_n^* kT}{h^2} \right)^{3/2} \quad (4.16)$$

$$N_v = 2 \left(\frac{2\pi m_p^* kT}{h^2} \right)^{3/2}. \quad (4.17)$$

In an intrinsic semiconductor, $n_i = p_i$; therefore,

$$N_c \exp\left(-\frac{\varepsilon_c - \varepsilon_F}{kT}\right) = N_v \exp\left(-\frac{\varepsilon_F - \varepsilon_v}{kT}\right) \quad (4.18)$$

Taking the logarithm and solving for ε_F , we obtain:

$$\varepsilon_F = \frac{\varepsilon_c + \varepsilon_v}{2} + \frac{kT}{2} \ln \frac{N_v}{N_c}. \quad (4.19)$$

The value of $\frac{kT}{2} \ln \frac{N_v}{N_c}$ is much smaller than $\frac{\varepsilon_c + \varepsilon_v}{2}$, so the Fermi level in an intrinsic semiconductor is approximately located in the middle of the forbidden gap.

The concentration of equilibrium charge carriers depends on the position of the Fermi level. In an n -type semiconductor, the electron concentration is primarily determined by the transition of electrons from the donor energy levels ε_d to the conduction band energy levels. Therefore, the electron concentration n_n should be equal to the concentration of ionized donors:

$$n_n = N_d [1 - f(\varepsilon_d)]. \quad (4.20)$$

$1 - f(\varepsilon_d)$ is the probability of the absence of an electron at the energy level ε_d , therefore,

$$n_n = N_d \exp \frac{\varepsilon_d - \varepsilon_F}{kT}. \quad (4.21)$$

Equating the right-hand sides of equations (4.14) and (4.21), we obtain:

$$N_c \exp\left(-\frac{\varepsilon_c - \varepsilon_F}{kT}\right) = N_d \exp\frac{\varepsilon_d - \varepsilon_F}{kT}. \quad (4.22)$$

Solving this equation for ε_F , we obtain the expression:

$$\varepsilon_F = \frac{\varepsilon_d + \varepsilon_c}{2} - \frac{kT}{2} \ln \frac{N_c}{N_d}. \quad (4.23)$$

From the obtained expression, it follows that the position of the Fermi level depends on the temperature and impurity concentration. It can be shown that

$$n_n = n_i \exp\frac{\varepsilon_F - \varepsilon_i}{kT} \quad (4.24)$$

$$p_n = n_i \exp\left(-\frac{\varepsilon_F - \varepsilon_i}{kT}\right). \quad (4.25)$$

Multiplying the obtained relations together, we get:

$$n_n p_n = n_i^2. \quad (4.26)$$

Thus, for any impurity concentration, the product of the electron and hole concentrations remains constant.

In a *p*-type semiconductor, the hole concentration is primarily determined by the transition of electrons from the valence band energy levels to the acceptor energy levels. Therefore, the hole concentration should be equal to the concentration of ionized impurities, i.e.,

$$p_p = N_a \exp\left(-\frac{\varepsilon_a - \varepsilon_F}{kT}\right) = n_i \exp\frac{\varepsilon_i - \varepsilon_F}{kT} \quad (4.27)$$

$$n_p = n_i \exp\left(-\frac{\varepsilon_i - \varepsilon_F}{kT}\right). \quad (4.28)$$

From the above, the following conclusions can be drawn:

- The concentration of both majority and minority charge carriers depends on the position of the Fermi level;
- The introduction of impurities into the semiconductor shifts the Fermi level relative to the middle of the forbidden gap: upwards in an *n*-type semiconductor and downwards in a *p*-type semiconductor;
- An increase in the semiconductor temperature shifts the Fermi level toward the middle of the forbidden gap;
- Increasing the impurity concentration increases the concentration of majority charge carriers and decreases the concentration of minority charge carriers.

The dependence of the concentration of mobile carriers on temperature can be divided into three characteristic regions (Fig. 4.15):

1. At sufficiently low temperatures, the carrier concentration mainly changes due to the transition of electrons from the donor level to the conduction band or due to the transition of electrons from the valence band to the acceptor level, forming

free holes. This is the freezing-out region, which ends when a certain temperature $T_1 \approx 100$ K is reached, at which point the impurity levels are completely ionized.

2. A further increase in temperature does not lead to an increase in the concentration of mobile carriers (impurity depletion region).

3. Starting from a higher temperature $T_2 \approx 400$ K, the concentration of mobile carriers begins to rise again due to the process of electron-hole pair formation when electrons transition from the valence band to the conduction band. This region is referred to as intrinsic conductivity.

In practice, many semiconductor devices operate primarily in the impurity depletion region.

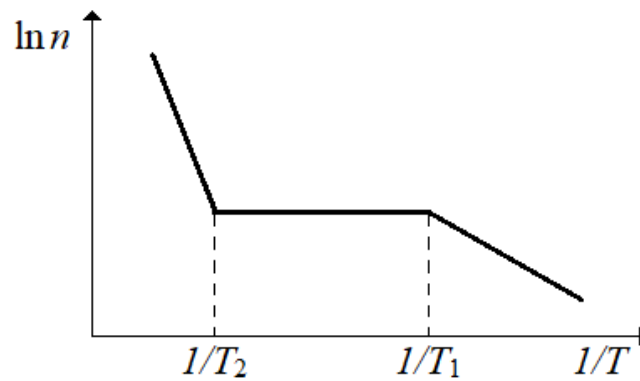


Fig. 4.15. Dependence of electron and hole concentrations on temperature.

4.3. Optical and photoelectric phenomena in semiconductors

Optoelectronics is a branch of microelectronics based on the use of both electrical and optical methods of signal processing. The scientific foundation of optoelectronics consists of the processes of converting electrical signals into light and vice versa, as well as the processes of generation, transmission, processing, and storage of information carried by light. These processes and phenomena primarily include light absorption and photoconductivity in semiconductors, the photoelectric effect in p - n junctions, electroluminescence, and stimulated emission processes in semiconductors.

To convert optical signals into electrical ones, optoelectronics employs p - n junctions operating in rectifying or photodiode mode, phototransistors, and photoresistors made from thin films of $A^{II}B^{VI}$ and $A^{III}B^V$ compounds, as well as thin-film devices based on the effect of abnormally high photovoltages.

To convert electrical signals into light, various types of electroluminescence are used, as well as the phenomenon of stimulated coherent emission. Electroluminescent devices are based on spontaneous radiative transitions that occur in crystals as a result of injection of nonequilibrium charge carriers through an external contact or a p - n junction, impact ionization, or ionization by a strong electric field. Stimulated coherent emission also arises from the injection of charge carriers

through a $p-n$ junction, but under conditions that create a very high (inverted) population of the upper energy levels. In this case, the stimulated component of the emission dominates over spontaneous electroluminescence. Devices for converting electrical signals into light can be manufactured in both thin-film and monolithic designs.

Most of the phenomena forming the scientific basis of optoelectronics have been known for quite some time, and many of them have found widespread practical application in electronics. However, the term “optoelectronics” does not encompass all areas of application of photoelectric and optical phenomena. Rather, it is used in a narrower sense, referring specifically to microelectronic devices based on solid-state materials or thin films, whose signal processing capabilities are realized through electronic and photonic processes.

In such devices, the interaction necessary for active functioning is achieved through both electrical and optical channels.

Photoconductivity and Light Absorption in Semiconductors. The phenomenon of photoconductivity refers to the change in a material's resistance under the influence of infrared, visible, or ultraviolet radiation. In most cases, exposure to radiation leads to a decrease in resistance (a normal photoelectric effect). However, there are instances where the opposite occurs — an increase in resistance — known as the anomalous photoelectric effect. This phenomenon is relatively rare. Numerous experimental studies have shown that the decrease in resistance is due to an increase in the concentration of mobile charge carriers.

The increase in the concentration of mobile charge carriers in semiconductors under light exposure can occur in various ways. As illustrated in Fig. 4.16, the generation of carriers under illumination may occur through one of the following mechanisms:

1. Photons of electromagnetic radiation excite electrons, transferring them from the valence band to the conduction band, which results in a simultaneous increase in both electron and hole concentrations;
2. Electrons are excited from the valence band to impurity levels, leading to an increase in hole conductivity only;
3. Electrons are excited from impurity levels to the conduction band, resulting in increased electron conductivity.

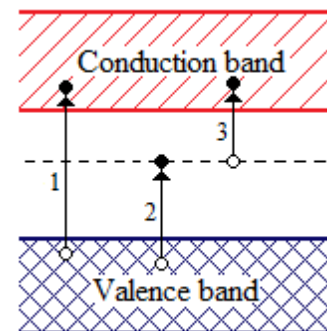


Fig. 4.16. Diagram of possible pathways for the generation of free charge carriers under light exposure:
1 – Band-to-band transition;
2 – Valence band to impurity level transition;
3 – Impurity level to conduction band transition.

The increase in the concentration of free carriers due to light absorption leads to an increase in electrical conductivity. Let us examine the emergence of photoconductivity using the example of electron excitation from impurity levels to the conduction band.

Suppose that under the influence of light, g electrons are generated per unit volume of the semiconductor per unit time. Then, from the moment illumination begins, the electron concentration will begin to increase. However, this growth cannot continue indefinitely, as the probability of recombination increases with the rising concentration of free carriers. After a certain period of time, a steady state is reached, in which the rate of carrier generation equals the rate of recombination over a given time interval.

For the case under consideration, the continuity equation can be written as follows

$$\frac{d\Delta n}{dt} = g - \frac{\Delta n}{\tau_n}, \quad (4.29)$$

where Δn is the concentration of photo-generated electrons, defined as $\Delta n = n - n_0$, n is the total electron concentration, n_0 is the equilibrium concentration of carriers, τ_n is the electron lifetime. The solution to this equation is:

$$\Delta n = \Delta n_{st} \left[1 - \exp\left(-\frac{t}{\tau_n}\right) \right], \quad (4.30)$$

where Δn_{st} is the steady-state concentration of photo-generated electrons, which is equal to:

$$\Delta n_{st} = g\tau_n. \quad (4.31)$$

After the illumination is turned off ($g=0$), equation (4.29) takes the form:

$$\frac{d\Delta n}{dt} = -\frac{\Delta n}{\tau_n}. \quad (4.32)$$

The solution to this equation is:

$$\Delta n = \Delta n_{st} \exp\left(-\frac{t}{\tau_n}\right), \quad (4.33)$$

this expression describes the process of carrier recombination and the return of the semiconductor to its equilibrium state.

The photoconductivity of the semiconductor, given by

$$\Delta\sigma = q\mu_n\Delta n, \quad (4.34)$$

follows the same pattern as the variation in electron concentration. Figure 4.17 shows the curve of photoconductivity variation under illumination of the semiconductor with rectangular light pulses of intensity I_0 . The steady-state value of the photoconductivity is, naturally, expressed by the formula

$$\Delta\sigma_{st} = q\mu_n\Delta n_{st} = q\mu_n g\tau_n. \quad (4.35)$$

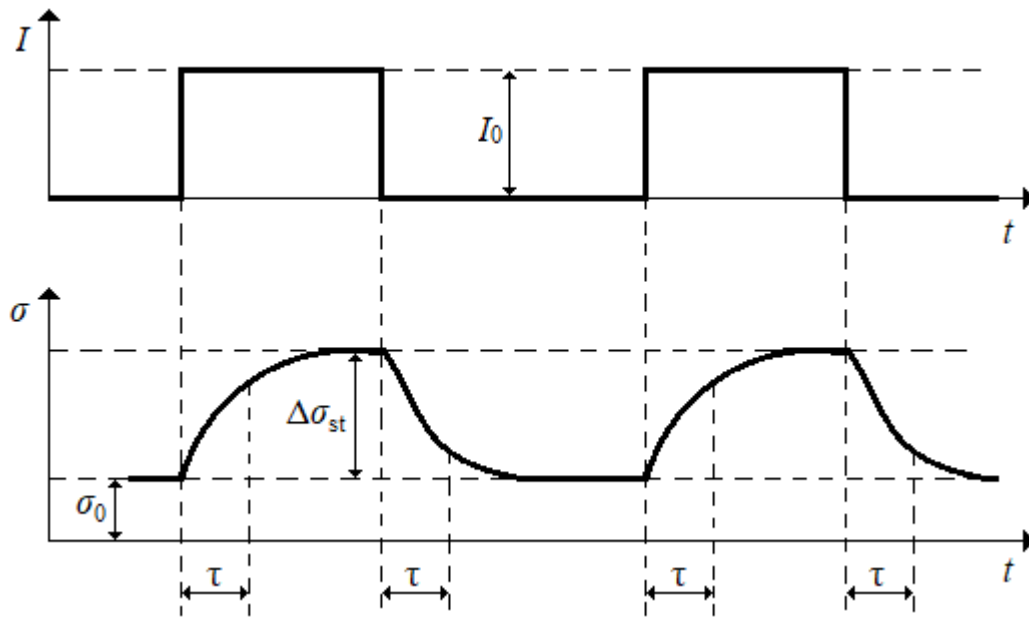


Fig. 4.17. Variation of semiconductor photoconductivity under illumination with rectangular light pulses (I_0 and σ_0 are the pulse amplitude and dark conductivity, respectively).

From the obtained formula, it is evident that the longer the carrier lifetime, the higher the semiconductor's photoconductivity.

The mechanisms of light absorption considered above, which lead to the generation of free charge carriers, are referred to as photoactive. However, there are several possible mechanisms of photon absorption that do not result in the creation of free carriers. Among them are excitonic absorption, absorption by free carriers, and absorption by optical lattice vibrations.

Excitonic Absorption. Excitonic absorption of photon energy refers to a type of excitation in which an electron does not leave its atom but instead transitions to an unoccupied energy level while remaining close to its nucleus. Therefore, excitonic excitation does not create free charge carriers and does not alter the electrical conductivity of the crystal.

However, the excitonic excitation can move through the crystal. That is, if a particular atom is in an excited state at a given moment, the excitation may be transferred over time to another atom. An electron in an excited state returns to the ground state, and the released energy is transferred to a valence electron of a neighboring atom, and so on.

This propagation of excitation — called an exciton — does not cause an electric current in the crystal since no charge is physically moving, only an excited state is being transferred. An exciton can also be described as the coupled motion of an electron and a hole bound by Coulomb interaction, rotating around their common center of mass.

Since less energy is required to create an excited atomic state than to ionize the atom, the exciton is associated with an energy level located within the bandgap. As a result, an exciton band or even a series of exciton bands appears in the energy diagram of the crystal.

It should be noted, however, that excitonic absorption may indirectly affect photoconductivity. As it travels through the crystal, an exciton may be disrupted by thermal vibrations or by interaction with another photon, leading to the generation of a free electron-hole pair. Moreover, an exciton may encounter an impurity atom and transfer its energy to a weakly bound electron, exciting it into the conduction band.

Absorption by Free Carriers. Radiation incident on a semiconductor may also be absorbed by free electrons. This type of absorption is observed in heavily doped semiconductors with high concentrations of free carriers. The mechanism of absorption can be described as follows: under the influence of an electromagnetic field, free electrons do not absorb the energy directly but begin to oscillate in phase with the field. If during these oscillations, the electron undergoes scattering by the lattice (lattice scattering), it transfers the field's energy to the lattice. This absorption occurs only when the relaxation time is much shorter than the period of the electromagnetic wave. Otherwise, the electron re-emits the absorbed energy back into the wave.

Therefore, the likelihood of absorption by free electrons increases as the frequency of the incoming radiation decreases — that is, it becomes significant in the infrared region of the spectrum. Absorption by free carriers is not a photoactive process and does not affect the semiconductor's photoconductivity.

Absorption by Optical Lattice Vibrations. In complex crystals containing several types of atoms, not only acoustic but also optical lattice vibrations are observed. Unlike acoustic vibrations, optical vibrations are short-wavelength, and the phase shift between neighboring atoms during such oscillations is significant. This results in the formation of an alternating electric dipole moment with a large amplitude.

If the frequency of the incident electromagnetic radiation matches the frequency of the optical phonon mode, resonance absorption occurs via interaction with the electric dipole. This type of absorption enhances the intensity of optical lattice vibrations but does not alter the concentration of free charge carriers.

Multi-Electron Photoexcitation. In contrast to the previously discussed absorption mechanisms, there are cases in which a single photon may generate more than one photoelectron. This phenomenon may occur when the photon energy exceeds twice the bandgap energy. An electron excited into the conduction band by such a photon may receive energy far greater than the bandgap width. As shown in

Fig. 4.18(a), this electron can then lose part of its excess energy via scattering processes, transferring energy to the lattice or creating additional electron-hole pairs.

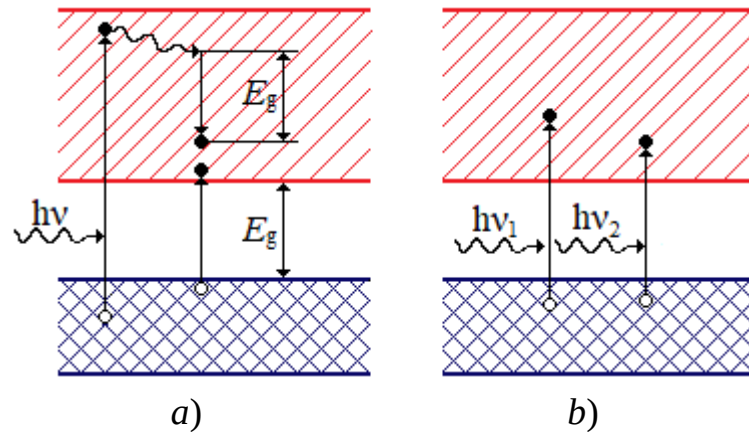


Fig. 4.18. Diagram of electronic transitions during the absorption of light quanta with energy significantly exceeding the bandgap width:

***a* – absorption of a quantum followed by impact ionization;**

***b* – absorption of a quantum in accordance with the Compton effect.**

However, during a subsequent collision with the lattice, this high-energy electron may transfer part of its energy to a bound electron, exciting it into the conduction band. As a result, the absorption of a single photon can, due to the secondary process of impact ionization, lead to the generation of two electrons and two holes. It should be noted that a similar ionization process occurs when the semiconductor is irradiated not with photons but with high-energy charged particles. These particles, through primary ionization events, produce fast electrons which, via a multistep cascade multiplication process, subsequently free a large number of electrons and holes into their respective bands.

The absorption of a high-energy photon may occur not only as a single act of internal photoelectric effect, but also as a result of the Compton effect. In this case, when a photon of energy $h\nu_1$ collides with an electron, only part of the photon's energy is transferred to the electron — enough to free it and generate a corresponding hole. The remaining energy is retained in the form of a secondary photon $h\nu_2$, with a lower frequency ν_2 , as illustrated in Fig. 4.18b. This secondary photon, as it propagates through the crystal, may itself be absorbed and generate another electron-hole pair.

