6. Semiconductors

6.1 Classification of Substances in Accordance with Their Conductivity

The specific conductivity σ characterizes a substance. The substances with $\sigma \approx$ (10^7 - 10^6) Sim·m^{-1} are called conductors or metals. The substances with $\sigma \approx$ (10^{-8} - 10^{-18}) Sim·m^{-1} are called dielectrics

The substances of intermediate features are called semiconductors. Thus, the specific electric conductivity of semiconductors is from 10^{-8} up 10^6 Sim·m^{-1},

The electrical resistance of semiconductors increases with temperature:

$$R(t) = R_0(1+\alpha t) \tag{6.1}$$

R_0 – resistance at 0°C, $R(t)$ – resistance at t°C, α - the resistance thermal coefficient, the magnitude of which is of order of 1/273.

For metals:

$$\alpha = dR/dT > 0 \tag{6.2}$$

The resistance of semiconductors decreases rapidly with temperature. The empiric formula describing the dependence of the resistance on absolute temperature T:

$$R(T) = R_0 e^{B/T} \tag{6.3}$$

The quantities R_0 and B characterizes the semiconductor (in a certain temperature interval). The specific electric conductivity;

$$\sigma = \sigma_0 e^{-B/T} \tag{6.4}$$

Multiplying the numerator and denominator of the power index of the exponent by the Bolzmann constant k_B and designating $k_B B = E_a$, we get:

$$\sigma = \sigma_0 e^{-E_a/k_B T} \tag{6.5}$$

The quantity E_a is called the **activation energy.**

The resistance temperature dependence of metals and semiconductors is shown in Fig.6.1.

The electric conductivity of semiconductors strongly depends on external factors (heating, radiation, pressure, electromagnetic field and others).

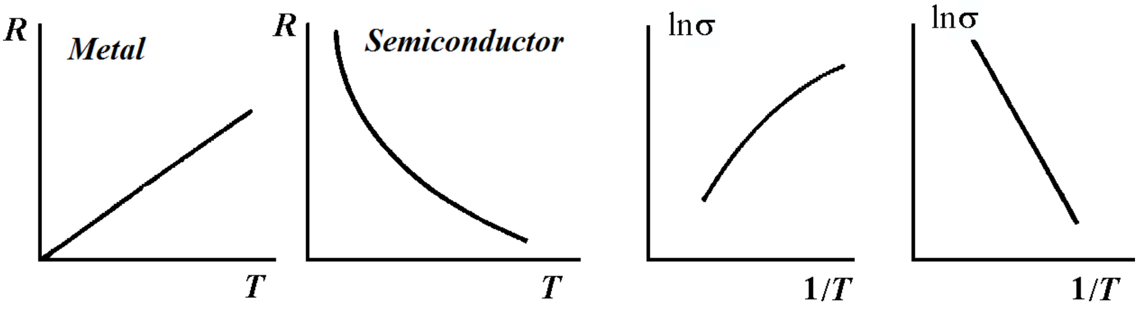

Fig.6.1. The temperature dependence of resistance and dependence of *lnσ* on reversible temperature for metals and semiconductors.

When T→0 the conductivity of semiconductors tends to zero. Thus, the semiconductors conduct the electric current only when excited.

The difference between dielectrics and semiconductors is quantitative; the difference between semiconductors and metals is qualitative.

Twelve simple compounds are known as semiconductors: B, C, Si, P, S, Ge, As, Se, Sn (gray), Sb, Te, and J. Germanium and silicon are most popular.

Many binary compounds are semiconductors. Compounds of $A^{I}B^{VII}$ type: AgC1, CuBr, KBr. Compounds of $A^{II}B^{VI}$ type: compounds of S, Te, Se, oxides of the second group. For example: CdS, CdSe, ZnS. Very perspective are the compounds of the type $A^{III}B^{V}$: compounds of Asand F, nitrides of Al, Ga, In, B.

