CONDUCTION PECULIARITIES IN $ZrNiSn_{1-x}In_x$ SEMICONDUCTOR SOLID SOLUTION

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The temperature and concentration dependences of resistivity and thermoelectric power for the $ZrNiSn_{1-x}In_x$ semiconductor solid solution are studied in the wide temperature ($T = 80 \div 380$ K) and concentration ($x = 0 \div 0.15$) ranges. It is shown for the first time that, in the heavily doped and completely compensated semiconductor, the maximal amplitude of fluctuations of the continuous energy bands is equal to the half-width of the band gap and the Fermi level is located in the middle of the band gap. The correlation between the fluctuation parameters of the continuous energy bands, the fluctuation amplitude, and the potential well depth of small-scale fluctuations was established experimentally.

1. Introduction

This work is devoted to the study of the *n*-ZrNiSn intermetallic semiconductor heavily doped with an In acceptor impurity and is a continuation of the investigations of the influence of high level doping (N_A, $N_D \approx 10^{18} \div 10^{22}$ cm^{-3}) in intermetallic semiconductors of the MgAgAs structural type on the electron density distribution, band structure, electrokinetic, magnetic, thermoelectric, resonance, and structural properties. For the given class of semiconductors, the preliminary investigations made it possible to specify the dominating mechanisms of electric conduction within wide temperature and concentration intervals [1–3] and to determine the conditions for the appearance of maximal values of the thermoelectric power factor Z^* ($Z^* = \alpha^2\sigma$, where α is the thermopower and σ is the specific conductivity) [4]. As follows from work [4], the necessary condition for Z^* to achieve a maximum in intermetallic compounds is the high level of doping with acceptor and/or donor impurities, which leads to the fixation of the Fermi level μ by a mobility edge of one of the continuous energy bands.

This result is also of great importance from the practical point of view, since the intermetallic semiconductors of the MgAgAs structural type are mostly promising and studied as materials for the work elements of thermoelectric current generators [5–11]. The features of the fabrication technique of the intermetallic semiconductors (a melting of a charge mixture of starting components with a subsequent non-controlled fast cooling of the melt), as well as the high concentrations of charged impurities, have favored the simultaneous development of a few fabrication methods of completely (amorphous) or partially (with a local amorphization) disordered solids [12,13].

In this respect, the results of theoretical investigations of the heavily doped and compensated semiconductors are very interesting [14, 15]. The authors of work [14] showed that, in such semiconductors, electrons are distributed non-uniformly in space, which leads to the spatial fluctuations of the continuous energy

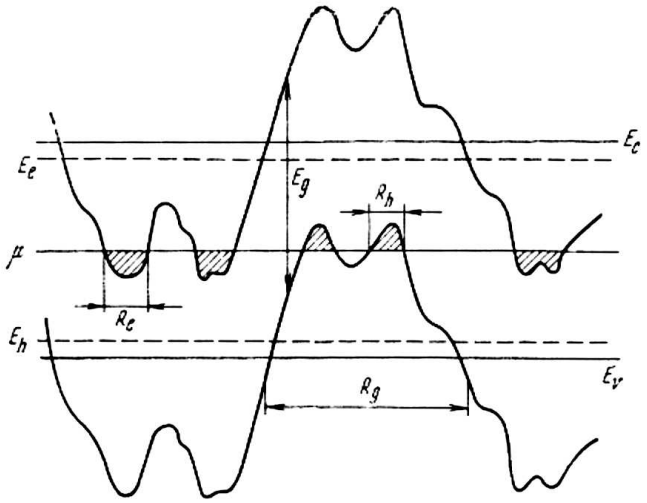

Fig. 1. Energy band scheme for the completely compensated heavily doped semiconductor [15]. The upper and lower straight solid lines show the non-excited positions of the bottom of the conduction band and the top of the valence band, respectively. The middle straight line is the Fermi level. The curved solid lines denote the bottom of the conduction band and the top of the valence band, modulated by the electrostatic potential of charged impurities. The dashed lines show the mobility edges for electrons and holes. The regions occupied by carriers are shaded. The quantities R_e, R_h, and R_g are the mean-square potential well depths for small-scale fluctuations of the conduction band, valence band, and fluctuation amplitude, respectively

