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ЗАСТОСУВАННЯ МОДЕЛЕЙ МАШИННОГО НАВЧАННЯ ДЛЯ ЕФЕКТИВНОЇ ОЦІНКИ РУХЛИВОСТІ НОСІЇВ У КРЕМНІЇ

УДК 004.932:537.311:621.382.2

The temperature and concentration dependences of the resistivity ρ and the thermopower coefficient α of a $Zr_{1-x}Y_xNiSn$ intermetallic semiconductor heavily doped with an acceptor Y impurity have been studied in the ranges $T = 80 \div 380$ K and $N_A^Y = 3.8 \times 10^{10}$ cm^{-3} ($x = 0.02$) $\div 4.8 \times 10^{21}$ cm^{-3} ($x = 0.25$). A conclusion on the mechanisms of conductivity in this compound is made. The dependences between the impurity concentration and the parameters of the modulation amplitude of the continuous energy bands have been established. The results obtained are discussed in the framework of the Shklovskii–Efros model for a heavily doped and strongly compensated semiconductor.

Ключові слова: mechanism of defect formation, Shklovskii–Efros model, strongly compensated semiconductor, heavily doped semiconductor.

1. Introduction

In the previous work [1], the structure characteristics of the intermetallic semiconductor n-ZrNiSn heavily doped with an Y impurity have been studied, and the corresponding calculations of the electron density distribution and the band structure have been carried out. The doping of n-ZrNiSn was demonstrated to be accompanied by the ordering of its crystal structure, when the impurity atoms occupy only the positions of Zr ones and generate acceptor-type defects. By detecting the conductivity transition insulator–metal, the existence range of the solid solution $Zr_{1-x}Y_xNiSn$ and the dependences between the impurity concentration, on the one hand, and the direction and the rate of Fermi level drift, on the other hand, have been established. In particular, the introduction of an acceptor Y impurity into the n-ZrNiSn crystal structure is accompanied by a redistribution of the electron concentration, a monotonous motion of the Fermi level from the conduction band edge to the valence band, and its intersection at $x = 0.137$. A conclusion was drawn that the mechanism of hopping conductivity in $Zr_{1-x}Y_xNiSn$ takes place at concentrations of the Y impurity, when the Fermi level is located below the percolation levels in the conduction band or the valence band ($x < 0.137$).

This work is a sequel of work [1]. Here, we report the results of our researches concerning the electrotransport and energy characteristics of n-ZrNiSn heavily doped with an acceptor Y impurity. The temperature dependences of the electroresistivity ρ and the thermopower coefficient α were measured. The impurity concentration was changed in the range from $N_A^Y = 3.8 \times 10^{20}$ cm^{-3} (at $x = 0.02$) to 4.8×10^{21} cm^{-2} (at $x = 0.25$). The techniques applied for the measurements of the electroresistivity and the thermopower coefficient relative to copper in the temperature interval $T = 80 \div 380$ K are discussed in work [2].

2. Electro-Transport Researches of $Zr_{1-x}Y_xNiSn$

The temperature dependences of the electrical resistivity $\ln \rho(1/T)$ and the thermopower coefficient

Рис. 1. Temperature dependences of the resistivity ρ and the thermopower coefficient α for $Zr_{1-x}Y_xNiSn$ at $x = 0.02$ (*1*), 0 (*2*), 0.08 (*3*), and 0.2 (*4*)