Compounds of the type of $A^{IV}B^{IV}$ are SiC, SiGe. Compounds of $A^{IV}B^{VI}$ are PbS, PbSe, PbTe. Compounds of $A^{I}B^{VI}$ type are CuS, CuO. More complex compounds and hard solutions are of great interest, for example the hard solutions of GaAsP and InGaSb.

Certain organic substances are semiconductors: antrathen methilenic blue, phtalocianin, caronen.

The great numbers of semiconductors with different parameters are very profitable in engineering.

6.2 Models of Electric Conductivity of Semiconductors

Let us take as an example the silicon. Fourteen electrons of the silicon atom are distributed as follows: $1s^2 2s^2 2p^6 3s^2 3p^2$.

There are four electrons in the external (unfilled) shell. The crystalline structure is tetragonal and analogues to that of a diamond. An atom is bound with four closest atoms by the pair-electron bound, which is produced by four valence electrons. она. In an ideal lattice, all electrons are bound. There are no free charge carriers. In an external electric field there is no electric current. To produce an electric current, some number of electrons must be free. To break the bond, certain quantity of energy is needed. That energy can be given in the form of heat, photons or corpuscular radiation. The energy 1.08eV is needed to free an electron at room temperature. That process produces a free bond.

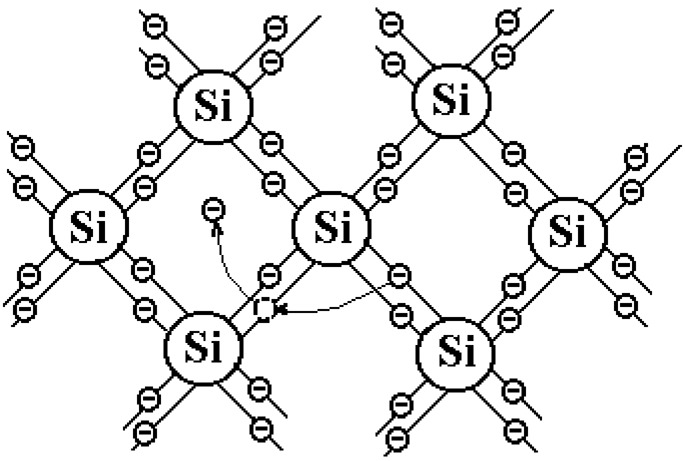

Fig.6.2. Generation of electric conduction as a result of thermal oscillation of a lattice

The Fig.6.2 is the scheme of generation of a free electron by the heat oscillation of the crystalline lattice in an ideal crystal. The freed electron moves chaotically inside the crystal. If the electron approaches the native atom, it can be attached having given away its energy in the form of a quantum of light. The process of transforming of a free electron into bound one is called the **recombination.** That process is reciprocal to the process of generation of the free electron**.** Recombination leads not only to annihilation of a free electron, but also annihilate one free bond between the atoms.

The number of free electrons and vacant bonds is not the same. In that situation, in the region of the vacant bond there is an additional positive charge (not compensated by the negative electric charge of an electron). It should be noted that the electrical neutrality of entire crystal is not violated.

When an external electric field ***E*** is applied across a crystal, the free electrons will undergo the force e**E** and begin drift in the direction opposite to that of the field. Let us designate the electron concentration by *n* and their mobility by μ_n**.** The electric current density:

$$\mathbf{j}_n = e\mu_n n\mathbf{E} = \sigma_n \mathbf{E}, \tag{6.6}$$

The quantity of free electrons in a metal practically does not change when the external factors are varied. The opposite situation takes place for semiconductors. The concentration of free charge carriers strongly depends on radiation, temperature, and external field. That circumstance is not unique difference between semiconductors and metals. In semiconductors there are two mechanisms of conductivity.

The uncompleted bond can chaotically move through a crystal. When an external field is applied, the electrons move against the field and take the vacant bond. In ideal crystal where all the bonds are filled, the motion of bounded electrons is not possible (in accordance with the exclusion principle). The vacancies in bonds permit the valence electrons to move against the field. Thus, the vacant electrons produce the electric conduction of semiconductors. The mobility of bound electrons depends on the quantity of vacancies.

