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FEATURES OF FORMATION OF RESISTIVE STATES WITH ABNORMALLY SMALL TEMPERATURE COEFFICIENTS OF ELECTRICAL RESISTANCE IN THE HETEROGENEOUS SYSTEMS FeSi–FeSi$_2$

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An approach describing the influence of thermoelectric effects on the electrical resistance of the heterogeneous system metal–semiconductor is developed. The values of the parameters for which the minimum values of the temperature coefficient of resistance are realized are calculated using the heterogeneous system FeSi–FeSi$_2$ as an example. It is shown that a marked influence on the electrical resistances in certain temperature intervals can be attained by creating temperature drops different in value at the specimen ends.

Semiconductor and submetallic silicides of transition metals are promising materials for electronic engineering [1, 2]. The analysis of experimental data on their electronic properties shows that temperature and concentration transitions of the semiconductor–metal type occurring in silicides of transition metals with abnormally low temperature coefficients of electrical resistance are mainly responsible for the formation of their resistive state [3–5]. However the nature of the formation of the temperature coefficients of electrical resistance in electron transformations which are observed in heterogeneous systems based on the silicides of transition metals has not been studied at present [6]. In particular, this is true of the heterogeneous systems FeSi–FeSi$_2$ [7], where we have electron transitions caused by a change in the topology and concentration of the monosilicide and disilicide phases. The submetallic phase FeSi experiences a sudden closing of the gap between the valence band and the conduction band (due to the splitting of these bands in fluctuating exchange fields [5]), while FeSi$_2$ is a semiconductor with the band gap $E_g = 0.2$ eV (which remains constant with change in the temperature).

In this connection, of interest is computer simulation of the features of flow of a current in the heterogeneous systems submetal–semiconductor using FeSi–FeSi$_2$ with different geometry of the conducting phases as an example. It should be borne in mind that the influence of the additional heat fluxes occurring due to thermoelectric effects on the character of electric flows which is possible in such systems has not yet been studied [8].

To compute the effective electrical conductivity of a heterogeneous system we use the equations of electrotransfer and heat transfer:

$$\mathbf{j} = -\frac{\sigma}{e}\,\mathrm{grad}\,(e\varphi - \mu)\; S\sigma\,\mathrm{grad}\,T\,, \quad \mathbf{q} = \frac{\pi}{e}\,\mathbf{j} - \chi\,\mathrm{grad}\,T\,. \tag{1}$$

In calculating the effective electrical conductivity of a heterogeneous system, we primarily find the distribution of the electrochemical potential $\tilde{\varphi}(x, y) = \varphi(x, y) - \frac{\mu(x, y)}{e}$ and of the temperature $T(x, y)$ over the specimen. To find the electrochemical potential in the vicinity of the arbitrary point (x, y) we subdivide the heterogeneous region into N finite cells each of which is homogeneous. The finite cell is used as the analog of an infinitely small vicinity of the point (x, y). By virtue of the finite size of the cell the functions defined in this region cannot be linear. In the ith cell $(i = 1, ..., N)$, we determine the electrochemical potential $\varphi_i(x, y)$ and the temperature $T(x, y)$ in the form of quadratic functions

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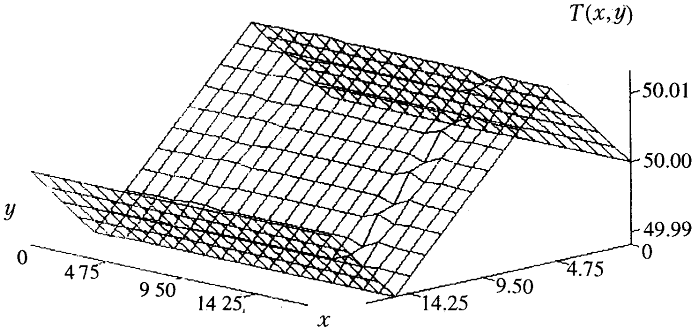


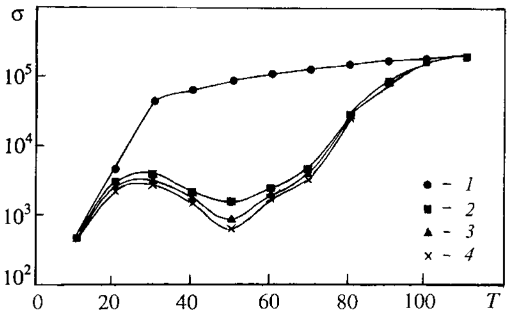


Fig. 1. Local distribution of the temperature in the FeSi–$FeSi_2$ system in calculating the electrical conductivity at a temperature point of 50 K.