Given the variety of absorption mechanisms in semiconductors — some photoactive and others not — the concept of quantum efficiency (or quantum yield) is introduced. Quantum efficiency is defined as the ratio of the number of free electrons (or holes) generated as a result of photon absorption to the total number of photons absorbed:

$$\eta = \frac{g}{N}. \quad (4.36)$$

If all photon absorption events are photoactive, the quantum efficiency is equal to one. However, the presence of absorption mechanisms that do not result in the generation of photocarriers leads to the quantum efficiency being, in most cases, less than one. Finally, when a semiconductor is irradiated with ultraviolet light or even higher-energy radiation — where the photon energy is significantly greater than the bandgap width — conditions may arise, as previously noted, in which a single photon excites multiple electrons. In such cases, the quantum efficiency exceeds one.

The concept of light absorption by a crystal must also have a quantitative spatial characteristic. Indeed, even strongly absorbed radiation will be only partially absorbed in an extremely thin sample. Conversely, radiation with weak absorption, when directed into a sufficiently thick body, may eventually be almost completely absorbed. With this in mind, let us consider how radiation is absorbed as a function of depth within the material.

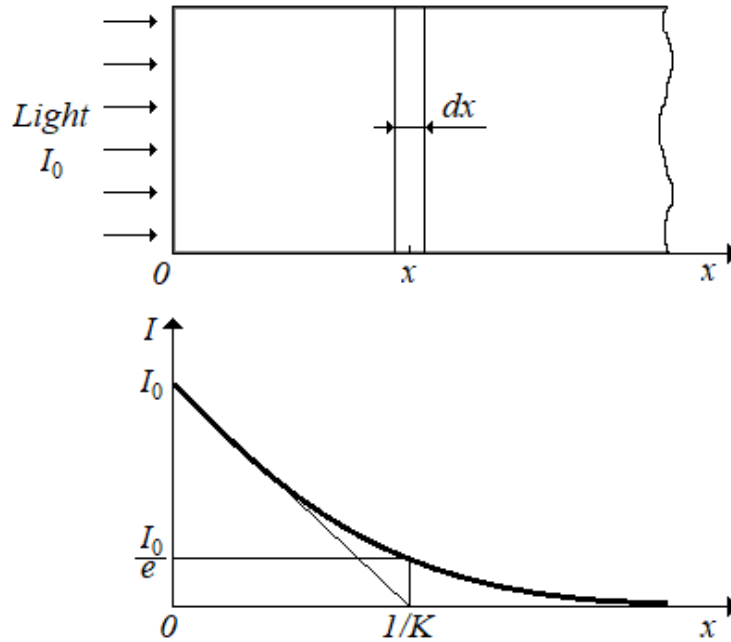


Fig. 4.19. Distribution of absorbed radiation intensity as a function of depth in the material.

Let a light flux with an initial intensity I_0 strike the surface of the sample perpendicularly, as shown in Fig. 4.19. The amount of light energy dI absorbed per unit time in a layer of unit area and thickness dx is proportional to the intensity of the light I at a depth x , and the thickness dx of the layer:

$$-dI = \alpha I dx, \quad (4.37)$$

where α is the proportionality constant known as the absorption coefficient. Integrating this equation, we obtain:

$$I = I_0 \exp(-\alpha x). \quad (4.38)$$

The derived distribution of radiation intensity as a function of depth in the sample is illustrated in Fig. 4.19. From the figure, it is clear that the reciprocal of the absorption coefficient, $1/\alpha$, represents the distance over which the light intensity decreases by a factor of e .

The more strongly a particular type of radiation is absorbed by the crystal, the greater the absorption coefficient α . Naturally, the value of α does not depend on whether the absorption process is photoactive or not.

As shown earlier, photons of different energy — and therefore different frequencies — undergo different absorption mechanisms within the crystal. The probability of absorption also varies with energy. Therefore, the absorption coefficient α is a frequency-dependent characteristic. For example, for photons whose energy exceeds the bandgap energy E_g , the absorption coefficient can reach very high values, on the order of $10^4 \div 10^6 \text{ cm}^{-1}$, whereas for $h\nu < E_g$, the absorption coefficient may decrease by six to seven orders of magnitude.

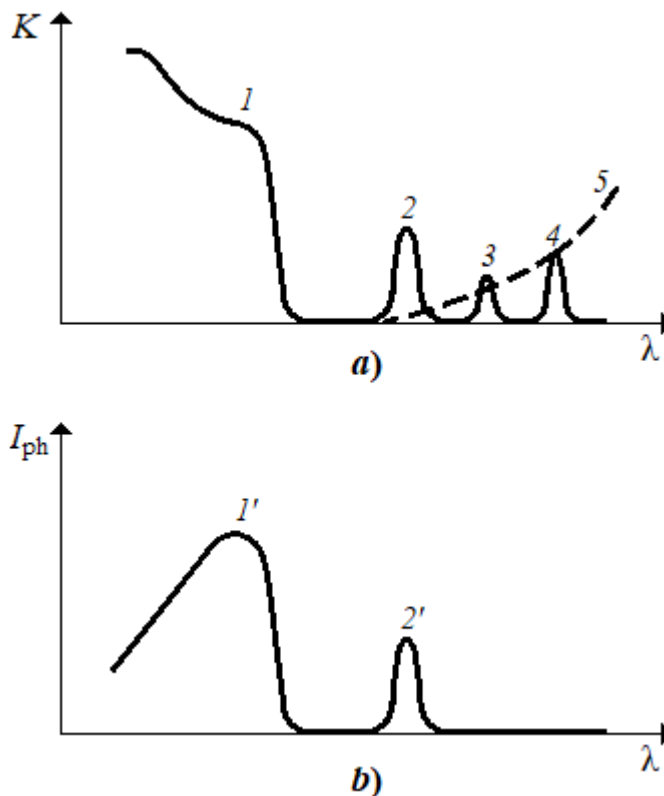


Fig. 4.20. Spectral curves of light absorption and photocurrent in a semiconductor:

1 – intrinsic absorption band; 2, 3, 4 – impurity absorption band, excitonic absorption band, and absorption by optical lattice vibrations, respectively; 5 – absorption curve due to free electrons; 1' – intrinsic conductivity band; 2' – impurity conductivity band.

The dependence of the absorption coefficient on frequency is referred to as the absorption spectrum or spectral absorption curve. A qualitative spectral absorption curve for a semiconductor is shown in Fig. 4.20a. Section 1 of the curve corresponds to interband transitions (the intrinsic absorption band), while sections 2, 3, and 4 represent impurity absorption, exciton absorption, and absorption due to optical lattice vibrations, respectively.

The dashed line (5) in Fig. 4.20a corresponds to absorption by free charge carriers. In Fig. 4.20b, the spectral response curve of the photocurrent is shown. Non-photoactive absorption processes do not contribute to the photocurrent. In practice, the observed spectral curves are usually more complex due to absorption by various uncontrolled impurities and numerous crystal lattice defects.

It should be noted that the decrease in photocurrent with decreasing wavelength of the radiation in the intrinsic absorption region is due to the fact that spectral curves are typically recorded at a constant incident light power. Since the energy of each photon increases with frequency, the number of photons decreases, leading to a corresponding reduction in the number of light-excited electron-hole pairs as the wavelength decreases.

4.4. Electrical conductivity of semiconductors in a strong electric field

The motion of an electron in an external electric field can be illustrated using an energy band diagram. The horizontal axis represents the electron's coordinate x , while the vertical axis shows the electron's energy E as it moves in the periodic potential of the crystal lattice. The energy levels are depicted as horizontal lines.

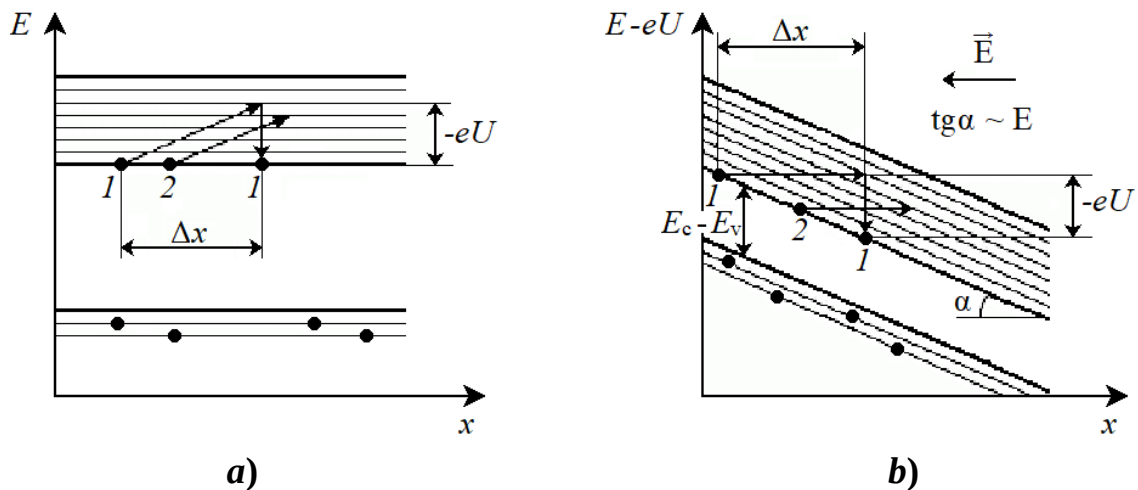


Fig. 4.21. Electron motion in an external electric field.

As an electron moves in an electric field, both its coordinate and energy change, causing it to transition from one energy level to another (Fig. 4.21a). In this process, its kinetic energy increases by an amount eU (where U is the potential difference traversed by the electron), while its potential energy decreases by the

same amount, keeping the total energy constant. The accumulated energy may be lost during scattering, with the electron returning to a lower level (electron 1).

Sometimes it is more convenient to plot the total energy of the electron, including the effect of the external electric field, on the vertical axis. In this case, the electron's motion is shown as a horizontal line, while the energy levels are drawn as slanted lines (Fig. 4.21b). The tangent of the inclination angle of these levels is proportional to the strength of the electric field.

As the electron moves in the applied field, it gains additional energy $\Delta\varepsilon$, which is later transferred to the lattice through electron-phonon interactions (electron 1). If the field strength E is not high (i.e., $E < 10^5$ V/m), the electrons transfer all the excess energy to the lattice, and their energy remains nearly constant. As the field strength increases further, the electrons cannot transfer energy to the lattice fast enough, and it begins to accumulate. As a result, the temperature of the charge carriers becomes higher than the lattice temperature. This effect is known as electron gas heating, and the electrons and holes are referred to as “hot” carriers.

In order for Ohm's law to be valid, the mobility and concentration of charge carriers must be independent of the electric field strength.

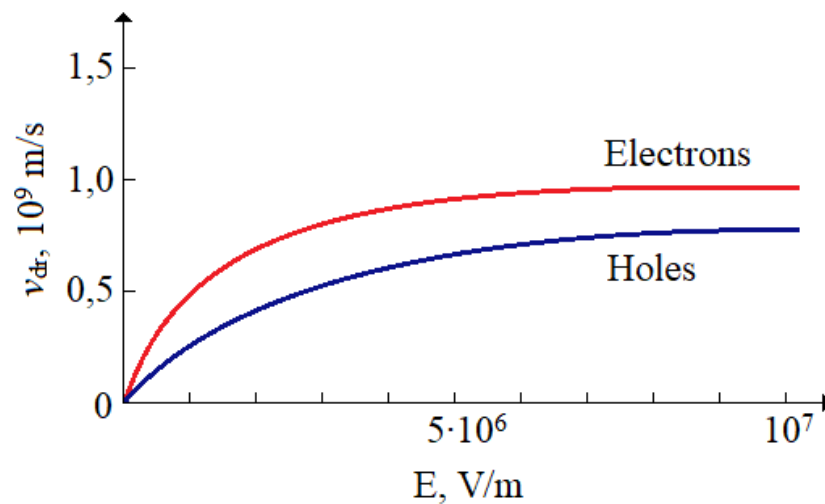


Fig. 4.22. Dependence of electron and hole drift velocities in Si on the electric field strength.

In the region of weak electric fields, the mobility remains independent of field strength due to the negligibly small change in the thermal velocities of charge carriers in the semiconductor. However, at sufficiently high field strengths, electron gas heating occurs, leading to an increase in the thermal velocity of the charge carriers. In this case, according to expression

$$\mu = \frac{qL}{m^* \bar{u}} \quad (4.39)$$

the mobility of charge carriers in strong fields decreases with increasing field strength. As a result, the drift velocity $v_{dr} = \mu E$ remains constant with increasing field strength and becomes equal to the saturation velocity (Fig. 4.22).

In practice, however, it is often difficult to observe a decrease in the conductivity of semiconductors in strong electric fields due to the reduced mobility of charge carriers. This is because, in most cases, increasing the electric field strength leads to a significant increase in the concentration of charge carriers.

When the applied electric field reaches values on the order of $10^6 \div 10^7$ V/m, processes of impact and electrical ionization of atoms begin, which are also accompanied by an increase in the concentration of free carriers. In impact (avalanche) ionization, an electron moving in a strong field accumulates kinetic energy sufficient to ionize atoms in the material. The newly released electron is also accelerated by the field and can ionize another atom. These electron collisions are inelastic, as evidenced by a change in the electron's energy after each collision. Repeated collisions with the generation of new free electrons lead to an avalanche process. Impact ionization is most characteristic of doped semiconductors, where the energy required to excite an electron from an impurity level to the conduction band is relatively low.

Electrostatic ionization (Zener effect) is observed in strong electric fields ($E \sim 10^6 \div 10^7$ V/m) due to tunneling of electrons from the valence band into the conduction band. The tunneling effect arises from the band bending that occurs at such high field strengths. On the energy band diagram, this appears as a tilt of the energy bands proportional to the electric field E (Fig. 4.23). In this case, a given electron energy may correspond to states in both the valence and conduction bands. When $E \sim 10^7$ V/m, the distance between equivalent positions in the bands is about $1 \text{ \AA}$.

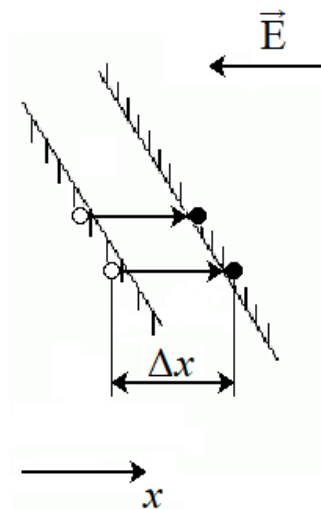


Fig. 4.23. Electron tunneling from the valence band to the conduction band under the influence of a strong electric field.

Chapter Review Questions

1. What are the properties of semiconductors, and how do they differ from metals and insulators?
2. What are the main differences between intrinsic and extrinsic semiconductors?
3. Explain the concepts of majority and minority charge carriers. Under what conditions do they become significant?
4. What is the role of donor and acceptor impurities in a semiconductor?
5. How are *n*-type and *p*-type semiconductors formed?
6. How does a change in temperature affect the concentration of charge carriers?
7. How does the conductivity of an intrinsic semiconductor change with increasing temperature, and what physical phenomenon explains this?
8. Describe the three main temperature-dependent conductivity regions in extrinsic semiconductors.
9. How does impurity ionization occur with increasing temperature, and how does this affect the charge carriers?
10. How can a nonlinear graph be used to explain the temperature dependence of carrier concentration?
11. How does the photoelectric effect manifest in semiconductors?
12. How does light energy affect the band gap of a semiconductor?
13. What physical processes underlie the phenomenon of photoconductivity?
14. What does quantum efficiency mean in photoelectric phenomena?
15. How do semiconductor-based photodetectors work, and which effects do they utilize?
16. How does a strong electric field affect charge carrier motion and conductivity in a semiconductor?
17. How does nonlinear behavior in a strong field differ from normal (linear) conductivity?
18. Explain the phenomena that cause a decrease in conductivity with increasing electric field strength (e.g., changes in collision frequency).
19. What role do thermal effects play under the influence of an electric field?
20. Explain the Gunn effect and its relation to conductivity in a strong electric field.
21. How is conductivity achieved in semiconductors?
22. Where are the energy levels of donor and acceptor impurities located within the band gap of a semiconductor?
23. Why is the ionization energy of an impurity lower in germanium than in silicon?

24. How are the concentrations of electrons and holes related in an intrinsic semiconductor?
25. Explain the temperature dependence of carrier concentration in a semiconductor. What is a “degenerate” (heavily doped) semiconductor?
26. What causes charge carrier scattering in a semiconductor?
27. Can the conductivity of a semiconductor decrease with increasing temperature?
28. What causes the appearance of non-equilibrium charge carriers in a semiconductor?
29. What is the difference between trapping centers and recombination centers?
30. What factors influence the lifetime and diffusion length of non-equilibrium charge carriers?
31. Why does additional photoconductivity shift toward longer wavelengths?

CHAPTER 5. BASIC PROPERTIES, TECHNOLOGY FEATURES AND APPLICATION OF SEMICONDUCTOR MATERIALS

Semiconductor materials are classified according to various criteria. The most common classification is based on the chemical composition of the material. Accordingly, semiconductors are divided into organic and inorganic types. In turn, inorganic semiconductors are further subdivided into elemental (simple) and compound (complex) semiconductors.

Elementary semiconductors consist primarily of atoms of a single chemical element, such as boron (B), silicon (Si), phosphorus (P), sulfur (S), germanium (Ge), arsenic (As), gray tin (Sn), antimony (Sb), selenium (Se), and tellurium (Te).

Compound semiconductors are composed of atoms of two or more chemical elements. Examples include:

Type $A^{IV}B^{IV}$ compounds (e.g., silicon carbide, SiC);

Type $A^{III}B^V$ compounds (e.g., aluminum antimonide, AlSb; gallium arsenide, GaAs; gallium phosphide, GaP; gallium antimonide, GaSb; indium antimonide, InSb; indium arsenide, InAs; indium phosphide, InP);

Type $A^{II}B^{VI}$ compounds (e.g., cadmium sulfide, CdS; cadmium selenide, CdSe; zinc oxide, ZnO; zinc sulfide, ZnS);

Type $A^{IV}B^{VI}$ compounds (e.g., lead sulfide, PbS; lead selenide, PbSe; lead telluride, PbTe).

In addition to inorganic substances, certain organic compounds — such as benzene, naphthalene, and others — also exhibit semiconductor properties.

Depending on their physical state, semiconductors may be classified as crystalline, amorphous, or liquid.

In some cases, narrow-bandgap semiconductors, oxide semiconductors, magnetic semiconductors, and others are considered separately, taking into account the specific physical processes that occur within them.

