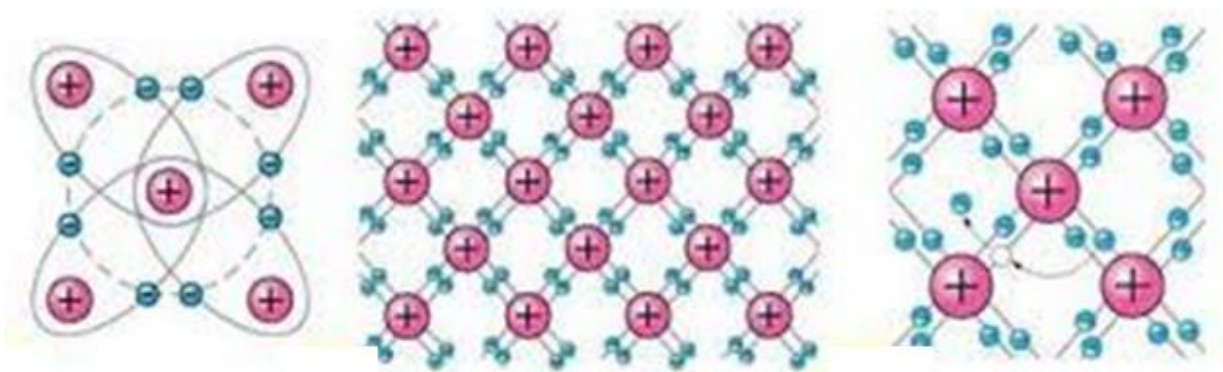


Drohobych Ivan Franko State Pedagogical University

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SEMICONDUCTOR MATERIALS SCIENCE



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Навчальний посібник “Напівпровідникове матеріалознавство” написаний відповідно до програми навчальної дисципліни “Напівпровідникове матеріалознавство” для підготовки фахівців другого рівня вищої освіти напряму підготовки 01 Освіта / Педагогіка спеціальності 014 Середня освіта (Фізика), затвердженої вченою радою Дрогобицького державного педагогічного університету імені Івана Франка. У посібнику подано матеріали для самостійної роботи з основних розділів напівпровідникового матеріалознавства. Посібник буде корисним для підготовки фахівців третього рівня вищої освіти спеціальності “Прикладна фізика та наноматеріали”.

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INTRODUCTION

Scientific and technological progress is closely linked to the development and use of new materials. It is no coincidence that even historical chronology is based on the names of materials – the Stone Age, Copper Age, Bronze Age, Iron Age. As people's knowledge and skills accumulated, new materials appeared. It is difficult to characterize the present time with a specific material. It is called the era of semiconductors, the era of polymers, the era of superconductors, etc.

Materials science is the science of the interrelationships between the electronic structure and structure of materials and their composition, physical, chemical, technological and operational properties. The properties studied include the structure of substances, electronic, thermal, chemical, magnetic, optical and other properties of these substances. In addition, this science uses a number of techniques to study the structure of materials. When manufacturing high-tech products in industry, especially when working with objects of micro- and nanoscale, it is necessary to know in detail the characteristics, properties and structure of materials. The science of materials is called upon to solve these problems.

The course "Semiconductor Materials Science" is taught to students as a professional training discipline. The course aims to provide information about semiconductor materials of various classes and their applications. The lecture course is based on the courses in quantum mechanics, thermodynamics, solid state physics, physics of semiconductors and dielectrics.

After studying the course, the student should know the basics of crystal-chemical classification of materials, the main classes of semiconductor materials, the main properties and applications of these materials, know the basics of chemical thermodynamics and their practical use to describe systems containing semiconductor materials used in semiconductor micro- and optoelectronics.

The development of semiconductor optoelectronics and microelectronics has led to the widespread use of semiconductor

compounds. The interaction of various compounds leads to the formation of solid solutions, which makes it possible to obtain materials with predetermined properties and parameters by changing the composition of the solution.

The problem of reproductive doping of semiconductor compounds to obtain crystals with the required parameters is quite difficult to solve. This is due to the fact that the properties themselves vary within a very wide range, and it is usually necessary to grow such crystals with a certain combination of different properties (for example, optical and electrophysical), taking into account the high homogeneity of the distribution of the latter in the volume. In addition, many impurities in semiconductor compounds exhibit rather complex behavior, and, therefore, the correct choice of an optimal dopant generally depends on the results of a thorough study of the effect of various impurities on the electrophysical and optical properties of such crystals.

Point defects, dislocations, and structural defects cause diffusion processes and significantly affect the electrical, thermal, and other properties of crystals. The study of defects has not only revealed a number of new, previously unknown phenomena, but also developed recommendations for controlling the properties of semiconductor materials.

COURSE LECTURE NOTES

**1. General characteristics of semiconductor materials
and their classification**

1.1. The subject is materials science

1. Materials science belongs to those sections of physics and chemistry that study the properties of materials. Materials science is the basis for the study of many special disciplines.
2. Fabrication, development of new materials, methods of their processing are the basis of modern production and determine the level of development of scientific and technical progress and economic potential of the country.
3. The variety of properties of materials is the main factor determining their wide application in technology.
4. The main properties of materials can be divided into physical, mechanical, technological and operational.
5. Materials science uses the following methods: electron microscopy, X-ray structural analysis, mechanical methods, calorimetry, nuclear microscopy, etc.
6. Areas of materials science research:
 - Nanotechnology – fabrication and study of materials and structures with sizes of about several nanometers.
 - Crystallography – study of the structure of crystals and violations of this structure, the inclusion of foreign particles and their influence on the properties of the main material of the crystal.
 - Diffraction technologies, such as X-ray structural analysis, used to study the phase state of matter.
7. Sections of science on which materials science is based:
 - Thermodynamics – to study stability, phase changes, to construct phase diagrams.
 - Thermal analysis – to study changes in the properties of materials under the influence of temperature and when interacting with various gases.

-
- Kinetics – when studying changes in the phase state of matter, thermal decomposition of the structure and diffusion.
 - Solid state chemistry – for the study of chemical processes taking place in the solid phase.
 - Solid state physics – for the study of classical and quantum effects in solid materials (for example, in semiconductors and superconductors)
8. The success of the development of semiconductor technology and related industries (electronics, power engineering, etc.) is one of the most important tasks of science and technology.
 9. Currently, in Ukraine, research and development in the field of semiconductor materials science has sharply narrowed, while there is a significant increase in interest in them in world science and technology.

1.2. General information about semiconductors

1. With the discovery of transistors (USA, 1949), the widespread use of semiconductors (primarily germanium and silicon) in radio electronics began. At the same time, an intensive study of the properties of semiconductors began, which was facilitated by the improvement of crystal purification methods and their doping.
2. Semiconductors differ from other classes of solid materials by many specific features, the main of which are:
 - Positive temperature coefficient of electrical conductivity, i.e. with increasing temperature, the electrical conductivity of semiconductors increases.
 - The specific electrical conductivity of semiconductors is lower than that of metals, but higher than that of insulators.
 - Large values of thermoelectromotive force compared to metals.
 - High sensitivity of semiconductor properties to ionizing radiation.
 - The ability to dramatically change physical properties under the influence of very small concentrations of impurities.
 - Current rectification effect or non-ohmic behavior at the contacts.

General characteristics of semiconductor materials and their classification

3. The properties of semiconductors are explained by the band theory of solids. If the valence band is completely filled with electrons, and the next band of allowed energies (conduction band) is empty and the range of forbidden energies (width of the energy gap E_g) does not exceed 1–3 eV, then such solids will be semiconductors.
4. As a result of certain energy action (temperature, radiation), electrons from the valence band can be transferred to the conduction band. The number of electrons that have entered the conduction band, and therefore the number of holes, increases with increasing temperature or illumination. This is a significant difference between semiconductors and metals, in which, on the contrary, conductivity decreases with increasing temperature.
5. At a temperature of absolute zero and in the absence of other external actions, electrons in semiconductors do not have enough energy to cross the energy gap. Therefore, the semiconductor under these conditions is a dielectric. Therefore, the division of substances into semiconductors and dielectrics is conditional.
6. The electrical conductivity of an intrinsic semiconductor in an equilibrium state is due to both conduction electrons and holes, and their concentrations are equal.

1.3. Classification of semiconductor materials

1. Semiconductor materials include most minerals, non-metallic elements of groups IV, V, VI of the periodic system of chemical elements, inorganic compounds (oxides, sulfides), some metal alloys, organic dyes.
2. Widely used semiconductor materials are elements of the IV group of the periodic system of chemical elements – germanium and silicon.
3. Semiconductor materials are divided into simple (elemental) and complex (compounds).
4. The group of complex semiconductor materials includes chemical compounds that have semiconductor properties and that include two, three or more chemical elements.

-
5. The total number of elementary semiconductors is small, their electrophysical properties are not diverse enough to meet the requirements of modern semiconductor technology. The number of semiconductor compounds is practically unlimited and, therefore, there will always be substances with practical properties.
 6. The classification of semiconductor compounds can be based on the following principles: crystal chemical (by structure), by the location of the initial elements in the periodic table (for example, $A^{II}B^{VI}$ compounds), by the name of the anion (silicides, arsenides, etc.).
 7. Semiconductor materials consisting of two elements are called binary. Binary compounds containing arsenic are called arsenides, sulfur – sulfides, tellurium – tellurides, carbon – carbides.
 8. The classification of semiconductor compounds by the name of the anion is most often used for oxides, sulfides, selenides, etc. This classification applies only to compounds formed according to the rules of valency.
 9. For other binary compounds, it is convenient to classify them according to the location of the initial elements in the Periodic Table.
 10. Complex semiconductor materials are united by the number of the group of the Periodic System to which the components of the compound belong, and denoted by letters of the Latin alphabet (A – the first element, B – the second, etc.).
 11. In addition to binary semiconductors, ternary and more complex compounds containing three or more components are known. Complex semiconductors also include solid solutions of elementary semiconductors and semiconductor compounds with semiconductor properties.
 12. Semiconductor materials are divided by structure into crystalline, solid, amorphous, and liquid. Inorganic crystalline semiconductor materials find the most practical application.

1.4. Application of semiconductors

1. The most important field of application of semiconductor materials is microelectronics. Semiconductor materials form the basis of modern large and ultra-large integrated circuits, which are made mainly on the basis of Si.
2. Further progress in increasing the speed and reducing the power consumption of integrated circuits is associated with their fabrication on the basis of GaAs, InP and their solid solutions from other compounds of type $A^{III}B^V$.
3. Semiconductor materials are used on a large scale for the manufacture of power electronic devices (rectifiers, thyristors, powerful transistors). Here, too, Si is the main material, and further advancement into the area of higher operating temperatures is connected with the use of GaAs, SiC and other wide-gap semiconductor materials.
4. The use of semiconductor materials in solar energy is expanding every year. The main semiconductor materials for the manufacture of solar cells are Si, GaAs, heterostructures $Ga_xAl_{1-x}As/GaAs$, Cu_2S/CdS .
5. The use of non-crystalline semiconductor materials in solar cells is associated with the prospect of a sharp decrease in the cost of solar cells.
6. Important areas of application of semiconductor materials: nuclear radiation detectors (especially pure Ge, Si, GaAs, Cd, etc. are used), manufacture of refrigerators, strain sensors, very sensitive thermometers, magnetic field sensors, and other devices.

1.5. Basic concepts and definitions

1. Materials science is a science that studies the structure of materials in close connection with their properties.
2. A semiconductor is a material whose main property is the strong dependence of its electrical conductivity on the action of external factors, such as temperature, electric field, light, etc.

-
3. Intrinsic semiconductor – a semiconductor whose electrical conductivity is determined by its own current carriers.
 4. An impurity semiconductor is a semiconductor whose electrical conductivity is determined by current carriers caused by impurities.
 5. Doping – the introduction of certain impurities into the semiconductor.
 6. Acceptors are impurities that determine the hole conductivity of a semiconductor. 7. Donors are impurities that determine the electronic conductivity of a semiconductor.
 7. A compensated semiconductor is a semiconductor in which conductivity will be provided by an equal concentration of donor and acceptor impurities.
 8. The width of the energy gap is the smallest energy required for the transition of an electron from the valence band to the conduction band, and determines the energy interval between these two bands.

1.6. Questions for self-control

1. What causes the widespread use of semiconductor materials in technology?
2. When did the widespread use of semiconductors begin?
3. How do semiconductors differ from other classes of solid materials?
4. What principles are the basis for the classification of semiconductor compounds?

2. Influence of the structural state on the properties of materials

2.1. Dependence of the physical properties of substances on the structure of crystals

1. The physical properties of crystals are determined primarily by the nature of the chemical elements that make up their composition, that is, the type of chemical bond plays a decisive role.
2. The manifestation of certain physical properties is connected with the geometric nature of the structure, with the mutual arrangement of atoms in the crystal structure of substances, as well as with the imperfection of the structures of real crystals, which reflect the conditions of their formation.
3. The most characteristic feature of the physical properties of crystals is their symmetry and anisotropy.
4. Anisotropic crystals exhibit a number of properties that are not possessed by isotropic crystals.
5. Manifestation of a number of physical characteristics, such as mass, density, heat capacity, melting point, depends on interatomic distances in crystal structures. In this case, the crystal can be considered as a discrete environment.
6. Regarding a number of macroscopic properties, such as thermal and electrical conductivity, optical and other properties, it is possible to abstract from the discrete structure and consider the crystalline substance as a continuous homogeneous anisotropic medium.
7. Since the manifestation of many physical properties depends on the direction in the crystal, the crystal can be considered a continuous anisotropic medium.
8. To describe the physical properties of crystals, scalar, vector and tensor quantities are used, therefore the properties of crystals are divided into scalar, vector and tensor properties.

2.2. Crystalline structure

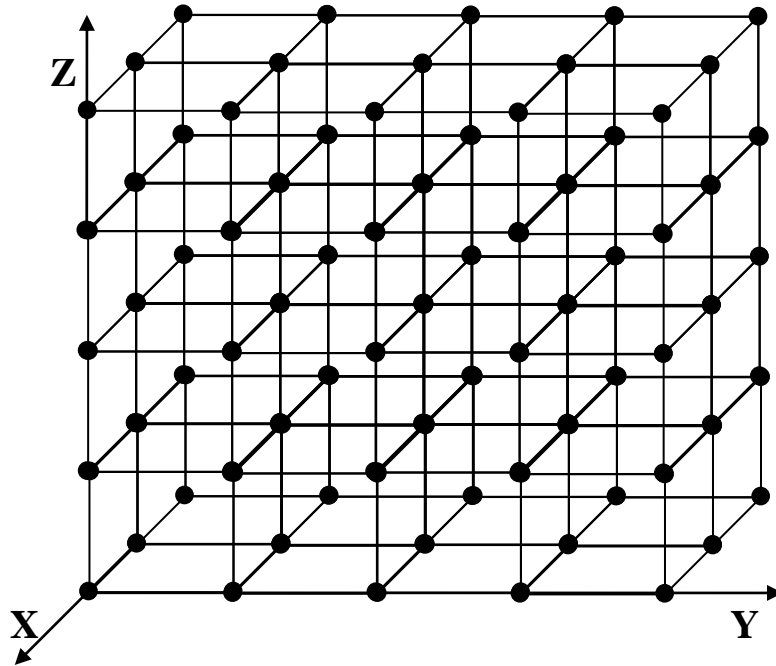


Fig. 2.1. Crystalline lattice

1. All crystalline solids are characterized by a certain order – periodicity, both in different directions and in different planes. This order is determined by the concept of a crystal lattice (Fig. 2.1).
2. Geometrical characteristics of the crystal structure, data on the distribution of electron density, amplitudes of atomic oscillations are found using diffraction research methods (X-ray structural analysis, neutron and electronography of crystals), oscillation frequencies – using spectroscopy methods (IR, Raman scattering, inelastic neutron scattering).
3. From ideas about the homogeneity of the crystal, the three-dimensional periodicity in the arrangement of its constituent identical material particles, an abstract geometric image emerges – an infinite spatial lattice – a kind of element of symmetry, which is set and realized as a result of the repetition of equivalent points of the crystal space. Spatial lattice is the main element of symmetry, without it the structure of the crystal cannot be represented.

2.3. Location of atoms or ions in a crystal

1. To describe the crystal lattice, it is enough to know the location of the particles in the unit cell of the crystal, the repetition of which forms the crystal lattice.
2. The choice of an elementary cell is ambiguous, but its volume in three-dimensional space (area in two-dimensional and length in one-dimensional) is unchanged with any choice.

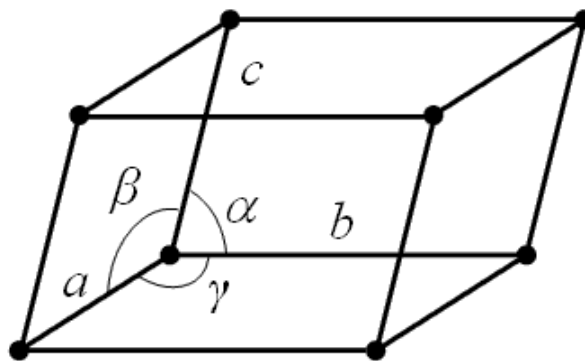


Fig.2.2. Elementary cell

3. An ideal crystal structure is characterized by an infinite spatial lattice, that is, it consists of identical elementary cells. The latter have the form of parallelepipeds with sides a , b , c and angles α , β , γ (lattice parameters) and face each other (Fig. 2.2).
4. A cell is called primitive if the nodes are located only at the vertices of the cell (empty cell). A non-primitive cell contains additional nodes outside the cell contour (Fig. 2.3).

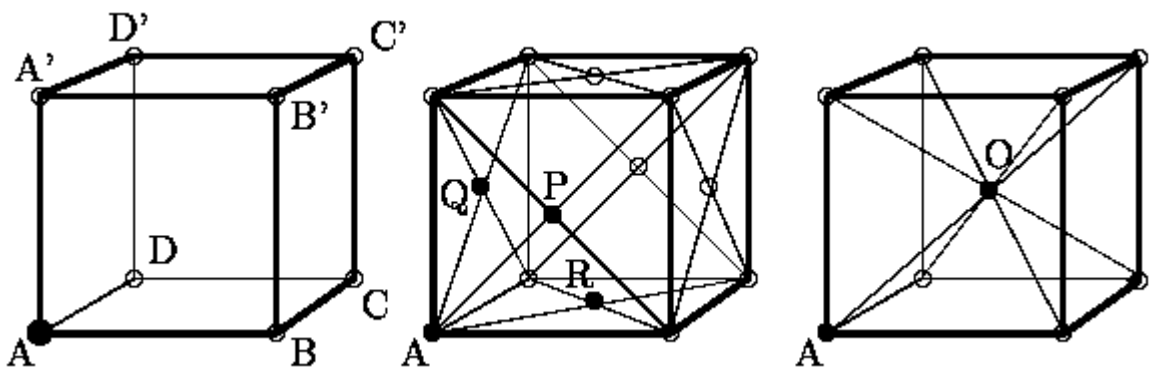


Fig. 2.3. Elementary cells of cubic lattices: a) primitive;
b) face-centered; c) volume-centered

-
5. The classification of possible types of crystal lattices was carried out by the French scientist O. Bravais, accordingly they received the name "Bravais lattice".
 6. There are a total of fourteen crystal lattices divided into four types for crystalline bodies.
 7. It is customary to mark the cells with Latin letters: primitive P, base-centered C, side-centered A, B, face-centered F, volume-centered I.
 8. It is often said that a crystal is a Bravais lattice plus a basis. This expression should be understood in the sense that, having the contents of the elementary cell and periodically extending it by parallel transfer to all the translation vectors given by the Bravais lattice, we will obtain the entire infinite crystal.
 9. All kinds of symmetry that can be observed in a crystal lattice give rise to 32 so-called point groups of symmetry, which in turn form 17 types of lattices, which are called crystallographic systems. Point groups correspond to 14 types of different spatial structures, which are called Bravais lattices. These lattices differ in the type of elementary cells.
 10. The main parameters of the crystal are:
 - dimensions of the edges of the elementary cell (a, b, c);
 - γ, β, α angles between axes;
 - coordination number (K);
 - lattice base;
 - packing density of atoms in the crystal lattice.
 11. For the elementary cell of a simple cubic lattice (Fig. 2.3), there are 8 points at the vertices of the cube, but each of these 8 points simultaneously belongs to 8 cubes converging at the selected vertex; in this way, we have $8(1/8)=1$ point corresponding to the elementary cell.
 12. For a volume-centered lattice, we have 8 vertices, each of which corresponds to 8 cubes, and, in addition, each cube contains one point. It follows that one elementary cell contains $8/8+1/1=2$ points.

13. For a face-centered cubic lattice, we have 6 points located on the faces of tangent cells, as well as one point each at the vertices of the cube. We find: $8/8+6/2=4$ points belonging to the elementary grid.
14. With multiple parallel transfers (translations) of the cell in three different directions, a spatial crystal lattice will result. Having specified three elementary translations a , b , c and the required number n of particle vectors in the cell (basis), we obtain a set of vectors of all crystal particles: $\vec{r} = k\vec{a} + l\vec{b} + m\vec{c}$
15. The unit cell can be specified in many ways. One of the most common methods is related to the construction of a Wigner-Seitz cell. It is formed from planes that are perpendicular to segments connecting various points of the grid. Planes should be located in the middle of these segments.
16. Parallelepiped (or rather, rhombohedron) $APR'QRQ'C'R'$ in Fig. 2.4 is the minimal unit cell of a lattice containing only one node. Similarly, it is possible to construct a minimal cell of a volume-centered lattice. Such a cell can serve, for example, as a parallelepiped built on three vectors AB , AD , AO .