bands. In the case of the complete compensation of a semiconductor [15], the maximal fluctuation amplitude for these bands equals a half of the semiconductor band gap ($\varepsilon_g/2$), and the Fermi level is located in the middle of the energy gap (Fig. 1).

Fluctuations of continuous energy bands manifest themselves in that the activation energies deduced from the temperature dependence of resistivity (ε_1^ρ) and the thermopower (ε_1^α) differ from each other within the same temperature range [12]. In ordinary and slightly doped semiconductors, where the band fluctuations are absent, the energy barrier height is invariant with respect to the ways of its determination.

The results presented below not only confirm the theoretical conclusions of works [14,15], but also lay the foundation for the views that, in a heavily doped and compensated semiconductor, the activation energy ε_1^α deduced from the temperature dependence of the thermopower is comparable with the average amplitude of fluctuations of the continuous energy bands, and its determination allows the estimation of the fluctuation amplitude. Moreover, these results illustrate the experimentally established dependence between the fluctuation parameters of the continuous energy bands, fluctuation amplitude, and depth of the potential well of small-scale fluctuations.

The work concentrates on the studies of the temperature dependences of resistivity ρ and the thermoelectric coefficient α, as well as on the structural characteristics of the ZrNiSn intermetallic semiconductor upon its doping with an acceptor impurity through the substitution of In ($4d^{10}5s^25p^1$) atoms for Sn ($4d^{10}5s^25p^2$) ones. It is worth noting that the high level doping of the semiconductor makes it possible to observe the peculiar features of its kinetic and thermoelectric properties at high temperatures [13].

The features of a specimens' fabrication method, the modes of a homogenizing annealing as well as the details of structural studies, measurements of resistivity and the thermoelectric coefficient (the latter – relative to copper) over the temperature range 80–380 K are presented in [4].

2. Experimental Results and Their Discussion

The X-ray phase, structure, and microprobe analyses confirmed that all the $ZrNiSn_{1-x}In_x$ specimens under investigation are single-phase (the structural type MgAgAs, the space group $F\bar{4}3m$: 4Ni in 4(c) 1/4 1/4 1/4; 4Sn in 4(a) 0 0 0; 4Zr in 4(b) 1/2 1/2 1/2).

The layer-to-layer analysis of the interplane distances for a unit cell of the ZrNiSn compound showed that the occupation of the Zr, Ni, and Sn atomic positions is not constant, as it is expected for the MgAgAs structural type. Some of the crystallographic positions of Zr and Sn atoms are statistically occupied by the atoms of Ni which is a donor impurity relative to these atoms. These facts provide the evidence of the local amorphization of the structure and explain the n-type of conductivity in the undoped semiconductor ZrNiSn.

The temperature dependences of the resistivity and the thermopower for $ZrNiSn_{1-x}In_x$ specimens under investigation are shown in Fig. 2. The high-temperature activation regions are discernable on all the $\ln\rho(1/T)$ and $\alpha(1/T)$ curves. What is more, for the specimens with the concentrations of the acceptor impurities corresponding to the compositions of $ZrNiSn_{1-x}In_x$ with $x = 0.005$, 0.01, 0.2, and 0.15, the low-temperature activation regions, which can be associated with a hopping conductivity, are characteristic of the $\ln\rho$ vs $1/T$ dependences. In two other alloys, with $x = 0.05$ and 0.1, the low-temperature activation regions are not observed and the resistivity