5.1. Classification of semiconductor materials. Silicon, germanium, silicon carbide and semiconductor compounds

Modern electronics is primarily based on inorganic crystalline semiconductors. These materials are classified by composition into elemental semiconductors and compound semiconductors. Semiconducting properties are exhibited by twelve chemical elements (Table 5.1), among which silicon (Si), germanium (Ge), and selenium (Se) are used as standalone semiconductor materials. The remaining elements are primarily utilized as dopants (impurities used for doping).

The electrical and physical characteristics of the main elemental semiconductors — silicon and germanium — are presented in Table 5.2.

Table 5.1

Elementary semiconductors

Element	Bandgap width E_g , eV*	Element	Bandgap width E_g , eV*
Boron (B)	1,1	Arsenic (As)	1,2
Carbon (diamond) (C)	5,6	Antimony (Sb)	0,12
Germanium (Ge)	0,665	Sulfur (S)	2,5
Silicon (Si)	1,12	Selenium (Se)	1,8
Tin (Sn_a)	0,08	Tellurium (Te)	0,36
Phosphorus (P)	1,5	Iodine (I)	1,25

*The band gap is given at 20°C.

Table 5.2

Electrophysical characteristics of germanium and silicon

Characteristics	Silicon	Germanium
Lattice period, nm	0,542	0,566
Density at 20°C, g/cm ³	2,3	5,3
Melting point, °C	1414	936
Intrinsic resistivity ρ , $\Omega \cdot m$	$2 \cdot 10^3$	0,47
Intrinsic carrier concentration N_o , m ⁻³	$1 \cdot 10^{16}$	$2,5 \cdot 10^{19}$
Bandgap width at 20°C E_g , eV	1,12	0,665
Mobility of charge carriers, m ² /V·s:		
• electrons μ_n	0,14	0,39
• holes μ_p	0,05	0,19
Relative permittivity ϵ	12	16

Silicon

Silicon is one of the most abundant elements in nature, ranking second only to oxygen in terms of prevalence. It is the primary semiconductor material used in microelectronics, accounting for up to 70% of all electronic devices produced.

Main applications of silicon include:

- Very-large-scale integrated (VLSI) circuits for electronic equipment and computers;
- Bipolar and field-effect transistors;
- Planar rectifier diodes;
- Zener diodes and thyristors;

- Photodiodes operating in the wavelength range from 0.3 to 1.1 μm ;
- Solar cells;
- Nuclear radiation detectors;
- Hall effect sensors.

Silicon-based devices can operate at temperatures up to 180°C.

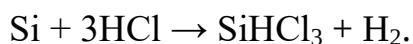
Like germanium, silicon is a Group IV element with a complex cubic crystal lattice of the diamond type. However, compared to germanium, it has stronger chemical bonds, resulting in a higher melting point, wider bandgap, lower charge carrier mobility, and lower intrinsic electrical conductivity (see Table 5.2).

Distinctive properties of silicon include:

- Chemical resistance;
- Thermal stability up to 900°C;
- High reactivity in the molten state with materials used to manufacture crucibles and reactors for single crystal growth (such as quartz and graphite), which complicates the production of pure silicon.

Obtaining semiconductor silicon:

1. Reduction of silicon dioxide with carbon in electric furnaces to obtain technical-grade silicon, which contains up to 1% impurities.
2. Synthesis of liquid trichlorosilane (SiHCl_3) by treating technical-grade silicon with dry hydrogen chloride at a temperature of 300–400°C:



3. Purification of trichlorosilane using advanced chemical refining methods.
4. Hydrogen reduction of trichlorosilane to obtain polycrystalline silicon.
5. Production of monocrystalline silicon:
 - By the Czochralski (CZ) method using a quartz crucible, large single crystals of low-resistivity silicon (ρ up to 2.5 $\Omega \cdot \text{m}$) are grown, with diameters up to 150 mm and lengths up to one meter.
 - Silicon reacts with SiO_2 in the crucible, forming silicon monoxide (SiO), which contaminates the crystal with oxygen atoms — deep acceptors in the silicon lattice.
 - By the float-zone (FZ) method (crucible-free zone melting), high-resistivity single crystals (ρ up to 200 $\Omega \cdot \text{m}$) up to 100 mm in diameter are produced, free from undesirable impurities.

Doping and Electrical Conductivity in Silicon. To form electrical conductivity in silicon, dopants from Groups III and V of the Periodic Table are used. The ionization energy of dopants in silicon is higher than in germanium, typically ranging from 0.03 to 0.06 eV. The main *n*-type dopant is phosphorus, the main *p*-type dopant is boron.

Vacancies in silicon are electrically active and act as deep acceptor levels. Impurities from Groups I and II of the Periodic Table form deep energy levels and significantly reduce the lifetime of nonequilibrium charge carriers.

Effect of Impurity Concentration on the Electrical Properties of Silicon.

The general trends in how impurities affect the electrical properties of silicon are similar to those observed in germanium (see Figs. 5.1 and 5.2).

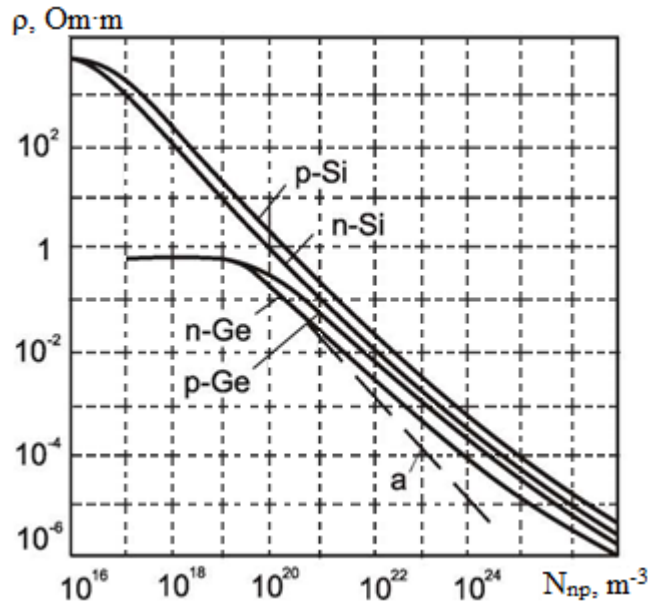


Fig. 5.1. Dependence of the specific electrical resistance of germanium and silicon on the impurity concentration at 20°C.

At room temperature (300 K), all dopant atoms are ionized. Intrinsic conductivity at this temperature is theoretically possible only when the impurity concentration $N < 10^{16} m^{-3}$, but such a high level of purification is technologically unachievable.

The baseline impurity concentration in silicon is comparable to that in germanium. However, the temperature at which intrinsic conductivity begins in silicon is $T_n > 200^\circ C$.

A decrease in carrier mobility due to scattering by ionized impurity atoms becomes noticeable when $N > 10^{21} m^{-3}$ (see Fig. 5.2). Impurity concentration strongly affects resistivity: as N increases, the resistivity ρ decreases from $10^3 \Omega \cdot m$ to $10^{-6} \Omega \cdot m$. For the same dopant concentration, $\rho_{Si} > \rho_{Ge}$ (see Fig. 5.1).

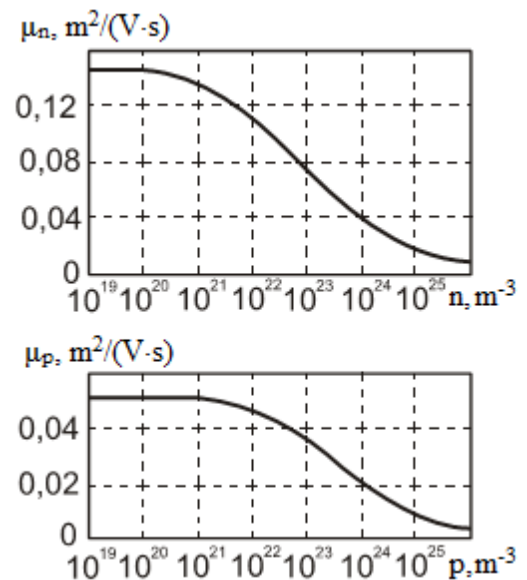


Fig. 5.2. Carrier mobility as a function of dopant concentration in silicon.

Semiconductor silicon marking:

Example 1: SEP 4.5/0.4 – silicon (S) with *n*-type conductivity (E), phosphorus-doped (P), resistivity at 300 K $\rho = 4.5 \, \Omega \cdot \text{cm}$, and diffusion length $L = 0.4 \, \text{mm}$.

Example 2: SHB 7.5/0.5 – silicon (S) with *p*-type conductivity (H), boron-doped (B), resistivity at 300 K $\rho = 7.5 \, \Omega \cdot \text{cm}$, and diffusion length $L = 0.5 \, \text{mm}$.

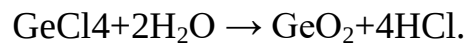
The letter "B" at the beginning of a designation indicates crucible-free (float-zone) silicon.

Germanium

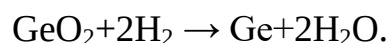
Germanium was historically the first semiconductor material to be developed, due to its relative ease of purification. It is a Group IV element with a diamond-like cubic crystal lattice. Distinctive properties of germanium include: chemical resistance to acids, high hardness and brittleness.

Obtaining semiconductor germanium. Germanium is rare in the Earth's crust (<0.001%) and does not form its own mineral ores. It is obtained as a by-product of copper-zinc and lead-zinc ore processing in the metallurgical industry. The main stages of production are:

1. Extraction of germanium concentrate.
2. Production of liquid germanium tetrachloride (GeCl_4) via chemical processing.
3. Production of germanium dioxide (GeO_2) through hydrolysis:



4. Hydrogen reduction of GeO_2 at 650–700 °C to produce germanium powder:



5. Melting of polycrystalline germanium from the powder.
 6. Zone refining to purify polycrystalline germanium.
 7. Crystal pulling (Czochralski method) to grow monocrystalline germanium.
- During crystal growth, carefully dosed dopants are added to obtain either *n*-type or *p*-type conductivity.

Doping and Conductivity Formation in Germanium. Germanium is used with extrinsic conductivity. Donor dopants (*n*-type): Group V elements – antimony (Sb), arsenic (As), phosphorus (P). Acceptor dopants (*p*-type): Group III elements – boron (B), aluminum (Al), gallium (Ga). These dopants create shallow energy levels in the bandgap, with an average ionization energy of ~0.01 eV. The most common dopants are antimony for *n*-type Ge and gallium for *p*-type Ge.

Copper and gold (Group I elements) form deep energy levels in the bandgap and act as efficient recombination centers, reducing the lifetime of nonequilibrium carriers, thereby increasing the switching speed of devices.

Effect of Dopant Concentration N_{np} on the Electrical Properties of Germanium. At temperatures above $90 \div 100$ K, dopant atoms in germanium are fully ionized, meaning the charge carrier concentration is equal to the dopant concentration: $n = N$.

The typical working dopant concentration in germanium is in the range of $N = 10^{21} \div 10^{24} \text{ m}^{-3}$. At room temperature ($T_n = 20 \div 25$ °C), intrinsic conductivity arises only at very low dopant concentrations ($N < 10^{19} \text{ m}^{-3}$). As the dopant concentration increases, the temperature at which intrinsic conductivity begins also increases. At standard dopant levels, this temperature exceeds $T_n > 100$ °C.

Thus, for dopant concentrations $N < 10^{19} \text{ m}^{-3}$, the resistivity ρ of germanium is primarily determined by intrinsic conductivity. In lightly doped semiconductors ($N < 10^{21} \text{ m}^{-3}$), resistivity increases due to scattering on thermal vibrations of the crystal lattice. At typical dopant concentrations, the resistivity is inversely proportional to N

$$\gamma = \frac{1}{\rho} = \frac{1}{en\mu} = \frac{1}{eN\mu},$$

i.e., as the dopant concentration increases, resistivity decreases. However, the actual dependence deviates from a linear trend (dashed line “a” in Fig. 5.1) due to the reduction in charge carrier mobility caused by scattering on ionized impurity atoms (Fig. 5.3). The resistivity of p -type germanium is higher than that of n -type germanium, because hole mobility is lower than electron mobility.

For concentrations $N > 10^{24} \text{ m}^{-3}$, germanium becomes a degenerate semiconductor.

Semiconductor germanium marking:

Example 1: GES 1.0/0.5 — germanium (G), electron conductivity type (E), doped with Antimony (S), resistivity at 300 K: $\rho = 1.0 \Omega \cdot \text{cm}$, diffusion length: $L = 0.5$ mm.

Example 2: GHG 5.0/1.0 — germanium (G), hole conductivity type (H), doped with Gallium (G), resistivity at 300 K: $\rho = 5.0 \Omega \cdot \text{cm}$, diffusion length: $L = 1.0$ mm.

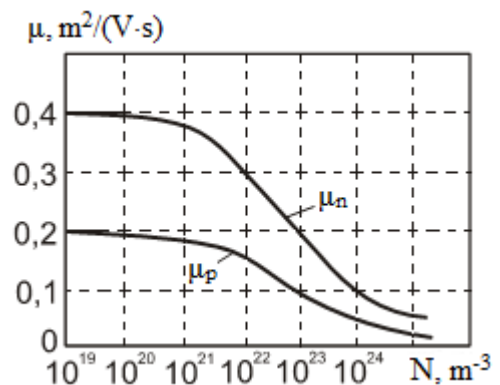


Fig. 5.3. Carrier mobility as a function of dopant concentration in germanium.

Semiconductor Compounds

Binary semiconductor compounds are commonly designated according to the group numbers of their constituent elements in the Periodic Table: $A^{IV}B^{IV}$, $A^{III}B^V$, $A^{II}B^{VI}$, $A^{IV}B^{VI}$.

Silicon Carbide. The only representative of the $A^{IV}B^{IV}$ group of compounds is silicon carbide (SiC). This compound exists in two polymorphic modifications:

- **β -SiC**, with a cubic diamond-like lattice ($T < 2000^\circ\text{C}$);
- **α -SiC**, with a hexagonal lattice ($T > 2000^\circ\text{C}$).

Key Properties of Silicon Carbide:

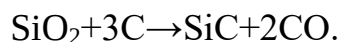
- Predominantly covalent bonding;
- High hardness, chemical resistance, and thermal stability;
- Nonlinear current-voltage characteristics;
- Luminescence in the visible spectral range;
- Wide bandgap, low charge carrier mobility (see Table 5.3), and impurity resistivity in the range of $0.03 \div 0.15 \, \Omega \cdot \text{cm}$.

Table 5.3

Properties of silicon carbide

Modification	β -SiC	α -SiC
Lattice period, nm	0,436	0,308
Band gap width E_g , eV	2,39	3,02
Electron mobility μ_n , $\text{m}^2/\text{V} \cdot \text{s}$	0,1	0,033
Hole mobility μ_p , $\text{m}^2/\text{V} \cdot \text{s}$	0,006	0,006
Sublimation temperature, $^\circ\text{C}$	>2600	2700

Production of Silicon Carbide. The starting raw material is quartz sand (SiO_2). Technical-grade silicon carbide is produced by reducing silicon dioxide with carbon in electric furnaces according to the reaction:



Semiconductor-grade SiC crystals are obtained by sublimation in furnaces with graphite heaters under an argon atmosphere at temperatures ranging from 2400 to 2600°C .

Ceramic silicon carbide is produced from SiC powder mixed with binders (such as clay, feldspar, or water glass), followed by pressing and firing at $T = 1000^\circ\text{C}$.

Conductivity Formation in SiC. Silicon carbide is primarily used with extrinsic conductivity (intrinsic conductivity is only significant at $T > 1400^\circ\text{C}$).

Group V dopants (N, P, As, Sb, Bi) act as donors, resulting in *n*-type green SiC. Group II (Ca, Mg) and Group III (B, Al, Ga) elements act as acceptors, producing *p*-type SiC, which appears blue, violet, or black in thick layers. Electrically active intrinsic defects also influence conductivity: excess silicon creates *n*-type conductivity and excess carbon results in *p*-type conductivity.

Applications of Silicon Carbide:

- Visible-spectrum LEDs based on monocrystalline hexagonal SiC. Depending on dopant type and concentration, emission ranges from red to violet. Yellow LEDs, obtained by boron diffusion into nitrogen-doped *n*-type SiC, exhibit the highest emission stability and are used as reference standards.
- High-power rectifier diodes and field-effect transistors (FETs) capable of operating at temperatures up to 700°C.
- High-energy particle detectors suitable for use in aggressive environments.
- Nonlinear resistors (varistors) made of ceramic SiC, used in automation systems, computing, and instrumentation for current and voltage stabilization and power line protection.
- High-temperature heaters (silicon carbide rods, or "silit" elements) operating up to 1800°C, and high-temperature strain gauges made from ceramic SiC.

$A^{III}B^V$ Semiconductor Compounds. These compounds are formed from elements of Groups III and V of the Periodic Table (see Table 5.4).

Table 5.4

Semiconductor chemical compounds $A^{III}B^V$

Groups of compounds	Nitrides	Phosphides	Arsenides	Antimonides
$A^{III} \backslash B^V$	N	P	As	Sb
B	BN	BP	BAs	BSb
Al	AlN	AlP	AlAs	AlSb
Ga	GaN	GaP	GaAs	GaSb
In	InN	InP	InAs	InSb

Most of these compounds possess a complex cubic crystal structure (zinc blende or sphalerite), while nitrides typically crystallize in a hexagonal structure (wurtzite). The chemical bonding is covalent-ionic in nature:

- *Covalent component:* Each atom of element A is surrounded by four atoms of element B, and vice versa. These atoms occupy the vertices of tetrahedra. Three valence electrons from atom A form three covalent pairs with electrons from atoms B, while the fourth pair is formed solely by electrons from B (A–B, A–B, A–B, B–B).

- *Ionic component:* The electron cloud is shifted toward the B atom, creating a partial negative charge near atom B and a positive charge near atom A. The magnitude of the effective charge determines the degree of ionicity of the compound.

Within each group, as the total atomic mass of the compounds increases, the following trends are observed due to weakening of covalent bonding, increased delocalization of electron clouds, and an enhanced metallic character of the bonds:

- Bandgap width decreases;
- Melting point decreases;
- Charge carrier mobility increases, and electrical resistivity decreases;
- Hardness decreases, and ductility increases, meaning that mechanically, the material becomes more metal-like (see Table 5.5).

