Investigation of structural, electrokinetic and energy state properties of the semiconductive Zr$_{1-x}$V$_x$NiSn solid solution

Structural, electrokinetic and energy state characteristics of the Zr$_{1-x}$V$_x$NiSn semiconductive solid solution ($x = 0 - 0.10$) were investigated in the temperature interval 80 – 400 K. It was shown that doping of the ZrNiSn compound by V atoms ($r_V = 0.134$ nm) due to substitution of Zr ($r_Zr = 0.160$ nm) results in increase of lattice parameter $a(x)$ of Zr$_{1-x}$V$_x$NiSn indicating unforecast structural change. Based on analysis of the motion rate of the Fermi level $\Delta \varepsilon_F/\Delta x$ for Zr$_{1-x}$V$_x$NiSn in direction of the conduction band it was concluded about simultaneous generation of the structural defects of the donor and acceptor nature (donor-acceptor pairs) by unknown mechanism and creation of the corresponding energy levels in the band gap of the semiconductor.

Keywords: solid solution, electrical conductivity, thermopower coefficient, Fermi level.

Article acted received 23.01.2019; accepted for publication 15.03.2019.

Introduction

The importance of the study of electroconductivity mechanism of the thermoelectric materials based on the $n$-ZrNiSn, $n$-HfNiSn and $n$-TiNiSn intermetallic semiconductors is due to the fact that thermoelectric materials based on the above-mentioned semiconductors have high efficiency of conversion of thermal energy into electric, and optimization of their characteristics is carried out by appropriate doping [1, 2].

The crystal structure of the intermetallic semiconductors was studied earlier. However, an analysis of the research results of the semiconductive solid solutions based on half-Heusler phases showed the difference (of several orders) between experimental measurements, for example, electrical resistivity and thermopower coefficient values and modeling of these characteristics by calculation of electronic structure. It’s worth to note, that the basis of the calculation of the electronic structure by any method is the correct construction of the Wigner-Seitz cell in reciprocal space, which is the first Brillouin zone [1]. In other words, the degree of accordance of crystal structure model to real distribution of the atoms in the sites of the unit cell (or their absence - vacancies) determines the degree of accordance of the semiconductor’s characteristics, obtained by modeling, to the results of experimental measurements.

What is the reason of such unpredictability and discrepancy?

Analysis of the Zr-Ni-Sn phase diagram in Ref. [3] showed a coexistence of the two related compounds, namely ZrNiSn (half-Heusler phase, space group $F43m$) and ZrNi$_2$Sn (Heusler phase, space group $Fm\overline{3}m$) [4]. Absence of center of symmetry in ZrNiSn is caused by covalent bonds between atoms, which results in the semiconductor properties, and forms in the unit cell the volume, not occupied by atoms (tetrahedral voids) (Fig. 1a), which is ~ 24% of the total. The term “relation” means the following. If to assume, that these voids are occupied by smaller Ni atoms and to consider void as a vacancy (Vac) in $4d$ position of Heusler phase, then the filling of $4d$ position by Ni atoms results in change of symmetry and realization of the ZrNi$_2$Sn compound at certain Ni concentration (Fig. 1, b).

The complex investigation of crystal and electronic structures, thermodynamic, electrokinetic and energy state characteristics of ZrNi$_{1-x}$Rh$_x$Sn semiconductive solid solution showed complicate change in the crystal and electronic structures [5, 6] caused by simultaneous...
generation of the structural defects of acceptor and donor nature. It was shown an energy advantage of occupation 4\(e\) position of Ni (3d\(^4\)4s\(^2\)) atoms by Rh (4d\(^5\)5s\(^2\)) atoms which generates the structural defects of acceptor nature (Ni has more \(s\)-electrons) and creates an impurity acceptor band \(\varepsilon_{\text{a}}\) in the band gap. At the same time, part of the replaced Ni atoms is accumulated in tetrahedral voids (vacancies), generating the structural defects of donor nature, and in the band gap the deep donor band \(\varepsilon_{\text{D}}\) appears.