$\alpha(1/T)$ of $Zr_{1-x}Y_xNiSn$ are depicted in Fig. 1. They demonstrate that $Zr_{1-x}Y_xNiSn$ specimens with $x = 0 \div 0.08$ reveal semiconducting properties: the resistivity decreases with the temperature growth, and the dependences $\ln\rho(1/T)$ and $\alpha(1/T)$ manifest high- and low-temperature activation sections. The specimen with $x = 0.08$ is an exception: its dependence $\ln\rho(1/T)$ contains no low-temperature activation section. For specimens with the content of Y impurity $x \geq 0.2$, the conductivity has a metallic character, and their electroresistance grows, as the temperature increases. The dependences $\ln\rho(1/T)$ can be approximated with a high accuracy by the known relation

$$\rho^{-1}(T) = \rho_1^{-1} \exp\left(-\frac{\varepsilon_1^\rho}{k_B T}\right) + \rho_3^{-1}\left(-\frac{\varepsilon_3^\rho}{k_B T}\right), \qquad (1)$$

where the first high-temperature term describes the charge carrier activation from the Fermi level onto the percolation level in the continuous energy bands, and the second low-temperature term describes hopping conduction [3].

In turn, the temperature dependences $\alpha(1/T)$ of the $Zr_{1-x}Y_xNiSn$ thermopower coefficient can be approximated by the following formula:

$$\alpha = \frac{k_B}{e}\left(\frac{\varepsilon_V^\alpha}{k_B T} - \gamma + 1\right), \qquad (2)$$

where γ is a parameter dependent on the scattering origin, and, in the case of n-ZrNiSn, it equals 1.04.

The introduction of the lowest concentrations of Y impurity is accompanied by a reduction of the electroconductivity $\sigma(x)$ (see Fig. 2). For instance, at $T = 80$ K, the conductivity diminishes from $\sigma = 7.6\times 10^{-3}$ $(\mu\Omega\times\mathrm{m})^{-1}$ at $x = 0$ to 1.2×10^{-4} $(\mu\Omega\times\mathrm{m})^{-1}$ at $x = 0.02$. Such a behavior of $\sigma(x)$ is connected with a reduction of the density of states at the Fermi level, when the compensation degree in a semiconductor of the electron conductivity type changes owing to the introduction of an acceptor impurity. The minimum in the dependence $\sigma(x)$ corresponds to a state close to the complete compensation of the semiconductor: the concentrations of donor- and acceptor-type defects are almost in equilibrium, and the electroconductivity is caused by free electrons and holes simultaneously, as well as by the hops of charge carriers between localized states. We associate the increase of $\sigma(x)$ at $x \geq 0.02$ with the intersection of the energy gap midpoint by the Fermi level ε_F and with increase in the concentration of free holes by their thermal throwing from the Fermi level onto the percolation level in the valence band.

The character of variations of the thermopower coefficient $\alpha(x)$ in $Zr_{1-x}Y_xNiSn$ agrees with the arguments given above on the simultaneous participation of charge carriers of several types in the electroconductivity. The charge carrier concentration changes as either the number of introduced Y atoms or the temperature varies; this occurs through the variation of the number of ionized acceptors. We connected the decrease of $\sigma(x)$ in the interval $x = 0 \div 0.02$ with a reduction of the contribution made by free electrons of the semiconductor, due to their capture by acceptors. In the same concentration range, the values of $\alpha(x)$ are negative, which testifies to the electron type of conductivity of the semiconductor, whereas a reduction of $\alpha(x)$-values indicates a reduction of the electron contribution to the $Zr_{1-x}Y_xNiSn$ conductivity. The minimum in the dependences $\sigma(x)$, when the concentrations of electrons and holes become close, is associated with the conductivity type change, and the values of $\alpha(x)$ are close to zero there. At Y contents $x > 0.02$ in $Zr_{1-x}Y_xNiSn$, free holes determine the conductivity of the semiconductor, and the positive sign of the thermopower coefficient evidences for that. A practical invariance of $\alpha(x)$-values in $Zr_{1-x}Y_xNiSn$ at $x \geq 0.12$ testifies to the intersection between