Table 5.5

Properties of some A^{III}B^V compounds

Compound	Density, g/cm ³	T_m , °C	E_g , eV	μ_n , m ² /V·s	μ_p , m ² /V·s	ϵ
GaN	6,11	1700	3,4	0,03	-	12,2
AlP	2,37	2000	2,45	0,008	0,003	9,8
GaP	4,07	1467	2,26	0,019	0,012	11,1
InP	4,78	1070	1,35	0,46	0,015	12,4
AlAs	3,6	1770	2,16	0,028	-	10,1
GaAs	5,32	1238	1,43	0,95	0,045	13,1
InAs	5,67	942	0,36	3,3	0,046	14,6
AlSb	4,28	1060	1,58	0,02	0,055	14,4
GaSb	5,65	710	0,72	0,4	0,14	15,7
InSb	5,78	525	0,18	7,8	0,075	17,7

In A^{III}B^V semiconductors, charge carrier mobility is primarily limited by scattering due to thermal lattice vibrations. As the atomic mass increases, the amplitude of these thermal vibrations decreases, resulting in higher carrier mobility and lower intrinsic resistivity (ρ).

In many commonly used A^{III}B^V compounds, the electron mobility (μ_n) is significantly higher than the hole mobility (μ_p), i.e., $\mu_n \gg \mu_p$, meaning that the intrinsic resistivity is predominantly determined by electron mobility.

Formation of Conductivity in A^{III}B^V Compounds. Group II elements (Zn, Cd, Mg) are used as acceptors, substituting Group III atoms in the crystal lattice and producing *p*-type semiconductors. Group VI elements (S, Se, Te) act as donors, replacing Group V atoms and forming *n*-type semiconductors. The ionization energy of impurities decreases with increasing atomic mass and, for heavier compounds, ranges from 0.001 to 0.005 eV.

Transition metals (Fe, Ni, Co) form deep acceptor-type energy levels and serve as effective recombination centers (traps).

Notable Properties of $A^{III}B^V$ Compounds. These compounds exhibit photoelectric sensitivity and a high efficiency of radiative recombination of non-equilibrium charge carriers. The emission spectrum is determined by the bandgap width, making these materials well-suited for various optoelectronic applications, including: high-speed photodetectors and light emitters, photovoltaic cells, photocathodes, light-emitting diodes (LEDs), semiconductor lasers.

$A^{II}B^{VI}$ Semiconductor Compounds. These compounds are formed from elements of Groups II and VI of the Periodic Table (see Table 5.6).

Table 5.6

Groups of compounds	Sulfides	Selenides	Tellurides
$A^{II} \backslash B^{VI}$	S	Se	Te
Zn	ZnS	ZnSe	ZnTe
Cd	CdS	CdSe	CdTe
Hg	HgS	HgSe	HgTe

$A^{II}B^{VI}$ compounds typically crystallize in either a complex cubic structure (zinc blende, or sphalerite) or a hexagonal structure (wurtzite); some compounds adopt the NaCl-type (rock salt) structure. The chemical bonding is covalent-ionic, with a more pronounced ionic character compared to $A^{III}B^V$ compounds. This is due to the greater electronegativity difference between the constituent elements.

In terms of bonding: two valence electrons from atom A form two covalent pairs with electrons from atom B, two additional electron pairs are contributed solely by atom B (A–B, A–B, B–B, B–B). Compared to $A^{III}B^V$ compounds, property correlation with atomic mass in $A^{II}B^{VI}$ compounds is weaker (see Table 5.7).

Table 5.7

Properties of $A^{II}B^{VI}$ semiconductor compounds

Compound	Density, g/cm ³	T_m , °C	E_g , eV	μ_n , m ² /V·s	μ_p , m ² /V·s	λ , nm
ZnS	4,1	1780	3,74	0,014	0,0005	330
CdS	4,82	1750	2,53	0,034	0,011	500
HgS	7,73	1713	2,0	0,025	-	-
ZnSe	5,42	1520	2,73	0,026	0,0015	454
CdSe	5,81	1264	1,85	0,072	0,0075	600
HgSe	8,26	867	0,12	2,2	-	-
ZnTe	6,34	1239	2,23	0,053	0,003	-
CdTe	5,86	1041	1,51	0,12	0,006	790
HgTe	8,42	577	0,08	2,3	0,01	-

$A^{II}B^{VI}$ compounds are typically obtained by crystallization from metal and non-metal vapors, with precise control over the relative concentrations of the components.

Formation of Conductivity. Intrinsic conductivity arises from an excess of either Group II (A^{II}) or Group VI (B^{VI}) atoms. Structural defects — such as vacancies and interstitial atoms — are electrically active: interstitial A^{II} atoms act as shallow donors with ionization energies of $0.01 \div 0.03$ eV; A^{II} vacancies act as shallow acceptors (about 0.05 eV). The type of conductivity can be modified by adjusting the composition of the solid solution. For example, excess A^{II} atoms, introduced through metal vapor treatment, lead to n -type conductivity. To achieve reproducible electrical characteristics, precise control of the chemical composition is required.

Impurity (extrinsic) conductivity is less commonly used. Group I metals (Cu, Ag, Au) serve as acceptors (with ionization energies of $0.1 \div 0.3$ eV) by substituting Group II lattice sites.

Properties and Applications of $A^{II}B^{VI}$ Compounds. A key feature of $A^{II}B^{VI}$ compounds is the wide variation in bandgap energies across different materials, which enables emission across a broad range of wavelengths (λ) — from ultraviolet (UV) to infrared (IR) (see Table 12.7). They also demonstrate high radiative recombination efficiency.

Primary applications include photoelectric devices:

- Photoconductors (photodetectors) based on the internal photoelectric effect, made using cadmium sulfide (CdS) and cadmium selenide (CdSe). CdS photoconductors exhibit high sensitivity in the visible and UV regions, as well as sensitivity to X-rays and gamma radiation, which is used in radiation indicators and dosimeters. They also have a high quantum efficiency: up to 10^{14} electrons per absorbed photon.

- Phosphors (luminescent materials) based on zinc sulfide (ZnS) or solid solutions such as (Zn,Cd)S and Zn(S,Se). Photoluminescent phosphors with long-lasting green or blue afterglow (phosphorescence), based on ZnS doped with copper or Cu+Co, are used in luminous dials and emergency lighting. Cathodoluminescent phosphors (used in cathode-ray tubes) include: ZnS:Ag for blue emission, ZnS·CdS:Ag for yellow, their mixture produces white light — used in TV screens, oscilloscopes, and monitor displays.

- Infrared photodetectors are made from heavier compounds, particularly cadmium telluride (CdTe) and mercury telluride (HgTe).

- Semiconductor lasers based on AIIIBVI compounds operate across various spectral regions. Hall effect sensors, made from compounds with high carrier mobility (e.g., HgSe, HgTe, and their solid solutions), are also used. These sensors are often produced as thin films deposited on mica substrates. They exhibit stable

performance due to a low dependence of resistivity (ρ) on temperature and electric field strength.

$A^{IV}B^{VI}$ Semiconductor Compounds. This group of compounds includes lead chalcogenides — namely, the sulfides, selenides, and tellurides of lead (see Table 5.8). These materials are typically produced by fusing lead with the corresponding chalcogen element (S, Se, or Te). Single crystals are grown using the directional solidification method from the melt. In addition, natural single crystals of PbS can be found in nature (as the mineral galena).

Table 5.8

Properties of $A^{IV}B^{VI}$ compounds

Characteristics	PbS	PbSe	PbTe
E_g , eV	0,41	0,29	0,32
T_m , °C	1114	1065	910
Density, g/cm ³	7,6	8,15	8,16
μ_n , m ² /V·s	0,06	0,09	0,03
μ_p , m ² /V·s	0,04	0,05	0,02

Conductivity of $A^{IV}B^{VI}$ Compounds. These compounds exhibit intrinsic conductivity: an excess of lead results in *n*-type conductivity, an excess of the chalcogen element leads to *p*-type conductivity.

Key property – spectral sensitivity in the infrared region. Due to their high sensitivity to infrared (IR) radiation, $A^{IV}B^{VI}$ compounds are widely used in photoconductors with high-frequency response, such as PbS-based detectors. Other Applications Include:

- Strain sensors (piezoresistors) used in vibration, pressure sensors, and microphones. These are fabricated from materials whose bandgap width changes under mechanical deformation (e.g., PbS and PbTe).
- Thermosensitive devices, based on changes in electromotive force (emf) across *p-n* junctions with temperature variation. These devices, using PbS and PbTe, are employed in semiconductor thermostats and thermoelectric coolers.

Promising materials – solid solutions of lead and tin tellurides. Solid solutions based on lead telluride (PbTe) and tin telluride (SnTe) are of particular interest. These materials share the same crystal lattice structure (lattice constant $a = 0.603$ nm) and exhibit complete mutual solubility. They are used in photodetectors with high sensitivity in the 8–14 μm “atmospheric window”, corresponding to the peak blackbody radiation at 300 K, injection lasers based on $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$, which emit in the deep infrared spectral region — up to 30 μm , representing the practical wavelength limit for semiconductor lasers.

Chapter Review Questions

1. What criteria are used to classify semiconductor materials?
2. What are the main differences between elemental and compound semiconductors?
3. What are the properties of organic and inorganic semiconductors?
4. Why are silicon and germanium the most widely used elemental semiconductors?
5. What physical or chemical factors are decisive when choosing a semiconductor material?
6. What are the characteristics of the crystal lattice and conductivity of silicon?
7. What advantages do silicon's thermal stability and oxidation properties provide in the electronics industry?
8. Why have silicon-based devices become so widely used?
9. What is the role of the SiO_2 oxide layer in silicon integrated circuits?
10. What charge carriers are generated when donor and acceptor impurities are introduced into silicon?
11. How does the electrical conductivity of germanium differ from that of silicon?
12. What are the advantages and limitations of germanium as a semiconductor?
13. How does the carrier mobility in germanium compare to that in silicon?
14. How do differences in bandgap width between germanium and silicon affect the performance of various devices?
15. What physical properties of silicon carbide (SiC) allow it to be used in high-voltage devices?
16. Under what temperature and environmental conditions can SiC operate stably?
17. In which application areas are group III–V semiconductors, such as gallium arsenide (GaAs), used and why?
18. What are the advantages of binary and multicomponent compound semiconductors?
19. What do the terms direct and indirect bandgap mean in semiconductor compounds, and how do they influence device selection?
20. What purification and crystallization methods are used to obtain germanium and silicon? Which methods are widely used for growing large single crystals?
21. How does carrier mobility change with increasing impurity concentration in germanium and silicon, and why?
22. What advantages make silicon the primary material for the production of planar transistors and integrated circuits?

23. What type of chemical bonding is characteristic of $A^{III}B^V$ semiconductor compounds? How do their electrophysical properties change with increasing atomic mass?
24. What materials are used in pumped lasers and LEDs?
25. What materials are used in solar cells?
26. Under what doping conditions does germanium exhibit high resistivity at room temperature?

CHAPTER 6. ELECTRONIC AND TECHNICAL MATERIALS FOR SOLAR CELLS

Solar cells are considered one of the most critical components of solar energy systems. Depending on their functional and structural characteristics, solar cells — and the solar panels built from them — can vary in size, ranging from microscopic solar cells used in calculators to large-scale coverings for vehicles and buildings (they are often seen mounted on rooftops).

The shift from traditional hydrocarbon-based energy to renewable sources is primarily driven by two factors: the annual depletion of fossil fuel reserves (which are non-renewable) and the rapid increase in global energy consumption associated with the growing world population. As a result, steady and consistent progress is being made in the field of renewable energy.

A solar cell is a semiconductor device that directly converts light energy into electrical energy. Its operation is based on the photoelectric effect. The core component of the solar cell is a silicon crystal featuring a p - n junction, which naturally generates an electric field.

When photons from sunlight strike the semiconductor, and if their energy exceeds the bandgap energy of the material, they excite electrons in the valence band, promoting them to the conduction band. This process creates free electrons and holes (electron vacancies). Under the influence of the electric field in the p - n junction, these charge carriers are separated: electrons move toward the n -region, and holes move toward the p -region.

These charge carriers travel through an external electrical circuit, generating an electric current. Thus, the energy of sunlight is converted into electrical energy — a process known as the photovoltaic effect.

6.1. Main types of solar cells

On a global scale, crystalline silicon-based (c-Si) solar cells are the primary technology used for large-scale electricity generation from solar energy. Despite the wide variety of designs and materials, all such solar cells are fundamentally based on a p - n junction contact region. Depending on the types of semiconductor materials used to form the junction, p - n junctions are classified into two main categories: homojunctions – junctions formed between regions of the same semiconductor material with different doping types and heterojunctions – junctions formed between different semiconductor materials. Solar cells are also classified based on the type of material used, the structure of the p - n junction, and the dimensions of the cell.

The development of solar cells is divided into **three main generations** depending on the stages of technological progress:

First generation solar cells (1G) — classic silicon solar cells (mono-Si, poly-Si, a-Si);

Second generation solar cells (2G) — technologies based on thin-film materials (CdTe, CIGS, a-Si);

Third generation solar cells (3G) — new generations with innovative approaches (perovskite, quantum dots, organic, tandem/hybrid systems and two-dimensional (2D) structures).

Each generation has its own unique characteristics in terms of the materials used, technological solutions and efficiency. Below we will consider the main ones.

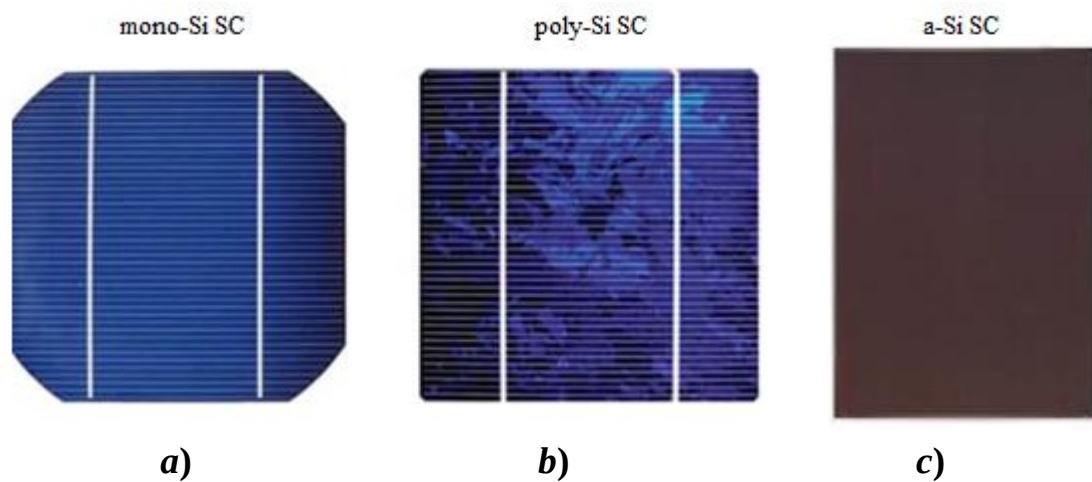


Fig. 6.1. Types of silicon solar cells.

Silicon solar cells. The most common solar cells are semiconductor silicon solar cells. Depending on the modification of silicon in their composition, silicon solar cells are mainly divided into monocrystalline, polycrystalline and amorphous silicon solar cells (Fig. 6.1).

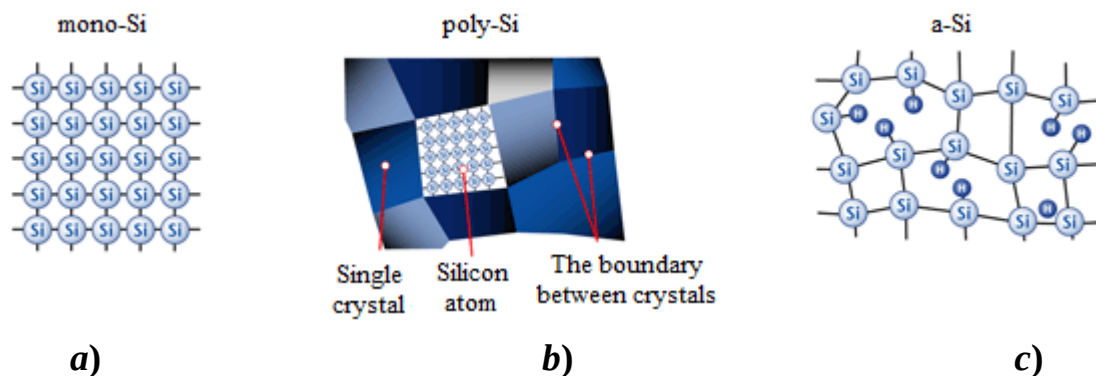


Fig. 6.2. Monocrystalline (a), polycrystalline (b) and amorphous silicon (c) used in solar cells.

1. Monocrystalline silicon (mono-Si) solar cells are the most established and widely used photovoltaic technology due to their high efficiency and long-term stability. These cells are manufactured from high-purity single crystal silicon, in which the atoms are arranged in a continuous and unbroken lattice structure with minimal defects (Fig. 6.2a). This uniformity allows for efficient charge carrier transport and low recombination rates, making monocrystalline cells particularly effective for converting solar radiation into electricity.

The production process typically begins with the Czochralski method, where a seed crystal is slowly pulled from molten silicon under controlled conditions, allowing a cylindrical ingot to form with a single crystalline orientation (Fig. 6.3). Once the ingot is fully grown, it is sliced into thin wafers using precision wire saws. These wafers serve as the base material for solar cells, undergoing further treatments such as surface texturing, doping, diffusion, and anti-reflective coating to optimize their electrical and optical performance.

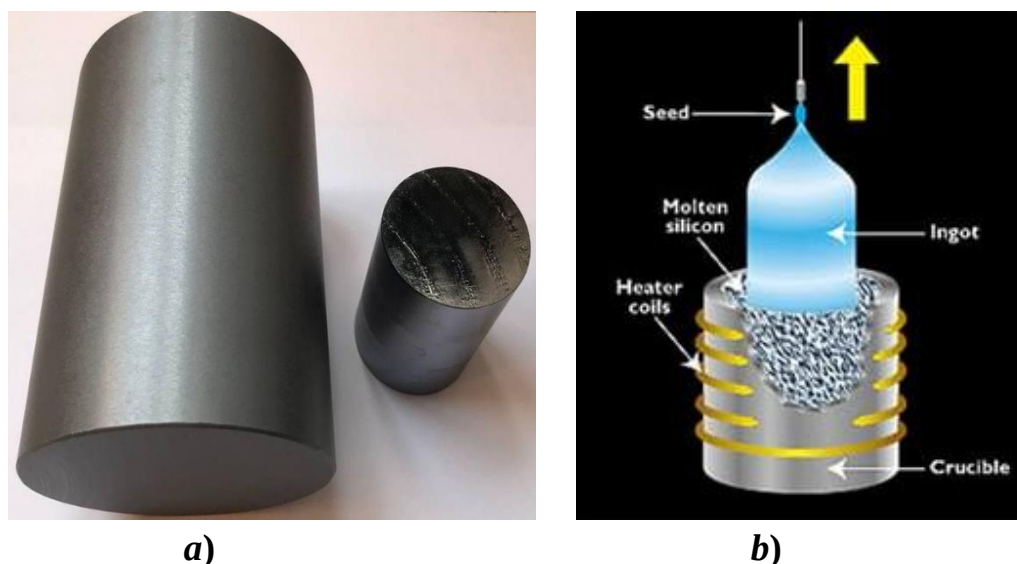


Fig. 6.3. A cylinder of monocrystalline silicon (a) and the process of its growth (b).