According to previous studies it was established that structure of the basic ZrNiSn compound is disordered as a result of partial, up to \(\sim 1\%\) (\(z = 0.01\)), occupation of 4\(a\) position of Zr (4d\(^2\)5s\(^2\)) atoms by Ni (3d\(^4\)4s\(^2\)) atoms, which generates the structural defects of donor nature and corresponding donor band \(\varepsilon_{\text{D}}\) (Ni has more \(d\)-electrons). Formula of the compound can be written as \((\text{Zr}_{1-x}\text{Ni}_x)\text{NiSn}\) [3].

Recent investigations of TiNiSn\(_{1-x}\)Ga\(_x\) [7] and ZrNiSn\(_{1-x}\)Ga\(_x\) [8] semiconductive solid solutions revealed an earlier unknown mechanism of generation of the structural defects of donor nature which suggests the appearance of vacancies in 4\(b\) position of Sn atoms. It was established that in the case of doping of \(n\)-TiNiSn and \(n\)-ZrNiSn by Ga (4s\(^2\)4p\(^2\)) atoms due to substitution of Sn (5s\(^2\)5p\(^2\)) in the same crystallographic position 4\(b\) the defects of acceptor nature (Ga has less \(p\)-electrons than Sn) and donor nature (vacancies in position of Sn atoms) are generated. The concentration of the defects increases with Ga content, and semiconductors become heavily doped and highly compensated (HDHCs) [9]. At first sight, such unexpected result is logical, since the stability of structure and the principle of electroneutrality for the crystals of TiNiSn\(_{1-x}\)Ga\(_x\) and ZrNiSn\(_{1-x}\)Ga\(_x\) in the case of significant number of acceptors (\(N_{\text{Ga}} = 3 \times 10^{21} \text{ cm}^{-3}\)) are provided by the generation of structural defects of donor nature, the effective charge of which is the opposite. In this case, the formulas of the solid solutions can be written as TiNiSn\(_{1-x}\)Ga\(_x\) and ZrNiSn\(_{1-x}\)Ga\(_x\), where \(\gamma\) is the concentration of vacancies in 4\(b\) position of Sn atoms.

In this context, the question arises why in case of doping of ZrNiSn compound by Rh atoms \((r_{\text{Rh}} = 0.134 \text{ nm})\) the part of the smallest size Ni atoms \((r_{\text{Ni}} = 0.124 \text{ nm})\) occupies the tetrahedral voids generating donors, and in case of doping by Ga atoms \((r_{\text{Ga}} = 0.141 \text{ nm})\) this mechanism is not identified? What factor, dimensional, charge or other determines the method of generation of structural defects in semiconductive solid solutions based on half-Heusler phases, forming the electronic structure and electrical conduction mechanisms?

The search of answer for these questions a first experimental stage of the study of generation mechanisms for structural defects in \(n\)-ZrNiSn doped by V atoms \((r_{\text{V}} = 0.134 \text{ nm})\) due to substitution of Zr, since V (3d\(^2\)4s\(^2\)) atom has one \(d\)-electron more than Zr, the structural defects of donor nature should be generated in Zr\(_{1-x}\)V\(_x\)NiSn, and corresponding impurity donor level would have appear in the band gap. It worth to note that atomic radii of Rh and V are the same, but the way of their introduction in the structure of the compound is different.

## I. Experimental

The samples of the Zr\(_{1-x}\)V\(_x\)NiSn solid solution were synthesized by direct arc-melting of the constituent elements (content of the basic component not lower than 99.9 wt. \%) in electric arc-furnace under inert atmosphere. The pieces of the alloys were homogenized in evacuated silica tubes at 1073 K for 720 h and subsequently quenched in ice water. Phase analysis was performed using X-ray powder diffraction of the synthesized samples (diffractometer DRON-4.0 with FeK\(_\alpha\) radiation). The calculation of the crystallographic parameters was performed using the Fullprof program package [10]. Chemical and phase compositions of the samples were examined by electron microprobe analysis (EPMA) (scanning electron microscope REMMA 102-02). Temperature and concentration dependences of the electrical resistivity \((\rho)\) and thermopower coefficient \((\alpha)\)
(copper as a reference material) of the Zr$_{1-x}$V$_x$NiSn samples were measured in the temperature range $T = 80 - 400$ K and concentration interval $N_0V \approx 3.8 \times 10^{15}$ cm$^{-3}$ ($x = 0.005$) to $1.9 \times 10^{21}$ cm$^{-3}$ ($x = 0.10$).