Таблиця 1. **Concentration and energy characteristics of $Zr_{1-x}Y_xNiSn$ alloys**

x	N_A, cm^{-3}	ε_1^ρ, meV	ε_1^α, meV	ε_3^ρ, meV	ε_3^α, meV
0	–	28.9	44.6	1.6	11.5
0.02	3.8×10^{20}	61.8	133.4	2.3	2.4
0.05	9.5×10^{20}	16.3	21.1	1.7	2.2
0.08	1.5×10^{21}	12.9	17.3	1.1	0.8
0.12	2.3×10^{21}	8.3	7.9	0	0.7
0.2	3.8×10^{21}	0	8.6	0	0.5
0.25	4.8×10^{21}	0	8.4	0	0.3

Рис. 2. Y-content dependences of the specific conductivity σ (*a*) and the thermopower coefficient α (*b*) of $Zr_{1-x}Y_xNiSn$ at various temperatures: $T = 80$ (*1*), 250 (*2*), and 370 K (*3*)

Рис. 3. Y-content dependences of the activation energies in $Zr_{1-x}Y_xNiSn$: (*a*) ε_1^α (*1*) and ε_1^ρ (*2*), (*b*) ε_3^α (*1*) and ε_3^ρ (*2*)

the Fermi level ε_F and the percolation level in the valence band, i.e. the electroconductivity transition insulator–metal is realized.

Analyzing the high- and low-temperature activation sections in the dependences $\ln\rho(1/T)$ and $\alpha(1/T)$ for $Zr_{1-x}Y_xNiSn$ and using the relations (1) and (2), we calculated the activation energies (see Table). In particular, we determined the energies of activation ε_1^ρ from the Fermi level onto the percolation level in the conduction (valence) band from the high-temperature activation sections in the dependences $\ln\rho(1/T)$ and the activation energies ε_3^ρ of hopping conduction from the low-temperature ones. Similarly, from the analogous activation sections in the dependences $\alpha(1/T)$, we calculated the activation energies ε_1^α and ε_3^α. In work [4], it was shown that the values for ε_1^ρ and ε_1^α determined from the activation sections of the dependences $\ln\rho(1/T)$ and $\alpha(1/T)$, respectively, are substantially different: ε_1^ρ gives the difference between the Fermi and percolation levels, whereas ε_1^α evaluates the amplitude of continuous energy band fluctuations. The activation energies ε_3^ρ and ε_3^α are related to the occupation degree and the amplitude of a small-scale fluctuation, respectively (Fig. 3). On the one hand, the results obtained confirm the conclusions made above on the role of carriers of different types and the mechanisms of conductivity in $Zr_{1-x}Y_xNiSn$. On the other hand, they evaluate the drift rate of ε_F and determine the modulation amplitudes and the "fine structure" parameters of the energy bands [5, 6].

The value $\varepsilon_1^\rho(x = 0) = 28.9$ meV estimates a remoteness of the Fermi level from the mobility edge of the conduction band in *n*-ZrNiSn, which is evidenced by the negative values of $\alpha(x)$. The introduction of the lowest experimental concentration of the Y impurity moves the Fermi level away from the percolation one in the conduction band. The value $\varepsilon_1^\rho(x = 0.02)$ reflects the position of the Fermi level in a practically completely compensated semiconductor – close to the energy gap mid-point. However, in our specimen, there is an insignificant overcompensation by acceptors, which is evidenced by the positive values of $\alpha(x)$. In this case, the value $\varepsilon_1^\rho(x = 0.02) = 61.8$ meV corresponds to the remoteness of the Fermi level from the percolation level in the valence band. A drastic recession in the dependence $\varepsilon_1^\rho(x)$ in the interval $x = 0.02 \div 0.05$, together with a practically linear reduction in the interval $x = 0.05 \div 0.2$, describes the dynamics of the Fermi level drift toward the percolation level in the valence band of $Zr_{1-x}Y_xNiSn$. Basing on the linear character of the dependence $\varepsilon_1^\rho(x)$ in the interval $x = 0.05 \div 0.2$, we determined the drift rate of ε_F toward the conduction band to be $\Delta\varepsilon_F/\Delta x = 1.1$ meV/at.%. The fact that $\varepsilon_1^\rho(x) = 0$ at $x \geq 0.2$ testifies to the intersection between the Fermi level and the percolation level in the valence band. For such specimens, no high-temperature activation sections would be observed in the dependences $\ln\rho(1/T)$ (Fig. 1).