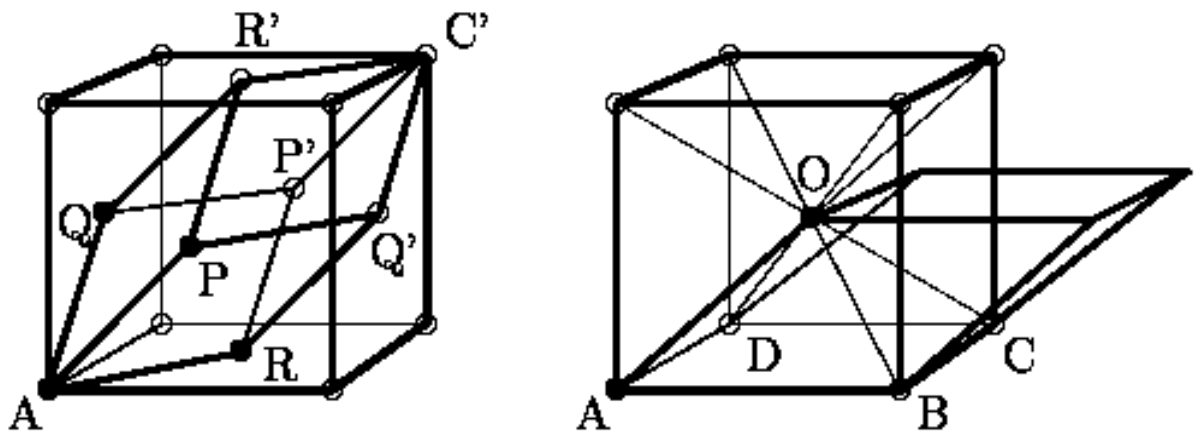


Fig. 2.4. Minimum elementary cells of cubic lattices:
a) face-centered; b) volume-centered

17. For VCC and FCC, it is accepted and more convenient to work with a cubic cell, despite the fact that it contains several particles. At the same time, the main properties of symmetry are better visible and it is easier to perform calculations.

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18. The crystal lattice of a diamond (Fig. 2.5) has the following property: each particle has 4 nearest neighbors that are equidistant and the angle between the directions of any two of them is equal to 120° . Thus, each particle is in the center of a regular tetrahedron with vertices in its neighbors.

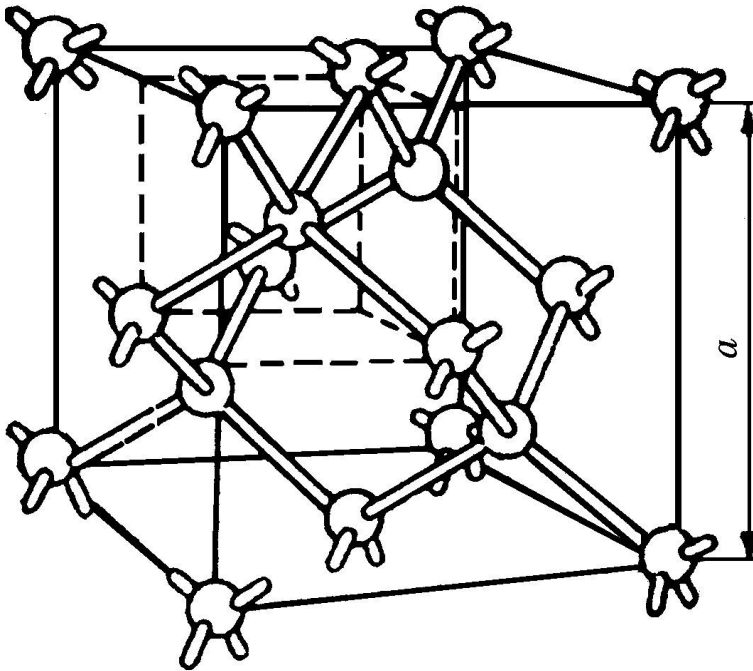


Fig. 2.5. The crystal lattice of a diamond

19. The lattice of the diamond structure can be represented as two face-centered lattices, shifted relative to each other by a quarter of the main diagonal of the cube.
20. Some substances consist of atoms of different types. These can be various chemical compounds and alloys.
20. The structure of the crystal of common table salt NaCl (Fig. 2.6) can be represented as a simple cubic lattice, in the nodes of which atoms alternate Na and Cl. Such a cell is not elementary, because when it is transferred to elementary translations, Na atoms change to Cl atoms and vice versa. It is more correct to consider this structure as consisting of two cubic face-centered lattices of Na and Cl shifted by half of the elementary translation vector.

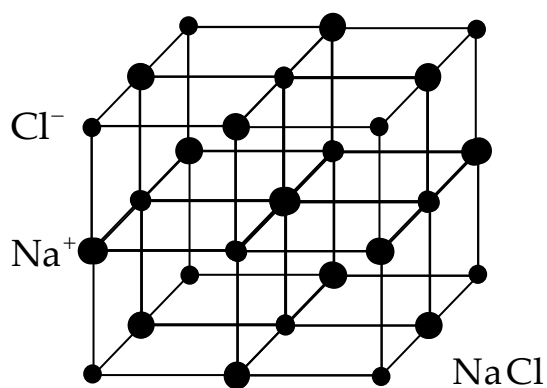


Fig. 2.6 The crystal lattice of table salt

21. In real crystals, the crystal structure is always distorted by defects, as well as by the presence of the crystal surface.
22. There is a huge number of crystal structures. They are united by the main property of the crystalline state of matter – the regular arrangement of atoms in the crystal lattice. The same substance can crystallize in different crystal lattices and have very different properties (a classic example is graphite – diamond) (Fig. 2.7). At the same time, different substances can form lattices of the same type.

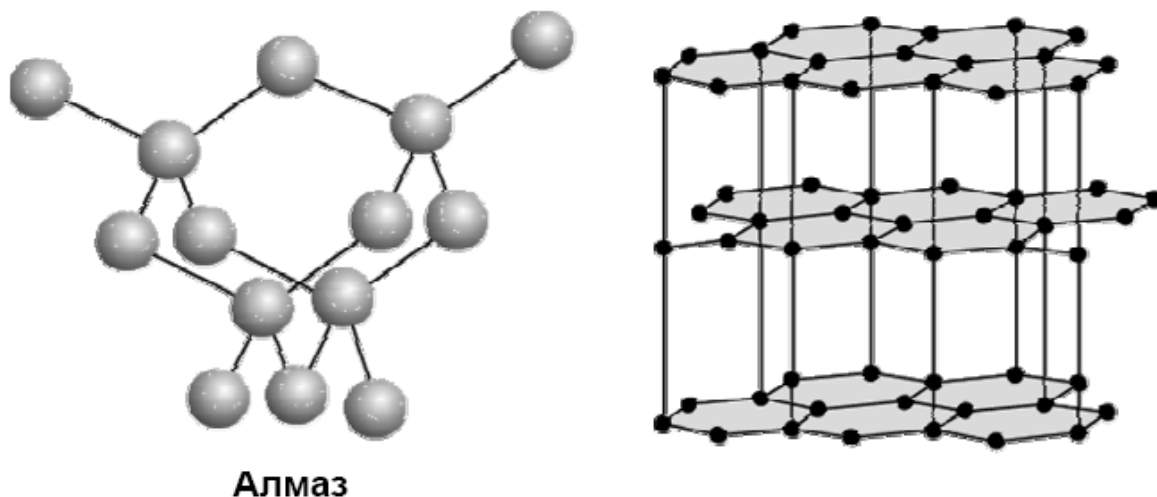


Fig. 2.7. Carbon can crystallize in different crystal lattices and have quite different properties (graphite – diamond)

23. The entire variety of crystal lattices is classified according to some of the most important features. The most important property of the crystal is spatial symmetry, and according to it the lattices are divided into 7 syngonias, 32 classes of symmetry. Another

important characteristic is the position of the atoms in the unit cell, which is the basis of Bragg's classification of crystal lattices.

2.4. Concept of isotropy and anisotropy

1. Due to the independence of various properties from the direction, substances are isotropic. These include gases, liquids and amorphous bodies (translated from Greek – formless). There are also isotropic crystals.
2. Crystalline materials can have anisotropy of physical properties (mechanical, electrical, optical, etc.), which consists in the fact that these properties depend on the direction chosen in the material.
3. The properties of a body depend on the nature of the atoms that make it up and on the strength of interaction between these atoms. The forces of interaction between atoms are largely determined by the distances between them.
4. In amorphous bodies with a chaotic arrangement of atoms in space, the distances between atoms in different directions are equal, therefore, the properties will be the same, that is, amorphous bodies are isotropic.
5. In crystalline bodies, atoms are correctly arranged in space, and in different directions the distances between atoms are not the same, which causes significant differences in the forces of interaction between them and, as a result, different properties.
6. To indicate crystallographic planes and directions, Miller indices are used (Fig. 2.8).

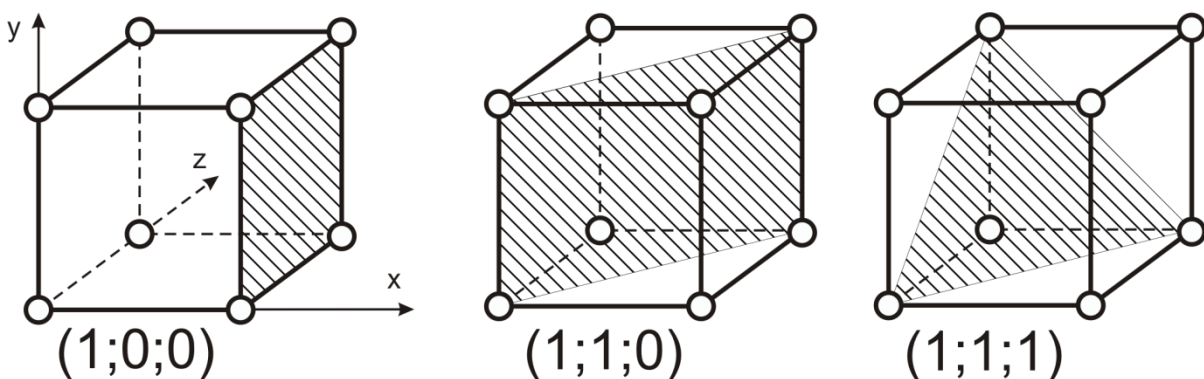


Fig. 2.8. Miller indices for planes

Influence of the structural state on the properties of materials

7. To determine the indices of the crystallographic plane, it is necessary:
 - set the coordinates of the intersection points of the plane with the coordinate axes in units of the grid period;
 - take the inverse values of these values;
 - reduce them to the smallest integer multiple of each of the received numbers.
8. Mueller's indices for the plane are simple integers that do not have a common factor (indicated in round brackets (hkl)). It follows that:
 - planes in the crystal crossing all three axes of the unit cell will have indices hkl ;
 - planes crossing two axes and parallel to the third axis will have indices $0kl$, $h0l$, $hk0$ if they are parallel to axes a , b and c , respectively;
 - planes crossing one axis and parallel to two other axes will have indices $00l$, $0k0$, $h00$ if they are parallel to axes a and b , a and c , b and c , respectively.
9. The orientation of a line is determined by the coordinates of two points. To determine the indices of the crystallographic direction, it is necessary:
 - align one point of the direction with the origin of the coordinates;
 - set the coordinates of any other point lying on a straight line in units of the grid period;
 - reduce the ratio of these coordinates to the ratio of the three smallest integers.
10. Indices of crystallographic directions are indicated in square brackets $[111]$.
11. In cubic lattices, the indices of the direction perpendicular to the plane (hkl) also have indices $[hkl]$.

2.5. Crystal lattice defects

1. In the crystal lattice of real crystals, there are various defects (imperfections) that disrupt the bonds between atoms and affect the properties of materials.
2. Crystal defects are any persistent violation of crystal translation symmetry – the ideal periodicity of the crystal lattice.
3. It is customary to divide all crystal lattice defects into two large groups: geometric defects and energy defects. Due to the appearance of geometric defects in the grid, it is locally distorted. In the presence of energy defects, the atoms remain in their places, but the energy of one or a group of atoms turns out to be increased.
4. It is customary to divide geometric defects into zero-dimensional (point), one-dimensional (linear), two-dimensional (flat) and three-dimensional (volumetric).
5. The extent of point defects in all directions is small. The length of linear defects is large in one direction and small in the other two directions. Surface defects have a large extent in two directions and small in one, volume defects have a large extent in all directions.
6. Defects play a significant role in shaping not only the mechanical properties of crystals (strength, plasticity, brittleness), but also affect the optical, electrical, and magnetic properties.

2.5.1. Lattice point defects

7. Lattice point defects include atoms of foreign elements (alloying element or impurities), internodal atoms (atoms of the main element that for certain reasons left the nodes of the crystal lattice and got stuck in the internodes), vacancies (nodes of the crystal lattice that are not occupied by atoms) (Fig. 2.9)

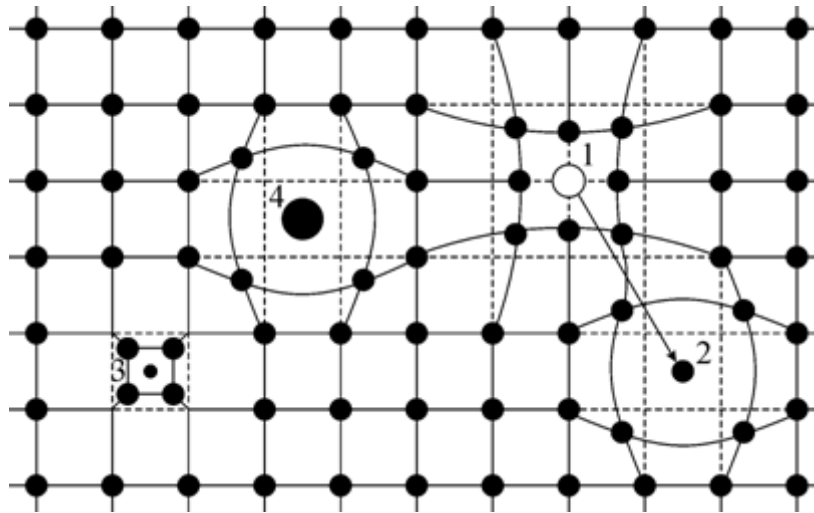


Fig. 2.9. Lattice point defects: 1 – vacancies (unoccupied atoms of the crystal lattice nodes); 2 – inter-nodal atoms (atoms of the main element, which for some reason left the nodes of the crystal lattice, and stuck in the interstices); 3, 4 – atoms of foreign elements (alloying element or impurities)

8. If there is a vacancy in the crystal lattice, an atom can jump from a lattice node to a vacant place. Thus, the vacancy shifts, and the diffusion process can be described as a sequential movement of atoms or as a movement of vacancies.
9. As the temperature rises, the bound energy of the system increases and the concentration of vacancies increases, therefore, as the temperature rises, diffusion becomes more active.
10. According to Frenkel's model, during the formation of vacancies, an atom from a crystal lattice node jumps into an interstitial space, and a pair of defects appears – a vacancy and an interstitial atom, or a Frenkel pair.
11. Schottky showed that the energy of elastic lattice distortions near an interstitial atom is significantly greater than the energy of distortions near a vacancy. This allowed him to propose another mechanism for creating vacancies. The atom comes to the surface of the crystal, and the resulting vacancy migrates (moves) deep into the crystal.

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12. The probability of vacancy formation by the Schottky mechanism is significantly higher than the probability of vacancy formation by the Frenkel mechanism.
 13. The presence of point defects affects not only diffusion processes in materials, but also their electrical properties.
 14. A simple complex of point defects – a bivacancy (divacancy) – two vacancies located in neighboring lattice nodes.
 15. Complexes consisting of two or more impurity atoms, as well as impurity atoms and intrinsic point defects, play an important role in semiconductors. In particular, such complexes can significantly affect the strength and electrical and optical properties of solids.
 16. In materials with an ionic bond, the appearance of any point defects leads to a decrease in electrical resistance.
 17. In materials with a covalent bond, only an increase in the concentration of vacancies leads to a decrease in electrical resistance.

2.5.2. Linear defects of the crystal lattice

18. Plastic deformation occurs by layer-by-layer shifting of one part of the crystal relative to another (like a deck of cards during shifting).
19. According to the geometric model of dislocation, there is a broken plane (extra-plane) in the crystal, near the break of which the remaining planes of the crystal lattice are bent. Thus, near the edge of the extraplane, the crystal lattice is distorted. The magnitude of crystal lattice distortions rapidly decreases when moving away from the edge of the extraplane, but remains the same when moving along the break line. Therefore, such a dislocation is called an edge dislocation (Fig. 2.10).

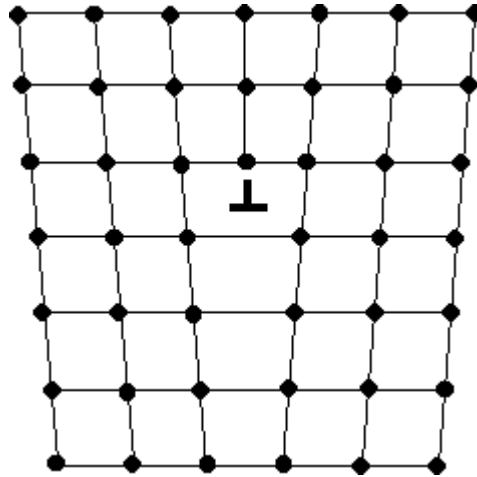


Fig. 2.10. Edge dislocation

20. Dislocations are linear defects of the crystal lattice. The presence of dislocations in the crystal lattice has a significant effect on the mechanical and electrical properties of materials. In the complete absence of dislocations, the strength of crystals would be the same as theoretical.
21. When an external stress is applied, dislocations are displaced and come to the surface of the crystal, and in this way plastic deformation is carried out.
22. The presence of dislocations in the material sharply increases the rate of diffusion. This is due to the fact that the presence of dislocations increases the local concentration of vacancies, and therefore accelerates diffusion.
23. The nature of the influence of dislocations on the electrical properties of materials is similar to the nature of the influence of point defects.

2.5.3 Methods of observing dislocations

24. Most methods of experimental observation of dislocations are based not on the detection of the dislocation line itself, which is practically difficult to do, but on the registration of stress or distortions in the lattice caused by the dislocation.
25. Selective etching method: in places where dislocations appear on the surface of the crystal near the dislocation due to the distortion of

the crystal lattice, the rate of chemical etching differs from the rate of etching of the crystal matrix, and so-called etching figures are formed on the surface, as a rule, "pits" or "bumps". The location and number of figures characterizes the dislocation structure of the crystal.

26. Photoelasticity method: the intrinsic stress fields of dislocations, adding up, make a noticeable stress inside the crystal, which can be observed due to the piezo-optical effect (photoelasticity). This method is especially convenient for observing dislocations in cubic crystals, which are optically isotropic in the unstressed state. The stress field of dislocations in them is registered by the birefringence that has arisen.
27. X-ray structural analysis: local lattice deformation associated with a defect changes the conditions of reflection and scattering of x-rays. The intensity of the diffracted x-beam near the defect decreases, as a result of which the defect is visible as a dark line on a general light background.
28. Electron microscopy: based on the dislocation contrast effect resulting from the interaction of the electron beam with displaced atoms in the stress field around the dislocation. As a result of the interference between the original and diffracted electron beams, it is possible to see images of dislocation lines, dislocation rows and walls in an electron microscope.

2.6. Basic concepts and definitions

1. Allotropy (polymorphism) is the property of crystals to change the type of crystal lattice when external conditions (temperature, pressure) change.
2. Amorphous bodies are bodies in which their simple constituent elements are chaotically arranged in the volume
3. Anisotropy is the dependence of crystal properties on the direction in it.

Influence of the structural state on the properties of materials

4. The basis of the crystal lattice is a set of atoms or molecules located in the unit cell of the crystal, in other words, the material filling of this unit cell.
5. Vacancy – a free place in a node of the crystal lattice (point defect).
6. Burgers vector – a vector that closes the contour (Burgers) drawn around the defective area in the crystal, characterizes the geometry and energy of dislocations.
7. The translation vector is a vector connecting two equivalent points of the crystal.
8. A screw dislocation is a dislocation whose Burgers vector is parallel to the line.
9. A Bravais lattice is a lattice formed by a set of equivalent points of a crystal, which are nodes of a Bravais lattice.
10. Crystal defects – any stable violation of crystal translation symmetry – the ideal periodicity of the crystal lattice.
11. Dislocation is the boundary of the region of incomplete displacement inside the crystal.
12. Diffusion is the movement of atoms at distances exceeding the parameters of the crystal lattice.
13. An impurity atom of introduction is an impurity atom that is located in an internode of the crystal lattice. In semiconductors, such defects create deep energy levels in the band gap, such as copper and gold in silicon.
14. Substitution impurity atom – replacement of an atom of one type by an atom of another type in a crystal lattice node. In the substitution positions, there may be atoms that differ relatively little from the atoms of the base in terms of their size and electronic properties.
15. Equivalent points of a crystal are points from which the same view of the surrounding infinite ideal crystal opens.
16. An extraplane is an incomplete atomic plane (half-plane) that breaks off inside the crystal.
17. An elementary cell is a cell with the smallest volume (volume element with the minimum number of atoms).