II. Study of crystallographic characteristics of Zr$_{1-x}$V$_x$NiSn

X-ray phase and structural analyses showed that the prepared Zr$_{1-x}$V$_x$NiSn samples were single phases, and the powder patterns were indexed with cubic Mg$_2$AgAs structure type (space group F-43m) [4]. Microstructure analysis of the atomic concentration on the surface of the ZrNi$_1$Rh$_x$Sn samples indicated their accordance to initial compositions of the ingots. Since the atomic radius of V ($r_v = 0.134$ nm) is smaller than that of Zr ($r_z = 0.160$ nm), it was expected to decrease the values of lattice parameter $a(x)$ for Zr$_{1-x}$V$_x$NiSn. However, the results of structural studies for Zr$_{1-x}$V$_x$NiSn showed a clear tendency to increase of $a(x)$ (Fig. 2) at least to values of $x = 0.07$.

![Fig. 2. Variation of lattice parameter $a(x)$ for Zr$_{1-x}$V$_x$NiSn](image)

Such behavior of the lattice parameter $a(x)$ of Zr$_{1-x}$V$_x$NiSn was unexpected, and the refinement of crystal structure due to the insignificant content of impurity which concentration is far beyond the precision of device did not give definite answer to the way of introduction of V atoms into the ZrNiSn structure. This experimental result is the first important feature that in the structure of Zr$_{1-x}$V$_x$NiSn semiconductor there are unpredictable changes which will be the source of structural defects that will determine its properties. The fact that the lattice parameter did not change in the concentration interval $x = 0.01 - 0.10$ may indicate the limited solubility of V in the semiconductor matrix, which can be caused by the appearance of small amount of metallic phase which we did not identify.

The growth of $a(x)$ dependence of Zr$_{1-x}$V$_x$NiSn is possible, for example, due to unexpected occupation of the crystallographic position 4c of the smaller Ni atoms ($r_{Ni} = 0.124$ nm) by V atoms. In this case, the structural defects of acceptor nature will be generated in the crystallographic position 4c, because Ni (3$d^8$) has more 3$d$-electrons than V (3$d^4$). On the other hand, in the case of occupation of tetrahedral voids by replaced Ni atoms similarly to ZrNi$_1$Rh$_x$Sn [5, 6], the structural defects of donor nature are also generated in the Zr$_{1-x}$V$_x$NiSn crystal. As a result, the obtained Zr$_{1-x}$V$_x$NiSn samples will be HDHCS [9].

III. Study of electrokinetic and energy state characteristics of Zr$_{1-x}$V$_x$NiSn

The temperature and concentration dependences of electrical resistivity $\rho$ and thermopower coefficient $\alpha$ for Zr$_{1-x}$V$_x$NiSn are shown in Figs. 3, 4.

The dependences $\ln(1/\rho)$ and $\alpha (1/\rho)$ for Zr$_{1-x}$V$_x$NiSn (Fig. 3) are typical for heavily doped and highly compensated semiconductors [9], and presence of activation regions indicates several mechanisms of charge transport. These mechanisms are the activation of current carriers from the Fermi level $\varepsilon_F$ to continuous energy band (high temperatures) and hopping conductivity within the energy states close to Fermi level $\varepsilon_F$ (low temperatures). The dependences of $\ln(1/\rho)$ for Zr$_{1-x}$V$_x$NiSn are described by known relation [9]:

$$\rho^{-1}(T) = \rho_1^{-1} \exp \left( \frac{\varepsilon_1}{k_BT} \right) + \rho_2^{-1} \exp \left( \frac{\varepsilon_2}{k_BT} \right)$$

(1)

where the first term describes an activation of current carriers from the Fermi level $\varepsilon_F$ to continuous energy band at high temperatures and second term at low temperatures – hopping conductivity $\varepsilon_F$.

The temperature dependences of thermopower coefficient $\alpha (1/\rho)$ for Zr$_{1-x}$V$_x$NiSn are described by relation [11]:

$$\alpha = \frac{k_B}{e} \left( \frac{\varepsilon_i}{k_BT} - \gamma + 1 \right)$$

(2)

where $\gamma$ – parameter which depends on the scattering mechanism. From the high temperature part of $\alpha (1/\rho)$ dependences the activation energy values $\varepsilon_i$ which are proportional to amplitude of high-scale fluctuation of the continuous energy bands were calculated. From the low temperature part of the $\alpha (1/\rho)$ dependences the activation energy values $\varepsilon_F$ which are proportional to amplitude of the small-scale fluctuation HDHCS [1, 9] were obtained.