Monocrystalline cells are characterized by their uniform dark appearance, usually black or deep blue, and by their distinctive round or clipped-corner shape, which reflects the geometry of the cylindrical ingots. They are known for their high-power conversion efficiencies, which in commercial modules typically range from 20% to 23%, while laboratory cells have achieved values above 26%. Their performance remains relatively stable under elevated temperatures, with temperature coefficients commonly around -0.3 to -0.4% per degree Celsius, which is favorable compared to other cell types.

The main advantages of monocrystalline silicon solar cells include their superior efficiency, long operational lifetime (often exceeding 25 years), and

compact footprint, which is especially important in applications with limited space. However, these benefits come at the cost of more complex and energy-intensive manufacturing, as well as greater material waste during the slicing of wafers from the round ingot.

Monocrystalline solar cells are widely deployed in both residential and commercial photovoltaic systems, as well as in portable solar products and grid-connected power plants. Their reliability, market maturity, and ongoing technological improvements, such as passivated emitter rear contact (PERC) designs, make them a cornerstone of modern solar energy generation.

2. Polycrystalline silicon (poly-Si) solar cells, also known as multicrystalline silicon cells, represent a foundational and widely adopted class of photovoltaic technology. Introduced as a cost-effective alternative to monocrystalline silicon, polycrystalline cells are distinguished by their unique material structure, fabrication processes, and performance characteristics. They have historically played a crucial role in the expansion of solar energy technologies, particularly in large-scale installations and budget-sensitive applications.

The core difference between polycrystalline and monocrystalline cells lies in the crystalline structure of the silicon used (See Fig. 6.1 *a* and *b*). While monocrystalline silicon consists of a single, continuous crystal lattice, polycrystalline silicon is composed of numerous small silicon crystals or grains, each with a different orientation. This polycrystalline nature results in grain boundaries – interfaces between crystals – which serve as sites of increased recombination of charge carriers, thus slightly reducing the overall efficiency compared to monocrystalline cells.

The manufacturing of polycrystalline silicon solar cells is generally more straightforward and less expensive than that of monocrystalline counterparts. The process typically begins with melting high-purity silicon in a crucible and allowing it to cool and solidify slowly in a square mold. Unlike the Czochralski process used for monocrystalline ingots, this method does not require precise control over crystal growth direction. As the silicon solidifies, it forms a block composed of randomly oriented crystals. This block is then sliced into square-shaped wafers, minimizing material waste and allowing for better packing density in solar panels.

The surface of polycrystalline cells exhibits a characteristic speckled or grainy texture, with visible crystal facets that scatter light in different directions. This appearance arises from the varying optical properties of the individual grains. The color of the cells often ranges from blue to dark blue, depending on the anti-reflective coating and surface texturing techniques applied during cell processing. These optical treatments are essential to minimize reflectance and enhance light absorption.

From an electrical standpoint, the presence of grain boundaries in polycrystalline silicon affects the movement of electrons and holes. These boundaries act as traps for carriers, leading to increased recombination losses and reduced carrier lifetimes. As a result, the power conversion efficiency of polycrystalline cells typically falls in the range of 15 %.

In terms of thermal performance, polycrystalline cells generally exhibit similar temperature coefficients to monocrystalline cells, typically around $-0,4\%/^{\circ}\text{C}$.

The lower cost of polycrystalline cells makes them particularly attractive for utility-scale solar farms and other applications where efficiency can be traded for affordability. Their simpler manufacturing process not only reduces energy consumption during production but also yields a shorter energy payback time — the time required for a solar panel to generate the amount of energy that was consumed in its production. This characteristic contributes to the favorable environmental footprint of polycrystalline PV technology.

Furthermore, polycrystalline solar modules are known for their mechanical robustness and durability. The square wafer geometry facilitates high packing density in panel arrays, optimizing the use of available space. These modules are often manufactured with standard aluminum frames and tempered glass, providing resistance against environmental stressors such as wind, hail, and moisture. With proper maintenance, polycrystalline modules can function effectively for 25 years or more.

Technological advancements in recent years have further improved the performance of polycrystalline cells. Techniques such as selective emitter formation, rear surface passivation, and advanced metallization have been adopted from monocrystalline technologies to enhance poly-Si cell performance. Additionally, research continues into reducing the adverse effects of grain boundaries through chemical passivation and advanced crystal growth control.

Despite the rise of newer technologies like PERC (Passivated Emitter and Rear Cell) and bifacial modules, polycrystalline silicon remains a significant player in the global PV market. While monocrystalline modules have gained popularity due to their higher efficiency and sleek appearance, polycrystalline modules continue to offer a compelling balance of cost, performance, and reliability, especially in markets where initial investment constraints are a primary consideration.

3. Amorphous silicon (a-Si) solar cells represent a distinctive class of thin-film photovoltaic technology characterized by their non-crystalline silicon structure. Unlike crystalline silicon materials, where atoms are arranged in an orderly, repeating pattern, amorphous silicon lacks long-range atomic order (Fig. 6.2c). This disordered structure allows a-Si cells to absorb sunlight more effectively over a

thinner layer, which is one of their key advantages compared to traditional crystalline counterparts.

The manufacturing process for a-Si solar cells involves the deposition of silicon atoms onto a substrate — typically glass, plastic, or metal — through a technique known as plasma-enhanced chemical vapor deposition (PECVD). In this method, silane gas (SiH_4) is broken down in a plasma environment, and the resulting silicon atoms form a thin amorphous film on the substrate. The entire process is carried out at relatively low temperatures (200-300 °C), which permits the use of flexible and low-cost substrates and reduces overall manufacturing energy requirements.

Amorphous silicon's high optical absorption coefficient allows it to absorb a significant portion of the solar spectrum within just a few micrometers of material thickness. As a result, a typical a-Si solar cell is only 0.3 to 0.5 micrometers thick, which significantly reduces material usage. To increase voltage output and efficiency, manufacturers often stack multiple layers of a-Si cells in a tandem or triple-junction configuration, where each layer is optimized to absorb different parts of the solar spectrum.

Despite the advantages of low-cost materials, flexible form factors, and minimal raw silicon consumption, a-Si solar cells typically exhibit lower conversion efficiencies compared to crystalline silicon. Commercial a-Si modules usually achieve efficiencies in the range of 6-10 %.

Another important challenge associated with a-Si technology is the Staebler-Wronski effect — a phenomenon in which prolonged exposure to light induces metastable defects in the silicon structure, leading to a gradual decline in cell efficiency over time. While some of this degradation is recoverable through thermal annealing or light cycling, it remains a critical factor in long-term performance evaluation.

Nevertheless, the low-temperature, scalable production process of a-Si solar cells makes them attractive for a variety of niche applications. They are particularly well-suited for building-integrated photovoltaics (BIPV), consumer electronics, and portable power solutions, where mechanical flexibility, weight constraints, and aesthetic integration are more critical than maximum efficiency. For example, a-Si modules are commonly used in calculators, camping gear, window-integrated panels, and solar-powered watches.

From a manufacturing standpoint, the ability to fabricate a-Si modules on large-area substrates using roll-to-roll processes contributes to their cost-effectiveness and scalability. Additionally, the potential to combine amorphous silicon with other thin-film materials, such as microcrystalline silicon (in so-called micromorph tandem cells), has enabled continued innovation within this class of

photovoltaics. These hybrid designs help to overcome some of the efficiency limitations of single-junction a-Si by broadening the absorption spectrum and improving carrier collection.

Environmentally, a-Si solar technology presents several benefits. It avoids the use of toxic heavy metals like cadmium or rare elements like indium, making its material profile more sustainable. The reduced energy input required for production also results in a lower energy payback time — typically under one year, depending on location and deployment.

While a-Si technology faces strong competition from more efficient and increasingly affordable crystalline silicon modules, it continues to hold relevance in specialized markets. Ongoing research is directed toward improving light trapping, optimizing layer thicknesses, passivating defect states, and enhancing long-term stability. These efforts aim to extend the application range of amorphous silicon photovoltaics while maintaining their inherent advantages in flexibility and manufacturability.

Thin-film solar cells constitute a diverse and rapidly evolving category of photovoltaic technologies that differ fundamentally from traditional wafer-based silicon cells in terms of materials, structure, and fabrication methods. These cells are characterized by the use of one or more thin layers — typically on the order of a few micrometers — of photovoltaic material deposited onto a supporting substrate such as glass, plastic, or metal foil. The reduced thickness of the active layers leads to significant material savings, lower production costs, and greater flexibility in application compared to crystalline silicon based solar cells.

Unlike bulk silicon solar cells, thin-film solar technologies encompass a variety of semiconductor materials, each with unique physical and electrical properties. The most prominent types of thin-film solar cells include *cadmium telluride (CdTe)*, *copper indium gallium selenide (CIGS)*, and *amorphous silicon (a-Si)*. Each of these materials offers distinct advantages and challenges in terms of efficiency, stability, manufacturing complexity, and environmental impact.

1. Cadmium telluride (CdTe) is currently the most commercially successful thin-film technology, accounting for a significant share of the global thin-film market. CdTe cells have a direct bandgap of approximately 1.45 eV, which is near optimal for solar energy conversion. This property allows for high light absorption in a very thin layer, reducing the need for thick material deposition. Commercial CdTe modules typically achieve efficiencies in the range of 16 %. Cadmium telluride (CdTe) thin-film solar cells represent one of the most commercially mature and cost-effective photovoltaic technologies in the global solar market. CdTe cells are known for their high absorption efficiency, relatively low production costs, and

short energy payback times, making them a leading alternative to crystalline silicon-based solar modules, especially in large-scale utility applications.

The fabrication of CdTe thin-film solar cells typically involves the deposition of thin layers of cadmium telluride and cadmium sulfide (CdS) onto a transparent conducting substrate such as fluorine-doped tin oxide (FTO) coated glass. The CdS layer acts as a buffer or window layer, while the CdTe layer serves as the primary photon absorber. These layers are deposited using methods such as close-spaced sublimation (CSS), vapor transport deposition (VTD), or chemical bath deposition (CBD), all of which are suitable for large-area and high-throughput manufacturing.

Despite their advantages, CdTe solar cells face certain challenges and limitations. One significant concern is the toxicity of cadmium, a heavy metal that can pose environmental and health risks if not properly managed. To address this issue, manufacturers implement strict recycling protocols and encapsulation standards that prevent cadmium leakage during operation and after decommissioning. Moreover, tellurium is a relatively rare element, which may constrain long-term scalability depending on supply chain developments and global demand.

Research in the CdTe field continues to focus on enhancing cell efficiency, improving long-term stability, and reducing the environmental impact of production. Innovations such as tandem CdTe-based cells, novel transparent contacts, and alternative window layers are being explored to further increase performance. Additionally, efforts to replace or minimize the use of cadmium or to find alternative absorber materials are under investigation to future-proof the technology.

CdTe solar technology is predominantly used in utility scale photovoltaic systems, particularly in regions with high solar irradiance and large tracts of available land. Companies such as First Solar have pioneered the industrial deployment of CdTe modules, contributing significantly to the global expansion of solar energy capacity. The ability to manufacture modules at scale using automated processes and low-cost materials has been key to the commercial success of CdTe photovoltaics.

Cadmium telluride thin-film solar cells provide a high-efficiency, low-cost alternative to traditional silicon-based modules. Their excellent absorption characteristics, competitive real-world performance, and scalable manufacturing processes make them well-suited for large-scale energy production. With ongoing research aimed at further improving performance and addressing material concerns, CdTe technology is expected to maintain its relevance as part of the diversified portfolio of next-generation solar solutions.

2. Copper indium gallium selenide (CIGS) thin-film solar cells are a highly efficient technology using a compound of copper, indium, gallium and selenium. It is a solid solution of copper indium selenide and copper gallium selenide, the

composition of which is expressed by the formula $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$. The material crystallizes in the chalcopyrite structure (Fig. 6.4). CIGS is a direct-gap semiconductor whose band gap can be adjusted from 1.7 eV (at $x=0$) to 1.0 eV (at $x=1$) depending on the composition. This adjustment allows the material to be optimized for different parts of the solar spectrum. In laboratory conditions, CIGS cells have demonstrated conversion efficiencies exceeding 23%.

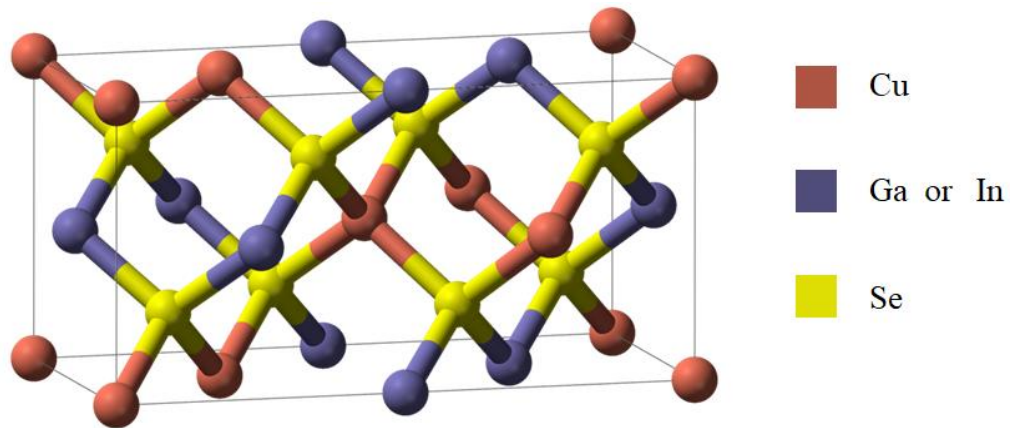


Fig. 6.4. Unit cell of chalcopyrite-type crystals.

The standard structure of a CIGS solar cell consists of several layers. Starting from the back, a molybdenum (Mo) contact layer is deposited onto a glass or flexible substrate. Above this is the CIGS absorber layer, which serves as the primary photon-absorbing material. A buffer layer — typically cadmium sulfide (CdS) — is applied next to form the *p-n* junction, followed by a transparent conductive oxide (TCO) layer such as zinc oxide (ZnO) or indium tin oxide (ITO) that allows light to enter the device while conducting electrical current. These layers are typically encapsulated with a protective covering to ensure long-term stability [7] (Fig. 6.5).

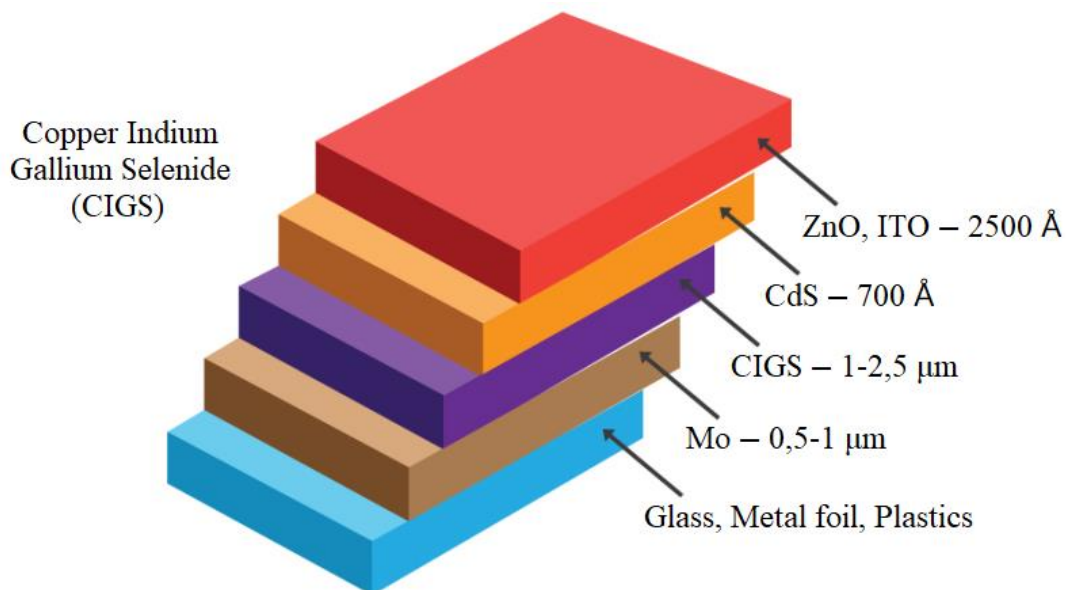


Fig. 6.5. A typical structure of solar cells based on CIGS [7].

Fabrication of CIGS solar cells can be achieved through various methods, including vacuum-based techniques such as co-evaporation and sputtering, as well as nonvacuum approaches like solution-based ink printing. The choice of deposition method impacts film quality, grain structure, and overall device performance. Co-evaporation remains the most successful method for achieving high-efficiency devices, as it allows precise control over elemental composition and film uniformity.

One of the distinguishing advantages of CIGS technology is its high absorption coefficient, which enables the complete absorption of incident sunlight within a film only 1 to 2 micrometers thick. This property significantly reduces the amount of active material needed and facilitates the production of lightweight, flexible modules.

CIGS modules demonstrate excellent performance under real-world conditions. They exhibit a relatively low temperature coefficient (around $-0.35\%/^{\circ}\text{C}$). Mechanical flexibility is another major benefit of CIGS technology. Because the thin-film layers can be deposited on flexible substrates such as polymers or metal foils, CIGS modules can be integrated into lightweight, bendable, or curved surfaces. This opens up new applications in building-integrated photovoltaics (BIPV), portable solar chargers, automotive surfaces, and even wearable electronics. Moreover, the technology supports roll-to-roll manufacturing processes that offer cost reductions through scalable, continuous production.

Despite these advantages, CIGS solar cells face some challenges that limit their widespread adoption. The presence of rare and costly elements such as indium and gallium poses concerns regarding resource availability and long-term scalability. Furthermore, the inclusion of cadmium in the buffer layer (when used) raises environmental and health concerns, prompting research into alternative buffer materials such as zinc oxysulfide ($\text{Zn}(\text{O},\text{S})$) and indium sulfide (InS).