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18. Isotropy is the independence of properties from direction in a solid body.
 19. Mueller's index is a natural integer characterizing a plane or direction in a crystal lattice.
 20. A cell is a part of a crystal, which can be moved multiple times in space to build the entire crystal.
 21. Coordination number (K) is the number of atoms located at the nearest equal distance from any atom in the lattice.
 22. An edge dislocation is a dislocation whose Burgers vector is perpendicular to the line.
 23. A crystal lattice is a spatial grid, in the nodes of which the conventional centers of the elements of the crystal lattice are located.
 24. Crystalline bodies are bodies in which their simple constituent elements are strictly fixed and periodically arranged in the volume.
 25. A crystallographic plane is a plane that passes through the nodes of the crystal lattice.
 26. Crystallographic direction is a straight line passing through the nodes of the crystal lattice.
 27. Translation operation (translation) – parallel transfer of the crystal to the translation vector.
 28. The packing density of atoms in a crystal lattice is the ratio of the volume occupied by atoms to the cell volume (for a volume-centered cubic lattice – 0.68, for a face-centered cubic lattice – 0.74).

2.7. Questions for self-control

1. What primarily determines the physical properties of crystals?
2. What substances are called isotropic?
3. Is the choice of elementary cell unambiguous?
4. Which elementary cell is called primitive?
5. Give examples of substances with crystal lattices: VCC, FCC, simple cubic.
6. State the difference between metals and semiconductors.

Influence of the structural state on the properties of materials

7. What is the Mueller index?
8. Specify the designation of the plane, the direction indicated in the figure, in Mueller indices.
9. What crystal defects are classified as: point, linear, surface, volume?
10. How many structural elements does a face-centered cubic lattice contain?
11. How is it customary to classify crystal lattice defects?
12. How is it customary to divide geometric defects?
13. What defects belong to point defects?
14. What are most methods of experimental observation of dislocations based on?

3. Relationship between the properties of semiconductor materials and the type of chemical bond

3.1. Types of chemical bonds

3.1.1. Covalent bond

1. This bond is formed between atoms of one or more chemical elements with close ionization potentials. In its pure form, the covalent bond is realized by the interaction of elements with half-filled electron shells.
2. The atom has minimum energy in the case when the electron shells are completely filled. Therefore, atoms with half-filled electron shells exchange electrons. In this case, pairs of electrons with oppositely directed magnetic spin moments are formed, and these pairs belong to both neighboring atoms.
3. The appearance of a pair of negatively charged electrons between positively charged ions leads to the fact that both ions are attracted to the shared electrons and, thus, attract each other.
4. Each atom interacts with a limited number of neighbors, and the number of neighbors is equal to the number of valence electrons of the atom. Hence, the covalent bond is saturated.
5. In addition, an atom interacts only with those neighbours with whom it has exchanged electrons, i.e. the covalent bond is directional.
6. Increasing the serial number of the element leads to an increase in the number of electron shells that shield the interaction of positively charged nuclei with valence electrons. Therefore, the force of mutual attraction decreases and the depth of the potential well decreases.
7. With the increase of the element's serial number, the melting point decreases, the coefficient of thermal expansion increases, and the modulus of elasticity decreases.

3.1.2. Ionic bond

8. This bond is formed by the interaction of atoms with a small number of valence electrons and atoms with a large number of electrons on the valence shells.

Relationship between the properties of semiconductor materials

9. External electrons of atoms with low ionization potentials transfer to the valence shells of atoms with high ionization potentials. As a result, positively and negatively charged ions are formed, which are mutually attracted by electrostatic forces.
10. In ionic crystals there are no molecules, so there are no boundaries between structural units. Ions can be represented as charged balls whose force fields are evenly distributed in all directions in space.
11. Ionic bonding is unsaturated, an ion can attract ions of the opposite sign in any direction.
12. Ionic bonding is directional because an ion attracts differently charged ions and repels ions of the same charge.
13. Structures with ionic type of chemical bonding are characterized by high coordination numbers and dense globular packing. The symmetry of ionic crystals is usually high.
14. Crystalline substances with ionic type of chemical bonding are characterized by dielectric properties, brittleness, average values of hardness and density, low thermal and electrical conductivity.
15. Reducing the size of the ion and increasing its charge leads to an increase in the binding energy, and hence to an increase in the melting point of the material, a decrease in the coefficient of thermal expansion and an increase in the modulus of elasticity.

3.1.3. Metal bond

16. This bond is formed between the atoms of one or more chemical elements in which the valence electron shells are less than half full.
17. Since the energy of the ion is minimal when the outer shell is completely filled, the atoms give up their outer valence electrons and turn into positively charged ions with free electrons between them (electron gas).
18. Each of the positively charged ions is attracted to free electrons and thus the ions are attracted to each other.
19. Metal bonding is non-directional and unsaturated, and the number of nearest neighbors of an ion is determined mainly by geometric and energy factors.

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20. Under the action of an electric field, electrons not associated with ions move, so metals have high electrical conductivity.
 21. Metal materials absorb quanta of electromagnetic field of any energy, i.e. metals are opaque to radio and light waves in a wide range of frequencies.
 22. After absorbing a quantum of the electromagnetic field, a free electron is excited, and when it returns to a stationary state, it emits a similar quantum. In other words, metallic materials reflect radio and light waves.
 23. Tightly packed lattice of metals is the reason for their high plasticity.

3.1.4. Polarization bond

24. This bond or van der Waals bond is formed when molecules or atoms of noble gases come together.
25. A single atom has a symmetrical electron shell. When two atoms approach, their electron shells interact electrically and deform. As a result, the atoms turn into dipoles, which are mutually attracted.
26. The higher the ordinal number of the atom, the more electron shells it has, and therefore the bonding of the valence electrons with the nucleus weakens, and it becomes easier to deform it. Consequently, the dipole moment of the atom increases and the binding energy between atoms increases. Therefore, the boiling point of heavy inert gases is much higher than the boiling point of light gases.
27. Similar processes occur when electrically neutral molecules come together. Moreover, the higher the molecular weight, the greater the dipole moment of the molecules and the higher the binding energy.
28. Substances with low molecular weight at room temperature are gases, substances with high molecular weight are liquids, and substances with even higher molecular weight are solids.

3.2. Features of chemical bond in semiconductors

1. Pure chemical bonds in semiconductor crystals are quite rare.

Relationship between the properties of semiconductor materials

2. Covalent bonding at different values of electronegativity undergoes polarization, i.e. the electron cloud is shifted towards the more electronegative atom. As a result, a certain proportion of ionicity is imposed on the covalence, and the bond becomes partially ionic.
3. In addition, there is a probability of breaking the electron pair responsible for the covalent bond. With increasing temperature this probability increases. And the break of the electron pair means the beginning of the metallization of the bond, since these electrons now belong to the entire crystal.
4. In general, the chemical bond between dissimilar atoms in solids is covalent-ionic-metallic in nature. Depending on which of the three bonds can be neglected in a real compound, one speaks of the dual nature of the chemical bond.
5. The contribution of one or another component predominates depending on the position in the Periodic Table of the elements that form the compounds and on the difference in relative electronegativities (REN) between the elements.
6. The contribution of ionic bonding increases with the increase of the REN difference. If the REN difference is small or equal to 0, in the case of simple substances, we can talk about covalent-metallic bonding.
7. The contribution of covalent bonding increases if both components are nonmetals and have high electronegativity values. If both components are metals, the contribution of metallic bonding increases.
8. In general, in the Periodic Table, both for simple substances and for binary compounds, the proportion of metal bonds increases in groups from top to bottom.
9. The criteria allowing to estimate which contribution to chemical bonding prevails in practice include coordination numbers in crystals. Covalent crystals are characterized by small coordination numbers 1–4, for ionic crystals the most characteristic number is 6. For metal crystals, coordination numbers 8 and 12 prevail.

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10. In semiconductors, the contribution of covalent bonding is always significant or predominant. The predominance of the covalent contribution to the chemical bond is considered one of the criteria that a substance can be a semiconductor.
 11. In most cases, semiconductors have coordination number 4, rarely – 6.
 12. To predict the properties of a semiconductor, it is important to establish the relationship between the nature of the chemical bond in it and such key parameters as band gap, carrier concentration, mobility.
 13. Some correlations are known that allow predicting the band gap width with good accuracy based on indirect criteria.
 14. With increasing proportion of covalent and ionic bonds, the width of the band gap increases. With increasing proportion of metallic bonding, the width of the band gap decreases.
 15. The influence of the nature of the chemical bond on the properties of semiconductors is well traced in a number of isoelectronic analogues. Thus, pure germanium has a band gap of 0.785 eV, and its isoelectronic analogues GaAs and ZnSe have band gaps of 1.4 eV and 2.7 eV, respectively.

3.3. Conductivity of silicon and germanium

1. Widely used semiconductor materials are elements of group IV of the periodic table – germanium and silicon. These are substances that crystallize in a diamond-like lattice.
2. The diamond lattice is a tetrahedron with four atoms at the vertices surrounding the atom. Here, each atom is bound to its four nearest neighbors by covalent bonding forces, since each of them has four outer valence electrons.
3. At temperatures near absolute zero, in an ideal silicon or germanium crystal, all covalent bonds are filled and all electrons are bound to the atoms and cannot participate in the conduction process.
4. For an electron to move, some work must be done to free it from the covalent bond.

Relationship between the properties of semiconductor materials

5. To break the valence bonds at very low temperatures, an energy of 1.2 eV (~ 0.1922 aJ) is required for silicon and 0.75 eV (~ 0.1201 aJ) for germanium.
6. The release of electrons can occur, for example, when the crystal is heated, when the vibrational energy of the atoms in the crystal lattice can increase so much that the bonds are broken and the electrons can be released. This process also occurs with the formation of holes.
7. In ideal crystals, where the number of electrons and holes are equal, the conductivity is called intrinsic. Since the resistivity of ideal semiconductor crystals depends only on temperature, its value can serve as a characteristic of a given semiconductor.
8. The resistance of ideal crystals is called the resistivity of the semiconductor, for example, for silicon at 300 K, the resistivity is equal to $63600 \Omega \cdot \text{cm}$ ($636 \Omega \cdot \text{m}$), and for germanium at the same temperature $47 \Omega \cdot \text{cm}$ ($0.470 \Omega \cdot \text{m}$).
9. Ideal crystals that do not contain any impurities are very rare. Impurities in semiconductor crystals can increase the number of electrons or holes.
10. In silicon and germanium the donors are elements of group V of the periodic table – antimony, phosphorus, arsenic and bismuth.
11. Acceptors in germanium and silicon are elements of the third group of the periodic table: gallium, thallium, boron, aluminum.
12. The number of current carriers arising from the introduction of each type of impurity separately depends on the concentration of the impurity and its ionization energy in a given semiconductor.
13. At an equal concentration of donor and acceptor impurities in the crystal, the conductivity will be provided, as in the native semiconductor, by electrons and holes due to the breaking of valence bonds. Such semiconductor is called compensated.
14. The most important characteristic that determines the quality of germanium and silicon in semiconductor devices is the lifetime of

minority current carriers. In most cases, it is desirable to have a maximum.

15. For the use of germanium and silicon in semiconductor devices (for example, solar cells that convert light energy into electrical energy) and infrared optics, it is important to know the refractive index, reflectivity and transmittance of light in a wide range of wavelengths.

3.4. Basic concepts and definitions

1. Isoelectronic analogues – substances having the same crystal structure and the same total charge of the nucleus of two partner atoms. For example, isoelectronic analogues are Ge, GaAs, ZnSe, as well as Sn, InSb, CdTe.
2. Ionic bond – a bond in which positively and negatively charged ions are formed, mutually attracted by electrostatic forces.
3. Covalent bond – a bond in which pairs of electrons with oppositely directed magnetic spin moments are formed, and these pairs belong to both neighboring atoms.
4. Metallic bond – a bond formed between the atoms of one or more chemical elements, the atoms give up external valence electrons and turn into positively charged ions, between which there are free electrons (electron gas).

3.5. Questions for self-control

1. Name the types of chemical bonds.
2. Why does the melting point decrease with increasing serial number of the element, the coefficient of thermal expansion increases, and the modulus of elasticity decreases?
3. With what type of chemical bonds substances are brittle, have low thermal and electrical conductivity?
4. What types of chemical bonds are unsaturated?
5. How do coordination numbers in crystals allow us to estimate which chemical bond prevails?

Relationship between the properties of semiconductor materials

6. What type of chemical bond is always significant or predominant in semiconductors?
7. How does the width of the band gap depend on the nature of the chemical bond?
8. Give examples of substances that have ionic, covalent, metallic and van der Waals bonds.

4. Elementary semiconductors

1. Chemical classification of semiconductors is based on the Periodic Table of elements. First of all, there are elementary semiconductors, i.e. semiconducting simple substances.
2. Semiconductor properties are exhibited by 12 chemical elements located near the great diagonal of the periodic table. Of the 12 elementary semiconductor elements, not all have instrumentation applications.
3. Semiconductor elements of the IVA subgroup include the main semiconductor materials germanium and silicon, as well as carbon (diamond) and polymorphic modification of tin.
4. These elements have a crystal lattice of diamond type (Fig. 2.5).
5. Such a lattice is a tetrahedron with atoms in the vertices and in the center
6. Here each atom is connected with four nearest neighbors by covalent bonding forces, since each of them has four outer valence electrons.

4.1. Silicon and its applications

1. At the first stage of microelectronic production development, germanium was used as a starting material.
2. Currently, 98% of the total number of integrated circuits are made on the basis of silicon.
3. Silicon (latin Silicium), Si, chemical element of group IV of the periodic table; atomic number 14. In compounds silicon (similar to carbon) is tetravalent.
4. Unlike carbon, silicon is not characterized by the formation of long chains and double bonds between Si atoms. In air, silicon is stable even at elevated temperatures due to the formation of a protective oxide film. In oxygen it oxidizes starting from 400°C, forming silicon dioxide SiO₂.
5. Silicon is a widespread element in nature. By distribution in the Earth's crust silicon is the second (after oxygen) element, its

average content in the lithosphere is 29.5% (by mass). Initial raw material in the form of silicon dioxide is widespread in nature.

6. Most of the applications of silicon in the world (almost 80%) remains traditional – it is a ligature in the production of special steels (electrical, heat-resistant) and various alloys (silumin, etc.).
7. Ferroalloys and other silicon alloys are mainly used in ferrous metallurgy. The composition of electrical steels, as a rule, includes 3.8–4.2% of silicon, so only these steel industries in the world consume more than 0.5 million tons of silicon per year as ligatures.
8. A significant part of silicon and its alloys is used in ferrous metallurgy as a very effective and relatively inexpensive deoxidizer of steels.
9. Some application of silicon (as silicon carbide and complex compositions) is found in the production of abrasive and carbide products and tools.
10. Geographically, silicon production in the world is not tied to the sources of raw materials, as in other metals. Silicon is a part of most minerals and ores. The necessary deposits of quartzite and quartz sands are available in many countries of the world.
11. The main feature of silicon production is their extremely high energy intensity (12–18 kWh/kg), so among the world's leading silicon producers for many years were primarily represented countries with developed energy (and inexpensive electricity), such as small Norway and Iceland.
12. In the production of silicon significant fuel consumption (coke).
13. Silicon is the material – the basis of most "high technologies" ("high-tech"). Modern and advanced information technologies (computers, electronics, telecommunications, etc.) are based on the use of semiconductor silicon.
14. The tonnage of world production of semiconductor silicon has been growing for several decades with an average rate of up to 20% per year.
15. The total amount of electronic silicon produced in the world only recently exceeded 20 thousand tons per year. By tonnage, this is only 5% of the world production of technical silicon.

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16. Other newer semiconductors (gallium arsenide, indium phosphide, etc.) or those that have been used for a long time (germanium, selenium) make up a minimal share of this market.
 17. Technically pure silicon (up to 98.5% Si), familiar to metallurgists, is absolutely not suitable for the needs of the electronic industry
 18. Purification of silicon to 99.99% and further goes through complex and science-intensive technologies. It is at these stages that the added value of high-purity silicon is formed, which is 1–2 orders of magnitude higher than the metallurgical one.
 19. Pure polycrystalline silicon is widely used in the world electronics and much less often – single crystals of silicon. At the same time, materials for semiconductors make up about 75% of this market, and materials for solar cells about 20%.
 20. The most popular semi-finished products now are precision (polished) silicon wafers with a diameter of up to 300 mm, on the basis of which the most modern microcircuits are made.

4.2. Metallurgy of silicon

1. The initial raw material for most products of microelectronic industry is electronic silicon. The first stage of its production is the manufacture of raw materials called metallurgical silicon.
2. In industry, silicon of technical purity (95–98%) is obtained by reducing the SiO_2 melt with coke in arc furnaces.
3. The furnace is loaded with SiO_2 quartzite and carbon in the form of coal, wood chips and coke. Reaction temperature is 1800°C , energy consumption is 13 kWh. A number of intermediate reactions take place in the furnace. The reduction proceeds according to the equation $\text{SiO}_2 + 2\text{C} = \text{Si} + 2\text{CO}$.
4. Since for practical use silicon of higher purity is required, the obtained silicon is chlorinated. Compounds of the composition SiCl_4 and SiCl_3H are formed. These chlorides are further purified in various ways from impurities and at the final stage are reduced with pure hydrogen.

5. Metallurgical silicon with a purity of 98% is crushed and placed in a hydrometallurgical plant to produce trichlorosilane.
6. The reaction temperature is 300° C: $\text{Si(s)} + 3\text{HCl(gas)} = \text{SiHCl}_3\text{(gas)} + \text{H}_2\text{(gas)} + \text{Q}$
7. Trichlorosilane at a temperature of 32 C becomes a liquid. Therefore, it can be easily purified by fractional method and recovered from the vapor-gas mixture in the reactor to obtain electron silicon.
8. Pure polycrystalline semiconducting silicon is obtained by reduction of SiCl_4 or SiHCl_3 with zinc or hydrogen, thermal decomposition of SiCl_4 and SiH_4 .
9. The germ of the future ingot is a heated silicon rod. The full deposition cycle lasts many hours. The result is a rod of polycrystalline structure of electronic silicon up to 20 cm in diameter and several meters long. The purity of silicon obtained in this way is about 99.9%.
10. For a number of semiconductor devices, semiconductor materials are mainly obtained in the form of single crystals, since in polycrystalline material there are uncontrolled changes in electrical properties.
11. Silicon marking is carried out according to the alphanumeric system. By letters, the numbers indicate the resistivity $\Omega\cdot\text{cm}$ ($\Omega\cdot\text{m}$), and if there are two groups, such as 0.3/0.2, then the first (0.3) means the resistivity, and the second (0.2) means the diffusion length of the minority current carrier, mm.
12. Silicon hole monocrystalline is marked KM-2, where the figure shows the resistivity $\Omega\cdot\text{cm}$; silicon electron monocrystalline is marked CME-2.

4.3. Obtaining single crystals of silicon

1. In connection with the development of semiconductor technology, methods for obtaining pure and especially pure silicon have been developed.

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2. The initial raw material for the microelectronic industry is electronic polycrystalline silicon, from which single crystalline ingots with the necessary electrophysical properties are then obtained.
 3. To obtain single crystals, the Czochralski method and crucible-free zone melting are used.
 4. The process of crucibleless zone melting, in which an additional deep zone purification of the initial polycrystalline billet from residual impurities is carried out in advance, is used to obtain the purest and most resistive single crystals.
 5. Single crystals obtained in this way have a resistivity of up to 100 kΩ·cm and a large diffusion length of charge carriers, have a low oxygen content, but the uniformity of the distribution of electrophysical properties in the volume of such material is lower than in the case of growing by the Czochralski method.
 6. The Czochralski method is the main method for obtaining single crystals of silicon.
 7. Installations for growing silicon crystals are fully automated and equipped with precision systems for maintaining a constant diameter of the ingot.
 8. The main disadvantage of the Czochralski method for growing semiconductor silicon is the contamination of the grown single crystals with oxygen and impurities contained in quartz crucibles, from which the ingot is usually extracted.
 9. To control the electrophysical properties (type of conductivity, resistivity, lifetime of charge carriers), doping processes with electrically active impurities are widely used.
 10. The main alloying impurities when obtaining single crystals of electronic type of conductivity are P, As, Sb, and when obtaining single crystals of hole type of conductivity – B and Al. These impurities form solid substitution solutions in silicon and have a sufficiently high solubility (10^{18} - 10^{19} atom/cm³) in a wide temperature range.
 11. Doping can be carried out both directly in the process of growing and at the stages of further processing.

12. Doping in the process of growing is carried out either with the help of special ligatures of silicon alloys with an alloying impurity, or from the vapor phase of volatile compounds of the alloying impurity.
13. To ensure a uniform distribution of the alloying impurity in the volume of the crystal, extraction from a double (floating) crucible, the effect of compensating for the accumulation of impurities in the melt by its evaporation (for volatile impurities), as well as various options for magnetohydrodynamic (MHD) action on the melt in order to control the mass flows in the molten bath are used.
14. The main structural defects in silicon single crystals are microdefects.
15. The main role in the formation of growth microdefects in single crystals grown by the Czochralski method is played by intrinsic point defects – vacancies and interstitial atoms, as well as oxygen. The presence of precipitates, for example, the SiO_2 phase in Si leads to the formation of mechanical stress and, consequently, the possible appearance of microcracks.
16. After the preparatory technological cycles (machining of ingots, preparation of main and additional base cuts, cutting of silicon ingot into wafers, etching of the surface and polishing) silicon should have the following properties:
 - be a chemically pure semiconductor (for example, the concentration of boron or carbon in silicon should not exceed 10^{-7} at. % and $2 \cdot 10^{-4}$ at. % respectively);
 - have the properties of a single crystal and have a small number of defects;
 - have homogeneous properties by volume, in particular, with respect to the controlled concentration of the alloying impurity;
 - have an ideal surface necessary for the implementation of planar technology.
17. In the final form, silicon is a single crystal plate with a diameter of 15-40 cm, a thickness of 0.5-0.6 mm with different surface orientation, mirror polished on one side. Additional and main cuts

are made for easier recognition of wafers with different types of conductivity and surface orientation.