It is very convenient to investigate the motion of the vacant bonds (not the electrons!). The motion of an electron opposite to the field corresponds to the motion of the vacancy in the direction of the field. The motion of the vacant bond is equivalent to the motion of a positive charge e^+. If *p* is the number of vacant bonds and μ_p is their mobility, the density current:

$$\mathbf{j}_p = e\mu_p p\mathbf{E} = \sigma_p \mathbf{E}. \tag{6.7}$$

A vacant bond is called the **hole.** An electric conduction by bound electrons is called the **hole conduction.** The quantity *p* is called the **hole concentration,** μ_p – the **hole mobility,** *e* – the **hole charge.** The holes are believed to be the quasi-particles. Their motion is equivalent that one of valence electrons. It is very important to establish all the properties of holes in order to describe the process properly.

6.3. The Intrinsic and Impurity Conduction

If the number of electrons is identical with that of the holes (n=p), the substance is called the **intrinsic semiconductor.** Then:

$$\mathbf{j} = \sigma\mathbf{E} = (\mu_n n + \mu_p p)e\mathbf{E} = (\sigma_n + \sigma_p)\mathbf{E}. \tag{6.8}$$

Generally, the quantities of electrons and holes are different. It appeared to be very profitable to construct the semiconductor devices. The different concentration of electrons and holes are produced by injection of impurities. The electric conduction caused by impurities is called the **impurity conduction.** To understand the problem, let us investigate the semiconductor of silicon with impurities of the elements of the third and fifth group.

In silicon crystal, the phosphorus atom substitutes the silicon atom (Fig.6.3). There are five electrons in the external shell of phosphorus atom. Four electrons build the covalent bond with four closest silicon atoms. The fifth electron can not form the bond because all bonds are engaged. At the same time the silicon atoms act upon it. It leads to decreasing of its bonding energy with the phosphorus atom by the factor ε^2. The permittivity of silicon is 12. It means that the fifth electron of the phosphorus atom can be liberated at the energy dispense tens times less than the energy needed to disrupt the electron from the basic substance (silicon).

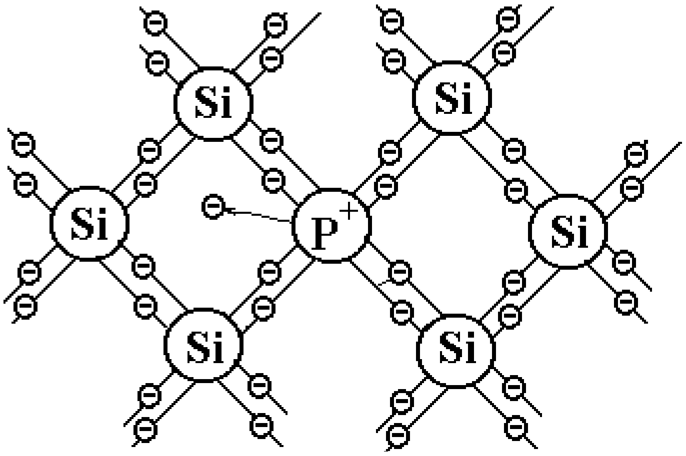

Fig.6.3. The silicon lattice with impurity of five valence phosphorus

The impurity can be ionized very easily. Thus a great number of free electrons will be generated. Their quantity will be greater then that one of the pure silicon. The impurity, which gives electrons, is called the **donor.** The impurity atoms having given off an electron transform into charged (P^+). The positive charged impurity ion does not produce the electric current. Thus, the donor impurity only produces the free electrons.