Multijunction and tandem (also referred to as cascaded or multilayer) solar cells represent some of the most advanced and high-performance photovoltaic technologies available today. These cells are specifically engineered to overcome the efficiency limitations of single-junction devices by stacking multiple p - n junctions, each optimized to absorb a distinct segment of the solar spectrum. By capturing more photons across a broader wavelength range, multijunction solar cells can achieve significantly higher conversion efficiencies than traditional single-layer solar cells.

Cascade solar cells are formed either by growing a monolithic multi-junction single-crystal structure or by mechanically stacking pre-fabricated elements. Most high-efficiency solar cells in this group are based on multi-junction (cascade) heterostructures. These are produced using molecular beam epitaxy (MBE) or metal-organic chemical vapor deposition (MOCVD) techniques. An example of a triple-

junction solar cell structure and the corresponding energy band diagram of solar energy conversion [8] is shown in Fig. 6.6.

The fundamental principle behind multijunction solar cells lies in the spectral selectivity of semiconductors. Each photovoltaic material has a characteristic bandgap, which determines the range of photon energies it can effectively absorb. In a single-junction cell, photons with energy below the bandgap are not absorbed, while those with energy above the bandgap generate excess thermal losses. Multijunction cells address this by incorporating multiple layers of different materials, each with a tailored bandgap, arranged in descending order of energy.

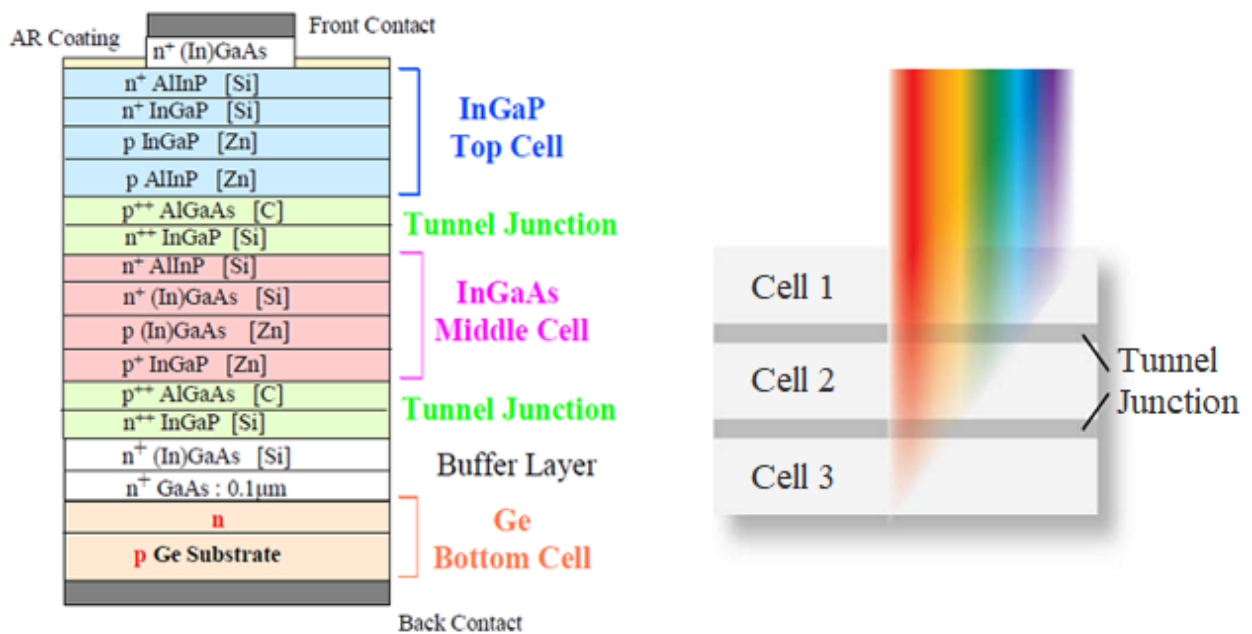


Fig. 6.6. Multijunction solar cell and energy scheme for the conversion of solar energy [8].

In a typical tandem structure, the top cell absorbs high-energy (short-wavelength) photons and transmits lower-energy photons to the underlying layers. Each subsequent layer absorbs a portion of the remaining spectrum, thereby minimizing thermalization and transmission losses. These subcells are electrically connected either in series (monolithic two-terminal configuration) or in parallel (four-terminal configuration), depending on the design and intended application.

The most well-established multijunction solar cells are those based on A^{III}B^V compound semiconductors such as gallium arsenide (GaAs), gallium indium phosphide (GaInP), and gallium indium arsenide (GaInAs). These materials offer high radiative efficiency and can be lattice-matched to reduce defect formation at interfaces. For example, a common triple-junction configuration includes GaInP (top cell, 1.9 eV), GaAs (middle cell, 1.4 eV), and GaInAs (bottom cell, 1.0 eV). This combination enables theoretical efficiencies exceeding 45%.

Multijunction solar cells manufactured in Germany (Fraunhofer ISE/Soitec) achieved an efficiency of 46.0% under solar radiation concentration at 500 suns. On January 14, 2015, the U.S. Department of Energy's National Renewable Energy Laboratory (NREL) in Golden, Colorado, announced the demonstration of 45.7% conversion efficiency for a four-junction solar cell under 234 suns concentration. NREL stated that this represented one of the highest efficiencies ever achieved among all types of solar cells. For comparison, in 2013, Solar Junction achieved a maximum efficiency of 44.4% for three-junction solar cells under 942 suns concentration.

However, the use of concentrators (e.g., Fresnel lenses) to achieve high efficiencies is associated with significant optical losses. It is important to note that these are laboratory-scale cells, tested under controlled illumination conditions. In practical applications, concentrator-based multijunction solar cells require mechanically complex support systems with sun-tracking mechanisms, suffer from poor performance under diffuse light, and require efficient cooling systems due to localized heating.

The highest efficiencies for non-concentrator multijunction solar cells were achieved by Boeing-Spectrolab (38.8% for five-junction cells) and Sharp (37.9% for three-junction cells). The main drawbacks in the production of MJSCs include the complexity of the fabrication process, the use of expensive equipment, and the reliance on high-cost monocrystalline substrates such as Ge and GaAs, along with other critical materials and components.

As noted by Zh. I. Alferov [9], multijunction solar cells are among the most structurally complex semiconductor devices.

In the production of two-junction solar cells via mechanical stacking, materials based on GaAs were used for the top cell and Ge for the bottom cell [10]. In [11], AlGaAs ($E_g \sim 1.7$ eV) was used for the top cell and Si for the bottom. However, record efficiencies of 37% [12] were achieved with mechanically stacked cells composed of a GaAs-based top junction and a GaSb-based bottom junction, under 100 suns concentration.

One of the advantages of mechanically stacked solar cells is that they are built on well-established single-junction technologies, eliminating the need to current-match the subcells. However, disadvantages include a complex interconnection system, high optical losses at junction interfaces, and the necessity to minimize absorption in the top cell of light intended for conversion in the bottom cell [13].

Despite these limitations, multijunction solar cells have found their niche in the photovoltaic market. They are not only widely used in space applications, but also in terrestrial concentrator photovoltaics. By 2008, companies such as Boeing, Emcore, and Spectrolab Inc. had already developed mature manufacturing

technologies with annual production capacities exceeding 1 MW each, established distribution systems, and a growing market for concentrator-based PV systems with cell efficiencies ranging from 36% to 39%.

Single-junction cells of the first technological generation achieve maximum efficiencies up to 27.5%, which is only slightly higher than silicon-based cells (25.6%), but at the cost of significantly more complex fabrication and expensive materials and equipment, driving up the levelized cost of electricity. Therefore, the main disadvantage of this generation remains its high cost.

Perovskite Solar Cells (PSCs). Perovskite (or calcium titanate) is one of the most abundant minerals on Earth. It was discovered by German geologists more than 170 years ago and, until recently, was primarily used as a dielectric material. When the first solar cells were developed, perovskite-based elements were not considered for their production. The main reason was the inability to achieve long-term stability during energy generation — an engineering challenge that remains difficult even today.

Perovskite solar cells have emerged over the past decade as one of the most promising new photovoltaic technologies, garnering widespread attention due to their high-power conversion efficiencies, ease of fabrication, and potential for low-cost production. These cells are based on a class of materials with the perovskite crystal structure — typically hybrid organic-inorganic lead or tin halide compounds — with the general formula ABX_3 , where “A” is an organic cation (such as methylammonium or formamidinium), “B” is a metal cation (commonly Pb^{2+} or Sn^{2+}), and “X” is a halide anion (Cl, Br, or I).

The success of PSCs is primarily due to the exceptional optoelectronic properties of perovskite materials. These include strong absorption in the visible spectrum, long charge carrier diffusion lengths, low exciton binding energy, and high defect tolerance. Together, these characteristics enable efficient light harvesting, charge separation, and transport even in relatively thin active layers, often less than one micrometer in thickness. This thinness contributes to reduced material usage and facilitates flexible and lightweight device configurations.

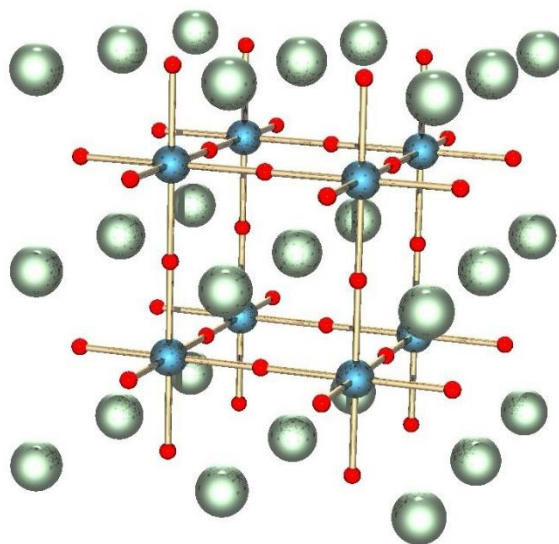


Fig. 6.7. The structure of perovskite ABX_3 : green balls are cations A, blue balls are cations B, red balls are anions X.

The typical structure of a perovskite solar cell consists of a transparent conductive oxide (TCO) front contact, followed by an electron transport layer (ETL), the perovskite absorber layer, a hole transport layer (HTL), and a metal back contact. Various materials can be used for the ETL (e.g., TiO₂, SnO₂, or ZnO) and HTL (e.g., Spiro-OMeTAD, PTAA, or PEDOT:PSS), depending on the device architecture. PSCs can be fabricated in both planar and mesoscopic configurations, the latter incorporating a porous scaffold to enhance charge collection.

A research team led by Seo Jang-won, a senior researcher at the Korea Research Institute of Chemical Technology, achieved a record efficiency of 22.7% for a perovskite solar cell in 2017.

These solar cells belong to the third generation of photovoltaic technologies. They are lightweight, flexible, and can be manufactured using relatively simple and low-cost methods. However, it is important to note that, at present, perovskite solar cells are prone to temporal degradation. This necessitates enhanced encapsulation requirements to ensure device stability and longevity. Currently, commercial-scale production of this class of solar cells has not yet been realized. Nevertheless, perovskite solar cells represent a potentially low-cost photovoltaic technology and remain the focus of ongoing laboratory research and development.

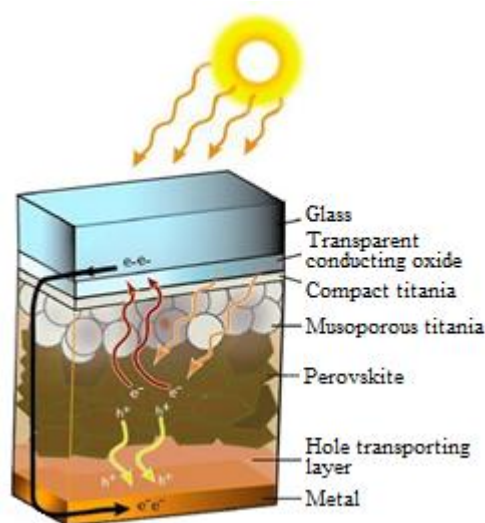


Fig. 6.8. Simple diagram of the operating mechanism of perovskite-based solar cells¹.

The fabrication of perovskite solar cells can be accomplished using low-temperature solution-processing methods such as spin coating, slot-die coating, and inkjet printing. This compatibility with roll-to-roll manufacturing on flexible substrates makes PSCs particularly attractive for scalable and cost-effective production. Moreover, the possibility of tuning the bandgap by adjusting the halide composition allows optimization for tandem cell integration and color-selective applications.

Despite their many advantages, PSCs face several critical challenges that must be addressed before widespread commercialization. Stability remains one of the foremost concerns, as perovskite materials are sensitive to moisture, oxygen, light, and heat, all of which can lead to degradation. Strategies to enhance stability include

¹ <https://ru.alfachemsp.com/info/an-overview-of-perovskite-solar-cells-42691096.html>

the use of all-inorganic compositions, encapsulation techniques, interface modifications, and additive engineering. In addition, efforts are underway to improve operational lifetimes under real-world conditions, with some devices now exceeding 1000 hours of continuous operation under standard test conditions.

Another important issue is the presence of lead in the most efficient perovskite compositions. While the amount of lead used is small, concerns about toxicity and environmental impact have prompted the exploration of lead-free alternatives based on tin (Sn) or bismuth (Bi). However, these alternative materials currently exhibit lower performance and stability, making them the subject of ongoing research.

Organic photovoltaic (OPV) cells, also known as organic solar cells, represent a class of thin-film solar technology that employs carbon-based semiconducting materials for light absorption and charge transport. These devices offer a unique set of advantages, including mechanical flexibility, low manufacturing costs, lightweight construction, and the potential for environmentally friendly processing. While OPV cells currently lag behind inorganic counterparts in terms of efficiency and long-term stability, ongoing research is steadily improving their performance and commercial viability.

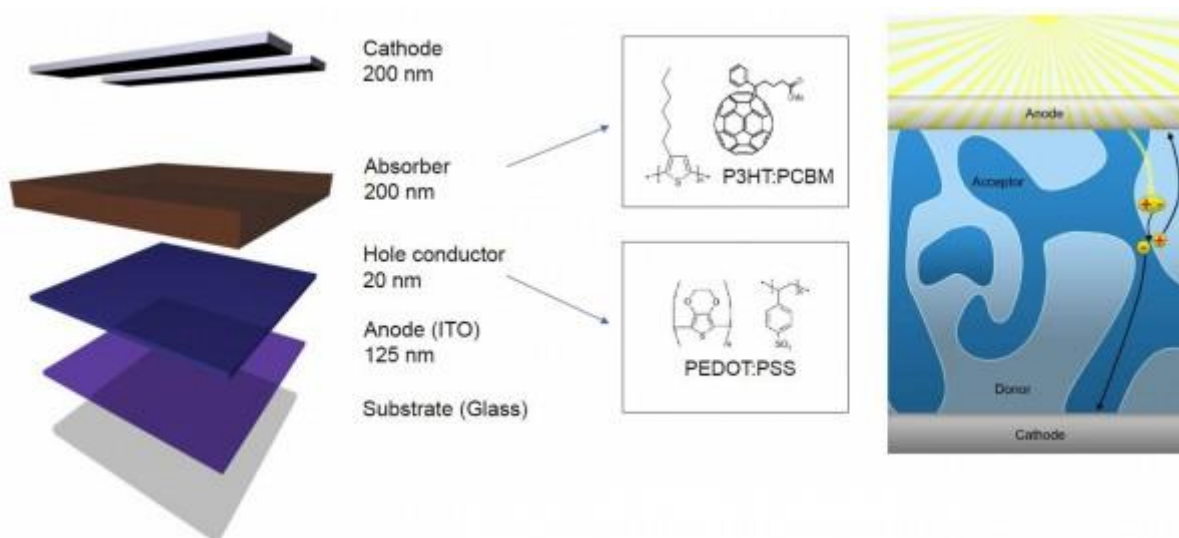


Fig. 6.9. The structure of an organic solar cell and the materials used to create it².

The active layer in an organic solar cell typically consists of a donor-acceptor blend of conjugated polymers or small molecules. When light is absorbed, excitons — bound electron-hole pairs — are generated rather than free carriers, due to the low dielectric constant of organic materials. Efficient operation therefore depends on the ability of the excitons to diffuse to a donor-acceptor interface where charge separation can occur. To maximize this process, OPVs are generally designed as

² <https://habr.com/ru/articles/202836/>

bulk heterojunction (BHJ) devices, in which the donor and acceptor materials are intermixed at the nanoscale to provide a large interfacial area.

A standard OPV device architecture comprises several layers (Fig. 6.9): a transparent electrode (often indium tin oxide, ITO), a hole transport layer (e.g., PEDOT:PSS), the active donor-acceptor layer, an electron transport layer (e.g., calcium or zinc oxide), and a metallic back electrode (such as aluminum or silver). The exact materials and architecture can be modified to optimize charge extraction, reduce recombination losses, and enhance optical absorption.

One of the most important features of organic solar cells is their compatibility with solution-based processing techniques. Techniques such as spin coating, doctor blading, inkjet printing, and roll-to-roll slot-die coating allow OPVs to be fabricated on flexible plastic substrates at low temperatures. This opens possibilities for large-area, lightweight, and semi-transparent solar panels that can be integrated into unconventional surfaces and portable electronics.

In terms of efficiency, OPV devices have made significant strides over the past two decades. Early devices achieved efficiencies of only 1-2%.

Nonetheless, OPVs face several limitations that continue to challenge their commercial competitiveness. Chief among these is their susceptibility to environmental degradation from moisture, oxygen, and ultraviolet light, which can lead to rapid performance loss. While encapsulation technologies and barrier films help mitigate these effects, they add complexity and cost. Improving the intrinsic stability of organic materials through molecular design and formulation remains a major research priority.

Another hurdle is the relatively short operational lifetime of OPV modules compared to silicon-based photovoltaics. While recent studies have demonstrated OPV devices operating beyond 10,000 hours under controlled conditions, achieving long-term stability in real-world outdoor environments is still a work in progress. Moreover, variability in material batches and sensitivity to fabrication parameters can complicate large-scale production and quality control.

Despite these challenges, the distinctive advantages of OPV technology continue to drive interest in specialized applications. These include building-integrated photovoltaics (BIPV), wearable electronics, portable power sources, and indoor energy harvesting. For example, OPVs perform well under low-light and diffuse lighting conditions, making them suitable for indoor IoT devices and smart sensors. Their aesthetic versatility, including transparency and color tunability, further enhances their appeal for architectural integration.

Quantum dot solar cells (QDSCs) are an emerging class of third-generation photovoltaic technologies that utilize semiconductor nanocrystals — known as quantum dots (QDs) — as the light-absorbing material. These nanometer-scale

particles exhibit quantum confinement effects, where the motion of charge carriers is restricted in all three spatial dimensions. As a result, quantum dots have tunable electronic and optical properties that can be precisely controlled by adjusting their size, composition, and surface chemistry.