4.4. Silicon

1. At present, silicon is the main semiconductor material in the field of solid-state microelectronics.
2. The advantage of silicon over germanium is the greater width of the band gap. Therefore, silicon devices can operate at higher temperatures.
3. If the operating temperature of germanium devices does not exceed 60–80°C, then silicon diodes can operate up to 200°C.
4. Silicon is a technologically convenient material: it is easy to process, it is easy to obtain dielectric films SiO₂, which are then successfully used in technological cycles; silicon technology is less expensive. Production of chemically pure Si is 10 times cheaper than Ge.
5. The main physical properties of silicon and germanium are given in Table 4.1.
6. Silicon is a dark gray, shiny crystalline substance, brittle and very hard. Only when heated above 800°C it becomes ductile.
7. Silicon forms crystals that have a cubic face-centered diamond-like lattice with a lattice period of 0.54 nm (the shortest distance between atoms is 0.23 nm).
8. A new (apparently hexagonal) modification with a density of 2.55 g/cm³ was obtained at very high pressure.
9. Silicon melts at 1417°C, boils at 2600°C.
10. Silicon is transparent for long-wave infrared rays; refractive index 3.42 (for 6 microns); dielectric constant 11.7.
11. Elemental silicon is a typical semiconductor. The band gap at room temperature is 1.09 eV.
12. The electrophysical properties of crystalline silicon are greatly influenced by the micro impurities contained in it.
13. To obtain silicon single crystals with hole conductivity, additives of elements of the III group – boron, aluminum, gallium and indium –

Elementary semiconductors

are introduced into silicon, with electronic conductivity – additives of elements of the V group – arsenic phosphorus or antimony.

Table 4.1. Basic physical properties of germanium and silicon

	germanium	silicon
Thermodynamic properties		
Lattice parameter, nm	0,5657	0,5431
Density, g/cm ³ :		
solid	5,33	2,33
liquid (at melting point)	5,62	2,53
Melting point, K	1210,6	1688
Boiling point, K	3103	2623
Coefficient of thermal expansion ($\cdot 10^{-6}$), K ⁻¹	4,2	6,0
Specific heat of melting, kJ/mol	36,8	50,6
Specific heat of vaporization, kJ/mol	328	383
Molar heat capacity J/(K·mol)	23,32	20,16
Molar volume, cm ³ /mol	13,6	12,1
Semiconductor properties		
Static dielectric constant	16,0	12
Band gap width (at 300 K), eV	0,66	1,10
Intrinsic concentration of charge carriers (at 300K), cm ⁻³	$2 \cdot 10^{13}$	10^8
Mobility of charge carriers in an impurity-free semiconductor (at 300 K), cm ² /(V·c)		
Electrons	3900	1450
Holes	1000	480

14. The electrical properties of silicon can be varied by changing the processing conditions of single crystals, in particular by treating the surface of silicon with various chemical agents.
15. The band gap of silicon at absolute zero is 1.21 eV and decreases with increasing temperature:

$$E_g = 1.21 - 3.6 \cdot 10^{-4} T \text{ [eV]}.$$

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16. Due to the high value of the bandgap width, the resistivity of silicon is about $10^5 \Omega \cdot \text{cm}$, silicon of such purity should not contain impurities more than 10^8 cm^{-3} .
 17. Empirical Hall mobilities of electrons n and holes p at 300 K $n = 1500$ and $p = 480 \text{ cm}^2/\text{V s}$.
 18. Since the mobility of electrons is greater than the mobility of holes, the sign of the Hall effect and thermoelectric constant in silicon corresponds to n-type conductivity.
 19. Group III elements (B, Al, Ga) create acceptor levels in silicon at a distance of about 0.05 eV from the top of the valence band. The ionization energy of the same impurities in silicon is higher than in germanium.

4.5. Application of semiconductor silicon

1. Silicon is widely used in microelectronics. Microprocessors are produced on its basis.
2. The complexity of microcircuits is accompanied by increased requirements for the quality of wafers (general and local planarity, reduction of surface contamination, increase of structural perfection and homogeneity of the initial material) while increasing their diameter and reducing the cost.
3. A sharp increase in the density of installation and reduction of the size of the working elements of microcircuits necessitates the reduction of operating currents and voltages. In these conditions, the role of extraneous noise increases significantly.
4. Increasing requirements for purity, structural perfection and microheterogeneity of the active area of the device composition. Particularly high requirements for the content of impurities capable of forming electrically active and recombination centers.
5. In power electronics, a wide range of high-power transistors and various power integrated circuits has been added to the powerful diodes and thyristors based on silicon.
6. Power silicon electronic devices are successfully used to transmit electricity over long distances with minimal losses, in energy-

intensive metallurgical and chemical industries, in transport, in electric drive and power supply systems.

7. In optoelectronics silicon is used in various sensor devices, precision micromechanical systems. Most photoelectric converters are made of silicon.
8. In solar energy, silicon-based solar cells are used. Solar cells and batteries (photovoltaic generators, photocells) belong to the class of renewable (ecological) power sources that convert solar energy into electricity. The total power of electricity generated by silicon solar cells has exceeded the level of thousands of megawatts.
9. Silicon is an indirect bandgap semiconductor, the efficiency of interband radiative recombination in it is very low. Doping silicon with erbium allows to form effective radiative recombination centers in the crystal lattice.
10. One of the ways to create effective radiators is to build up on silicon substrates heteroepitaxial structures of direct band compounds $A^{III}B^V$ (GaAs, InGaAs).
11. For the manufacture of waveguides, Si/SiO₂ structures are used, which have a difference in the refractive indices of the constituent components equal to 2, which provides a condition for reliable optical confinement.
12. In such a waveguide, light propagates through a thin layer of single-crystal silicon, which is transparent to radiation with a wavelength of 1.3-1.55 microns.
13. This waveguide structure provides reliable communication (with minimal optical losses) between the emitter and photodetector.

4.6. Germanium

1. Historically, the first semiconductor material used in the early stages of semiconductor device development was germanium.
2. Improvements in germanium technology have made a number of devices possible, including germanium point and alloy transistors.
3. However, germanium was soon replaced by silicon, which has such an important property as the ability to obtain a thin, durable and

moisture-proof dielectric layer of amorphous silicon dioxide (SiO_2) in an oxidizing environment.

4. Pure germanium has a metallic luster, quite hard. Differs in great fragility – with a light blow with a hammer it crumbles into pieces.
5. Germanium crystallizes, like silicon, in the structure of diamond. The lattice constant and the distance between adjacent atoms in germanium is larger than in silicon.
6. The covalent bond in germanium is less strong, resulting in a lower melting point and a smaller band gap than silicon.
7. The band gap of germanium at absolute zero is 0.785 eV. It decreases with increasing temperature: $E_g = 0.785 - 3.5 \cdot 10^{-4}T$ [eV].
8. The carrier concentration of $2.6 \cdot 10^{13} \text{ cm}^{-3}$ corresponds to the purity of germanium 99.99999999%, and such samples already at room temperature have their own conductivity, i.e. the impurities remaining in them do not affect their electrophysical properties.
9. The temperature dependence of the carrier mobility in the realized germanium single crystals is expressed by the formula: $u_n = 4.9 \cdot 10^7 T^{-1.66} [\text{cm}^2 / \text{V s}]$.
10. A large number of various impurities can be introduced into germanium, the energy levels of which are located in the band gap. These impurity levels can be donor or acceptor depending on their chemical nature. The activation energy of impurities of atoms of groups III and V of the periodic system in germanium is approximately 0.01 eV.
11. Germanium is characterized by an increase in the ionization energy of acceptors from boron to indium from top to bottom of the Periodic Table. This is explained by the fact that in the series B-Al – Ga-In-Tl metallic properties increase, and the ability to capture an electron naturally decreases.

4.7. Other elementary semiconductors

1. In the first two groups of the Periodic Table there are no elementary semiconductors.

4.7.1. Boron

2. Of the elements of the third group, boron is a semiconductor. This shows a diagonal analogy between the chemistry of boron and silicon – a typical elemental semiconductor.
3. As a semiconductor, boron has not yet found wide application due to insufficient study, but it is promising due to its widespread occurrence in nature and high melting point.
4. Boron is obtained in the form of several crystalline modifications, of which tetragon, α -rhombohedral and β -rhombohedral are stable. In addition, amorphous boron is known.
5. Tetragonal boron has a band gap of 1.55 eV.
6. The temperature dependence of the thermoelectric constant shows that in tetragon boron the mobility of holes exceeds the mobility of electrons.
7. α -Rhombohedral boron, also called "red" boron (in transmitted light it has a red color), is a semiconductor with an optical band gap of about 2 eV. In the temperature range from 0 to 500° C it has a constant resistivity.
8. β -Rhombohedral boron is also a semiconductor with a band gap of 1.45 eV.

4.7.2. Carbon

9. Of the elements of Group IV, in addition to typical semiconductors, carbon and its modifications, diamond and graphite, also exhibit semiconducting properties, although the former is closer to insulators and the latter to metals.
10. The electrophysical properties of the third polymorphic modification of carbon, carbene, are still unexplored due to the very small size of the crystals.
11. Since the emergence of civilization, diamond has attracted special attention of people. Its optical properties interested Isaac Newton. In the XIX century it was discovered that diamond is one of the forms of existence of elementary carbon.

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12. Diamond is one of the simplest homeopolar crystals; its closest relatives are single crystals of germanium, silicon and gray tin.
 13. Carbon atoms in diamond are extremely tightly bound to each other, and the equilibrium solubility of most impurities in it, with the exception of nitrogen and boron, is negligible.
 14. Diamond is the hardest material now known, and is less amenable to compression than any other material.
 15. Diamond also has a high thermal conductivity at room temperature, and if it has no defects and foreign inclusions, it is one of the most transparent materials for visible light.
 16. The transformation of graphite into diamond occurs by polymorphic transition with a change in the type of bonding. Under the action of high pressure graphite is compressed along the axis perpendicular to the layers. Their displacement and reduction of the distance between the layers is observed. After that, the flat layers of carbon atoms are corrugated, turning into a diamond structure with the formation of bonds between the layers.
 17. Thin diamond films are attracting more and more attention due to such unique properties as extremely high hardness, high thermal conductivity, transparency in a wide optical range, high resistivity. In addition, diamond films with specially introduced impurities can be used as semiconductor materials.
 18. One of the methods of obtaining diamond films is the growth of epitaxial semiconductor layers of diamond on a diamond insulating substrate during the decomposition of hydrocarbons in plasma.
 19. Diamond materials with various impurities that determine their semiconducting properties are also useful. Currently, one of the most used impurities is boron.
 20. It is generally accepted that carbon substituting boron atoms are stable acceptor centers. To obtain p-type semiconductor diamonds, arsenic can be used as an alloying additive.
 21. One of the methods of diamond doping is ion implantation. At present, it is possible to create areas of the required geometry with

hole conductivity using the introduction of boron ions according to specified programs.

22. The crystal form of carbine consists of parallel oriented chains of carbon atoms with sp-hybridization of valence electrons in the form of straight macromolecules.
23. Carbine has semiconducting properties and the presence of a band gap of ~ 1 eV, and under strong heating it transforms into graphite.
24. Under the influence of light, the electrical conductivity of carbine increases greatly. The first practical application of carbine is based on this property – in photocells. Carbine does not lose its photoconductivity at temperatures up to 500°C .
25. Carbon fibres, a super-strong structural material of recent years, can also consist of polycrystalline carbine. Carbon fibers are obtained by heat treatment of polymer fibers in a noble gas environment. These are super-strong threads with conductive properties. They are currently used to make bulletproof vests, structural elements of aircrafts and rockets, rocket engines themselves, suits heated by electricity and much more.

4.7.3. Tin

26. Of the two modifications of tin, white tin is a metal and grey tin is a semiconductor.
27. Tin exists in three polymorphic modifications.
28. Grey tin (α -Sn) has semiconducting properties. Up to a temperature of 13°C , the interatomic bonding in tin is covalent, and it is a typical semiconductor – gray tin. Grey tin crystallizes in the diamond lattice.
29. Above 13°C the bond becomes metallic and tin behaves as a typical metal – white tin. White tin crystallizes in the tetragonal lattice.
30. When heated above 161°C , it transforms into the rhombic modification γ -Sn with a density of 6.60 g/cm^3 , which is highly brittle.

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31. The mutual transformation of different modifications of tin can be depicted by the scheme: α -Sn (13.2°C) β -Sn (161°C) γ -Sn (231.9°C) liquid tin.
 32. As can be seen from the scheme, the rhombic modification of tin cannot be directly converted to gray tin. And the transition of white tin to gray tin is accompanied by a sharp change in density (from 7.298 to 5.846 g/cm³).
 33. The rate of transition β -Sn to the gray modification increases with supercooling and reaches a maximum at -34°C . This transformation proceeds more easily when white tin comes into contact with gray tin. Tin objects or products made of tin alloys under the appropriate temperature conditions are "infected" from each other, and in this way the "tin plague" spreads.
 34. The transformation of white tin into gray was the cause of the death of Robert Scott's expedition. Since the fuel cans were soldered with tin, the white tin turned to gray during cooling and the fuel leaked out.
 35. The thermal band gap of gray tin is between 0.064 and 0.094 eV at absolute zero. With increasing temperature, the band gap decreases with velocity: $E_g = 0.08 - 5 \cdot 10^{-5} T$ [eV].
 36. Impurity atoms Al, Ga, In, Cd, Au, Zn act on the type of conductivity of gray tin as acceptors; As, Sb, Bi – as donors; Cu, Si, Ge, Se, Ti, Tl, V, Mn, Fe, Co, Ni can function as acceptors and as donors depending on the conditions.

4.7.4. Semiconductor elements of group V

37. Of the elements of Group V of the Periodic Table, phosphorus, arsenic and antimony exhibit semiconducting properties under certain conditions. However, semiconductor modifications of these elements are not widely available and are not of interest in terms of their application.
38. In semiconductor elements of this group, chemical bonds are realized through the formation of p^3 -orbitals, they have structures

with a coordination number of 3, which refers to rhombohedral syngony.

39. Such crystals can be represented as consisting of two-layer plates. Each atom has three nearest neighbors in the adjacent layer of the same plate, with which it is connected by covalent bonds. Neighboring plates are bound together by weak van der Waals forces.
40. Elements of this subgroup are included as basic components in semiconductor compounds and are also used as donor impurities in $A^{III}B^V$ compounds.

4.7.5. Semiconductor elements of group VI

41. The following elements of group VI have semiconducting properties: sulfur, selenium and tellurium.
42. Hexagonal modification of selenium is used as a semiconductor material in microelectronics from elements of group VIA subgroup.
43. It is a semiconductor of p-type conductivity, the semiconductor properties of which are manifested and used in polycrystalline structures. The band gap is 1.8 eV.
44. Single crystals of hexagonal selenium are obtained by growing from the melt or deposition from the gas phase. Evaporation of Se in vacuum on the substrate can produce films with a thickness of 50-100 microns, which are used for the production of semiconductor devices.
45. Hexagonal selenium is used for the manufacture of semiconductor rectifiers of photocells, solar cells.
46. Selenium is characterized by an internal photoelectric effect: under the influence of light, the number of holes increases and its own electrical conductivity increases. The action of selenium photocells and many other devices is based on this property.
47. The effect of light on the electrical properties of selenium is twofold. The first is the reduction of its resistance to light. The second, no less important, is the photovoltaic effect, that is, the

direct conversion of light energy into electricity in a selenium device.

48. To implement the photovoltaic effect, it is necessary that the photon energy is greater than a certain threshold value, the minimum for a given photocell. A simple device that uses this effect is an exposure meter. More complex devices are solar panels operating on Earth and in space.
49. The world's first photoresistor was made of selenium more than 100 years ago, and the history of selenium rectifiers dates back to 1933. In addition, numerous metal selenides are obtained from selenium, which also exhibit semiconducting properties.
50. Tellurium as a semiconductor does not find independent application in technology. But numerous compounds of tellurium – tellurides – are widely used as semiconductor materials.
51. Technical selenium and tellurium are obtained from wastes of non-ferrous metallurgy and sulfuric acid industry.
52. Crystals of these elements consist of spiral chains or rings in which each atom has two covalent bonds with atoms of the same chain. The chains are bound together by van der Waals forces.
53. The width of the band gap decreases with increasing serial number and is 2.4 eV for sulfur, 1.7 eV for selenium, and 0.35 eV for tellurium.
54. Of the elements of group VII, only iodine belongs to semiconductors. In the solid state, it has semiconductor properties, p-bonds are realized in it.
55. When moving from element to element in the groups there is a natural change in the key properties of semiconductors. For example, in groups from top to bottom, the width of the band gap naturally decreases. In the same direction there is a decrease in the melting point of conductors. The hardness of semiconductor crystals decreases. The mobility of charge carriers increases. All these changes are associated with an increase in the metal contribution to the chemical bond and a decrease in the covalent bond. Similar

regularities are observed not only for elementary semiconductors, but also for semiconductor compounds.

56. All elementary semiconductors are p-elements, in the atoms of which p-orbitals are gradually filled with electrons. In simple substances with valence s- and p-electrons, the octet rule is fulfilled, according to which the coordination number $K = (8 - N)$, where N is the group number in the Periodic Table.
57. In group IVA semiconductors, the coordination number is four (tetrahedron). In the semiconductor modification of iodine (group VIIA) the coordination number is equal to one.

4.8. Basic concepts and definitions

1. Metallurgical silicon – silicon of technical purity (95–98%), which is obtained by reducing the SiO_2 melt with coke in arc furnaces.
2. Ligature (in metallurgy) – an alloy of two or more components designed to introduce refractory elements into liquid metal.

4.9. Questions for self-control

1. What is the basis of the chemical classification of semiconductors?
2. What type of crystal lattice have the main semiconductor materials: germanium and silicon?
3. What material was used at the initial stage of development of microelectronic production?
4. What is silicon mainly used for?
5. Why among the world's leading silicon producers for many years were primarily represented by the countries: Norway and Iceland?
6. What is the initial raw material for most products of the microelectronic industry?
7. What methods are used to obtain single crystals of silicon?
8. Why can silicon devices operate at higher temperatures?
9. What type of lattice does silicon form?
10. What physical characteristics of semiconductor materials determine the maximum operating temperature of semiconductor devices based on them?

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11. What impurities are introduced into silicon to obtain single crystals of silicon with hole and electronic conductivity?
 12. What elementary semiconductors are in the first two groups of the periodic table?
 13. What elementary semiconductors are in the third group of the periodic table?
 14. Does tin have semiconductor properties?
 15. What elements of group VI have semiconductor properties?

5. Semiconductor compounds of A^{III}B^V group

1. Together with elementary semiconductors, semiconductor compounds are widely used in semiconductor technology.
2. Of particular interest are compounds of the A^{III}B^V type.

5.1. Crystal structure and chemical bonding

1. A^{III}B^V compounds are the closest electron analogues of silicon and germanium. By a number of properties these compounds are close to semiconductor elements of group IV – germanium and silicon.
2. Semiconductor compounds A^{III}B^V are formed as a result of the interaction of elements of groups III and V of the periodic system.
3. In group III, compounds of A^{III}B^V type are formed by elements boron and aluminium, as well as metals of the gallium subgroup (thallium is an exception). In group V compounds of type A^{III}B^V give nitrogen, phosphorus, arsenic and antimony. Bismuth does not form compounds of this series.
4. A^{III}B^V compounds are classified according to the metalloid element. Accordingly, nitrides, phosphides, arsenides and antimonides are distinguished.
5. Of the A^{III}B^V compounds, nitrides and boron compounds have not yet been studied; the interaction of metals of the scandium subgroup, lanthanides and actinides with elements of group V of the Periodic Table has not been studied at all.
6. The most interesting semiconductor properties are possessed by nine compounds (AlP, AlAs, AlSb, GaP, GaAs, GaSb, InP, InAs, InSb), formed by combining, on the one hand, Al, Ga, In and, on the other hand, phosphorus, arsenic and antimony.
7. For this group of A^{III}B^V compounds the mechanism of occurrence and the nature of chemical bonding is of great interest.
8. A^{III}B^V compounds are characterized by a special type of chemical bond, called donor-acceptor.
9. In the A^{III}B^V structure, each A^{III} atom is valently bonded to four B^V atoms and vice versa.