Fig. 2. Temperature dependence of the electrical conductivity of the FeSi–$FeSi_2$ system: 1) without account taken of thermal effects; 2–4) with account taken of thermal effects (the temperature drop between the ends of the specimen is, respectively, 1, 3, and 5 K). σ, 1/(Ω·m); *T*, K.

$$\tilde{\varphi}_i(x,y) = a_{i,1}x^2 + a_{i,2}y^2 + a_{i,3}xy + a_{i,4}x + a_{i,5}y + a_{i,6}\,,$$
$$T_i(x,y) = a_{i,7}x^2 + a_{i,8}y^2 + a_{i,9}xy + a_{i,10}x + a_{i,11}y + a_{i,12}\,, \qquad (2)$$

where the coefficients $a_{i,j}$ are to be determined.

The electrochemical potential and the temperature are found from the assumption that the physical processes occurring in the vicinity of the point (x, y) depend on the physical properties of the vicinity itself of the point (electrical conductivity, thermal conductivity, thermoelectromotive force, and chemical potential of the vicinity of the point are considered to be prescribed) and on the conditions at the boundary of this vicinity. At the boundary which divides two neighboring cells, the average values of the electric current and the heat flux and the average values of the electrochemical potential and the temperature which are computed on the source side of both regions are equal by virtue of the continuity of these functions. The absence of the sources of electric charges and heat is taken into account by the equations

$$\oint_{S_i} \operatorname{grad} \tilde{\varphi}_i d\mathbf{s} = 0\,, \quad \oint_{S_i} \operatorname{grad} \tilde{T}_i d\mathbf{s} = 0\,, \qquad (3)$$

where S_i is the surface bounding the cell volume V_i.

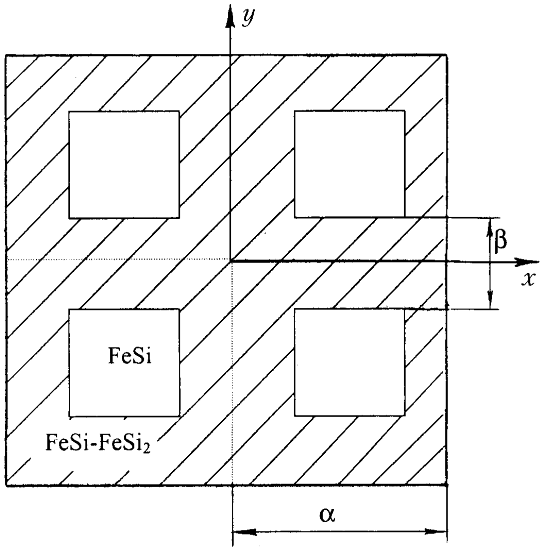
To unambiguously describe the physical processes in the system we must supplement Eqs. (1)–(3) with the following boundary conditions. We prescribe the heat flux and the flow of electricity and the electric potential and the temperature on the left side of the specimen (at the boundary of one cell). On the right side of the specimen (at the boundary of one cell), these quantities are not determined; the fluxes and flows and the potentials at this boundary of the cell must be obtained by solution of a system of algebraic equations. The adiabaticity condition is imposed on the remaining boundary of the specimen.

The conditions of equality of the potentials and the fluxes and flows at the boundary which divides two neighboring cells and Eqs. (3) for each cell and the boundary conditions for the heterogeneous system give the system of linear algebraic equations relative to the coefficients a_{ij}.