The number of electrons produced by the impurity is much greater than the number of electrons produced by the basic substance (in the process of ionization). Thus, the number of holes is much less than the number of electrons, which (in that situation) are the **fundamental** charge carriers. Such semiconductor is called the electron type or n-type) semiconductor. Its electric conductivity ($p \ll n$):

$$\sigma = e\mu_n n, \tag{6.9}$$

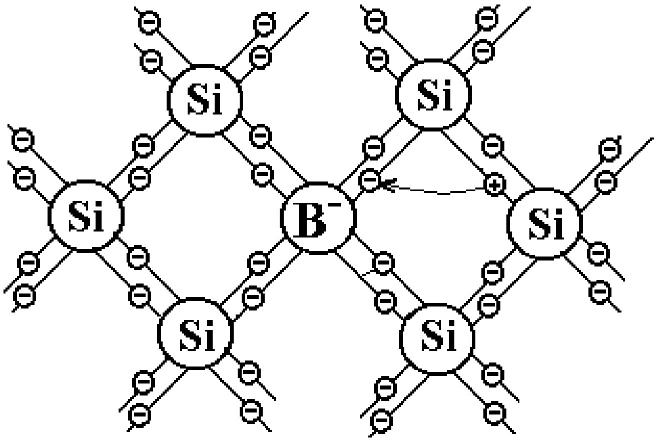

Fig.6.4.The silicon lattice with impurity of three valence boron

A boron atom (or another atom of the third group) introduced in silicon (see Fig.6.4). In boron atom there are three valence electrons. Thus, one bond is not occupied. To fill that bond, it is necessary to transmit an electron of a silicon to boron atom.

The energy needed to transmit an electron from the basic substance atom to the atom of impurity, winch transforms into negative ion, is much less than the energy needed to liberate the electron. Thus, the processes of transition of electrons from the basic substance atoms to the impurity atoms are more often than the processes of ionization of the basic substance.

The negative charge is located in the impurity atom, and does not produce the electric current. The unfilled bond between two basic atoms is a positive charge carrier. The impurity that takes electrons is called the **acceptor.** The number of holes is greater than that one of electrons. The electric conduction is of a hole-type or p-type (n<<p).

$$\sigma = e\mu_p p, \tag{6.10}$$

The substances with the valence less than that one of the basic substance are very often good acceptors.

The charge carrier concentration of an impurity semiconductor is greater than that one of the proper semiconductor. Thus, the electric resistance of a impurity conductor is less than the resistance of a pure substance. The process of introducing the impurities is called the **alloying.**

If in a substance there are the impurities of both types, the impurities compensate one another. When the concentration of donors and acceptors is identical the alloyed semiconductor is very like the proper one. Its electric resistance is high. The semiconductors of that kind are called **compensated.**

Semiconductors with the conductivity, which depends on the impurity type are called **amphoteric.**

6.4 An Elementary Theory of Impurity States

We remind our readers that impurities produce defects of the crystalline lattice. The donor and acceptor impurity levels are generated in the forbidden zone.

We will use the hydrogen model. The interaction between a weakly bounded donor electron (for examples, phosphorus, see Fig.6.3) and a positive impurity ion can be described by the Coulomb potential taking into account the dielectric permittivity of the substance.

$$U(r) = -\frac{e^2}{4\pi\varepsilon_0\varepsilon r} \tag{ 6.11}$$

In accordance with the hydrogen model, the energy levels are:

$$E_n = -\frac{m^* e^4}{8\pi^2\varepsilon_0^2\varepsilon^2}\cdot\frac{1}{n^2} = -\frac{me^4}{8\pi^2\varepsilon_0^2\varepsilon^2}\cdot\frac{m^*}{m}\cdot\frac{1}{n^2}, \tag{ 6.12}$$

n = 1, 2, ... ; m^* - the effective electron mass (the origin of the energy scales $E_c = 0$). In general case:

$$E_n = E_c - \frac{me^4}{8\pi^2\varepsilon_0^2\varepsilon^2}\cdot\frac{m^*}{m}\cdot\frac{1}{n^2}, \tag{ 6.13}$$

Hence, the level E_n is located in the forbidden zone i.e. is lower than E_c .

$$E_1 = E_c - \frac{me^4}{8\pi^2\varepsilon_0^2\varepsilon^2}\cdot\frac{m^*}{m} = E_d. \tag{ 6.14}$$

Thus, it is clear that the depth of the donor level:

$$\Delta E_d = E_c - E_d = \frac{me^4}{8\pi^2\varepsilon_0^2\varepsilon^2}\cdot\frac{m^*}{m} = \frac{13.5}{\varepsilon^2}\cdot\frac{m^*}{m}\,\text{эВ}. \qquad (6.15)$$

It follows from (6.15) that the ionization energy of the five valence impurities in the Ge and Si semiconductors is the same. For germanium ($m^* = 0{,}25\,m$, $\varepsilon = 16$) $\Delta E_d = 0{,}01$eV. In reality the quantities ΔE_d slightly differ.