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10. Of the four covalent bonds by which each atom is embedded in the lattice, three are formed by the sharing of valence electrons of A^{III} and B^V atoms, and the fourth bond is made by an unshared pair of valence electrons of B^V atoms.
 11. The formation of this bond corresponds to the energetically advantageous transition of electrons from the B^V atom to an energy state that is common to the donor (B^V atoms) and acceptor (A^{III} atom).
 12. Electronegativity and ionization potential of the elements of the fifth group are greater than those of the metals of the third group. Therefore, in $A^{III}B^V$ compounds, electron clouds will be more strongly pulled to the lattice nodes where B^V atoms are located.
 13. Due to this polarization of the bonds, the A^{III} atoms acquire some effective positive charge, and the B^V atoms – negative.
 14. The value of this effective charge determines the degree of ionicity of the compound, which naturally changes when moving from one compound to another.
 15. Four electron pairs of an octet, regardless of whether they belong to one or more atoms, tend to be located in space at the corners of a regular tetrahedron.
 16. The bonding of atoms in the crystal lattice is predominantly covalent with a share (up to 15%) of the ionic component.
 17. Except for nitrides, all $A^{III}B^V$ compounds crystallize in a zinc decoy lattice (Fig. 5.1) (sphalerite). Nitrides are characterized by a hexagonal structure (wurtzite) (Fig. 5.2).
 18. Some atoms (whether AI^{II} or B^V) occupy the vertices and centers of the cube faces, and others occupy the centers of four (out of eight) small cubes.
 19. In the lattice of both types, each atom of the element of group III is in a tetrahedral environment of four atoms of the element of group V and vice versa.
 20. The structure of $A^{III}B^V$ is similar to that of diamond with the only difference that the centers of the small cubes are occupied by atoms

of a different type than the vertices and centers of the faces of the large cube.

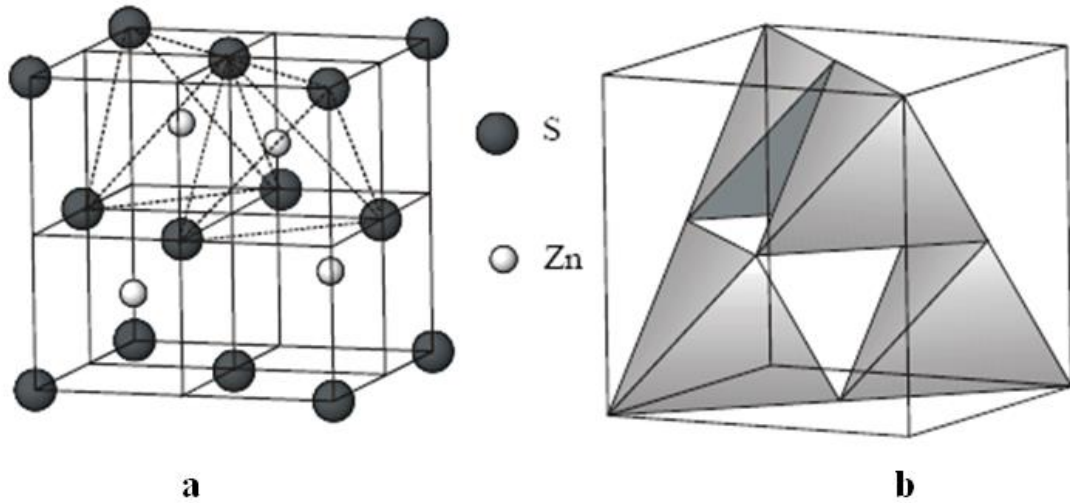


Fig. 5.1. ZnS elementary cell (a) and its representation as a frame of ZnS₄ tetrahedra (b)

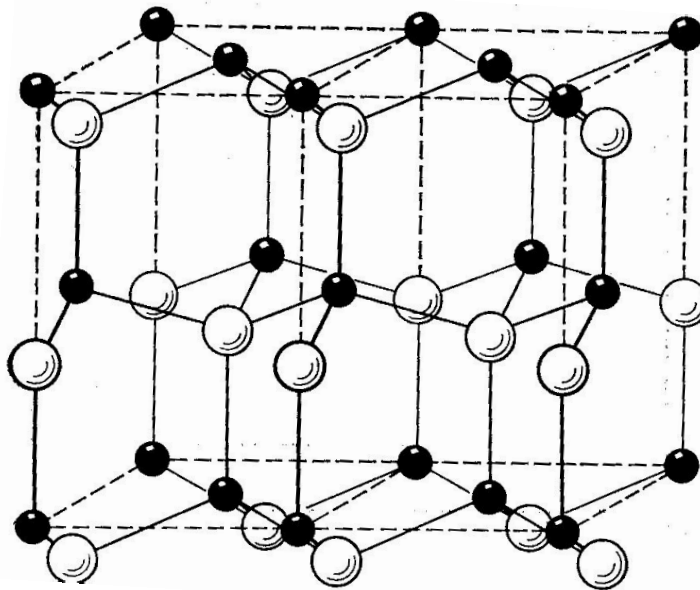


Fig. 5.2. Structure of wurtzite. Location of metal atoms (small black balls) and nonmetal atoms (large light balls)

21. In a unit cell (Fig. 5.1) there are four atoms of one kind and four of another, i.e. eight atoms in total.
22. Most A^{III}B^V compounds crystallize in structures that can be characterized based on the geometric position of the cations that fill the intermediate positions of the tightly packed anion layer in different sequences.

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23. If they occupy half of the tetrahedral voids so that the occupied and unoccupied tetrahedral interstices alternate, then the cubic structure of zinc decoy arises.
 24. If the cations occupy half of the tetrahedral voids in the hexagonal densely packed lattice, then the cubic structure of wurtzite appears.
 25. The structure of sphalerite can be represented as a three-dimensional frame formed by tetrahedral groups of ZnS_4 connected by vertices. Each vertex is common for four such tetrahedra.
 26. This becomes clearer if you break the cubic cell into eight cubes (Fig. 5.1a.) In this case, you can see how tetrahedral and octahedral voids are formed.
 27. The structure of sphalerite, unlike the structure of diamond, has no center of symmetry. This feature leads to differences in the properties of the surfaces (100) and (111), entirely composed of opposite-signed atoms. The different behaviour of the faces is revealed by etching, oxidation and crystal growth.
 28. $\text{A}^{\text{III}}\text{B}^{\text{V}}$ compounds melt congruently (without changing the composition). They have a sufficiently narrow region of homogeneity, i.e. the interval of compositions in which, depending on the state parameters (temperature, pressure, etc.), the predominant type of defects can be changed (change of defects type leads to change of conductivity type (n, p) and change of specific electrical conductivity dependence on composition).

5.2. Physicochemical and electrical properties

1. Semiconductor compounds $\text{A}^{\text{III}}\text{B}^{\text{V}}$ form a homologous series, in which there is a natural change in many properties when changing the atomic numbers of the components.
2. Table 5.1. shows data on the properties of semiconductor compounds $\text{A}^{\text{III}}\text{B}^{\text{V}}$. Compounds-analogues are grouped according to the principle of anion stability.

Table 5.1. Basic physical properties of A^{III}B^V semiconductor compounds

Compound	ρ , g/cm ³	T _m , °C	T _b , °C	Atomization energy, kJ/mol	E _g (300 K), eV	Electron mobility, cm ² /V·s	Mobility of holes, cm ² /V·s
AlP	2,42		2000	795	2,42	–	–
GaP	4,10	945	1467	712	2,25	300	150
InP	4,74	410	1055	665	1,28	6000	650
AlAs	3,6	520	1700	712	2,16	–	
GaAs	5,4	750	1237	611	1,40	12000	400
InAs	5,68	330	943	544	0,46	33000	500
AlSb	4,15	400	1070	670	1,6	200	550
GaSb	5,65	448	712	561	0,79	4000	1420
InSb	5,78	220	536	506	0,18	100000	

3. There is a natural change in the width of the band gap within the compounds-analogues.
4. Within each group of compounds-analogues there is a decrease in the width of the band gap with increasing total atomic number and atomic masses of the elements included in the compounds.
5. This is due to a stronger blurring of the electron clouds of covalent bonds as one moves down the Periodic Table, thereby enhancing the metallic character of the bond.
6. This does not mean that the electrons become the property of the whole lattice, but there is an increasing blurring of the electron clouds of covalent bonds.
7. Simultaneously with the weakening of covalent chemical bonds, the melting point and hardness of the material decrease, i.e. the semiconductor becomes more plastic, approaching the mechanical properties of metals.
8. With a decrease in the total serial number, that is, with the movement upward within the group of the Periodic System, a linear increase in the melting point of A^{III}B^V is observed.
9. It is interesting to note that the melting points of phosphides are a direct extension of the melting points of antimonides.

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10. Thus, the larger the band gap, the higher the melting point and vice versa.
 11. Within homologous compounds, the atomization energy changes symmetrically with the melting point and the width of the band gap. The atomization energy characterizes the energy strength of crystals with predominant covalent and metallic bonds.
 12. Mobility of current carriers in $A^{III}B^V$ compounds also, with the exception of GaSb, increases in a series of homologous compounds with increasing total atomic number.
 13. This is due to a decrease in the ionic contribution to the chemical bond and an increase in the covalent and metallic contributions in these series.
 14. The width of the band gap and carrier mobility depend primarily on the nature of the chemical bond. A large proportion of ionic bonds causes less mobility and increases the width of the band gap.
 15. Some $A^{III}B^V$ compounds – InP, GaAs, AlSb – have a wider band gap than silicon, but melt below its melting point.
 16. Gallium antimonide, which has a large band gap compared to germanium, melts at 225°C below germanium.
 17. The lower the melting point of a substance, the simpler the technology of purification and obtaining single crystals.
 18. The relative lowering of the melting point in $A^{III}B^V$ substances compared to A^{IV} is due to the presence of a certain proportion of ionic bonds.
 19. The ionicity of the chemical bond is related to the polarization of the ions. Polarization of ions always contributes to lowering the melting point.
 20. Hence it becomes clear why such a compound as InSb has huge electron mobility and at the same time melts at a relatively low temperature.
 21. With the exception of antimonides, all $A^{III}B^V$ compounds decompose on heating.
 22. The equilibrium pressure of saturated vapor, consisting practically of molecules of component B, increases with increasing temperature

and at the melting point reaches values of $10^4 - 10^5$ Pa for arsenides and $10^6 - 10^7$ Pa for phosphides.

23. The mobility of charge carriers in A^{III}B^V semiconductors is mainly limited by the scattering of electrons and holes on optical thermal vibrations of the lattice, which should be understood as a shift in the antiphase of neighboring atoms.
24. Since atoms A^{III} and B^V have some ionic charge, their antiphase shift leads to the appearance of dipole moment, which is an effective center of electron and hole scattering. The more pronounced the ionic component of the chemical bond, the more the scattering on optical vibrations increases and the mobility of charge carriers decreases.
25. In a number of covalent semiconductors, the electron mobility increases in the transition from diamond to silicon and then to germanium, i.e. it can be assumed that the mobility of charge carriers increases with increasing atomic mass.
26. A similar dependence, more pronounced for electrons than for holes, takes place in A^{III}B^V compounds.
27. Increasing the atomic mass of components leads to a decrease in the amplitude of thermal vibrations of atoms, which in turn leads to a decrease in the scattering of charge carriers on these vibrations.
28. An increase in the atomic mass of the components leads to a weakening of the ionic bond, which means that the mobility of charge carriers increases sharply. Among all semiconductors indium antimonide has a record of high electron mobility.
29. The absolute value of electron mobility for most compounds significantly exceeds the mobility of holes. The only exception is aluminum antimonide, in which the mobility of holes is almost three times higher than the mobility of electrons.
30. Due to the large difference in the values of electron and hole mobilities in InSb, InAs, InP and GaAs, their own resistivity is almost completely determined by the electron motion.

5.3. Impurities and structural defects

1. Most $A^{III}B^V$ compounds are characterized by insignificant deviations from the stoichiometric composition, so they are relatively simple in terms of the alloying mechanism, electron-hole transitions are easily formed in them.
2. As a rule, the introduction of an excess of one of the components into the crystallization medium does not significantly affect the electrophysical properties of the material.
3. The exception is nitrides, in which there are difficulties with the inversion of the type of electrical conductivity. In particular, gallium nitride, regardless of the conditions of obtaining crystals, always exhibits n-type electrical conductivity.
4. Substitution impurities in the crystal lattice of $A^{III}B^V$ compounds are distributed so that there are no centers with a large excess charge.
5. Impurities of elements of group II – Ve, Mg, Zn and Cd, which create solid solutions of substitution, always occupy in the lattice of $A^{III}B^V$ nodes of the metal component and at the same time are acceptors, due to the lower valence compared to the valence of the atoms that are replaced.
6. Impurities of the elements of group VI – S, Se, Te – are always located in the nodes of B^V and play the role of donors.
7. The behavior of impurities of elements of group IV is more complicated. Atoms of impurities of group IV can occupy both nodes A and B, showing donor or acceptor properties, respectively.
8. Substitution should be accompanied by the smallest deformation of the crystal lattice. Therefore, the criterion for the donor or acceptor action of impurities can be the correspondence of the size of the substituent atoms that are replaced.
9. In most cases, impurity atoms of group IV elements are localized in one of the sublattices. For example, in indium antimonide silicon and germanium replace only antimony atoms and are only donors.
10. However, in some compounds amphoteric behavior of these impurities is observed. Thus, in gallium arsenide and gallium phosphide there is a pair entry of silicon and germanium atoms into

the crystal lattice of the compound with the simultaneous replacement of A^{III} and B^V nodes.

11. Depending on the degree of alloying, growth temperature and composition of the crystal environment, the preferential entry of these impurities into one or another sublattice takes place.
12. Impurities of elements of III-b and V-b subgroups usually replace A^{III} and B^V atoms in the lattice of the compound, forming neutral centers. The solubility of these elements in most cases is so high that it is possible to obtain crystals of solid solutions in the entire concentration range.
13. Impurities of transition group elements (Fe, Co, Ni, etc.) create deep energy levels of acceptor type in $A^{III}B^V$ semiconductors and are effective recombination traps.
14. Doping of gallium arsenide with iron or chromium is used to obtain crystals with high resistivity (up to $10^2 \Omega m$). Such material is called semi-insulating.
15. In semiconductors with high electron mobility (InSb, InAs, GaAs), the ionization energy of shallow donors (S, Se, Te, Sn) is only from one to several thousandths of an electron volt.
16. An essential feature of the diffusion process in $A^{III}B^V$ semiconductors is its dependence on the vapor pressure of the volatile component of group B^V , which determines the concentration of defects in the lattice.
17. To obtain reproducible results, diffusion is preferably carried out in a sealed ampoule, in which, in addition to the alloying component, a weight of phosphorus and arsenic is placed.
18. It was found that in gallium arsenide with increasing arsenic vapor pressure, the diffusion coefficient of acceptor impurities decreases, and donor impurities increases. Similar regularities take place in other semiconductors of $A^{III}B^V$ type.
19. Donors in compounds of $A^{III}B^V$ type are characterized by extremely low values of diffusion coefficients. For the penetration of donors to reach measurable sizes, high temperature (in the range of 200–

300°C from the melting point of the main substance) and long diffusion time are required.

20. This leads to disturbance (erosion) of the surface due to the transfer of the volatile element of group V under the influence of small temperature gradients inside the ampoule. In addition, the diffusion of donors such as S, Se and Te is complicated by the formation of a layer of complex phase composition (chemical compounds such as Ga_2S_3) on the surface of the semiconductor.
21. In practice, only diffusion of zinc is used in the formation of p-n structures, which is an acceptor impurity and has a sufficiently high solubility in $\text{A}^{\text{III}}\text{B}^{\text{V}}$ semiconductors.
22. To reduce the surface concentration of acceptors, diffusion of zinc into GaAs is often carried out through a thin layer of SiO_2 applied to the wafer surface.
23. For the diffusion of zinc into GaP, ZnP_2 is successfully used as a source of alloying impurity, which is placed in an ampoule together with gallium phosphide wafers.
24. Large diffusion coefficients in semiconductors of $\text{A}^{\text{III}}\text{B}^{\text{V}}$ type have elements of group I, especially copper. The low activation energy of the diffusion process of these impurities indicates the inter-nodal mechanism of their migration in the crystal lattice of the compound.

5.4. Recombination of charge carriers

1. A valuable property of many $\text{A}^{\text{III}}\text{B}^{\text{V}}$ semiconductors is the high efficiency of radiative recombination of nonequilibrium charge carriers.
2. To generate radiation in the visible spectral region, the band gap of the semiconductor must exceed 1.7 eV.
3. Of the compounds of type $\text{A}^{\text{III}}\text{B}^{\text{V}}$, mastered in technological terms, this condition is satisfied by gallium phosphide and gallium nitride.
4. Materials with a narrower energy gap are able to radiate effectively in the infrared region. These include, in particular, gallium arsenide, which has a band gap of 1.43 eV.

5. Photon emission in GaAs occurs as a result of direct interband recombination of electrons and holes.
6. Effective luminescence in GaN and GaP occurs only with the introduction of special impurities.
7. When doping gallium nitride with zinc, depending on the concentration of the latter, recombination radiation can be obtained in the yellow, green or blue regions of the spectrum.
8. In gallium phosphide, the most intense luminescence is due to recombination with the participation of isoelectron traps. The role of such traps is played by nitrogen atoms or neutral Zn-O complexes.
9. The latter are formed when zinc atoms (shallow acceptor) and oxygen (deep donor) occupy adjacent nodes in the GaP lattice.
10. Nitrogen isoelectron traps cause luminescence of gallium phosphide in the green region of the spectrum, and Zn-O complexes are responsible for red emission.
11. The most practical interest is the injection electroluminescence excited by direct inclusion of p-n junctions.

5.5. Gallium arsenide

1. Gallium arsenide, one of the main semiconductor materials, belongs to the class of A^{III}B^V compounds. Due to the successful combination of properties, it ranks second (after silicon) in its importance in modern electronic technology.
2. Gallium arsenide has good thermophysical characteristics, a large band gap, high electron mobility, favorable features of the band structure, which determine the possibility of direct interband transitions of charge carriers.
3. Crystals of gallium arsenide crystallize in sphalerite lattice.
4. The equilibrium pressure of arsenic vapor at the melting point of gallium arsenide is 10^5 Pa (0.98 atm), which greatly complicates the technology of its production.
5. The electrophysical properties of unalloyed gallium arsenide strongly depend on the composition and concentration of intrinsic point

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- defects, the concentration of background impurities and the heat treatment regimes of ingots.
6. The main alloying impurities when obtaining n-type gallium arsenide single crystals are S, Se, Te, Si, Sn, and when obtaining p-type single crystals – Zn.
 7. Gallium arsenide does not interact with water, but actively decomposes under the action of acids with the release of toxic arsine.
 8. When heated in air to 300°C, gallium arsenide does not oxidize.
 9. Gallium arsenide belongs to decomposing compounds. Starting from 600°C, it decomposes with the release of arsenic.
 10. Molten gallium arsenide is very active and interacts with almost all known materials used for the manufacture of containers.
 11. One of the main technological characteristics of GaAs is the density of dislocations. The nature of the distribution and value of the dislocation density has an impact on the operating parameters of devices manufactured on its basis.
 12. The presence of dislocations in the active regions of light-emitting structures made on heavily doped GaAs wafers of n- and p-type conductivity leads to rapid degradation of the device characteristics. In this regard, low dislocation density is the main requirement for the material.
 13. Obtaining dislocation-free GaAs crystals is a complex technological problem, which is still practically unsolved.
 14. The exception is heavily doped crystals, since the introduction of alloying impurities, having reached a certain level of doping, is accompanied by the effect of "impurity strengthening" – a decrease in the density of dislocations – in gallium arsenide crystals.
 15. The density of dislocations in semiconductor crystals is determined by thermoplastic deformation, which manages to pass in the crystal in the process of relaxation of thermoelastic stress, i.e. depends on the conditions of obtaining (growth method), crystal diameter and concentration of the dopant.

5.5.1. Application of gallium arsenide

16. Undoped semi-insulating GaAs with high resistivity ($10^7 \Omega \cdot \text{cm}$) is used in the manufacture of high-frequency integrated circuits and discrete microelectronic devices.
17. In addition to high resistivity, single crystals of unalloyed GaAs used in the production of high-frequency devices (especially with the use of ion implantation technologies) must have high values of charge carrier mobility and high macro- and microscopic homogeneity of the distribution of properties both in cross-section and along the length of the grown ingots.
18. Strongly silicon-doped GaAs of n-type conductivity with low dislocation density is used in the manufacture of LEDs and lasers.
19. Single crystals of heavily silicon-doped (10^{17} - 10^{18} cm^{-3}) GaAs, in addition to high conductivity, must have a sufficiently perfect crystal structure.
20. They are widely used in optoelectronics for the manufacture of injection lasers, light- and photodiodes, photocathodes, and are an excellent material for microwave oscillators (so-called oscillators or Gunn diodes).
21. The Gunn effect was discovered by the American physicist J. Gunn in 1963 in a gallium arsenide (GaAs) crystal with electron conductivity.
22. When applying an electric field of 2-3 kV/cm to homogeneous samples of n-type gallium arsenide, spontaneous current fluctuations occur in the sample.
23. The physical basis that allows to realize such properties in a diode is the Gunn effect, which consists in the generation of high-frequency oscillations of electric current in a homogeneous semiconductor with an N-shaped volt-ampere characteristic.
24. The Gunn effect is observed mainly in two-valley semiconductors whose conduction band consists of one lower valley and several upper valleys.
25. Gallium arsenide Gunn generators can generate microwave oscillations from 1 to 50 GHz.