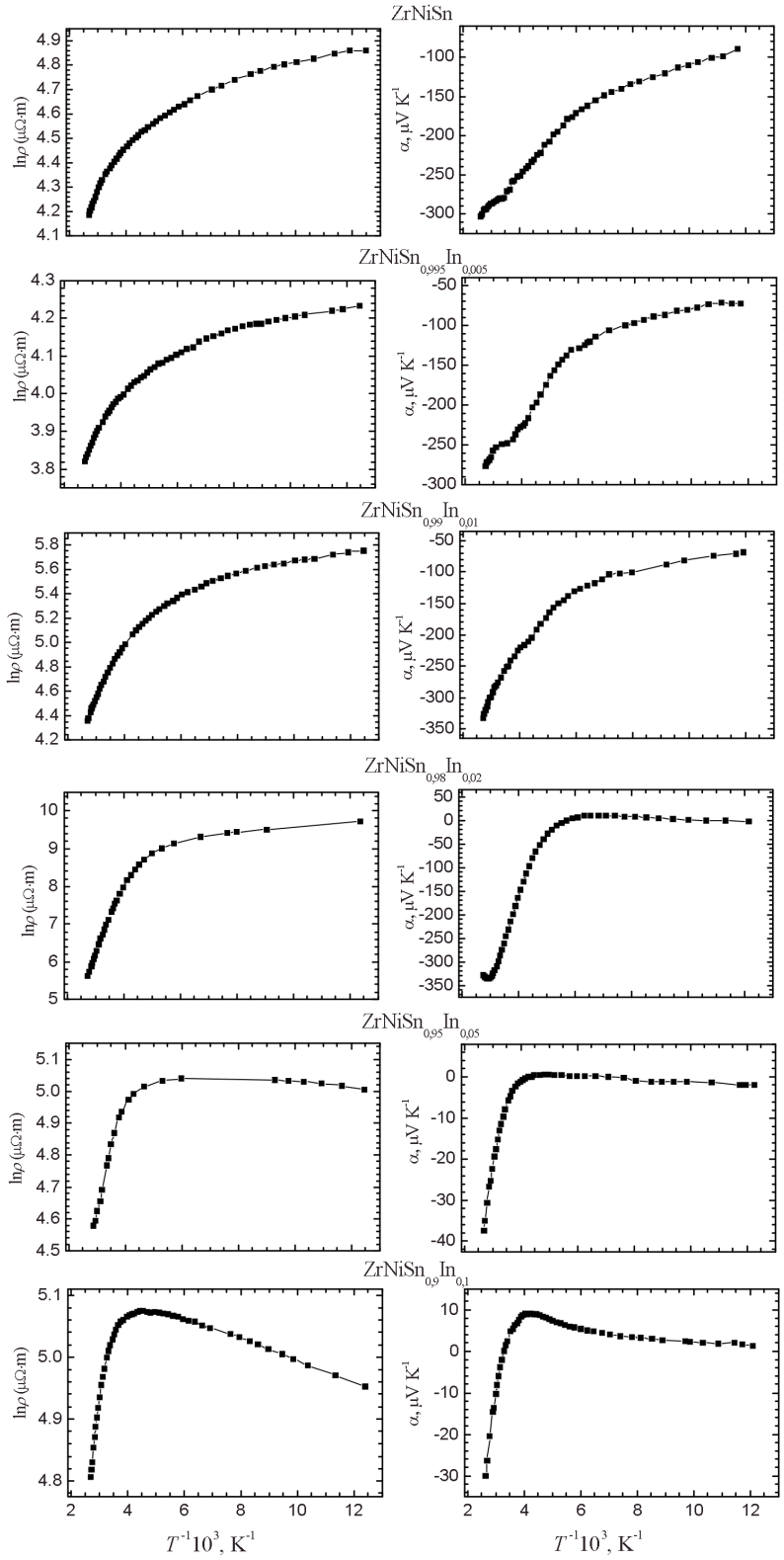

Fig. 2. Temperature dependences of resistivity ρ and the thermopower α for $ZrNiSn_{1-x}In_x$ for different concentration