From the high-temperature part of the $\ln(1/\rho)$ dependence for undoped n-ZrNiSn semiconductor (Fig. 3, a) the values of activation energy of electrons from donor band $\varepsilon_D$ to the percolation level of conduction band were calculated: $\varepsilon_D = 97.6$ meV. The activation of electrons to the conduction band was confirmed by negative values of the thermopower coefficient of n-ZrNiSn at all temperatures. Since the Fermi level $\varepsilon_F$ is fixed at the donor band $\varepsilon_D$, the calculated activation energy value of electrons $\varepsilon_D$ represents the location depth of the Fermi level $\varepsilon_F$ relatively to the edge of the conduction band. Obtained result agrees with previously one [1]. The presence of low-temperature activation on dependence of $\ln(1/\rho)$ indicated the existence of the hopping conductivity over the energy states of donor band $\varepsilon_D$ with activation energy $\varepsilon_D = 11.9$ meV. Additionally, from high- and low-temperatures parts of
\[ \alpha(1/T) \] dependence the activation energy values 
\[ \varepsilon_1^a = 83.8 \text{ meV} \] and \[ \varepsilon_3^a = 11.5 \text{ meV} \], respectively, were determined. Since the value of activation energy \( \varepsilon_1^a \) represents the modulation amplitude of continues energy band of \( n\text{-ZrNiSn} \) [1,9], the close values of \( \varepsilon_1^a \) and \( \varepsilon_3^a \) are a feature of high compensation of the semiconductor.

Doping of ZrNiSn compound by V impurity atoms results in the change of behavior of \( \ln(\rho/T)(1/T) \) and \( \alpha(1/T) \) dependences and the values of electrical resistivity and thermopower coefficient (Fig. 3, 4). Since the substitution of Zr atoms by V would have generate in the \( \text{Zr}_{1-x}\text{V}_x\text{NiSn} \) crystal the structural defects of donor nature, an increase of the concentration of free electrons should lead to the decrease of the electrical resistivity values \( \rho(x, T) \), as it’s shown in Fig. 4, a. At the same time, the sign of thermopower coefficient \( \alpha(x, T) \) for \( \text{Zr}_{1-x}\text{V}_x\text{NiSn} \) remains negative at all concentrations and temperatures (Fig. 4, b).

At higher V concentration \( x > 0.01 \) only the structural defects of donor nature should be generated in the semiconductor, that will result in enlarge of the electron concentration and decrease of the electrical resistivity values as shown in Fig. 3, a and 4, a.

The presence of high-temperature activation parts in the \( \ln(\rho/T)(1/T) \) dependences of \( \text{Zr}_{1-x}\text{V}_x\text{NiSn} \) even at “giant” concentration of the donor impurity \( N_D^V = 1.9 \times 10^{21} \text{ cm}^{-3} \) for \( x = 0.10 \) (Fig. 3, b) and negative values of the thermopower coefficient \( \alpha(x, T) \) indicate that the Fermi level \( \varepsilon_F \) is located in the band gap near the bottom of the

Fig. 3. Temperature dependences of electrical resistivity \( \ln(\rho/T)(1/T) \) (1) and thermopower coefficient \( \alpha(1/T) \) (2) for \( n\text{-ZrNiSn} \) (a) and \( \ln(\rho/T)(1/T) \) (b) and \( \alpha(1/T) \) (c) for \( \text{Zr}_{1-x}\text{V}_x\text{NiSn} \): 1 – \( x = 0.01 \); 2 – \( x = 0.03 \); 3 – \( x = 0.05 \); 4 – \( x = 0.07 \); 5 – \( x = 0.10 \).

Fig. 4. Variation of electrical resistivity values \( \rho(x) \) (a) and thermopower coefficient \( \alpha(x) \) (b) for \( \text{Zr}_{1-x}\text{V}_x\text{NiSn} \) at different temperatures: 1 – \( T = 80 \text{ K} \); 2 – \( T = 250 \text{ K} \); 1 – \( T = 380 \text{ K} \).
conduction band. This experimental fact is the second feature that in the semiconductor $Zr_{1-x}V_xNiSn$, besides donors, the defects of acceptor nature appear by unknown mechanism and compensate the donors (catch free electrons increasing their concentration). As a result the movement of Fermi level $\varepsilon_F$ to the conduction band becomes slower.