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26. The efficiency of the Gunn generators can be different (from 1 to 30%), since the technology of manufacturing devices and the quality of the initial semiconductor material differ significantly.
 27. GaAs single crystals are used to manufacture tunnel diodes capable of operating at higher temperatures and frequencies than germanium.
 28. Single crystals of semi-insulating gallium arsenide, doped with chromium, are used in infrared optics.
 29. GaAs single crystals doped with zinc or tellurium are used in the production of optoelectronic devices.

5.6. Indium phosphide

1. Indium phosphide, InP, is a single-crystal semiconductor material belonging to the class of compounds $A^{III}B^V$.
2. Single crystals of indium phosphide have the greatest prospects for wide industrial production and application after gallium arsenide.
3. Crystals of indium phosphide crystallize in the sphalerite lattice.
4. Energy gap of indium phosphide is 1.35 eV.
5. Indium phosphide is insoluble in water, resistant to acetic, dilute sulfuric and nitric acids, caustic soda.
6. The best solvent of indium phosphide is hydrochloric acid, the specific dissolution rate in which increases with increasing concentration.
7. It dissolves in mixtures of acids (hydrochloric and nitric, nitric, hydrofluoric and acetic).
8. When heated to 300°C, indium phosphide does not oxidize. At higher temperatures it decomposes with the release of phosphorus.
9. Indium phosphide is technologically more complex material than gallium arsenide, since the equilibrium pressure of phosphorus vapor over the melt of stoichiometric composition is high.
10. For the growth of InP single crystals the same methods are used as for gallium arsenide – the Czochralski method with liquid sealing of the melt and the method of vertical directional crystallization.

11. The peculiarity of InP and GaAs growth technologies is that both methods are implemented at high pressure of inert gas or phosphorus in the chamber.
12. To obtain crystals with adjustable electrophysical properties (type of conductivity, resistivity, concentration and mobility of charge carriers), the processes of doping indium phosphide with electrically active impurities are used.
13. The main alloying impurities in obtaining n-type single crystals are S, Se, Te, Si, Ge, Sn, and in obtaining p-type single crystals – Zn and Cd.
14. Doping with donor impurities to high concentrations leads to a decrease in the density of dislocations in them, but at the same time is accompanied by the appearance of microdefects.
15. These microdefects, as well as in gallium arsenide, are packing defects, small prismatic dislocation loops, dispersed second-phase separations. As in the case of gallium arsenide, the main role in their formation is played by their own point defects.
16. The main application for the production of integrated circuits is semi-insulating (with high resistivity) indium phosphide doped with iron.
17. The main technological problems in the growth of indium phosphide crystals are the tendency of crystals to twinning, the formation of dislocation clusters and segregation phenomena due to the high content of Fe impurities in semi-insulating crystals.
18. Field effect transistors and other microwave devices are created on the basis of indium phosphide.
19. Somewhat higher frequencies are obtained on indium phosphide Gunn generators, but the quality of devices made of this material is much lower due to insufficient development of the material manufacturing technology.
20. The Gunn effect is also observed in electronic semiconductors InSb and InAs.
21. Monocrystalline InP wafers are used as substrates for growing heterostructures, on the basis of which effective radiation sources (injection lasers, LEDs) and high-speed photodetectors for fiber-optic

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- communication systems at wavelengths of 1.3 and 1.55 microns (spectral range of high transparency of quartz glass fiber) are created.
22. Indium phosphide is promising for the development of ultrafast integrated circuits. According to some forecasts, it may in the future completely replace gallium arsenide in the production of integrated circuits.

5.7. Application of semiconductor compounds of $A^{III}B^V$ type

1. The variety of properties of semiconductors of $A^{III}B^V$ type determines their wide application in devices and devices for various technical purposes.
2. Particular interest in this group of materials was caused by the needs of optoelectronics in high-speed radiation sources and receivers.
3. Injection lasers and LEDs based on $A^{III}B^V$ semiconductors are characterized by high efficiency of conversion of electrical energy into electromagnetic radiation.
4. Significant advantages of such devices are small overall dimensions, simplicity of design, the possibility of internal modulation of radiation by changing the control voltage, compatibility with integrated circuit elements in terms of operating parameters and technological operations.
5. Due to this, semiconductor lasers and LEDs are successfully used in computing, information-measuring and defense technology, in astronautics and communications technology, as well as in household appliances.
6. Gallium arsenide was the first semiconductor on which an injection laser was made in 1962, i.e. generation of coherent radiation by means of p-n junction. The laser effect occurs only if the current density through the p-n junction exceeds a certain threshold value.
7. In optoelectronics devices mainly infrared emitters (gallium arsenide and solid solutions based on it) are used.
8. A large set of values of the band gap of $A^{III}B^V$ semiconductors allows to produce on their basis different types of photodetectors covering a wide range of spectrum.

9. Among them the most widespread are photodiodes and photocells.
10. Gallium arsenide is potentially one of the best photosensitive materials for use in solar cells.
11. Indium antimonide has important technical importance for the manufacture of infrared radiation receivers with photosensitivity up to 7 microns.
12. A kind of photon radiation receivers are photomultiplier tubes operating on the basis of external photoelectric effect.
13. A^{III}B^V semiconductors allow to produce efficient photocathodes and secondary electron emitters. For example, photocathodes made of p-type gallium arsenide activated by Cs₂O film to reduce work of the electron exit, have a quantum yield in the near infrared spectrum several orders of magnitude higher than that of photocathodes made of traditional materials.
14. Current instability in strong electric fields due to inter-valley transitions of electrons is used to produce microwave oscillators (Gunn generators) operating in the frequency range 10⁹-10¹⁰ Hz. In addition to gallium arsenide, promising materials for these purposes are InP, InAs and solid solutions based on them.
15. Compared to germanium diodes, gallium arsenide devices are characterized by a higher operating temperature, and InSb diodes have better frequency properties at low temperatures.
16. On the basis of narrow band semiconductors of A^{III}B^V type (InSb, InAs), which have high electron mobility, magnetoresistors and Hall converters are made.
17. Progress in gallium arsenide technology has opened wide prospects of application of this material for producing of field-effect transistors and high-speed integrated circuits.

5.8. Boron nitride and its physical and chemical properties

1. Group of semiconductor compounds of A^{III}B^V type based on boron is one of the least studied among semiconductor compounds with diamond-like structure.

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2. However, these compounds are of great interest because of their high chemical stability, large band gap and other specific properties. These properties are due to the special position of boron in the Periodic Table.
 3. Boron belongs to those elements of the second row of the Periodic Table, whose atoms are characterized by the strongest bonds.
 4. Boron is a very high-melting ($\sim 2300^{\circ}\text{C}$) and hard ($\sim 3000\text{kg/mm}^2$) conductor. All this gives reason to believe that compounds of $\text{A}^{\text{III}}\text{B}^{\text{V}}$ type based on boron will have interesting properties.
 5. Boron nitride (borazone) BN is an electronic analogue of carbon.
 6. Obtaining cubic boron nitride became possible only in the second half of the 50th, when the technique of ultra-high pressure developed so much that it allowed to obtain pressures of hundreds of thousands of atmospheres at temperatures of several thousand degrees.
 7. The phase diagram of boron nitride, as well as the state diagram of the B-N system, has not been developed. There is information in the literature that, in addition to boron nitride BN, there are other compounds of boron with nitrogen in this system.
 8. Borazon crystals do not change when heated in vacuum to temperatures above 2000°C . When heated in air, slow oxidation of borazon was observed only at 2000°C , while diamond burns in air already at 875°C .
 9. When borazone was heated under a pressure of 40000 atm, its transition to hexagonal boron nitride was observed at 2500°C .
 10. Borazon crystallizes in the structure of a zinc decoy (sphalerite).
 11. Borazon crystals obtained by the transition from BN (hex.) to BN (cub.) at high pressure are polyhedra, usually tetrahedra or octahedra. They are transparent, and their color depends on the presence of certain impurities.
 12. The density of borazone is 3.45 g/cm^3 (X-ray density 3.47 g/cm^3). Its hardness when evaluated on the Mohs scale was comparable to the hardness of diamond (10 points).

13. Borazon, as A^{III}B^V type compounds based on boron, has high chemical stability, large band gap, low ionization energy of impurity centers.
14. Production of borazon is associated with technological difficulties (use of ultrahigh pressure technique). Its properties are not fully studied at the moment, but we can already say that it is a good material for semiconductor devices designed to operate in a wide temperature range.

5.9. Basic concepts and definitions

1. *Relative electronegativity* (REN) is a quantitative characteristic of the ability of an atom in a molecule to shift electrons of other atoms to itself. The highest degree of electronegativity is in halogens and strong oxidizing agents (p-elements, F, O, N, Cl), and the lowest – in active metals (s-elements of group I).
2. *Sphalerite* is one of the polymorphic modifications of zinc sulfide, which crystallizes in cubic syngony.
3. *Gunn diode* is a semiconductor diode consisting of a homogeneous semiconductor that generates microwave oscillations when a constant electric field is applied.

5.10. Questions for self-control

1. What semiconductors are the closest electronic analogues of compound A^{III}B^V?
2. Which compounds of A^{III}B^V are called arsenides and which are called antimonides?
3. What type of chemical bonding is characteristic of A^{III}B^V compounds?
4. Name the most important representatives of the A^{III}B^V group?
5. What crystal structure do the representatives of the group A^{III}B^V have mainly?
6. How do impurities of group II elements (Be, Mg, Zn and Cd) affect the conductivity in A^{III}B^V semiconductors?
7. Where are the impurities of group VI elements (S, Se, Te) in A^{III}B^V semiconductors?

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8. How do impurities of group VI elements (S, Se, Te) affect the conductivity in $A^{III}B^V$ semiconductors?
 9. Describe the effect of impurities of transition group elements (Fe, Co, Ni, etc.) in semiconductors on the energy structure.
 10. What material is called semi-insulating?
 11. Why for the generation of radiation in the visible spectral region of the band gap of the semiconductor must exceed 1.7 eV?
 12. In what lattice crystallizes gallium arsenide?
 13. What is the main alloying impurity in the production of p-type single crystals?
 14. Why is obtaining dislocation-free GaAs crystals a very important technological task?
 15. What are the features of GaAs band structure?
 16. What frequency can be generated by oscillations of gallium arsenide Gunn oscillators?

6. Semiconductor compounds of the $A^{II}B^{VI}$ group

1. Among the materials of the near future, there is undoubtedly a whole class of semiconductor compounds of the $A^{II}B^{VI}$ type, which are established by elements of the second (Cd, Zn, Hg) and sixth (S, Se, Te) groups of the periodic table.
2. $A^{II}B^{VI}$ materials are much less developed, and their applications are not yet as numerous as those of semiconductors of group $A^{III}B^V$.
3. The widespread use of $A^{II}B^{VI}$ compounds is hindered by the lack of research of many processes associated with the production of these crystals, as well as technical difficulties arising from the producing of appropriate growth equipment.
4. Interest in $A^{II}B^{VI}$ compounds is due to the combination of many interesting physical properties that allow the use of these crystals in various devices of optics, acoustics, electronics, nuclear physics.
5. The band gap of $A^{II}B^{VI}$ semiconductors covers the range from hundredths of eV (in mercury chalcogenides) to 3.7 eV (in zinc sulfide).
6. From the point of view of optical applications, materials of this group cover the spectral range of wavelengths from 0.3 μm to several tens of μm .
7. Compounds $A^{II}B^{VI}$ are characterized by a wide mutual compatibility, which allows to construct new materials with a given band gap, spectral transmission range, crystal lattice parameters and other characteristics on the basis of solid solutions of these compounds.

6.1. Structure and chemical bonding

1. Compounds of type $A^{II}B^{VI}$ include chalcogenides of zinc, cadmium and mercury. Among them are sulfides, selenides and tellurides. This group does not include oxides of these metals.
2. Semiconductor compounds of type $A^{II}B^{VI}$ crystallize in the structure of a zinc decoy (sphalerite) or hexagonal (wurtzite) type.
3. Chemical bonding is of mixed covalent-ionic nature.

4. Compared to semiconductors of type $A^{III}B^V$, the ionic component of the bond is more pronounced in chalcogenides, which is due to large differences in the electronegativities of the elements that create the compounds. This is reflected in the properties of the compounds, which are systematized in Table 6.1.

Table 6.1. Basic physical properties of semiconductor compounds $A^{II}B^{VI}$

Compound	type of lattice structure *	Lattice period, Å	ρ , g/cm ³	T_m , °C	E_g , eV	Type of conductivity	μ_e , $\frac{cm^2}{V \cdot s}$	μ_h , $\frac{cm^2}{V \cdot s}$
ZnS	S	5,41	4,09	1020**	3,67	<i>n</i>	–	–
ZnS	W	3,82(a) 6,26(c)	4,10	1780	3,74	<i>n</i>	140	5 1100
CdS	W	4,13(a) 6,75(c)	4,82	1750	2,53	<i>n</i>	340 350	15
HgS	S	5,84	7,73	1480	1,78	<i>n</i>	700	–
ZnSe	S	5,66	5,43	1520	2,73	<i>n</i>	260	15
CdSe	W	4,30(a) 7,01(c)	5,81	1264	1,85	<i>n</i>	C 720	75
HgSe	S	6,08	8,25	790	0,12	<i>n</i>	20000	–
ZnTe	S	6,10	6,34	1239	2,23	<i>p</i>	530	30
CdTe	S	6,48	5,86	1041	1,51	<i>n, p</i>	1200	60
HgTe	S	6,46	8,09	670	0,08	<i>n, p</i>	25000	200

* S – sphalerite, W – wurtzite; ** β -hase transition temperature from to α -modification

5. As can be seen from Table 6.1, the width of the band gap and melting point of compounds naturally decrease with increasing average atomic mass in all three homologous series.
6. At the same time, the mobility of charge carriers increases. Due to the increase in interatomic distances, the strength of chemical bonds decreases in the transition from sulfides to selenides and then to tellurides.
7. Mercury telluride at all temperatures exhibits properties of semi-metals.

8. The large proportion of ionic bonds in compounds $A^{II}B^{VI}$ in comparison with semiconductors $A^{III}B^V$ leads to large values of the band gap and low mobility of charge carriers in the series of isoelectronic analogues.

6.2. Features of properties

1. The behaviour of impurities in compounds of type $A^{II}B^{VI}$ basically follows the same laws as in semiconductors of type $A^{III}B^V$.
2. Substitution impurities having a valence lower than that of the displaced atoms play the role of acceptors, and impurities with a higher valence are donors.
3. For example, impurity atoms of the elements of group I (Cu, Ag, Au), replacing Zn or Cd in the crystal lattice of a semiconductor, exhibit acceptor properties. In this case, as a rule, they form deep energy levels.
4. Atoms of elements of group III (Al, Ga, In), which also replace cations, behave as donors with low ionization energies.
5. Accordingly, the acceptor and donor properties are shown by elements of groups V and VII of the Periodic Table, which replace chalcogenide atoms in the lattice $A^{II}B^{VI}$.
6. At elevated temperatures all $A^{II}B^{VI}$ compounds decompose. The equilibrium vapor pressure of volatile components strongly depends on temperature.
7. An important feature of $A^{II}B^{VI}$ type semiconductors is that many of them exhibit electrical conductivity of only one type, regardless of the conditions of production and the nature of doping of crystals.
8. Sulfides and selenides of zinc, cadmium and mercury are always n-type semiconductors. In contrast, zinc telluride has only hole electrical conductivity.
9. Only CdTe and HgTe can have both n- and p-type electrical conductivity, depending on the manufacturing conditions and the type of alloying impurities.

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10. The lack of inversion of the type of electrical conductivity significantly limits the possibilities of practical use of semiconductors of type $A^{II}B^{VI}$.
 11. Conductivity of compounds of type $A^{II}B^{VI}$ can be significantly (by several orders of magnitude) changed by heat treatment in vapor of own components. For example, the specific conductivity of cadmium sulfide during heat treatment in sulfur vapor can change by 10 orders of magnitude.
 12. Such a strong change in electrical properties is due to violations of the stoichiometric composition of the compound.
 13. Since semiconductors of type $A^{II}B^{VI}$ are characterized by a significant proportion of ionic bonds, non-stoichiometric defects behave as electrically active centers, in particular, vacancies in the metalloid sublattice play the role of donors, and vacancies in the metal sublattice behave like acceptors.
 14. During heat treatment, defects with lower energy of formation are mainly formed.
 15. In sulfides and selenides, the dominant type of defects are vacancies in the anionic sublattice.
 16. Vacancies in anionic sites are formed when there is a lack of sulfur. The latter can leave the crystal only in the form of neutral S^0 atoms, leaving excess electrons on the vacancies.
 17. Each vacancy forms an energy level near the conduction band, filled with electrons at low temperature. A small action is enough to tear the electrons away from the defect in the structure, i.e. to transfer them to the conduction band.
 18. In ZnTe crystals, vacancies are mainly formed in the cation sublattice. Zinc ions, leaving the crystal, take the missing electrons from the nearest tellurium ions, due to which hole electrical conductivity appears.
 19. Unlike CdS and ZnTe, cadmium telluride can be an electronic and hole semiconductor. For example, heat treatment at a temperature of 900°C in cadmium vapor under a pressure of more than $7-10^4$ Pa leads to the appearance of electronic conductivity. If the pressure of

cadmium vapor during heat treatment is less than this value, then the material is p-type.

20. Chemical purity is a necessary but not sufficient condition for obtaining crystals of compounds of type $A^{II}B^{VI}$ with the specified properties. It is necessary to control the degree of defectiveness of the crystal lattice, i.e. the concentration of vacancies.
21. Self-compensation of sulfides and selenides by their own structural defects is the main reason that prevents the change of the type of electrical conductivity during their alloying.
22. Acceptors have low solubility in $A^{II}B^{VI}$ semiconductors and usually form deep levels.

6.3. Applications

1. Of all $A^{II}B^{VI}$ compounds, zinc sulfide ZnS and cadmium sulfide CdS are the most widely used. The former is the basis for many industrial phosphors, and the latter is widely used for the manufacture of photoresistors with high sensitivity in the visible part of the spectrum.
2. Solar cells and batteries are made of cadmium sulfide.
3. Until now, ZnS phosphors are superior to other materials in terms of internal quantum yield
4. Depending on the synthesis conditions, ZnS crystallizes in two modifications – high-temperature hexagonal and low-temperature cubic. The phase transition point lies near 1020° .
5. Preference is given to phosphors with a cubic structure due to the increased brightness of the glow. However, almost always in sulfide phosphors there is a mixture of both modifications.
6. An important feature of zinc sulfide is that it forms a continuous series of solid solutions with CdS, CdSe, ZnSe. In this case, the addition of CdS stabilizes the hexagonal modification, and the addition of ZnSe-cubic.
7. The emission spectrum of phosphors is determined by the type of luminescence activators introduced. The most widely used are

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- copper-activated phosphors, which emit in the green and blue regions of the spectrum.
8. Effective phosphors with radiation in the yellow region of the spectrum are obtained by activating zinc sulfide with manganese.
 9. The disadvantage of electroluminescent devices based on zinc sulfide is a relatively high rate of degradation of devices (deterioration of their properties), due to the strengthening of the ionic nature of the chemical bond, which stimulates the electrolysis processes.
 10. Impurities play a significant role in the mechanism of intrinsic photoconductivity of $A^{II}B^{VI}$ semiconductors, since the lifetime of nonequilibrium charge carriers depends on their nature and concentration, and it, in turn, determines the photosensitivity and photoresponse rate.
 11. At the same time, it is important not so much the donor or acceptor character of impurity atoms, but their belonging to recombination centers or traps.
 12. The introduction of special impurities, the so-called sensitization centers, can significantly increase the sensitivity of their own photoresistors.
 13. In cadmium sulfide, the sensitive centers are compensated (i.e. ionized) acceptors, which can be cadmium vacancies. The concentration of the latter increases when doped with donors. Accordingly, the intrinsic photoconductivity increases.
 14. The samples of cadmium sulfide doped with copper also have high photosensitivity. At strong copper doping the dominant role begins to play impurity photoconductivity, which is reflected in the shift of the spectral response.
 15. In addition to cadmium sulfide for the manufacture of photoresistors sensitive to visible radiation, films and sintered powdered salts of CdSe are used.
 16. Narrow band semiconductors of type $A^{II}B^{VI}$ are of interest for the manufacture of receivers of far infrared radiation.

17. Particular attention is attracted by solid solutions of Cd_xHg_{1-x}Te, the photosensitivity spectrum of which overlaps the atmospheric transparency window in the region of 8-14 microns.
18. Films of mercury selenide and telluride, due to the high mobility of electrons, are used for the manufacture of highly sensitive Hall sensors.
19. High efficiency of radiative recombination in semiconductors of type A^{II}B^{VI} allows to use single crystals of these compounds as a working body of semiconductor lasers excited by an electron beam.

6.4. Synthesis and crystal growth

1. The technology of growing single crystals of semiconductor compounds A^{II}B^{VI} is developed much less fully than the technology of semiconductors of type A^{III}B^V.
2. Wide bandgap semiconductors A^{II}B^{VI} are technologically difficult objects, because they have high melting points and high dissociation pressure at the melting point.
3. Synthesis of initial A^{II}B^{VI} compounds is most often carried out by exchange decomposition reactions in aqueous medium. Thus, zinc sulfide is obtained from an aqueous solution of ZnSO₄ sulfate by passing through it hydrogen sulfide – H₂S.
4. For the production of products with a low content of oxides, the synthesis is carried out by the interaction of the corresponding metals of group II with sulfur and selenium hydrogen.
5. Growth of single crystals of refractory compounds of type A^{II}B^{VI} in most cases is carried out by recrystallization of a previously synthesized compound through the vapor phase in sealed quartz ampoules.