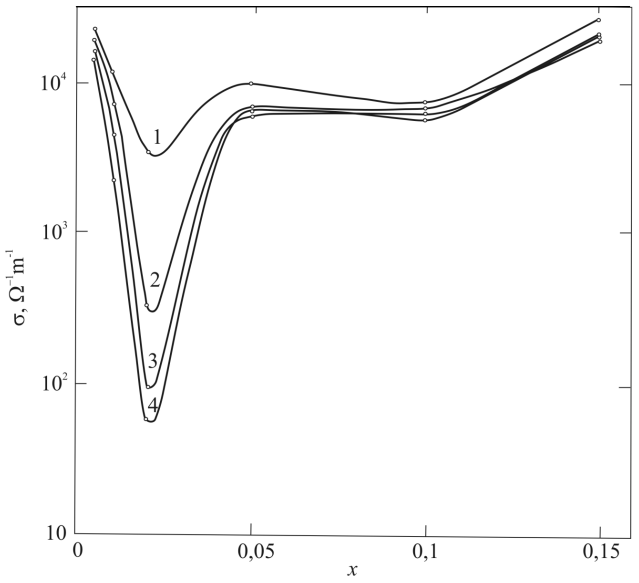

Fig. 3. Dependences of electric conductivity σ on the composition of the $ZrNiSn_{1-x}In_x$ solid solution at temperatures: 370 K (*1*), 250 (*2*), 160 (*3*), and 80 (*4*)

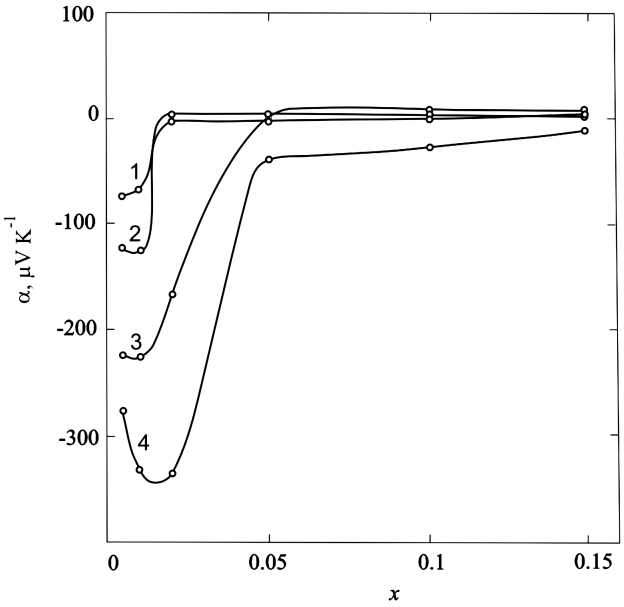

Fig. 4. Dependences of the thermoelectric coefficient α on the composition of the $ZrNiSn_{1-x}In_x$ solid solution at temperatures: 80 K (*1*), 160 (*2*), 250 (*3*), and 370 (*4*)

grows with the temperature rise, which is characteristic of the metallic type of conduction. For the specimens with $x = 0.005$ and 0.01, the low-temperature activation regions are also characteristic of the $\alpha(1/T)$ dependences.

The values of activation energies, ε_1^ρ and ε_1^α, deduced from the high-temperature regions of the $\ln\rho(1/T)$ and $\alpha(1/T)$ dependences, respectively, are presented in the Table for the various concentrations of the donor impurities introduced into *n*-ZrNiSn. The value of ε_1^α was calculated using the expression for the thermoelectric coefficient [12]

$$\alpha = k_B/e(\varepsilon/k_BT - \gamma + 1)$$

and assuming $\gamma = 1$. In ordinary semiconductors, both quantities, ε_1^ρ and ε_1^α, give the value of the energy barrier between a position of the Fermi level which is fixed by the Coulomb gap of the donor impurity band and a mobility edge of the corresponding continuous energy band.