To determine the effective electrical conductivity of the heterogeneous system we have the following formula:

$$\sigma_{\text{ef}} = \frac{I}{\Delta\varphi}\,. \qquad (4)$$

Next we note that for structures which are in parallel to the electric current or perpendicular to it the approach developed in the work yields a complete agreement with the well-known analytical formulas of parallel or series connection of semiconductors and, with account taken of the thermoelectric effects, with the formulas obtained in [9].



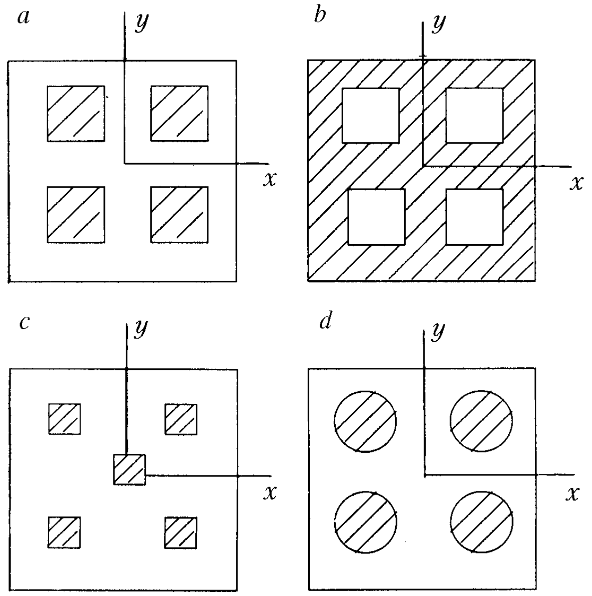


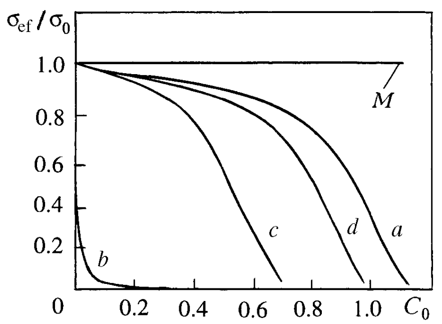
Fig. 3. Two-dimensional system formed by square FeSi grains along the boundaries of which the segregates of $FeSi_2$ are concentrated.

Fig. 4. Geometry of the eutectic of the FeSi–$FeSi_2$ system.

If the width of the interphase boundary is considered to be negligibly small, the temperature T and the electrochemical potential $\tilde{\varphi}$ will be continuous functions of coordinates in the heterogeneous system. The physical processes occurring in a homogeneous system in determining the electrical conductivity can be established by analysis of system (1). The flow of electrons transfers the Peltier heat, which is essentially the kinetic energy of the electrons. Thus, if the system experiences a heat flux equal to the Peltier heat the temperature gradient at any site of the specimen is equal to zero and the electrical conductivity is determined by the first equation of system (1) as the ratio of the current density to the electric-potential gradient. However the situation becomes more complicated when the heterogeneous systems have a complex geometric distribution of the components. In this case a heat flux must pass through the specimen due to the difference in the kinetic energy of the charge carriers in the components of the heterogeneous system. Thus, local temperature gradients will occur in the system when the temperature drop average over the specimen is equal to zero. The electrical conductivity of the system will be determined not only by the concentration of the components and their spatial arrangement but by the temperature dependence of the partial kinetic coefficients and their chemical potentials as well.

Figure 1 shows the temperature distribution in the FeSi–$FeSi_2$ system with the central square inclusion of the second component; the concentration of $FeSi_2$ is 0.25. The fact that the Peltier fluxes of FeSi and $FeSi_2$ are dissimilar leads to the heat exchange of the system with the thermostat. When the temperature drop between the ends of the specimen is nonzero the electrical conductivity can sharply change. Figure 2 shows the polytherms of electrical conductivity of the FeSi–$FeSi_2$ system for the structure with the central inclusion of $FeSi_2$ (the concentration of $FeSi_2$ is 50%). The first curve corresponds to the electrical conductivity calculated without account taken of thermal effects (the temperature along the specimen is constant). The remaining curves correspond to the electrical conductivity calculated with account taken of the Peltier heat for temperature drops of 1, 3, and 5 K along the specimen. From the analysis of the curves it is seen that in the vicinity of the temperature which corresponds to the maximum thermoelectromotive force the electrical conductivity with account taken of thermal effects is substantially lower than the electrical conductivity without account taken of them. The behavior of the curves is different only in the temperature region in which the electron thermal conductivities of the components are low (χ(50 K)$\approx$ 0.5 W/(m·K)) and the thermoelectromotive force of one component is rather large (S_{FeSi}(50 K)$\approx$ 700 μV/K) [10, 11].