6.5. Questions for self-control

1. In what structure do compounds of type A^{II}B^{VI} crystallize?
2. How does the large proportion of ionic bonds in compounds A^{II}B^{VI} in comparison with semiconductors A^{III}B^V affect the value of the band gap in the series of isoelectronic analogues?

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3. How do impurity atoms of elements of group I (Cu, Ag, Au) behave, replacing Zn or Cd in the crystal lattice of the semiconductor?
 4. What limits the practical use of semiconductors of type $A^{II}B^{VI}$?
 5. What leads to self-compensation of sulfides and selenides by their own structural defects?
 6. Where are used narrow band semiconductors of type $A^{II}B^{VI}$?
 7. Why are wide band gap semiconductors $A^{II}B^{VI}$ technologically difficult objects?

7. Other binary and ternary semiconductors

7.1. Silicon carbide

1. Silicon carbide refers to diamond-like semiconductors and is an electronic analogue of simple semiconductors – elements of IVB subgroup – modifications of tin, germanium, silicon, diamond.
2. Silicon carbide has many polytype modifications (more than 140), which are derived from hexagonal and cubic dense crystal packings.
3. The phenomenon of polytypism is quite common among semiconductors and allows to significantly increase the range of semiconductor materials.
4. Among the polytype modifications there are n-type and p-type semiconductors. Silicon carbides of n-type have anisotropy of electrical conductivity, in p-type polytypes there is no anisotropy.

7.1.1. Methods of growing SiC single crystals

5. Technical silicon carbide is produced in electric furnaces by reduction of silicon dioxide (quartz sand) with carbon.
6. The color of SiC crystals and the type of electrical conductivity depend on foreign impurities or excess of Si or C atoms over the number of them corresponding to the stoichiometric composition.
7. Since the own melt of silicon carbide can exist at abnormally high values of external pressure and temperature, the classical methods of growing single crystals from the melt for SiC are not applicable. In this regard, methods of growing crystals from the gas phase and from solutions in the melt are currently developed.
8. When growing crystals from solutions in the melt, Si, Si+Co, Si+Cr, Si+REM (rare earth metals), Ge, Sn, Ga, Cr are used as solvents.
9. Crystals are grown from the gas medium (phase) by three methods:
 - by thermal decomposition into aqueous compounds containing Si and C on graphite at a temperature of about 1700–1800°C;
 - by sublimation under conditions of spontaneous nucleation (mass crystallization);

- by sublimation with vapor deposition on baits.
10. Epitaxial layers of SiC and solid solutions on its basis can be obtained by all known methods of semiconductor technology.

7.1.2. Application of SiC

11. The main physical properties of SiC crystals are given in Table 7.1.

Table 7.1. Basic physical properties of SiC crystals

density, mg/m ³	3,2
thermal conductivity at 20°C, W/(m·K)	10 – 40
specific heat capacity, J/(kg·K)	620 – 750
temperature coefficient of linear expansion, K ⁻¹	(4 – 7)·10 ⁻⁶
hardness on the mineralogical scale	9,5
band gap width, eV	2,8 – 3,1
electron mobility at 20°C, m ² /(V·s)	0,01 – 0,05
hole mobility at 20°C, m ² /(V·s)	0,002 – 0,005
dielectric constant	6,5 – 7,5

12. Silicon carbide in electrical engineering is used
- for the manufacture of resistors of valve discharger protecting high voltage transmission lines and equipment;
 - for production of various low-voltage varistors used in automation, instrumentation;
 - in the technique of obtaining high temperatures, etc.
13. High-temperature power semiconductor devices; field-effect transistors, microwave devices, tunnel diodes, LEDs, photodiodes, thermistors, strain gauges, photoresistors are made on the basis of SiC.
14. Semiconductor devices based on SiC have stable parameters when working in aggressive environments, at elevated temperatures, in conditions of irradiation with high energy particles.
15. For example, LEDs based on SiC have exceptionally high reliability and stability, they can withstand a hundredfold current overloads,

cyclic overheating up to 400°C and then retain the stability of their readings with an accuracy of $\pm 1.5\%$, have exceptionally high radiation resistance.

16. These properties allow to use LEDs as light standards, reference light sources in measuring devices.
17. Luminescence colors cover the entire spectrum of visible radiation, up to violet, and can be controlled by introducing various luminescence activator impurities into a particular polytype, or by using crystals of different polytypes.
18. Varistors, high-temperature heaters, wave absorbers, as well as mirrors for powerful lasers emitting in the IR and UV parts of the spectrum are made on the basis of polycrystalline SiC.

7.2. $A^{IV}B^{VI}$ semiconductor compounds

1. Compounds of $A^{IV}B^{VI}$ type with NaCl crystal structure or orthorhombic and covalent-ionic type of chemical bonds are of great practical importance. The most important representatives are mainly direct band semiconductors PbS, PbSe, PbTe, SnTe.
2. Monochalcogenides of germanium, tin and lead belong to $A^{IV}B^{VI}$ semiconductor compounds. Formally, they are similar to semiconductor compounds $A^{II}B^{VI}$, since the A^{IV} atoms in them (as well as A^{II} in $A^{II}B^{VI}$) are in the oxidation state +2. Compounds of $A^{IV}B^{VI}$ type have interesting rectifying properties.
3. Among the compounds of elements of group VI with transition metals and rare earth elements there are many refractory semiconductor materials with ionic character of bonding and possessing ferromagnetic or antiferromagnetic properties.
4. Lead with sulfur, selenium and tellurium also forms one PbB^{VI} compound in $Pb - B^{VI}$ systems.
5. The main role here is played by the well-known in inorganic chemistry Sidgwick's inert vapor effect, due to which for metals of groups II – V of the periodic table the lower oxidation states are stabilized from top to bottom.

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6. Therefore, the $6s^2$ electron pair becomes inert for lead, and mainly $6p^2$ electrons participate in the formation of valence bonds. Only such a strong oxidizing agent as oxygen causes oxidation of lead to higher oxidation states than chalcogenes.
 7. Germanium with sulfur and selenium forms both mono- and dichalcogenides.
 8. In the system tin – selenium also fixed only two compounds: mono- and diselenide of tin.
 9. The most complicated interaction in the system tin – sulfur: in addition to mono- and disulfide of tin, intermediate sulfides Sn_2S_3 and Sn_3S_4 are formed. This is explained by the great affinity of tin to sulfur.
 10. According to the type of crystal lattice monochalcogenides of elements of the germanium subgroup are divided into two groups:
 - high-temperature modification of GeTe , lead and SnTe chalcogenides crystallize in the sodium salt lattice;
 - the second group of monochalcogenides crystallizing in the orthorhombic lattice includes GeS , GeSe , SnS and SnSe .
 11. There is no fundamental difference between these two groups of structures. In fact, the orthorhombic lattice is a deformed lattice of sodium chloride, in which each atom has a coordination environment in the form of a strongly distorted octahedron.
 12. The low-temperature polymorphic form of germanium telluride has a rhombohedral structure.
 13. The phase transition temperature depends on the composition and ranges from 390 to 460°C. Probably, SnTe is also characterized by low-temperature rhombohedral modification, which is observed at temperatures much lower than room temperature.

7.3. A_2B_3 type compounds

1. Semiconductor compounds with the general formula A_2B_3 are divided into two groups – $\text{A}_2^{\text{III}}\text{B}_3^{\text{VI}}$ and $\text{A}_2^{\text{V}}\text{B}_3^{\text{VI}}$.

2. In the first case, these are chalcogenides of metals of the third group (for example, Al_2S_3 , Ga_2Se_3), and in the second – compounds of elements of the fifth group in the oxidation state +3 (for example, As_2S_3 , Sb_2Se_3).
3. Many of these compounds have crystal structures of sphalerite type with one third of unfilled cationic sites (typical representatives: Ga_2Se_3 , Ga_2Te_3 , In_2Te_3).
4. The compounds are characterized by a crystal structure with low symmetry, so they exhibit strong anisotropy of properties.
5. Their structures are characterized by layered and chain lattices. Inside the layers and chains they are connected by covalent bonds, and between the layers – by van der Waals forces. Therefore, this group of compounds is characterized by low melting points.
6. $\text{A}^{\text{II}}\text{B}^{\text{V}}$ compounds (e.g., Zn_3P_2 , Cd_3As_2 , ZnP_2 , ZnAs_2 , ZnSb , etc.) are less studied. Several chemical compounds exist on their phase diagrams.

7.4. Compounds of group $\text{A}^{\text{II}}\text{B}^{\text{V}}$

1. They have long been studied due to their unusual properties and possibilities of application in technology.
2. They have complex phase diagrams, polymorphism of a number of compounds, metastable and amorphous phases, wide areas of homogeneity, distortion of structures and associated structural rearrangements.
3. Single crystals of $\alpha\text{-ZnP}_2$ and $\beta\text{-CdP}_2$ crystallize in a lattice with a space group D_4^4 . They have eight formula units in the unit cell.
4. They are characterized by a large band gap, mechanical and chemical resistance, as well as high optical activity.
5. Cadmium and zinc diphosphides are wide band gap semiconductors with band gap width $E_g = 2.03$ eV for $\beta\text{-CdP}_2$, $E_g = 2.05\text{-}2.22$ eV for $\sigma\text{-ZnP}_2$.

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6. The specific electrical conductivity measured at direct current varies in a wide range; for α -ZnP₂ and β -CdP₂ the conductivity σ is $(5 \cdot 10^{-1} - 10^{-3})$ and $(10^{-3} - 10^{-8}) (\Omega \cdot \text{cm})^{-1}$, respectively.
 7. Both crystals have in the unit cell three independent atoms P1, P2 and Zn (Cd), which occupy three equivalent eightfold positions.
 8. Each zinc (cadmium) atom is surrounded by four phosphorus atoms (two of each kind), and each phosphorus atom is bonded to two zinc (cadmium) atoms and two phosphorus atoms.
 9. The electrical properties of zinc and cadmium diphosphide compounds are determined by the energy levels of intrinsic defects, since the concentration of impurity defects is negligible $n_D = 10^{17} \text{ cm}^{-3}$ and their contribution can be neglected.
 10. Crystals obtained by gas-phase methods differ in the type of conductivity and resistivity. The electrical conductivity of semiconductors is associated with the ionization of deep donors and acceptors, whose concentration is $n_D \sim 10^{10} \text{ cm}^{-3}$.
 11. The concentration of holes in the crystals of the order of $10^{12} - 10^{15} \text{ cm}^{-3}$ and their Hall mobility $\mu_p = 60-70 \text{ cm}^2/\text{V}\cdot\text{s}$.
 12. The conductivity of crystals is determined by the presence of intrinsic defects, which are one- and two-charged vacancies of zinc and phosphorus – acceptors in the zinc (cadmium) node and donors in the phosphorus node. Interstitial zinc (cadmium) atoms and antistructural defects of zinc (cadmium) substitution by phosphorus form donor levels.
 13. The static dielectric constant of ϵ compounds shows significant anisotropy. This is due to the contribution of IR-active lattice vibrations.
 14. There are many features in the optical spectra of diphosphide crystals. IR-active phonons are observed in the infrared spectra of ZnP₂.
 15. In wide band gap semiconductors α -ZnP₂ and β -CdP₂ intrinsic defects in the form of vacancies, interstitial atoms and antistructural defects determine a wide range of electrical and dielectric properties of crystals.

16. Structural and packing defects together with the anharmonicity of thermal vibrations and the ionic-covalent nature of the bonding lead to the appearance of structural features in the form of lattice distortions, polymorphism and superstructures.

7.5. Solid solutions based on compounds $A^{\text{III}}B^{\text{V}}$

1. Solid solutions have significantly expanded, compared to semiconductor compounds, the set of electrophysical parameters that determine the possibility of using materials in specific semiconductor devices.
2. Among diamond-like semiconductors, in particular compounds of type $A^{\text{III}}B^{\text{V}}$, solid substitution solutions are widespread.
3. The necessary conditions for the formation of solid solutions are the crystallochemical similarity of the crystal lattices of the component compounds and the proximity of their identity periods.
4. The best studied are ternary solid solutions in which substitution occurs only in the nodes of one of the sublattices of a binary compound (metal or metalloid).
5. The composition of such solid solutions is usually characterized by the symbols $A_xB_{1-x}C$ and AC_yD_{1-y} , where A and B denote elements of group III, and C and D- elements of group V.
6. In the formula $A_xB_{1-x}C$ index x determines the mole fraction of compound AB in solid solution. If solid solutions exist in the entire concentration range, then x can vary from 0 to 1.
7. In ternary solid solutions, there is a statistically irregular distribution of atoms of substituted components at the nodes of the corresponding sublattice.
8. With a change in the composition of the solid solution, a linear change in the period of the crystal lattice is observed. This regularity is known in crystal chemistry as Vegard's law. It allows to determine the composition of a solid solution by changes in the lattice period using X-ray diffraction.

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9. As in binary compounds $A^{III}B^V$, in solid solutions there are no significant deviations from the stoichiometry, so they are simple by the mechanism of alloying.
 10. By the same methods as in binary compounds, electron-hole transitions can be obtained in them. Temperature changes of electrical parameters also do not fundamentally differ from the corresponding dependences for partner compounds.
 11. Particular interest in solid solutions is due to the possibility of smooth control of the band gap of semiconductors by changing their component composition.
 12. The dependence of the band gap width on the composition in some systems of solid solutions ($Ga_x In_{1-x}As$; $InPu_y As_{1-y}$) is very close to linear, but may differ significantly from it, showing an extreme or a break at a certain ratio between the components.
 13. The specific nature of the dependence of the band gap width on composition $E_g(x)$ is largely determined by the type of band structure of the partner compounds, i.e. the position of their energy valleys in the quasi-pulse space (k-space).
 14. In particular, the hacking of the $E_g(x)$ dependence is observed in those systems of solid solutions in which the initial binary compounds have band structures of different types, i.e. different locations of the main energy minima of the conduction band in k-space.
 15. Mobility of charge carriers in semiconductor solid solutions is mainly limited by the same factors as in binary compounds.
 16. In the general mechanism of charge carrier scattering, the share of scattering on statistical inhomogeneities of the material structure is relatively small. Otherwise, a minimum of carrier mobility should be observed for solid solutions with composition close to $x = 0.5$.
 17. The observed regularity in the behavior of charge carriers distinguishes semiconductor solid solutions from metal alloys, in which electron scattering on statistical inhomogeneities of the structure plays a very significant role.

18. At the same time, as in metal alloys, the effects of statistical disorder in the crystal lattice have a strong influence on the specific thermal conductivity of semiconductors, which in solid solutions is noticeably lower than in binary compounds.
19. For example, in solid solutions of $\text{GaAs}_{0.5}\text{P}_{0.5}$ and $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$, the value of the specific thermal conductivity is about an order of magnitude lower than that of pure GaAs crystals.
20. Changing the width of the bandgap in solid solutions is accompanied by a corresponding shift in the spectra of optical absorption and transmission, luminescence and photosensitivity.
21. With a change in the composition of the solid solution, the values of dielectric constant and refractive index change, there is a shift in the impurity energy levels.
22. In some systems, a qualitatively new combination of properties can be obtained at a certain ratio between the components. Thus, in solid solutions of $\text{GaAs}_{1-y}\text{P}_y$ and $\text{Al}_x\text{Ga}_{1-x}\text{As}$ (with x and y about 0.3-0.4), a sufficiently wide band gap (>1.7 eV) is combined with a high quantum yield of interband radiative recombination.
23. Such materials are used to create efficient electroluminescent sources of red radiation (LEDs and lasers). $\text{GaIn}_{1-x}\text{P}$ solid solutions with $x = 0.5-0.7$ have effective luminescence in the yellow-green spectral region.
24. Obtaining homogeneous solid solutions of a given composition is a very difficult technological task. Conventional methods of crystallization from the melt at best can produce homogeneous polycrystalline ingots.
25. Monocrystalline layers of solid solutions used in device structures are obtained exclusively by epitaxy methods.
26. Epitaxy of $\text{GaAs}_{1-y}\text{P}_y$ solid solutions is carried out on GaAs or GaP substrates by means of chemical reactions in the gas phase. At the same time, the most perfect epitaxial layers are $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and $\text{Al}_x\text{Ga}_{1-x}\text{Sb}$.
27. Solid solutions of $\text{Ga}_x\text{In}_{1-x}\text{As}$ and $\text{Ga}_x\text{In}_{1-x}\text{P}$ are obtained by liquid-phase epitaxy using gallium or indium as a solvent.

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28. Solid solutions open wide opportunities for the manufacturing of heterojunctions and devices based on them.
 29. To obtain heterojunctions with the properties of ideal contact, it is necessary to fulfil a number of conditions for the compatibility of materials in terms of mechanical, crystallochemical and thermal properties.
 30. The decisive criterion in the choice of materials of the contact pair is the equality of periods of their crystal lattices and their temperature coefficients of linear expansion.
 31. If the components of the heterocouple have mutual solubility in the entire concentration range, then there is a unique opportunity to create heterojunctions between the chemical compound AC and the solid solution $A_xB_{1-x}C$ based on it.
 32. This circumstance allows smoothly changing the properties of materials at the contact boundary, which is important in the manufacture of a number of optoelectronic devices and, above all, radiation sources and receivers.
 33. Among semiconductors of type $A^{III}B^V$ the best pairs of materials for producing ideal heterojunctions are GaAs-Al_xGa_{1-x}As and GaSb-Al_xGa_{1-x}Sb systems.
 34. The advantages of these heteropairs are that the lattice period of solid solutions of Al_xGa_{1-x}As and Al_xGa_{1-x}Sb weakly depends on the composition and is close to the lattice period of the corresponding binary compound GaAs or GaSb.

7.6. Other multicomponent semiconductors

1. Additional degrees of freedom for varying the parameters of the semiconductor materials that are combined to obtain ideal heterojunctions arise when using four-component solid solutions of the type $A_xB_{1-x}C_yD_{1-y}$.
2. Among this group of materials, the most interesting and studied are solid solutions of $Ga_xIn_{1-x}As_{1-y}P_y$, in which there is a substitution on both sublattices while maintaining the general stoichiometry, that is, the equality of the total number of metal and metalloid atoms.

3. Four binary compounds can be considered as the initial components of such a solid solution: GaP, InP, GaAs and InAs.
4. Of particular interest are $\text{Ga}_x\text{In}_{1-x}\text{As}_{1-y}\text{P}_y$ solid solutions with isoperiodic substitution with respect to InP. Depending on the composition, their band gap can vary from 0.75 to 1.35 eV.
5. Injection lasers based on the InP – $\text{Ga}_x\text{In}_{1-x}\text{As}_{1-y}\text{P}_y$ heterocouple are promising for use in fiber-optic communication lines, since the spectral range of their radiation corresponds to the minimum optical losses of quartz fiber.
6. Many compounds of the $\text{A}^{\text{II}}\text{B}^{\text{VI}}$ type form a continuous series of solid melts, the typical representatives of which $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$, $\text{Cd}_x\text{Hg}_{1-x}\text{Se}$ and $\text{CdTe}_x\text{Se}_{1-x}$.
7. The physical properties of $\text{A}^{\text{II}}\text{B}^{\text{VI}}$ compounds are largely determined by the content of intrinsic point defects in the structure, which have low ionization energy and exhibit high electrical activity.
8. Triple compounds of $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{C}^{\text{V}}_2$ type crystallize mainly in the chalcopyrite lattice.
9. They exhibit magnetic and electrical ordering. They form solid melts with each other. In many ways they are electronic analogues of type $\text{A}^{\text{III}}\text{B}^{\text{V}}$ compounds. Typical representatives: CuInSe_2 , CdSnAs_2 , CdGeAs_2 , ZnSnAs_2 .

7.7. Basic concepts and definitions

1. *Epitaxy* (from Greek epi – on and taxis – ordered) – a method of growing thin single crystal layers of semiconductor on single crystal substrates.
2. *Liquid phase epitaxy* – a method of obtaining various films and semiconductor crystals. In the formation of epitaxial films, a melt of semiconductor material with appropriate dopants is first obtained, and then the substrate is brought to the surface of the melt solution. After establishing thermal equilibrium between them, they are cooled according to the appropriate law for epitaxial deposition of the film on the substrate.

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3. *Heterojunction* – contact of two semiconductors with different band gap widths.

7.8. Questions for self-control

1. Why silicon carbide crystals are currently grown by methods from the gas phase and from solutions in the melt?
2. What is silicon carbide used for in electrical engineering?
3. Name the most important representatives of типу $A^{IV}B^{VI}$ type compounds.
4. What type of crystal structure have typical representatives of $A^{IV}B^{VI}$ compounds (e.g. Ga_2Se_3)?
5. What determines the conductivity of crystals of compounds of group $A^{II}B^V$?
6. What is the reason for the significant anisotropy of the static dielectric constant of compounds of group $A^{II}B^V$?
7. What intrinsic defects are most often present in wide band gap semiconductors α - ZnP_2 and β - CdP_2 ?
8. What are the necessary conditions for the formation of solid solutions?
9. What determines the index x in the formula $A_xB_{1-x}C$? Within what limits can it vary?
10. What has a strong influence on the specific thermal conductivity of solid solutions in comparison with binary compounds?
11. In what wavelength region do $GaIn_{1-x}P$ solid solutions with $x = 0.5-0.7$ have effective luminescence?
12. What parameters of the contact pair materials are the decisive criterion when choosing them to produce ideal heterojunctions?
13. Name the best pairs of materials for manufacturing ideal heterojunctions among semiconductors of type $A^{III}B^V$?