The behavior of $\varepsilon_1^\alpha(x)$ agrees completely with the Shklovskii–Efros model describing the energy state of a heavily doped and compensated semiconductor [5, 6]. Really, in a completely compensated semiconductor, the amplitude of a large-scale fluctuation is maximum, being equal to the activation energy from the Fermi level onto the percolation one, and the Fermi level ε_F is located in the middle of the energy gap. As is seen from Fig. 3, the dependence $\varepsilon_1^\alpha(x)$ is maximum at the $Zr_{1-x}Y_xNiSn$ content, $x \approx 0.02$, close to the complete compensation state. In the latter case, in accordance with the conclusions of work [6], the activation energies ε_1^ρ and ε_1^α coincide. In our case, the values $\varepsilon_1^\rho(x = 0.02) = 61.8$ meV and $\varepsilon_1^\alpha(x = 0.02) = 133.4$ meV are maximum but substantially different. This fact is related to the slight overcompensation of a $Zr_{1-x}Y_xNiSn$ specimen with $x = 0.02$. Above the overcompensation of $Zr_{1-x}Y_xNiSn$ (at $x > 0.02$), the reduction of $\varepsilon_1^\alpha(x)$-values testifies to a decrease of the continuous energy band modulation amplitude, which is accompanied by the ordering of the semiconductor crystal structure.

From Fig. 3, it also follows that the behaviors of the $Zr_{1-x}Y_xNiSn$ dependences $\varepsilon_1^\rho(x)$ and $\varepsilon_1^\alpha(x)$ correlate with each other. It is also true for the potential well depth of a small-scale fluctuation $\varepsilon_3^\alpha(x)$ and the occupation degree of this potential well, the latter being proportional to the energy of hopping conduction $\varepsilon_3^\rho(x)$. As soon as the potential well depth becomes less than 0.8 meV ($x = 0.12$), the activation energy of hopping conduction is nullified—the small-scale relief of the valence band becomes "flooded" with holes,

and electrons are activated from the Fermi level onto the percolation one in the valence band only.

3. Conclusions

Thus, the results of electro-transport researches dealing with the doping of n-ZrNiSn with an acceptor Y impurity agree with the results of structural researches and the calculations of the electron density distribution and the band structure of the semiconductor. It is shown that the doping of n-ZrNiSn with an Y impurity allows a predictable control over the fabrication of thermoelectric and thermometric substances with preassigned properties. On the basis of the results given above, we may assert that the obtained semiconductor solid solution $Zr_{1-x}Y_xNiSn$ is a promising thermoelectric substance.

The work was sponsored by the National Academy of Sciences of Ukraine (grant No. 0106U000594) and the Ministry of Education and Science of Ukraine (grants Nos. 0109U002069 and 0109U001151).

ДОДАТОК А. Оцінка рухливості відповідно до моделі Klaassen (Philips)

В цьому випадку для обчислення рухливості як електронів, так і дірок, незалежно від того, чи вони є основними чи неосновними носіями, застосовують схожі формули з різними коефіцієнтами. А саме

$$\mu^{\mathrm{K}} = \frac{\mu_{\mathtt{L}} \cdot \mu_{\mathtt{DA}}}{\mu_{\mathtt{L}} + \mu_{\mathtt{DA}}}\,, \qquad \text{(Д.1.1)}$$