In the region of room temperatures where the thermoelectromotive force of $FeSi_2$ attains values of 250 μV/K, the computations do not yield such a difference in the values of the electrical conductivity with account taken of ther-



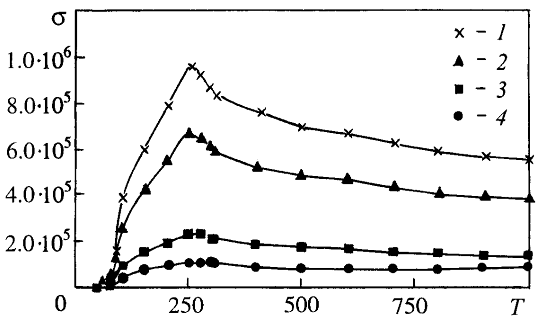


Fig. 5. Relative effective electrical conductivity of the heterogeneous system FeSi–FeSi$_2$ vs. concentration of FeSi$_2$ at $T = 300$ K. C_0, %.

Fig. 6. Temperature dependence of the effective electrical conductivity for a heterogeneous structure with eutectic *a* for concentrations of FeSi$_2$ in the eutectic of (%): 1) 0.85, 2) 0.64, 3) 0.25, and 4) 0.04. σ, 1/(Ω·m); *T*, K.

moelectric effects and without account taken of them since in this region of temperatures the electron thermal conductivities of the components are rather high.

For calculations we considered the heterogeneous systems formed by square FeSi grains along the boundaries of which the segregates of FeSi$_2$ are concentrated (hatched region in Fig. 3). The grain size is equal to α and the thickness of the two-phase boundary region is β; it is also taken into account that the boundary region is characterized by its heterogeneous structure [12]. The schemes of these heterogeneous systems are shown in Fig. 4. The above conducting systems correspond not only to thin films of the composition FeSi–FeSi$_2$ but also to polycrystalline three-dimensional structures in which the current pattern is two-dimensional (plane) [13, 14].

The effective electrical conductivity σ_{ef} of the heterogeneous system shown in Fig. 3 was calculated in two steps:

(1) the effective electrical conductivities σ_{ef} in the region of grain boundaries (hatched region in Fig. 3) which are characterized by the heterogeneous structures *a*–*d* (see Fig. 4) were computed;

(2) the effective electrical conductivities of the heterogeneous system were determined with account taken of the computed electrical conductivity of the hatched region.

Figure 5 shows the dependences of the relative effective electrical conductivity of the heterogeneous systems at issue (corresponding to structures *a*–*d* in Fig. 4) on the concentration of iron disilicide which are calculated for the relative thickness of the boundary region $\delta = 0.01$ (σ_0 is the electrical conductivity of monosilicide at a temperature of 300 K); *M* are the dependences of the effective electrical conductivity which occur in the case of a uniform distribution of the particles of the second phase in the grain (they are calculated from the Maxwell formula [15]). From the figure it is seen that the concentration of the segregates of the second phase along the grain boundaries leads to a sharp change in the value of the electrical conductivity as compared to the homogeneous system. The character of the concentration dependence of σ_{ef} substantially depends on the geometry of inclusions. For the critical concentrations C_c when the disilicide particles in the boundary region begin to join a sharp decrease in the electrical conductivity occurs and the metal–semiconductor transition is realized.

Figure 6 shows the characteristic polytherms of the relative electrical conductivity of the heterogeneous system FeSi–FeSi$_2$ with structure *a*. From the figure it is seen that the change in the content of the second phase leads to the transition from the dependence σ(*T*) which is characteristic of FeSi (curve 4) to a polytherm of the semiconductor type (curve 1). It should be noted that selection of the values of the concentrations of the second phase and the shape of inclusions makes it possible to obtain the state with a nearly zero temperature coefficient of electrical resistance in a comparatively wide interval of temperatures (see, for example, Fig. 6, curve 2).