8. Other semiconductor compounds

8.1. Oxide semiconductors

1. Oxide semiconductors are binary chemical compounds, one of the components of which is metal and the other is oxygen. This class of semiconductor materials includes such substances as Cu_2O , ZnO , CdO , NiO , Fe_2O_3 , MnO , Mn_3O_4 , etc.
2. These are polar type compounds with metal and metalloid components, which can be considered as ionic compounds.
3. Not all transition metal oxides have semiconducting properties, but only those in which the metal ion belongs to elements of the transition series of the periodic table (Zn, Cu, Ni, Co, Fe, Mn, Cr, V, Ti).
4. In addition to oxide semiconductors, more complex oxide compounds are also used (ZnFeO_4 , MnCr_2O_4), the electrical conductivity of which can be selected by changing the percentage of components.
5. The electrical conductivity of oxide semiconductors is due to the presence of at least two multivalent states in the ions of the same metal and is associated with the exchange of electrons between these ions.
6. The resistivity of oxide semiconductors is in the range from 10^5 to $10^9 \Omega \cdot \text{m}$. The presence of impurities significantly affects the electrical properties.
7. The technology of oxide semiconductor materials is relatively simple. Usually these materials are used in the form of polycrystals, or are made in the form of sintered materials using ceramic technology.
8. Oxide semiconductor materials are widely used.
9. The main materials used in the manufacture of sensors are semiconducting metal oxides (SnO_2 , WO_3 , ZnO , TiO_2).
10. Polycrystalline semiconductors such as SnO_2 , ZnO , In_2O_3 are widely used as active elements of gas sensors.

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11. Improvement of the sensing properties of oxide semiconductors: sensitivity, selectivity and stability is achieved by doping them with various metals or metal oxides, or by applying noble metal particles to their surface.
 12. By analogy with a field-effect transistor, metal nanoparticles play the role of a gate, which is controlled by adsorption of the analyzed gases on it.
 13. For example, the method of magnetron sputtering of metal with subsequent oxidation produces thin polycrystalline films of SnO₂, surface-doped with platinum.
 14. Surface doping with platinum by laser ablation significantly improves the sensitivity to hydrogen and is promising for the production of highly sensitive gas sensors of resistive type.
 15. Mixtures of oxides, on the basis of which thermal resistors, varistors, rectifiers and other devices are made, have been practically used.
 16. For example, copper underoxide Cu₂O is used for the manufacture of cuprox rectifiers. Copper underoxide is a typical semiconductor material with a resistivity of 10 to 10⁷ Ω·m, the value of which depends on the heat treatment. It has a hole type of conductivity due to the excess of oxygen relative to the stoichiometric composition. To obtain the electronic type of conductivity, copper diffusion is used.
 17. Zinc oxide ZnO is used in radio electronics for the manufacture of self-activated phosphor ZnO:Zn, which has a blue-green luminescence colour. On the basis of powdered zinc oxide, complex compounds are obtained, which are used for the manufacture of varistors, etc.
 18. Recently, a liquid crystal display (LCD) panel with particularly large diagonal dimensions was made. The new development uses thin-film-transistor (TFT) technology based on oxide semiconductors. The new TV panel supports three-dimensional images with a resolution that is four times higher than that of traditional Full High Definition (Full HD) TVs.

8.2. Polycrystalline semiconductors

8.2.1. Preparation of polycrystalline films and their properties

1. Obtaining a semiconductor in the form of a polycrystalline ingot or film is a technologically simpler and more productive process that reduces the cost of manufacturing semiconductor materials and devices based on them.
2. Polycrystalline semiconductors are the initial raw materials for growing single crystals.
3. The main problem in obtaining polycrystalline semiconductors is to achieve maximum purity. In some cases, technologists limit the content of certain impurities in semiconductors (silicon in semiconductor compounds, oxygen and carbon in elementary semiconductors).
4. Common methods of obtaining polycrystalline films of semiconductor compounds are vacuum and plasma sputtering processes.
5. Polycrystalline layers of GaAs and other $A^{III}B^V$ compounds are obtained by the MDS (metal-dielectric-semiconductor)-hydride technology, which provides low build-up temperatures, reproducibility of grain sizes and high uniformity of films in thickness. Films can be built up on different substrates.
6. Traditional methods of crystallization from the gas phase with the use of volatile silicon-containing substances (monosilane, dichlorosilane, trichlorosilane and tetrachlorosilane) are usually used to obtain polycrystalline silicon layers.
7. One of the most important characteristics of polycrystalline films is the grain size.
8. The grain size depends on the deposition temperature, gas phase composition, crystallization rate and the type of substrate used. Other things being equal, the grain size depends on the nature of the dopant to be introduced.
9. Polycrystalline layers obtained by crystallization from the gas phase are usually textured, and the degree of their texturing increases with increasing deposition temperature.

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10. The process of solid-state recrystallization is used to control the grain size and texture of polycrystalline films.
 11. For the recrystallization of thin layers, heating with a laser or electron beam, as well as heating with special tape resistive heaters is used.
 12. Polycrystalline films with controlled grain size and texture can be obtained by recrystallization of amorphous and fine crystalline layers deposited on amorphous substrates, on the surface of which a special relief is applied by etching, for example, in the form of micron-sized triangular or square grid (graphoepitaxy).
 13. To acquire the necessary electrical properties, polycrystalline semiconductors are doped. The most common doping methods are doping from the gas phase in the process of obtaining layers and ion implantation.
 14. In the diffusion technology of manufacturing devices based on polycrystalline silicon, low-resistance polycrystalline silicon layers heavily doped with traditional impurities are used as sources.
 15. This technology can significantly increase the reproduction of the thickness and properties of diffusion-doped layers and is used to form emitters in microwave transistors and gates in metal-dielectric-semiconductor structures.
 16. Grain boundaries are the main structural defects in polycrystalline layers and have a significant impact on the formation of electrophysical properties of such materials.
 17. The lifetime and mobility of charge carriers depend on the grain size.
 18. Grain boundaries in semiconductors have specific electrical and recombination properties that are implemented in a number of device applications.
 19. The presence of impurities and defects at the grain boundaries leads to the appearance of an unbalanced electric charge on them. In this case, the conductivity of the polycrystalline sample can vary by many orders of magnitude.

20. Intergranular boundaries, in general, affect the electronic properties of the material in two ways.
21. First, the potential barriers formed by intergranular boundaries significantly reduce the mobility of the majority charge carriers, which leads to an increase in the effective resistivity of the semiconductor.
22. This is undesirable for many practical applications not only because of the increased resistivity, but also because of the difficulty of obtaining samples with reproducible resistivity.
23. Second, intergranular boundaries are broken bonds that can be carrier traps, attract impurities or intrinsic defects. These conditions reduce the mobilities and lifetimes of minority charge carriers.
24. The grain boundary, which is a serious violation of the crystal lattice perfection, plays the role of an effective internal getter, which contributes to the purification of the main volume of the material from residual impurities and intrinsic point defects.

8.2.1. Use of polycrystalline films

25. Polycrystalline semiconductor materials have great potential for application in microelectronics and production of cheap thin-film solar cells.
26. The progress of polycrystalline film production technologies has already allowed to offer many new devices: resistors, diodes, bipolar and MDSFETs (metal-dielectric-semiconductor field effect transistor). The potential utility of polycrystalline semiconductors depends on the crystalline perfection of the grains and the electronic properties of their boundaries.
27. The most widely used in semiconductor instrumentation are polycrystalline silicon layers. These layers are used for such elements of integrated circuits as resistors, diodes, field effect and bipolar transistors.
28. High-resistivity polycrystalline silicon layers are used to isolate active elements of integrated circuits. Polycrystalline thin films are also promising for solar energy.

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29. Layers of polycrystalline semiconductor materials are used in the fabrication of solar cells for ground-based applications.
 30. If the grain size significantly exceeds the diffusion length of the charge carriers, then the grain boundaries should not have a major impact on the recombination processes in the material and the performance of photovoltaic solar energy converters.
 31. For silicon, which is an indirect band gap semiconductor, the thickness of the solar radiation absorption layer is 50–100 micrometers, this condition is fulfilled for the size of some crystallites.
 32. In direct band gap semiconductors such as GaAs and Cu_2S , the thickness of the absorption layer is units of micrometers, and the corresponding critical grain size does not exceed several tens of micrometers. Extremely high ability to absorb solar radiation in copper-indium diselenide (CuInSe_2) – 99% of light is absorbed in the first micron of this material (band gap – 1.0 eV).
 33. The most common material for the manufacture of solar cell windows based on CuInSe_2 is CdS.
 34. Cadmium telluride (CdTe) is another promising material for photovoltaics. It has an almost ideal band gap (1.44 eV) and a very high ability to absorb radiation.
 35. CdTe films are cheap enough to produce. In addition, it is technologically easy to obtain a variety of alloys of CdTe with Zn, Hg and other elements to make layers with desired properties.
 36. Polycrystalline films of PbS, PbTe, PbSe are used to fabricate effective IR detectors.
 37. Solar energy converters are fabricated on the basis of polycrystalline film heterostructures in $\text{Cu}_2\text{S}/\text{CdS}$, $\text{Cu}_2\text{S}/\text{Zn}_{1-x}\text{Cd}_x\text{S}$, $\text{CuInSe}_2/\text{CdS}$ systems.
 38. Thin polycrystalline films of metal oxide semiconductors based on SnO_2 , ZnO, etc. are widely used as gas-sensitive layers in solid-state gas sensors.

8.3. Glassy semiconductors

1. Glassy and amorphous semiconductors can be produced both in the form of bulk samples by melt cooling and in the form of thin films obtained by various vacuum deposition methods.
2. Solids obtained by cooling the melt below the melting point, depending on the ratio between the cooling and crystallization rates of the melt, have a crystalline or non-crystalline structure.
3. Lowering the temperature in the melt causes a sharp increase in viscosity, which makes it difficult to rearrange the atoms into a crystal lattice. If the cooling rate is small, the atoms have time to group into a crystal lattice before the increased viscosity of the melt limits the possibility of their mutual movement.
4. The probability of glass formation during the cooling of the melt is higher the higher the cooling rate and viscosity. Glassy materials are obtained at melt cooling rates from fractions of a degree to several degrees per minute.
5. Depending on the chemical composition, glassy materials can be dielectrics, semiconductors and conductors.
6. Glassy semiconductors are characterized by the presence of short-range and absence of long-range order.
7. A glassy semiconductor material, which can be considered as a special type of amorphous substance, is characterized by the presence of a spatial lattice in which, in addition to covalently bonded atoms, there are polar groupings of ions. In such materials, the connection between groups of atoms and ions is carried out by short-range van der Waals forces.
8. Inorganic glassy semiconductors have electronic conductivity.
9. Unlike crystalline semiconductors, glassy semiconductors have no impurity conductivity. Impurities in glassy semiconductors affect the deviation from stoichiometry, and thus change their electrophysical properties. These semiconductors are colored and opaque in thick layers.
10. Glassy semiconductor materials are characterized by a disoriented structure and unsaturated chemical bonds.

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11. Amorphous and glassy semiconductors by composition and structure are divided into oxide, chalcogenide, organic, tetrahedral.
 12. Oxide oxygen-containing glasses are obtained by alloying metal oxides with variable valence, for example, V_2O_5 - P_2O_5 -ZnO. Metal oxides that form these glasses have simultaneously at least two different valence states of the same element, which determines their electronic conductivity.
 13. Typical representatives of glassy semiconductors are chalcogenide glassy semiconductors, which are alloys of chalcogenes – elements of the alkaline group of the periodic system (sulfur S, selenium Se, tellurium Te) with elements of the fifth (As, Sb) or fourth (Si, Ge). This also includes the elemental halogen glassy selenium.
 14. Oxygen-free chalcogen glasses are obtained by alloying chalcogen (S, Se, Te) with elements of III, IV, V groups of the periodic system.
 15. Chalcogenide glassy semiconductors are mainly obtained either by cooling the melt or by evaporation in vacuum. Typical representatives are arsenic sulfide and selenide. They also include two- and multi-component glassy alloys of chalcogenides (sulfides, selenides and tellurides) of various metals (e.g. Ge-S, Ge-Se, As-S, As-Se, Ge-S-P, Ge-As-Se, As-S-Se, As-Ge-Se-Te, As-Sb-S-Se, Ge-S-Se, Ge-Pb-S).
 16. Chalcogenide glasses have high transparency in the infrared spectrum from 1 to 18 microns. Amorphous films of complex chalcogenide compounds have great possibilities of variation of their physical and chemical properties.
 17. Amorphous semiconductors include amorphous Si, Ga, a number of other elements and alloys. In the usual solid state Si and Ge are tetravalent and their atoms are bound by a strong covalent bond.
 18. Tetrahedral bonds lead to the formation in these materials not of individual molecules, but of a continuous three-dimensional grid of chemically bonded atoms. Such a grid has great rigidity. Therefore, it is difficult to obtain any other structure when cooling the melt. It is not possible to form a non-crystalline material in this way.

19. Due to the specificity of the electrical conduction process in amorphous semiconductors, it is almost impossible to control the electrical properties of such materials.
20. Introduction of hydrogen into amorphous silicon films significantly changes its electrophysical properties. Dissolving in amorphous silicon, hydrogen closes the bonds (saturates them), as a result, in such a hydrogenated material, called Si:H, the density of states in the band gap (up to 10^{16} - 10^{17} cm⁻³) is sharply reduced. Such material can be doped with traditional donor (P, As) and acceptor (B) impurities, giving it an electronic or hole type of conductivity, forming p-n junctions in it.
21. A number of amorphous hydrogenated semiconductors with interesting electrical and optical properties Si_{1-x}C_x:H, Si_{1-x}Ge_x:H, Si_{1-x}N_x:H, Si_{1-x}Sn_x:H were synthesized on the basis of silicon.
22. The practical application of amorphous and glassy semiconductors is diverse.
23. Amorphous silicon is a cheaper alternative to monocrystalline silicon, for example, in the manufacture of solar cells based on it.
24. Optical absorption of amorphous silicon is 20 times higher than that of crystalline silicon. Therefore, for a significant absorption of visible light, a Si:H film with a thickness of 0.5-1.0 microns is sufficient instead of expensive 300- μ m silicon substrates. Compared to polycrystalline silicon cells, Si:N-based products are manufactured at lower temperatures (300°C).
25. Hydrogenated silicon is an excellent material for the fabrication of photosensitive elements in xerography, primary image sensors (sensors), targets of windows for transmitting television tubes.
26. Optical sensors made of hydrogenated amorphous silicon are used for recording video information in memory, for the purposes of flaw detection in the textile and metallurgical industries, in automatic exposure and brightness control devices.
27. Glassy semiconductors are photoconductive semi-insulators and are used in electrophotography, information recording systems and a number of other areas.

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28. Due to their transparency in the long-wave region of the spectrum, chalcogenide glassy semiconductors are used in optical instrumentation, etc.
 29. Films of chalcogenide glassy semiconductors are used to form memory elements in chips of reprogrammable permanent storage devices, transmitting television tubes (vidicons), photosensitive media for recording optical information, as well as inorganic photo- and electronic resistors in the manufacture of microelectronics products.

8.4. Semi-metals

1. According to their chemical properties, semimetals are nonmetals, but by the type of conductivity they belong to conductors. They are characterized by the presence of a covalent crystal lattice and metallic conductivity.
2. Semimetals include boron, arsenic, antimony, tellurium and polonium, sometimes bismuth and germanium, as well as tin, which has a semiconducting form, and allotropic modifications of carbon – graphite, and phosphorus – metallic phosphorus. Unlike semiconductors, semimetals have electrical conductivity at absolute zero temperature, and unlike metals, their conductivity increases with increasing temperature.
3. A characteristic feature of semimetals is the weak overlap of the valence band and the conduction band, which leads, on the one hand, to the fact that semimetals remain conductors of electric current up to absolute zero temperature, and on the other hand, with increasing temperature, the number of current carriers (electrons and holes) increases, but nevertheless remains small, reaching a concentration of 10^{18} - 10^{20} cm^{-3} , or 10^{-3} per atom.
4. Current carriers in semimetals are characterized by high mobility and low effective mass. Due to this, semimetals are the most suitable objects for observing size effects, semimetal-dielectric phase transitions in strong magnetic fields and a number of other phenomena.

5. Semimetals are of different types:
 - elements closer in properties to metals (antimony, polonium);
 - elements that are average in properties, i.e. have metallic external features, but in chemical reactions are closer to non-metals (boron, arsenic, tellurium);
 - elements that are almost completely metals, but show slightly noticeable non-metallic features (beryllium, aluminum, bismuth, tin, gallium, zinc);
 - elements that exhibit non-metallic properties, but in some modifications are similar to metals (hydrogen (non-metal completely in all external features, but in chemical reactions behaves like a metal), carbon (mod. graphite), phosphorus (mod. black phosphorus), selenium (mod. gray selenium) and iodine).
6. It turns out that only nitrogen, oxygen, fluorine, sulphur, chlorine, bromine and all inert gases fully belong to the class of “non-metals”.

8.5. Basic concepts and definitions

1. *Texture* is the predominant orientation of crystals in a polycrystalline sample.
2. *Laser ablation* – a method of removing substance from the surface by laser pulse and obtaining complex film structures. This method is successfully used to obtain multicomponent oxide systems.
3. *Semimetals* – substances that occupy an intermediate position between metals and semiconductors in terms of electrical properties.

8.6. Questions for self-control

1. What binary chemical compounds belong to oxide semiconductors?
2. What causes the electrical conductivity of oxide semiconductors?
3. Where are polycrystalline semiconductors such as SnO_2 , ZnO , In_2O_3 widely used?
4. Why are polycrystalline films widely used for the manufacture of semiconductor devices?

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5. What are the most common methods of obtaining polycrystalline films of semiconductor compounds?
 6. What are the most common methods of doping polycrystalline films of semiconductor compounds?
 7. What determines the lifetime and mobility of charge carriers in polycrystalline semiconductor compounds?
 8. What leads to the presence of impurities and defects at the intergranular boundaries in polycrystalline semiconductor compounds?
 9. Where are high-resistance polycrystalline silicon layers used?
 10. Where are polycrystalline silicon layers used?
 11. Why is cadmium telluride (CdTe) and its alloys a promising material for solar energy?
 12. What are thin polycrystalline films of metal oxide compounds used for?
 13. What type of conductivity have inorganic glassy semiconductors?
 14. How are glassy semiconductors divided by composition and structure?
 15. Name the typical representatives of chalcogenides glassy semiconductors.
 16. What chemical elements belong to the semimetals?

Suggested readings

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Appendix

Appendix 1

**List of individual educational and research tasks
(examples)**

1. The main stages of the development of physical materials science of semiconductors, the contribution of domestic researchers.
2. Basic properties and main groups of semiconductor materials.
3. Types of chemical bonding in solids.
4. The relationship between the structure and properties of materials and the type of chemical bonding.
5. Classification and basic properties of classical semiconductors.
6. Elementary semiconductors. The most important representatives of this group are silicon and germanium.
7. Advantages of silicon technology.
8. Semiconductor compounds of the $A^{III}B^V$ group. Crystal structure and chemical bonding.
9. Semiconductor compounds of group $A^{III}B^V$. Classification.
10. Semiconductor compounds of group $A^{III}B^V$. Donor-acceptor type of chemical bond.
11. Basic properties of semiconductor compounds $A^{III}B^V$.
12. Mobility of charge carriers in $A^{III}B^V$ semiconductors.
13. Application of semiconductor compounds of $A^{III}B^V$ type.
14. Semiconductor compounds of the $A^{II}B^{VI}$ group. The crystal structure. Classification.
15. Semiconductor compounds of the $A^{II}B^{VI}$ group. Features of properties.
16. Semiconductor compounds of the $A^{II}B^{VI}$ group. Impurities and structure defects. Application.
17. Solid solutions based on $A^{III}B^V$ compounds. Isoelectronic series.
18. Other semiconductor compounds. Silicon carbide SiC.
19. Glassy and oxide semiconductors.
20. Defects in semiconductor materials.

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21. Basic mechanisms of formation of point defects.
 22. Dislocations. Properties of dislocations. Influence of dislocations on some physical properties of semiconductors. Basic methods of dislocation observation.
 23. Impurities: substitution and introduction; electrically active (donors, acceptors and amphoteric impurities) and electrically inactive (isoelectronic).

Appendix

Appendix 2. Sample of the title page of the IS

Drohobych Ivan Franko state pedagogical university
department of physics and information systems

Semiconductor compounds $A^{IV}B^{IV}$

Individual educational and research task of the student
**group F-103M of Faculty of Physics, Mathematics,
Economics and Innovation Technologies**

Vasylenko Ivanna

for the 1st semester of the 2023/24 academic year

Date of submission to the teacher	
Date of checking	
Checked by	
The maximum possible number of points for the implementation of the IT	
Number of points for the implementation of this IT	

Електронне навчальне видання

Yuriy Uhryn, Mykola Stan'ko, Oleh Kuzyk

SEMICONDUCTOR MATERIALS SCIENCE

Юрій Угрин, Микола Станько, Олег Кузик

НАПІВПРОВІДНИКОВЕ МАТЕРІАЛОЗНАВСТВО

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