However, as follows from the data of the Table, the activation energies determined in different ways essentially differ from each other. This result, with regard for the remark presented above and the structural studies of the $ZrNiSn_{1-x}In_x$ solid solution, implies that such peculiar features are characteristic of the semiconductors under investigation: (i) a high degree of disorder (compositional fluctuations) [12], (ii) the fluctuations of charged impurities with high values of their concentrations [13], and, as a result, the fluctuations of the continuous energy bands [14]. For this reason, the ordinary approaches which are usually used in the analysis of the weakly doped semiconductors are invalid in our case.

It was shown in work [16] that, in a heavily doped and compensated semiconductor, the activation energy ε_1^α is changed by an increment of the fluctuation band amplitude, and ε_1^ρ varies by the value of the energy distance between the Fermi level and the mobility edge. In this case, ε_1^α cannot be smaller than ε_1^ρ, and this is actually observed in experiment (see the Table). What is more, as a compensation degree grows in an *n*-type semiconductor, the Fermi energy is expected to diminish, while the potential relief – to increase [14], which is also observed in our experiments (see the Table).

We pay attention to the fact that the thermoelectric power reverses its sign at the concentrations of the acceptor impurity in $ZrNiSn_{1-x}In_x$ which correspond to the compositions with $x \geq 0.02$. This means that the overcompensation occurs and the conduction type is changed from the electron to hole one. For the concentrations of the acceptor impurity which correspond to the compositions with $x = 0.01 \div 0.02$, the complete compensation occurs in the semiconductor (Figs. 3 and 4). In this case, according to the Shklovskii–Efros model for a heavily doped and completely

compensated semiconductor [15], the Fermi level should be in the middle of the energy gap, and the energy ε_1^ρ of the carrier activation from the Fermi level to the mobility edge should be maximal. As follows from the data of the Table, it is at $x = 0.02$ that the value of ε_1^ρ reaches a maximum in the $ZrNiSn_{1-x}In_x$ solid solution.

Of interest is the fact that the values of ε_1^ρ and ε_1^α coincide in the case of the complete compensation of the semiconductor ($x = 0.02$) (see the Table). This experimental result is the first direct proof of the Shklovskii–Efros theoretical conclusions [15] that, in a completely compensated semiconductor, the amplitude of fluctuations of the continuous energy bands cannot exceed $\varepsilon_g/2$, and the Fermi level is in the middle of the band gap (see Fig. 1).

In fact, let us agree that, in a heavily doped and compensated semiconductor, ε_1^α and ε_1^ρ are equal, respectively, to the average amplitude of fluctuations of the continuous energy bands [16] and to the energy distance between the Fermi level and the mobility edge [14,15]. Then the values of ε_1^ρ and ε_1^α can only coincide when the semiconductor is completely compensated. In this case, the amplitude of fluctuations and the distance from the Fermi level to the mobility edge equal $\varepsilon_g/2$ (Fig. 1).

The analysis of the $\alpha(x)$ dependences (Fig. 4) shows that the overcompensation phenomenon in $ZrNiSn_{1-x}In_x$ is temperature-dependent. At $T = 80$ K (curve *1*), the $\alpha(x)$ curve exhibits a tendency to the sign reversal at the lowest concentrations of the acceptor impurity ($x = 0.005 \div 0.02$). At higher temperatures, the $\alpha(x)$ curves display a minimum, and such a tendency becomes apparent at $x \approx 0.01$ (80 K $< T <$ 370 K) or 0.015 ($T = 370$ K).