де

$$\mu_{\mathtt{L}} = \mu_{\max}\left(\frac{300}{T}\right)^{2{,}25}, \qquad \text{(Д.1.2)}$$

$$\mu_{\mathtt{DA}} = \frac{\mu_{\max}^2}{\mu_{\max}-\mu_{\min}} \cdot \frac{N_{\mathrm{sc}}}{N_{\mathrm{eff}}} \cdot \left(\frac{N_{\mathrm{ref}}}{N_{\mathrm{sc}}}\right)^{\alpha} \cdot \left(\frac{T}{300}\right)^{3\alpha-\frac{3}{2}} + \\ + \frac{\mu_{\max}\,\mu_{\min}}{\mu_{\max}-\mu_{\min}} \cdot \frac{n+p}{N_{\mathrm{eff}}} \cdot \left(\frac{300}{T}\right)^{\frac{1}{2}}, \qquad \text{(Д.1.3)}$$

а константи, що входять до рівнянь (Д.1.2)-(Д.1.3) наведені у Табл. Д.1.1.

Величини N_{sc} та N_{eff} є функціями, вигляд яких залежить від типу носіїв, а саме при визначенні рухливості електронів

$$N_{\mathrm{sc}} = N_d^+ + N_a^- + p\,, \qquad \text{(Д.1.4а)}$$

$$N_{\mathrm{eff}} = N_d^+ + N_a^- \cdot G_n(P_n,T) + \frac{p}{F_n(P_n,T)}\,, \qquad \text{(Д.1.5а)}$$

Таблиця Д.1.1. **Коефіцієнти для розрахунку рухливості відповідно до моделі Klaassen, формули (Д.1.2)-(Д.1.3)**

Тип носіїв	Параметр			
	$\mu_{\max}$, $\frac{\text{см}^2}{\text{В·с}}$	$\mu_{\min}$, $\frac{\text{см}^2}{\text{В·с}}$	α	N_{ref}, см^{-3}
Електрони	1414	68,5	0,711	$9,2 \cdot 10^{16}$
Дірки	495	44,9	0,719	$2,23 \cdot 10^{17}$

а для дірок

$$N_{\mathrm{sc}} = N_a^- + N_d^+ + n\,, \qquad \text{(Д.1.4б)}$$

$$N_{\mathrm{eff}} = N_a^- + N_d^+ \cdot G_p(P_p,T) + \frac{n}{F_p(P_p,T)}\,. \qquad \text{(Д.1.5б)}$$

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Received 22.01.22

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MACHINE LEARNING MODELS FOR EFFICIENT MOBILITY ESTIMATION IN SILICON

Досліджено вплив акцепторної домішки Y на зміну

Таблиця Д.1.2. **Concentration and energy characteristics of $Zr_{1-x}Y_xNiSn$ alloys**

x	N_{A}, cm^{-3}	ε_1^{ρ}, meV	ε_1^{α}, meV	ε_3^{ρ}, meV	ε_3^{α}, meV
0	–	28.9	44.6	1.6	11.5
0.02	3.8×10^{20}	61.8	133.4	2.3	2.4
0.05	9.5×10^{20}	16.3	21.1	1.7	2.2
0.08	1.5×10^{21}	12.9	17.3	1.1	0.8
0.12	2.3×10^{21}	8.3	7.9	0	0.7
0.2	3.8×10^{21}	0	8.6	0	0.5
0.25	4.8×10^{21}	0	8.4	0	0.3

питомого електроопору (ρ), коефіцієнта термо-ерс (α), енергетичних характеристик інтерметалічного напівпровідника n-ZrNiSn у діапазонах: $T = 80 - 380$ K, $N_{\text{A}}^{Y} \approx 3,8 \cdot 10^{20}$ см$^{-3}$ ($x = 0{,}02$)–$4{,}8 \cdot 10^{21}$ см$^{-3}$ ($x = 0{,}25$). Зроблено висновки про механізми електропровідності $Zr_{1-x}Y_xNiSn$. Встановлено залежності між концентрацією домішки та характеристиками амплітуди модуляції зон неперервних енергій. Обговорення результатів проводиться у межах моделі сильнолегованого і сильнокомпенсованого напівпровідника Шкловського–Ефроса.

K e y w o r d s: механізм дефектоутворення, модель Шкловського–Ефроса, сильнокомпенсований напівпровідник, сильнолегований напівпровідник.