One of the most attractive features of quantum dots is their size-dependent bandgap. Unlike bulk semiconductors, the energy levels in quantum dots shift as the particle size changes, enabling customization of the absorption spectrum across a wide range of wavelengths. This allows QDSCs to be engineered for specific spectral regions or designed in multi-junction architectures to maximize solar energy capture. For example, lead sulfide (PbS), lead selenide (PbSe), cadmium selenide (CdSe), and indium phosphide (InP) quantum dots have all been used in QDSCs due to their favorable optoelectronic properties.

The basic structure of a QDSC typically consists of a photoactive layer composed of a dense film of quantum dots sandwiched between electron and hole transport layers [14] (Fig. 6.10). The electron transport layer (ETL) is often made from materials such as titanium dioxide (TiO₂) or zinc oxide (ZnO), while the hole transport layer (HTL) may include materials like nickel oxide (NiO) or organic polymers. These devices can be fabricated in several architectures, including Schottky junction, heterojunction, and sensitized structures, depending on the quantum dot type and intended application.

Quantum dots can be synthesized through colloidal methods, which are solution-based and amenable to low-cost, scalable production. The nanocrystals are typically capped with organic ligands to maintain colloidal stability, though these ligands can hinder charge transport [15] (Fig. 6.11). To improve electronic coupling and charge extraction, ligand exchange processes are employed, where insulating ligands are replaced with shorter or inorganic alternatives. Film formation methods such as spin coating, dip coating, and layer-by-layer deposition are commonly used to assemble QD films for solar cell fabrication.

One of the key advantages of QDSCs is the potential for multiple exciton generation (MEG) and carrier multiplication (CM), a phenomenon in which a single high-energy photon creates two or more electron-hole pairs, thereby increasing the

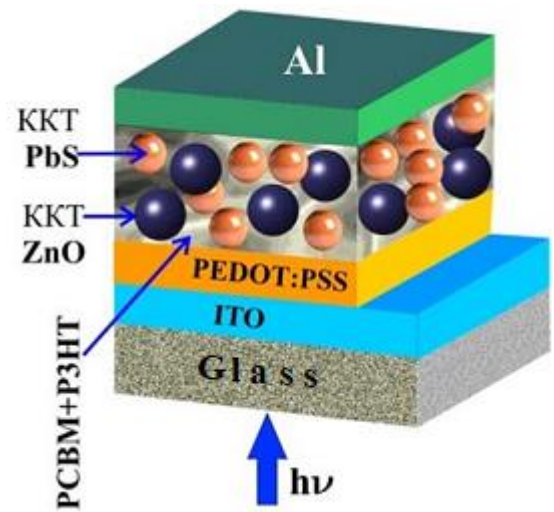


Fig. 6.10. Structure of a quantum dot solar cell based on a heterojunction CQDPbS-PCBM-P3HT-CQDZnO [14].

theoretical efficiency beyond the Shockley-Queisser limit of conventional single-junction solar cells.

In QDSCs, the absorption of high-energy photons is accompanied by carrier multiplication (also known as multiexciton generation), resulting in a quantum yield equivalent to the production of an equal number of low-energy secondary photons. These, in turn, generate new charge carriers. The fundamental mechanism involves the relaxation of excited high-energy electrons through impact ionization, leading to the creation of multiple electron-hole pairs. Consequently, the solar cell's efficiency increases through the subsequent absorption of these generated low-energy secondary photons.

While MEG and CM has been demonstrated in QDs under idealized conditions, practical implementation in devices remains a topic of active research.

QDSCs also exhibit strong light absorption, particularly in the near-infrared region, making them suitable for tandem integration with wide-bandgap materials like perovskites or organic semiconductors. Their solution-processable nature and compatibility with flexible substrates enable novel applications in lightweight, portable, and transparent solar technologies.

However, quantum dot solar cells still face significant challenges that limit their commercial readiness. Chief among these are issues related to material toxicity, particularly with lead-based QDs, and the environmental stability of the devices. Degradation under light exposure, oxygen, and moisture can severely impact performance and longevity. Encapsulation strategies, surface passivation, and the development of environmentally benign quantum dots (e.g., using indium phosphide or copper indium sulfide) are being explored to address these concerns.

Another important avenue of development involves integrating QDs into hybrid or tandem configurations. For instance, QD-perovskite tandem cells aim to exploit the complementary absorption spectra of both materials, enabling higher overall efficiencies. Similarly, QDs are being explored as photon downshifting layers to improve the response of conventional silicon or thin-film solar cells.

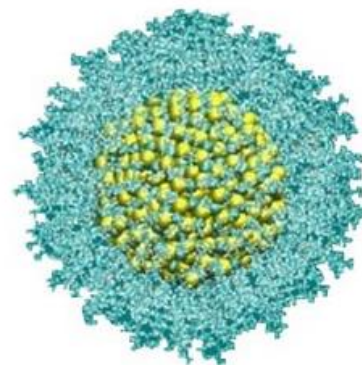


Fig. 6.11. Schematic representation of a colloidal quantum dot with a core made of a binary semiconductor and a stabilizing ligand shell (the upper part of the ligand layer is removed for clarity) [15].

6.2. Materials for solar cells

Materials used in solar cells (photovoltaic cells) can be divided into the following main groups:

1. Conventional semiconductor materials. Silicon (Si) is the most widely used material. Its forms — such as monocrystalline, polycrystalline, and amorphous silicon — dominate the global photovoltaic market.

2. Other semiconductor compounds (thin-film materials). These include CdTe (cadmium telluride), GaAs (gallium arsenide), and CIGS (Cu(In,Ga)Se₂ – copper indium gallium selenide).

3. Organic materials (OPV – organic photovoltaics). These operate based on polymers and small molecules.

4. Perovskites. Materials with a perovskite structure (e.g., CH₃NH₃PbI₃).

5. Quantum dots. Nanoparticles based on PbS, CdSe, InP, and others.

We will now take a closer look at some of these.

Silicon (Si) is the most widely used and historically significant material in the production of solar cells. As a group IV elemental semiconductor, silicon offers an optimal combination of electrical, optical, and mechanical properties, along with abundant availability and well-established processing technologies.

The key attribute that makes silicon attractive for photovoltaic applications is its semiconducting nature, with an indirect bandgap of approximately 1.12 eV at room temperature. This bandgap is near the ideal value for solar energy conversion, enabling the absorption of a significant portion of the solar spectrum while minimizing thermalization losses. However, because silicon is an indirect bandgap material, it requires a relatively thick layer — on the order of 150 to 200 micrometers in typical crystalline silicon cells — to absorb sunlight efficiently. This contrasts with direct bandgap materials, which can achieve similar absorption in much thinner layers.

Silicon exists in several allotropic forms, but in PV technology, it is predominantly used in its crystalline phase. The three main categories are:

1. Monocrystalline Silicon (mono-Si). Produced using the Czochralski process, monocrystalline wafers are cut from a single-crystal ingot and exhibit a uniform atomic structure with minimal defects. This uniformity leads to superior charge carrier mobility and long diffusion lengths, contributing to high cell efficiencies (typically 20-23%).

2. Polycrystalline Silicon (poly-Si). Manufactured by casting molten silicon into square molds and allowing it to solidify into multiple crystal grains. Although more cost-effective, poly-Si contains grain boundaries that act as recombination centers, resulting in slightly lower efficiencies (typically 15-18%).

3. Amorphous silicon (a-Si). In addition to these, silicon is also used in amorphous form in certain thin-film technologies. Amorphous silicon features a disordered atomic structure and allows for very thin layers due to its higher absorption coefficient. However, a-Si has lower efficiency (typically 10-12%) and is more prone to light-induced degradation, limiting its widespread use.

In addition, there are also modifications of silicon, such as metallurgical and technical silicon. Purity is critical in silicon-based solar cell manufacturing. For example, for metallurgical silicon (MG-Si), it is about 98-99%.

The silicon wafers are subjected to a series of processes to form functional solar cells. These include surface texturing to reduce reflectivity, phosphorus diffusion to form a *p-n* junction, anti-reflective coating deposition, metallization for electrical contacts, and encapsulation for protection. Modern advancements such as passivated emitter and rear cell (PERC) structures, heterojunction technology (HJT), and interdigitated back contact (IBC) designs have significantly improved the performance of silicon solar cells.

From a mechanical and chemical standpoint, silicon is robust, non-toxic, and stable under a wide range of environmental conditions. Its hardness and thermal conductivity contribute to long-term durability in photovoltaic modules. Silicon-based solar panels typically have operational lifetimes exceeding 25 years, with annual degradation rates below 0.5%.

In terms of availability, silicon is the second most abundant element in the Earth's crust, mainly found in the form of silicon dioxide (SiO₂) in sand, quartz, and other minerals. Although extracting high-purity silicon requires significant energy input, the material's abundance and recyclability make it a sustainable choice for large-scale PV deployment.

The dominance of silicon in the photovoltaic market is further reinforced by an established industrial ecosystem, including mature supply chains, standardized manufacturing equipment. The scalability of silicon technology and continuous cost reductions through innovation and economies of scale have led to a steady decrease in the levelized cost of electricity (LCOE) from solar power.

Cadmium telluride (CdTe) is a compound semiconductor material composed of cadmium (Cd) and tellurium (Te), and it plays a central role in thin-film photovoltaic technology. CdTe is one of the few commercially successful alternatives to crystalline silicon, widely used in utility-scale solar power installations due to its cost-effectiveness, relatively simple manufacturing processes, and favorable optoelectronic properties.

CdTe has a direct bandgap of approximately 1.45 eV, which is very close to the theoretical optimum for solar energy conversion under the AM1.5 solar spectrum. This optimal bandgap allows CdTe to absorb a large fraction of the

incident sunlight with minimal thermal losses, and its direct bandgap nature enables high absorption coefficients — more than 10 cm^{-1} — allowing for efficient light absorption in films only a few micrometers thick. As a result, CdTe solar cells use less material than crystalline silicon cells, leading to lower production costs.

The standard architecture of a CdTe solar cell includes a transparent conducting oxide (TCO) front contact, such as fluorine-doped tin oxide (FTO), followed by a cadmium sulfide (CdS) window layer, a *p*-type CdTe absorber layer, and a metal back contact (e.g., graphite, molybdenum, or a multilayer alloy). The CdS layer forms a *p-n* junction with the CdTe, enabling the separation of photogenerated electron-hole pairs and their subsequent collection at the electrodes. A cadmium chloride (CdCl) treatment is often applied post-deposition to improve grain growth, reduce recombination sites, and enhance device performance.

The manufacturing process for CdTe modules typically involves high-throughput vacuum deposition techniques such as close-spaced sublimation (CSS), vapor transport deposition (VTD), or sputtering. These methods allow for large-area uniform film deposition, facilitating gigawatt-scale production. CdTe modules are often manufactured using a fully integrated process that includes glass preparation, semiconductor layer deposition, laser scribing for cell interconnection, encapsulation, and framing.

However, CdTe technology faces some notable challenges. One primary concern is the toxicity of cadmium, a heavy metal that poses environmental and health risks if not properly handled or disposed of. Manufacturers mitigate this risk through strict encapsulation protocols and end-of-life recycling programs. The availability of tellurium is another limitation; although it is obtained as a byproduct of copper refining, its global supply is limited and may become a bottleneck as demand for CdTe increases.

Recent research efforts have focused on improving the efficiency and sustainability of CdTe solar cells. This includes exploring alternative buffer layers (e.g., ZnSe, SnO), developing transparent back contacts, and integrating tandem structures to enhance light utilization. Passivation strategies, such as alloying with selenium (CdTeSe), have been employed to broaden absorption and reduce non-radiative recombination.

CdTe solar modules are widely deployed in large-scale ground-mounted systems, particularly in regions with high solar irradiance. They have proven field reliability and exhibit lower degradation rates compared to some other thin-film technologies. Companies like First Solar have been instrumental in advancing CdTe PV, scaling production to multi-gigawatt levels and contributing significantly to the global renewable energy supply.

Gallium arsenide (GaAs) is a $A^{III}B^V$ compound semiconductor that has long been recognized for its exceptional electronic and optoelectronic properties, making it a key material in high-performance solar cell technologies. Although more expensive and complex to manufacture than silicon, GaAs offers numerous advantages in terms of efficiency, radiation hardness, and suitability for specialized applications, particularly in aerospace and concentrator photovoltaics (CPV).

GaAs possesses a direct bandgap of approximately 1.42 eV at room temperature, which is close to the optimal value for single-junction solar energy conversion. Its direct bandgap allows for very high absorption coefficients, enabling the use of extremely thin active layers (a few micrometers) without compromising photon capture. This characteristic results in high short-circuit current densities and contributes to GaAs cells' outstanding power conversion efficiencies.

One of the most remarkable features of GaAs solar cells is their high efficiency. Laboratory-scale single-junction GaAs cells have achieved power conversion efficiencies above 29 %.

The basic structure of a GaAs solar cell typically includes a highly doped *p*-type or *n*-type substrate, a lightly doped active absorber layer, and window/contact layers made from lattice-matched $A^{III}B^V$ compounds such as AlGaAs or GaInP. These structures are grown using epitaxial techniques like metal-organic chemical vapor deposition (MOCVD) or molecular beam epitaxy (MBE), which provide atomic-level control over layer thickness, composition, and doping. The resulting heterojunction architecture allows for minimal recombination and precise energy band alignment.

An important aspect of GaAs-based solar cell fabrication is substrate reuse. Since GaAs wafers are expensive, manufacturers often employ techniques such as epitaxial lift-off (ELO) to remove the thin photovoltaic layer from the growth substrate, enabling the substrate to be recycled. This approach significantly reduces material costs and enhances the economic feasibility of GaAs PV technologies.

GaAs solar cells are known for their excellent performance under extreme environmental conditions. Their superior resistance to radiation damage makes them the material of choice for powering satellites, space probes, and high-altitude drones. They also exhibit a low temperature coefficient (typically around -0,1 %/°C to -0,2 %/°C).

In concentrator photovoltaics, GaAs cells are often used in multijunction configurations with lenses or mirrors that focus sunlight by factors of several hundred. Because GaAs devices can tolerate high photon flux without significant performance degradation, they are well suited for CPV systems where maximizing power per unit area is critical.

Copper indium gallium selenide (CIGS) and its related variant, **copper indium selenide (CIS)**, are important materials in the class of thin-film photovoltaics. These I-III-VI compound semiconductors are characterized by their direct bandgaps and high absorption coefficients, making them highly efficient absorbers for solar energy conversion. CIGS has gained particular attention for its potential to deliver high performance while maintaining compatibility with flexible substrates and scalable manufacturing techniques.

CIGS is a quaternary alloy composed of copper (Cu), indium (In), gallium (Ga), and selenium (Se), with the chemical formula CuInGaSe . The inclusion of gallium allows for tuning of the bandgap from approximately 1.0 eV (pure CIS) to around 1.7 eV (with higher Ga content). Optimal device performance is typically achieved with a bandgap in the range of 1.1–1.3 eV, balancing strong absorption and high voltage output.

CIGS and CIS materials are direct bandgap semiconductors, which means they can absorb light very efficiently in a thin film — usually 1 to 2 micrometers thick. Their high absorption coefficient (10 cm^{-1}) enables nearly complete absorption of the solar spectrum within this short distance. This makes them suitable for lightweight, flexible, and low-material-use solar modules.

The typical device architecture of a CIGS solar cell includes a back contact (often molybdenum deposited on glass or metal foil), the CIGS absorber layer, a buffer layer (commonly cadmium sulfide, CdS), and a transparent conductive oxide (TCO) layer such as zinc oxide or indium tin oxide (ITO). The CdS forms a heterojunction with the *p*-type CIGS absorber, facilitating charge separation. Alternative buffer layers, such as Zn(O,S) or InS , are being developed to avoid the use of cadmium.

Fabrication techniques for CIGS and CIS solar cells include co-evaporation, sputtering, and solution-based approaches such as inkjet printing and spray coating. Co-evaporation, in which elemental precursors are evaporated simultaneously onto a heated substrate, offers precise compositional control and has been used to produce laboratory cells with efficiencies exceeding 23 %.

CIGS and CIS materials also lend themselves well to flexible and lightweight applications. By depositing the active layers onto polymer or metal foil substrates, manufacturers can produce bendable solar modules ideal for use in portable electronics, building-integrated photovoltaics (BIPV), transportation systems, and space limited environments.

Challenges for CIGS/CIS technologies include the relative scarcity and high cost of indium and gallium, which may pose barriers to large-scale deployment. Furthermore, the presence of cadmium in some buffer layers introduces environmental concerns, prompting efforts to transition to cadmium-free

alternatives. Additional issues include complexity in achieving compositional uniformity and control over defect densities, which can impact reproducibility and module yield.

Recent research has focused on improving light management, passivating interfaces, and understanding the role of grain boundaries in device performance. Strategies such as sodium incorporation, alkali post-deposition treatments, and bandgap grading have been employed to enhance open-circuit voltage and fill factor. Tandem structures integrating CIGS with other materials, as well as bifacial designs and advanced encapsulation, are also under development.

CIGS and CIS modules have seen deployment in both residential and commercial markets, with niche applications in mobile and off-grid systems due to their flexibility and durability. Companies like Solar Frontier, Avancis, and MiaSoie have commercialized CIGS-based products and contributed to advancing the technology's competitiveness.

Copper indium gallium selenide (CIGS) and copper indium selenide (CIS) are promising absorber materials for thin-film solar cells, offering high efficiency, tunable bandgaps, and mechanical versatility. While challenges related to material availability and environmental impact remain, ongoing innovation in materials engineering, processing techniques, and device architecture supports their continued relevance in the evolving landscape of photovoltaic technologies.

Hybrid organic-inorganic perovskites, exemplified by methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}$ or MAPbI), are a groundbreaking class of materials that have revolutionized the field of photovoltaics and optoelectronics. These perovskites possess the general formula ABX_3 , where “A” is an organic cation (e.g., methylammonium or formamidinium), “B” is a metal cation (commonly Pb_2), and “X” is a halide anion (I, Br, or Cl). Their distinctive structural and electronic properties, along with ease of processing, have led to rapid advances in solar cell performance and attracted widespread scientific interest.

The crystal structure of hybrid perovskites consists of a three-dimensional network of corner-sharing BX_3 octahedra, with the A-site organic cation occupying the voids between them. In $\text{CH}_3\text{NH}_3\text{PbI}$, methylammonium (MA) cations stabilize the lead iodide framework, resulting in a cubic or tetragonal lattice depending on temperature. This hybrid configuration combines the processability and tunability of organic compounds with the stability and efficient charge transport properties of inorganic frameworks.