At the concentrations of the acceptor impurity corresponding to the compositions of $ZrNiSn_{1-x}In_x$ with $x > 0.02$, N_A becomes greater than N_D, and we have a heavily doped and strongly compensated p-type semiconductor. The subsequent increase in the acceptor impurity concentration will diminish the compensation degree and, as a result, the decrease in the amplitude of fluctuations of the bands is expected to occur [14]. In this case, the Fermi level drifts towards the valence band and, thus, the distance between the Fermi level and the mobility edge of the valence band is expected to decrease. It is this result that we observe in experiment (see the Table and Figs. 3 and 4).

Concentration and energy characteristics of the $ZrNiSn_{1-x}In_x$ alloys

x	Specimen number	N_A, cm^{-3}	ε_1^ρ, meV	ε_1^α, meV	ε_3^ρ, meV	ε_3^α, meV
0	01	0	28.9	44.6	1.6	11.5
0.005	13	9.5×10^{19}	18.3	64.9	1.0	4.9
0.01	14	1.9×10^{20}	48.7	133.1	2.9	5.0
0.02	39	3.8×10^{20}	182.0	182.6	5.6	–
0.05	40	9.5×10^{20}	42.4	59.0	–	–
0.1	19	1.9×10^{21}	42.0	60.1	–	–
0.15	105	2.9×10^{21}	24.2	24.0	0.3	–

For the specimens which contain the low-temperature activation sections on the $\ln\rho(1/T)$ and $\alpha(1/T)$ dependences, the values of the corresponding activation energies, ε_3^ρ and ε_3^α, were determined (see the Table). As follows from the data of the Table, the growth of the acceptor impurity concentration through the value, where the overcompensation phenomenon occurs, leads to the rise in both the fluctuation amplitude and the hopping conductivity energy ε_3^ρ, which agrees with the results of calculations in [17]. At the same time, one can observe a decrease in the potential well depth for small-scale fluctuations (the value of ε_3^α diminishes from 11.5 to 5 meV). As soon as the potential well depth for small-scale fluctuations gets equal to the hopping conduction energy ($\sim$ 5 meV), the subsequent increase in the acceptor impurity concentration gives rise to the disappearance of the low-temperature activation sections on the $\ln\rho(1/T)$ dependences due to the metallization of conduction. It is the substantial decrease in the depth of small-scale fluctuations that brings about the filling up of the small-scale relief with electrons. As a result, the hopping conduction is no longer observed.

The similar correlation between the fluctuation amplitude and the intensity of its small-scale fluctuations, as well as the phenomenon of the hopping conduction disappearance when ε_3^ρ becomes comparable with ε_3^α, were also observed in the n-ZrNiSn and p-TiCoSb heavily doped with the donor admixture Cu [16, 18].

3. Thermoelectric Power Factor for $ZrNiSn_{1-x}In_x$

It was noted above that the condition for the appearance of the maximal thermoelectric power factor Z^* is the fixation of the Fermi level by the mobility edge of one of the continuous energy bands. Taking into account that ZrNiSn is an n-type semiconductor, we can expect *a priori* proceeding from the results of work [4] that the Fermi level in $ZrNiSn_{1-x}In_x$ will start to drift towards the valence band already at the lowest concentrations of the acceptor impurity. This should result in a substantional diminishing of the Z^* value. The results presented in Fig. 5 are in full compliance with the conclusions of work [4]. It is seen that, for the impurity