For the acceptor three-valence impurities (for example in germanium):

$$E_a = E_v + \frac{me^4}{8\pi^2\varepsilon_0^2\varepsilon^2}\cdot\frac{m^*}{m}; \qquad (6.16)$$

$$\Delta E_a = E_a - E_v = \frac{13.5}{\varepsilon^2}\cdot\frac{m^*}{m}\,\text{эВ}. \qquad (6.17)$$

For $m^* = 0{,}25m$ and $\varepsilon = 16$ $\Delta E_a = 0{,}01$eV. The experimental data for the impurities of the third and fifth group in germanium are close to 0.01eV. For silicon the range of ΔE_d and ΔE_a is wider. The corresponding quantities are greater than those ones of germanium.

In the forbidden zone besides the basic impurity states there can be excited impurity states. Those states (n=2,3,4…) are higher than the basic donor state [see **Рис. 6.5.** (6.13)]. While investigating the long-wave infra red radiation absorption at the liquid helium temperature, the excited states in silicon were found. Their position coincides with theoretical ones.

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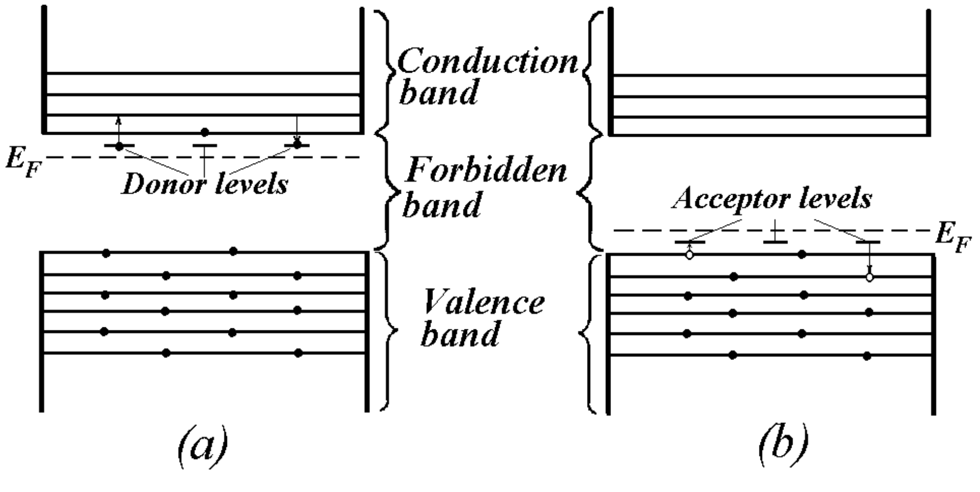

Fig.6.5.The zones of semiconductors and dielectrics

In compounds $A^{III}B^{V}$ (GaAs and InSb), the effective mass is isotropic (the hydrogen model). The levels of the donor and acceptor impurities formed by the elements of the III and V group in covalent semiconductors of germanium type are shallow. Their ionization energy is small.

Atoms of I, II, VI, VIII group introduced in the germanium type semiconductors form the deep impurity levels. The impurities can be in the form of neutral atoms of a donor or acceptor, one-charge and two-charge ions. The situations are known when a certain impurity can form the donor and acceptor levels at the same time (amphoteric centers).

The impurity atoms and structure defects generate the impurity levels in the semiconductor forbidden zone, which separates the conduction and valence zones. The distance between the conduction zone bottom and the donor level is called the **donor ionization energy** (Fig.6.5a). The distance between the acceptor level and the valence zone ceiling is called the **acceptor ionization energy** (Fig.6.5b).

Thus, the elementary theory of impurity states is based upon the hydrogen model.