It’s worth to remind that the doping of $n$-$ZrNiSn$, for example, by donor impurity Sb ($4d^{10}5s^25p^3$) due to substitution of Sn ($4d^{10}5s^25p^2$) leads to rapid drift of the Fermi level $\varepsilon_F$ to the bottom of the conduction band and crossing of this band at the concentration $Sb = 0.02$, which was accompanied by metallization of the conductivity of $ZrNiSn_{1-x}Sbx$ [1]. In the case of $Zr_{1-x}V_xNiSn$ the metallization of conductivity (disappearance of activation part in $\ln \rho(1/T)$ dependence) was not observed at all temperatures and concentrations.

On the other hand, the presence of high-temperature activation parts in $\ln \rho(1/T)$ dependence of $Zr_{1-x}V_xNiSn$ (Fig. 3, b) allows to calculate the values of activation energy of electrons $\varepsilon_i^i(x)$ from the Fermi level $\varepsilon_F$ to the mobility edge of the conduction band and to trace dynamics of the Fermi level position $\varepsilon_F$ in the band gap of the semiconductor. From the activation parts of $\alpha(1/T)$ dependences we can obtain information concerning with the change of compensation degree for $Zr_{1-x}V_xNiSn$ by calculation of activation energy values $\varepsilon_i^a(x)$ which are proportional to the amplitude of large-scale fluctuation of continuous energy bands in HDHCS.

The variation of activation energy values $\varepsilon_i^i(x)$ and $\varepsilon_i^a(x)$ for $Zr_{1-x}V_xNiSn$ is presented in Fig. 5. At the lowest impurity concentration of $Zr_{1-x}V_xNiSn$, $x = 0.01$, the Fermi level $\varepsilon_F$ with motion rate $\Delta \varepsilon_F/\Delta x \approx 77.8$ meV/%V rapidly approached the percolation level of conduction band at the distance of 19.8 meV, while in $n$-$ZrNiSn$ it was located at the distance of 97.6 meV. And this despite the fact that in this concentration range there was a decrease of the electron concentration due to the disappearance of impurity donor band $\varepsilon_i^i(x)$ caused by ordering of $Zr_{1-x}V_xNiSn$ structure, which would have to slow down the Fermi level $\varepsilon_F$ in the direction of conduction band. With the same rate the Fermi level $\varepsilon_F$ moved to the percolation level of conduction band in the case of doping of $n$-$ZrNiSn$ by donor impurity Sb [1].

However, at higher concentrations V, the rapid decrease of motion rate of Fermi level $\varepsilon_F$ in the direction to conduction band takes place. Thus, in the concentration interval $x = 0.01 - 0.03$, the motion rate of Fermi level $\varepsilon_F$ is $\Delta \varepsilon_F/\Delta x = 2.2$ meV/%V, at concentrations $x = 0.03 - 0.10$ becomes even smaller and is equal $\Delta \varepsilon_F/\Delta x = 0.7$ meV/%V. Since the concentration of impurity V atoms, which should generate donors, is introduced into the matrix of $n$-$ZrNiSn$ semiconductor according to the linear law, then the Fermi level $\varepsilon_F$ would have to move to the percolation level of conduction band of $Zr_{1-x}V_xNiSn$ in the same way. What is the reason for “braking” of this motion?

From the point of view of semiconductor physics it is possible only if simultaneously with donors the generation of acceptors takes place by unknown mechanism. Thus, obtained experimental result is the third indisputable feature, which confirms, except donors, the appearance of some number of acceptors in $Zr_{1-x}V_xNiSn$, which generation rate is lower than generation rate of donors, because the Fermi level $\varepsilon_F$ is still approaching to the percolation level of conduction band, as indicated by negative values of thermopower coefficient.

This conclusion is consistent with the results of change of activation energy values $\varepsilon_i^i(x)$ for $Zr_{1-x}V_xNiSn$, $x \geq 0.01$, (Fig. 5, b), which reflects the compensation degree of semiconductor. Since the dependence of $\varepsilon_i^i(x)$ represents the ratio of ionized acceptors and donors, the total number of donors exceeds the number of acceptors in $Zr_{1-x}V_xNiSn$, provided that the sign of thermopower coefficient is negative. The compensation degree and $\varepsilon_i^a(x)$ values become lower with increasing this exceedation.