MAPbI and related materials exhibit remarkable optoelectronic characteristics that make them well suited for solar energy applications. These include:

- A direct bandgap of approximately 1.55 eV, ideal for single junction solar cells;

- Strong optical absorption, allowing nearly complete photon harvesting in thin layers (300-600 nm);
- High carrier mobilities and long diffusion lengths ($\sim 1 \mu\text{m}$), which minimize recombination losses;
- Low exciton binding energies, enabling efficient charge separation at room temperature;
- Defect tolerance, with benign defect states that do not severely impact performance.

One of the key advantages of hybrid perovskites is their compatibility with solution-based, low-temperature fabrication processes. MAPbI can be deposited using simple methods such as spin coating, blade coating, or inkjet printing, making it accessible for large-area, flexible, and low-cost solar module production. The ability to tune the bandgap by substituting the halide (e.g., using Br or Cl) or the organic cation (e.g., formamidinium instead of methylammonium) further extends their applicability to tandem cells and color-selective devices.

Since their introduction into photovoltaics around 2009, hybrid perovskites have achieved an unprecedented rise in power conversion efficiencies, reaching over 25 %.

Despite their impressive photovoltaic properties, hybrid perovskites like $\text{CH}_3\text{NH}_3\text{PbI}$ are known for their sensitivity to environmental factors such as moisture, oxygen, heat, and UV light. Degradation can result from decomposition of the organic cation, migration of halide ions, or reactions at material interfaces. To address these challenges, researchers have explored encapsulation techniques, compositional engineering (e.g., replacing MA with FA or Cs), and the use of additive passivation to improve structural stability and device longevity.

Hybrid organic-inorganic perovskites such as $\text{CH}_3\text{NH}_3\text{PbI}$ represent a transformative development in materials science. Their unique combination of high performance, low-cost processing, and structural tunability positions them at the forefront of next generation photovoltaic and optoelectronic technologies. While further work is needed to resolve issues related to stability and toxicity, the rapid pace of research and innovation continues to drive progress toward the commercialization of perovskite-based solar cells and related applications.

6.3. Modern innovations and promising materials in solar energy

Modern solar energy requires unconventional innovative approaches, without which it cannot compete with hydrocarbon energy. The main primary component of solar energy is the solar cell, which is responsible for its efficiency. The efficiency of solar cells can be improved through the following methods:

1. Reducing the cost and simplifying the technology for manufacturing materials, which leads to a decrease in the cost of the photovoltaic cells themselves;
2. Increasing the service life of the equipment;
3. Expanding the spectrum of efficiently absorbed radiation;
4. Improving the efficiency factor (efficiency).

Thus, solar energy as an industry requires the implementation of innovative technologies and advanced materials for the production of solar cells to improve their efficiency, reduce costs, and expand their areas of application.

Next, we will take a closer look at such technologies and materials.

Tandem solar cells, also known as multijunction or multi-terminal solar cells, are among the most promising innovations in the pursuit of higher photovoltaic efficiencies. These devices are engineered to overcome the fundamental efficiency limits of single-junction solar cells, as described by the Shockley-Queisser limit, by stacking multiple layers of materials with complementary bandgaps. Each layer (or subcell) is designed to absorb and convert a specific portion of the solar spectrum, thus enabling more complete utilization of incident solar energy.

In a tandem architecture, the top cell captures high-energy (short-wavelength) photons, while allowing lower-energy photons to pass through to subsequent layers. This minimizes energy losses due to thermalization and non-absorption, resulting in higher theoretical efficiencies. Depending on the electrical configuration, tandem cells can be monolithic (two-terminal), mechanically stacked (four-terminal), or optically coupled with intermediate reflectors or filters. Monolithic tandem cells are the most compact and scalable but require precise current matching between subcells.

The most prominent tandem configuration under active development today is the perovskite-silicon tandem solar cell. In this design, a wide-bandgap perovskite top cell (1.7-1.8 eV) is deposited over a standard crystalline silicon bottom cell (1.1 eV). This combination leverages the high efficiency and bandgap tunability of perovskites with the stability and industrial maturity of silicon. Perovskite-silicon tandems have achieved certified power conversion efficiencies exceeding 32 %.

Beyond perovskite-silicon tandems, other tandem combinations are also being explored:

- **A^{III}B^V multijunction cells**: These include combinations of GaInP, GaAs, GaInAs, and related alloys, achieving record efficiencies above 47 %.
- **All-perovskite tandems**: These devices use two different perovskite compositions with tailored bandgaps to form the top and bottom cells. They offer high performance potential while maintaining low-temperature processing and flexibility.

- **Perovskite-CIGS tandems:** Combining wide-bandgap perovskites with narrow-bandgap CIGS absorbers offers high spectral utilization and better mechanical compatibility.

Key technical challenges in tandem solar cell development include:

- **Current matching and optical losses:** For monolithic designs, mismatches in current generation between subcells can limit overall performance.

- **Interface engineering:** The quality of interlayer contacts and charge transport layers is critical to reduce recombination and resistive losses.

- **Stability and durability:** Tandem cells, particularly those incorporating perovskites, must withstand thermal, moisture, and light-induced stress without degradation over operational lifetimes.

Significant research is being dedicated to developing advanced transport layers, robust encapsulation methods, and scalable fabrication processes such as blade coating, vapor deposition, and hybrid ink-based techniques. The integration of intermediate layers with tailored optical and electrical properties is also critical to achieving high-efficiency tandem devices.

From a commercialization perspective, tandem solar cells are rapidly gaining traction. Several start-ups and major PV companies are investing in pilot production lines for perovskite-silicon tandems, and early demonstrations have shown promising module efficiencies with pathways to cost-competitive manufacturing. The ability to retrofit existing silicon production infrastructure with perovskite deposition techniques makes this innovation particularly attractive for industrial adoption.

Organic photovoltaic (OPV) technology continues to evolve as a promising candidate for next-generation solar energy applications, driven by a growing understanding of organic semiconductors and advances in molecular design. Recent innovations in OPV research have significantly improved device efficiency, stability, and scalability, positioning organic solar cells as a viable option for a range of emerging markets, including flexible electronics, portable power sources, and building-integrated photovoltaics (BIPV).

One of the key breakthroughs in modern OPV development has been the shift from fullerene-based acceptors to non-fullerene acceptors (NFAs). Traditional fullerene derivatives such as [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) offered limited tunability and stability. In contrast, NFAs — such as ITIC, Y6, and their derivatives — provide enhanced absorption in the near-infrared region, better morphological stability, and tunable energy levels, resulting in significantly improved device performance. The incorporation of NFAs has pushed the power conversion efficiency (PCE) of single-junction OPVs beyond 18 %.

Molecular engineering plays a central role in advancing OPV materials. By modifying donor and acceptor chemical structures, researchers can optimize energy level alignment, light absorption, crystallinity, and phase separation within the bulk heterojunction. New classes of donor-acceptor conjugated polymers and small molecules offer improved charge mobility, exciton dissociation, and charge transport, contributing to higher fill factors and open-circuit voltages.

Device architecture has also seen important innovations. Tandem OPVs, which stack two or more subcells with complementary absorption spectra, are being actively developed to surpass the limitations of single junction devices. These structures enable broader solar spectrum coverage and can theoretically achieve efficiencies over 20 %.

Another major focus is enhancing the environmental stability and operational lifetime of OPV devices. Strategies include encapsulation with advanced barrier films, use of intrinsically stable organic semiconductors, and incorporation of stabilizing additives or interfacial layers. Recent devices have demonstrated lifetimes exceeding 10,000 hours under standard operating conditions, a significant improvement over earlier generations.

Scalability is a critical factor for commercial adoption of OPV technology. Solution-based, roll-to-roll compatible fabrication techniques such as slot-die coating, gravure printing, and spray coating have been refined to produce large-area OPV modules with high uniformity and reproducibility. These methods allow the production of lightweight, flexible solar panels suitable for curved surfaces and custom form factors.

Quantum dot solar cells (QDSCs) represent a dynamic area of innovation in photovoltaics, offering unique opportunities to transcend the efficiency limitations of conventional materials through the quantum confinement effect. Recent advances in material synthesis, surface passivation, and device integration have significantly enhanced the performance and applicability of quantum dot-based photovoltaics. These innovations are propelling QDSCs toward becoming a competitive platform for next-generation solar energy harvesting.

The foundational concept behind QDSCs lies in the size-tunable electronic properties of semiconductor nanocrystals. By adjusting the diameter of quantum dots, their bandgap can be finely tuned to absorb specific regions of the solar spectrum. This makes it possible to design QDSCs that optimize spectral utilization across a broad wavelength range. Current research is focused on synthesizing highly monodisperse quantum dots with precise control over bandgap and minimal trap states.

Innovations in surface chemistry have been central to improving quantum dot performance. Advanced ligand exchange strategies have replaced long-chain

insulating ligands with shorter or inorganic ones, enhancing charge transport and electronic coupling between quantum dots. In addition, surface passivation techniques using shell layers (e.g., core/shell structures like PbS/CdS or InP/ZnS) are employed to reduce non-radiative recombination and improve photostability.

One of the most promising areas of innovation in QDSCs is the implementation of multiple exciton generation (MEG), where one high-energy photon can produce two or more electron-hole pairs. Although MEG has been demonstrated in several quantum dot systems, integrating it into efficient device operation remains an ongoing challenge. Nevertheless, this mechanism has the potential to push power conversion efficiencies beyond the Shockley-Queisser limit for single-junction cells.

Device architectures are also being refined to maximize performance. New designs include depleted heterojunctions, Schottky junctions, and hybrid QD-organic or QD-perovskite configurations. These hybrid systems aim to combine the tunable absorption and high carrier multiplication of QDs with the charge transport efficiency and mechanical flexibility of organic or perovskite materials. Such hybrid structures are particularly promising for lightweight, flexible solar panels and wearable energy systems.

Material diversification is another key area of innovation. While lead chalcogenides like PbS and PbSe have dominated early QDSC development due to their superior optoelectronic properties, concerns about lead toxicity have motivated the development of environmentally friendly alternatives. Quantum dots based on indium phosphide (InP), copper indium sulfide (CIS), and carbon dots are being actively explored. These materials aim to retain the favorable properties of quantum confinement while improving safety and sustainability.

Integration techniques have advanced toward scalable manufacturing. Solution-processable QDs can be deposited via techniques such as spin coating, layer-by-layer assembly, inkjet printing, and spray coating. These methods support roll-to-roll production and enable integration into flexible substrates, making QDSCs compatible with modern fabrication lines. Encapsulation strategies using barrier films and UV-stable polymers are also being developed to enhance environmental stability.

Recent QDSC prototypes have achieved power conversion efficiencies exceeding 13-14 %. In terms of applications, QDSCs are particularly attractive for building-integrated photovoltaics (BIPV), indoor photovoltaics, and mobile energy solutions due to their tunable appearance, transparency, and form factor. Their infrared sensitivity also makes them suitable for niche uses such as thermophotovoltaics and photodetectors.

Two-dimensional (2D) materials have recently emerged as a novel and promising class of semiconductors for photovoltaic applications due to their unique structural, electrical, and optical properties. Defined by their atomically thin nature, 2D materials offer new opportunities for ultrathin, flexible, lightweight, and transparent solar cells. Materials such as graphene, transition metal dichalcogenides (TMDs), black phosphorus (BP), and hexagonal boron nitride (h-BN) have been the focus of intense research in the context of next-generation solar energy devices.

Transition metal dichalcogenide (TMD) monolayers are atomically thin crystals of the MX_2 type, where M is a transition metal (Mo, W, etc.) and X is a chalcogen (S, Se, or Te). One layer of M atoms is sandwiched between two layers of X atoms (Fig. 6.12). They are part of a larger family of two-dimensional crystals, so named to emphasize their extraordinary thinness. For example, a monolayer of MoS_2 is only 6.5 Å thick.

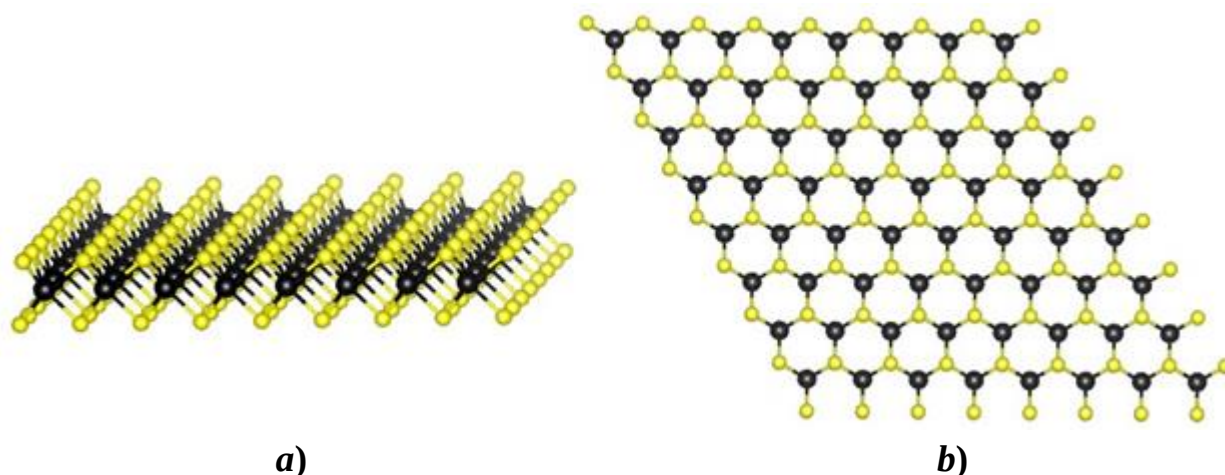


Fig. 6.12. (a) Structure of a hexagonal TMD monolayer. M atoms are shown in black, X atoms in yellow. (b) Hexagonal TMD monolayer, top view³.

Transition metal dichalcogenides (TMDs), such as molybdenum disulfide (MoS_2), tungsten disulfide (WS_2), and molybdenum diselenide (MoSe_2), are among the most widely studied 2D semiconductors for photovoltaics. These materials possess tunable direct or indirect bandgaps in the range of 1–2 eV, depending on the number of layers and the specific composition. Monolayer TMDs often exhibit direct bandgaps and strong light-matter interactions, making them suitable for high-absorption, ultrathin solar absorbers.

The extremely high surface-to-volume ratio of 2D materials enhances their sensitivity to light and electronic interactions, enabling efficient exciton generation and charge separation in devices only a few nanometers thick. Their mechanical flexibility and transparency also make them ideal candidates for wearable and

³[https://en.wikipedia.org/wiki/Transition_metal_dichalcogenide_monolayers#:~:text=Transition%2Dmetal%20dichalcogenides%20\(TMDs\),not%20have%20an%20inversion%20center.](https://en.wikipedia.org/wiki/Transition_metal_dichalcogenide_monolayers#:~:text=Transition%2Dmetal%20dichalcogenides%20(TMDs),not%20have%20an%20inversion%20center.)

embedded photovoltaic applications. Additionally, 2D materials can be integrated into van der Waals heterostructures without the constraints of lattice matching, allowing for customized band alignments and novel device architectures.

One promising direction is the development of 2D-2D heterojunctions, where two different 2D materials with complementary electronic properties form a type-II interface for effective charge separation. For example, vertical stacks of MoS and WSe have demonstrated photovoltaic activity due to built-in electric fields at the interface. Another approach involves combining 2D semiconductors with conventional materials like silicon, perovskites, or organic semiconductors to enhance carrier extraction and stability.

Graphene, a zero-bandgap 2D material, is commonly employed as a transparent electrode due to its exceptional electrical conductivity, optical transparency 97 %.

Black phosphorus (BP), another emerging 2D semiconductor, offers a layer-dependent bandgap that ranges from 0.3 eV in bulk to 2 eV in monolayer form. Its high hole mobility and anisotropic charge transport properties make it attractive for optoelectronic applications, although its air sensitivity remains a challenge for practical deployment.

Several device architectures utilizing 2D materials have been demonstrated, including Schottky junction solar cells, planar p-n heterojunctions, and hybrid devices. Reported power conversion efficiencies are still modest — typically below 5 %.

Another active area of research is the integration of 2D materials in tandem solar cells and photonic structures. Their thinness enables them to serve as intermediate absorbers or energy filters, enhancing light management and device performance. Moreover, 2D materials can be engineered to exhibit plasmonic or quantum confinement effects, which may be leveraged for light trapping and hot carrier extraction.

Challenges for 2D-material solar cells include environmental stability, contact resistance, uniform large-area film growth, and interlayer defect control. Encapsulation techniques and substrate engineering are critical for improving long-term durability and device reproducibility.

In summary, solar cells based on 2D materials offer a compelling vision for ultrathin, flexible, and tunable photovoltaic platforms. While currently in the early stages of development, rapid progress in materials synthesis, heterostructure assembly, and device engineering suggests that 2D materials will play an increasingly important role in the future of solar energy technologies.

Chapter Review Questions

1. What physical phenomena form the basis of solar cells?
2. How does the photoelectric effect work in solar cells?
3. What are the key technological features of first-generation (1G) solar cells?
4. What materials and technologies are used in second-generation (2G) solar cells?
5. How do third-generation (3G) solar cells differ from previous generations?
6. What are the differences between monocrystalline and polycrystalline silicon solar panels?
7. What are the advantages and disadvantages of amorphous silicon-based solar cells?
8. What underlies the high efficiency of gallium arsenide (GaAs) solar cells?
9. How do tandem (multi-junction) solar cells work, and what increases their efficiency?
10. What is the operating principle of organic solar cells, and in which applications are they used?
11. What are the main semiconductor materials used in solar cells?
12. What role does silicon (Si) play in solar cells, and what are its advantages?
13. What are the properties of perovskite materials, and why are they considered promising?
14. What are the features of CdTe (cadmium telluride) and CIGS (copper indium gallium selenide) solar cells?
15. What factors affect the lifespan and efficiency of organic photovoltaic materials?
16. What is the significance of the bandgap for each type of solar cell?
17. Which material properties determine the light absorption coefficient in a semiconductor layer?
18. What materials are used for anti-reflective coatings, and what benefits do they provide?
19. What properties should materials used in electrodes (e.g., ITO — indium tin oxide) possess?
20. What are the current achievements and limitations of perovskite-based solar cells?
21. What is the operating principle of quantum dot solar cells?
22. What technologies are used to improve the efficiency of tandem solar cells?
23. What materials are used to manufacture flexible and transparent solar panels?
24. What is the principle of operation of photoelectrochemical solar cells?
25. What advantages do nanostructures offer in modern solar cells?

26. What technological methods are used to enhance solar cell efficiency?
27. What environmental issues and disposal challenges are associated with solar cells?
28. What are the prospects for quantum dot-based solar cells?
29. What are the advantages and challenges of solar cells based on two-dimensional (2D) materials?
30. What new materials and technologies are expected in the near future in solar energy?

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