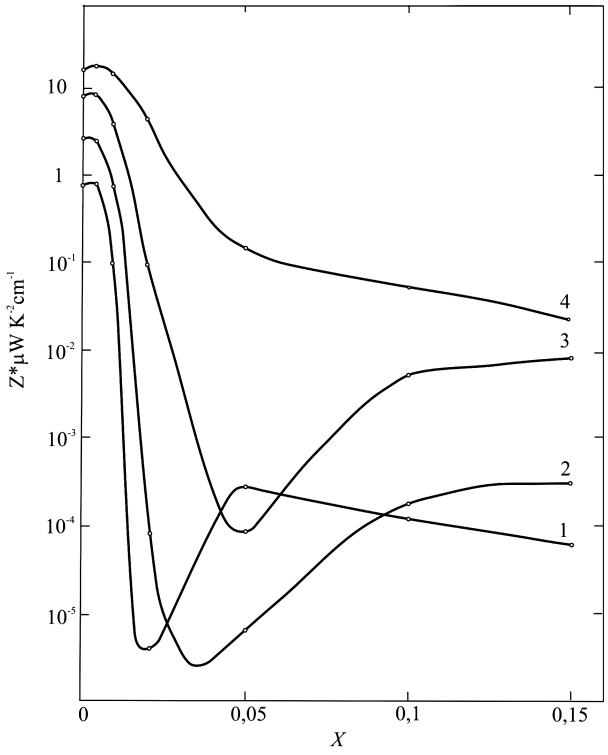

Fig. 5. Dependences of the thermoelectric power coefficient Z^* on the composition of the $ZrNiSn_{1-x}In_x$ solid solution at temperatures: 80 K (*1*), 160 (*2*), 250 (*3*), and 370 (*4*)

concentration region which corresponds to the compositions of $ZrNiSn_{1-x}In_x$ with $0 < x < 0.05$, the decrease in Z^* is observed in the whole temperature range under study, with the width of such concentration region increasing with temperature.

As the Fermi level approaches the mobility edge of the valence band (after the overcompensation has occurred), one can observe the growth of Z^* and the achievement of its maximal value (for example, at $x \approx 0.05$ for $T = 80$ K). As follows from the analysis presented above, it is at these concentrations of the acceptor impurity that the Fermi level crosses the mobility edge of the valence band. Such features of the behavior of the $Z^*(x)$ dependences as the shift of both minimal and maximal values towards the region of higher concentrations of impurities, observed at higher temperatures, confirm the additive influence of temperature and impurity concentration on the value of Z^*. The absence of the minimum on the $Z^*(x)$ dependence at $T = 370$ K, as well as the negative sign of the thermoelectric power coefficient within the temperature range under study, can be a consequence of both the narrowness of the concentration interval under investigation and the high concentration of the non-controlled donor impurities.

4. Conclusions

In summary, the doping of the *n*-ZrNiSn intermetallic semiconductor with the In acceptor impurity is accompanied by a change in the compensation degree of the semiconductor and the drift of the Fermi level from the conduction band towards the valence band. The correlation between the fluctuation parameters of the continuous energy bands, the fluctuation amplitude, and the potential well depth of small-scale fluctuations, predicted in [15,17], is established experimentally. The doping of *n*-ZrNiSn with the In impurity up to the concentrations, which correspond to the compositions of $ZrNiSn_{1-x}In_x$ with $x \leq 0.02$, leads to the rise in the fluctuation amplitude ε_1^α, the energy distance between the Fermi level and the mobility edge ε_1^ρ, and the decrease in the depth of small-scale fluctuations ε_3^α. As x exceeds 0.02, the hopping conductivity disappears due to the smallness of the amplitude of small-scale fluctuations.

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ОСОБЛИВОСТІ ПРОВІДНОСТІ НАПІВПРОВІДНИКОВОГО ТВЕРДОГО РОЗЧИНУ $ZrNiSn_{1-x}In_x$

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Р е з ю м е

Досліджено температурні та концентраційні залежності питомого опору та коефіцієнта термо-ерс напівпровідникового твердого розчину $ZrNiSn_{1-x}In_x$ у діапазонах $T = 80 \div 380$ K, $x = 0 \div 0{,}15$. Вперше показано, що в сильнолегованому та повністю компенсованому інтерметалічному напівпровіднику максимальна амплітуда флуктуації зон неперервних енергій дорівнює половині ширини забороненої зони напівпровідника, а рівень Фермі розташовується посередині забороненої зони. Експериментально встановлено залежність між параметрами флуктуації зон неперервних енергій, глибиною флуктуації та глибиною потенціальної ями дрібномасштабної флуктуації.