Thus, in $Zr_{1-x}V_xNiSn$ the reduction of compensation degree initially takes place, as indicated by decrease of energy activation values from $\varepsilon_i^i(x = 0) = 83.8$ meV to $\varepsilon_i^i(x = 0.01) = 60.1$ meV and $\varepsilon_i^a(x = 0.03) = 52.5$ meV. Such decrease of $\varepsilon_i^a(x)$ values, as well as the motion rate of Fermi level $\varepsilon_F$ to the conduction band, is also nonlinear. However, at concentration $x > 0.03$, the...
dependence \( \varepsilon_1 (x) \) rapidly increases with maximum at \( x = 0.07 \), indicating that in the crystal acceptors are generated with larger rate than donors, but the total number of ionized donors is still higher than ionized acceptors. The obtained result is an additional factor that indicates the simultaneous generation of acceptors and donors in Zr\(_{1-x}\)V\(_x\)NiSn. Taking into account the structural investigations, we consider that the activation energy values \( \varepsilon_1 (x = 0.10) = 50.7 \) meV do not correspond to real state in the semiconductor due to possible shunting of current by channels of admixture phase.

Consequently, the presented experimental results of electrokinetic and energy state studies confirmed the predicted complicated character of introduction of V atoms into the structure of Zr\(_{1-x}\)V\(_x\)NiSn semiconductor, as evidenced by the unexpected increase of unit cell parameter \( a(x) \) (Fig. 2). Performed analysis shows that an increase of lattice parameter \( a(x) \), on the one hand, and the appearance of acceptors in Zr\(_{1-x}\)V\(_x\)NiSn, on the other hand, can only be achieved by the partial occupation of 4c position of smaller Ni atoms \( (r_{\text{Ni}} = 0.124 \) nm) by V atoms. If the displaced Ni atoms occupy the tetrahedral voids of the structure, as in the case of ZrNi\(_{1-x}\)Rh\(_x\)Sn \([5, 6]\), then structural defects of the donor nature will also be generated in Zr\(_{1-x}\)V\(_x\)NiSn. These considerations need confirmation by electronic structure calculations for various variants of atomic distribution in the matrix of semiconductor, which will show the motion of Fermi level \( \varepsilon_F \). The comparison of calculations with experimental results described above will give final answer about mechanism of introduction of V atoms into the n-ZrNiSn structure. That will be the subject of our next studies.

**Conclusions**

Thus, based on the abovementioned results we can suppose that to provide the stability of the structure and the principle of electroneutrality in Zr\(_{1-x}\)V\(_x\)NiSn the structural defects of acceptor and donor nature (the effective charge of which is opposite) are generated simultaneously, the concentration of which enlarges with the increase of V content. Determination of the mechanisms for generation of acceptors and donors need additional investigation of the Zr\(_{1-x}\)V\(_x\)NiSn solid solution, to which our next work will be devoted.

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Investigation of structural, electrokinetic and energy state properties …

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Дослідження структурних, кінетичних та енергетичних властивостей напівпровідникового твердого розчину Zr1-xVxNiSn

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Досліджено особливості структурних, кінетичних та енергетичних характеристик напівпровідникового твердого розчину Zr1-xVxNiSn (x = 0 – 0,10) в інтервалі температур 80 – 400 К. Показано, що уведення атомів V (rV = 0,134 нм) у структуру сполуки ZrNiSn шляхом заміщення Zr (rZr = 0,160 нм) супроводжується неочікуваним збільшенням значень періоду елементарної комірки a(x) Zr1-xVxNiSn, вказуючи на непрогнозовані структурні зміни. На основі аналізу швидкості руху рівня Фермі ΔεF/Δx Zr1-xVxNiSn у напрямі зони провідності зроблено висновок про одночасне генерування у кристилі структурних дефектів донорної та акцепторної природи (донорно-акцепторні пари) за невідомим механізмом, які породжують відповідні енергетичні рівні у забороненій зоні напівпровідника.

Ключові слова: щирдій розчин, електропровідність, коефіцієнт термо-ерс, рівень Фермі.