Thus, using the analysis of the thermoelectric properties of the heterogeneous system FeSi–FeSi$_2$ as an example, one can see that by selecting the concentration and geometry of the inclusions of the second phase one can control the values of the temperature coefficients of electrical resistance, creating, in particular, rather low values of them. One can attain a marked influence on the electrical conductivity in certain temperature intervals by creating temperature drops different in value at the specimen ends.

Furthermore, from the analysis made it follows that the electron transitions in the heterogeneous systems in question are possible even in the case of small deviations from the stoichiometric composition of iron silicides and are related to a large extent to the uncontrolled geometry of the specimen. The latter circumstance seems important for other heterogeneous systems in which the value of the specific electrical resistances of the components markedly differ.

NOTATION

$\mathbf{j}$, density of the flow of electricity; $\mathbf{q}$, density of the heat flux; σ, specific electrical conductivity; χ, specific thermal conductivity; S, differential thermoelectromotive force; π, Peltier coefficient; e, electron charge; φ, electric potential; μ, chemical potential; T, temperature; I, electric current; $\tilde{\varphi}$, electrochemical potential; $\Delta\varphi$, electric-potential difference; α, grain size; β, thickness of the two-phase boundary region in the grain; $\delta = \beta/\alpha$, relative thickness of the boundary region in the grain.

REFERENCES

1. S. P. Murarka, *Silicides for VLSI Applications* [Russian translation], Moscow (1986).
2. L. I. Vinokurova, A. V. Vlasov, and É. T. Kulatov, *Tr. IOFAN*, **32**, 26–66 (1991).
3. P. V. Gel’d, A. A. Povzner, and A. G. Volkov, *Dokl. Akad. Nauk SSSR*, **283**, No. 2, 358–360 (1985).
4. P. V. Gel’d, A. A. Povzner, Sh. Sh. Abel’skii, and L. F. Romasheva, *Dokl. Akad. Nauk SSSR*, **313**, No. 5, 1107–1109 (1990).
5. A. G. Volkov, A. A. Povzner, V. V. Kryuk, and P. V. Bayankin, *Fiz. Tverd. Tela*, **41**, Issue 10, 1792–1796 (1999).
6. A. G. Volkov, A. A. Povzner, V. V. Kryuk, and P. V. Bayankin, *Fiz. Tverd. Tela*, **41**, Issue 6, 1054–1056 (1999).
7. Z. Schlezinger, Z. Fisk, H.-T. Zhang, M. B. Maple, J. F. Di-Tusa, and G. Aeppli, *Phys. Rev. Lett.*, **71**, No. 11, 1748–1751 (1993).
8. I. N. Sachkov and A. A. Povzner, *Fiz. Tverd. Tela*, **38**, No. 10, 2969–2972 (1996).
9. G. N. Dul’nev and V. V. Novikov, *Transport Processes in Inhomogeneous Media* [in Russian], Leningrad (1990).
10. B. Buschinger, C. Geibel, F. Steglich, D. Mandrus, D. Young, J. L. Sarrao, and Z. Fisk, *Physics B*, **230–232**, 784–786 (1997).
11. M. B. Hunt, M. A. Chernikov, E. Felder, H. R. Ott, Z. Fisk, and P. Canfield, *Phys. Rev. B*, **50**, No. 20, 14933–14941 (1994).
12. I. N. Sachkov, A. G. Gofman, F. A. Sidorenko, and P. V. Gel’d, *Izv. Vyssh. Uchebn. Zaved.*, *Fizika*, No. 5, 17–23 (1996).
13. S. I. Vecherskii and F. A. Sidorenko, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **27**, No. 1, 117–120 (1991).
14. S. I. Vecherskii and F. A. Sidorenko, *Poroshk. Metall.*, No. 8, 64–68 (1992).
15. E. A. Mityushov, P. V. Gel’d, and R. A. Adamesku, *Generalized Conductivity and Elasticity of Macrohomogeneous Heterogeneous Materials* [in Russian], Moscow (1992).