Journal of Engineering Physics and Thermophysics, Vol. 74, No. 1, 2001

CONDITIONS FOR FORMATION OF A ZERO TEMPERATURE COEFFICIENT OF RESISTANCE IN MATRIX SYSTEMS OF METAL–SEMICONDUCTOR

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UDC 537.311+536.212

Using the method of finite elements, the authors have calculated the parameters of a heterophase metal–semiconductor system for which the minimum temperature coefficients of resistance (TCRs) are realized. The temperature-concentration region in which the TCR acquires values approaching zero has been established.

In developing resistive materials, multiphase compositions in which the resistivity polyterms $\rho(T)$ are U-shaped draw particular attention [1]. These materials are characterized by a certain critical temperature T_c in the vicinity of which states with vanishingly small values of the temperature coefficient of resistance (TCR) (of the order of several units of 10^{-6} K^{-1}) are realized. The main problem of resistive materials science is searching for methods for controlled displacement of the minimum of the U-shaped characteristic $\rho(T)$ and methods for decreasing its curvature sharply to obtain vanishingly small TCRs in the working temperature range.

Such systems represent composite resistive materials which are heterogeneous multiphase systems consisting of fine particles (100–1000 Å) with conductivity of the metal and semiconductor type. As the conducting phase, use is commonly made of palladium oxides, ruthenium oxide, bismuth ruthenate, and palladium and silver alloys, while various lead boron aluminosilicate glasses are used as the semiconducting phase [1, 2]. Changing the concentration ratio and the geometry of the phase components, one is able to control both the sign of the TCR and the position of the $\rho(T)$ minimum. In practice the temperature of the minimum of $\rho(T)$ has a very large spread and often it is beyond the limits of the working temperature range. The problem of optimization of the composition and structure of the resistive material can be solved using the methods of computer-assisted modeling of the processes of electrotransfer in a heterophase system.

At present there are several principal methods that allow calculation of the conductivity of multiphase materials. They include methods based on leakage theory [3] and the theory of effective media [4]. A common drawback of these methods lies in the impossibility of taking into account the effect of the geometry of inclusions on the system's conductivity. The geometry of inclusions is taken into account in the method of sectionalization of a medium by adiabatic and isopotential surfaces that has been developed in the works of G. N. Dul'nev [5]. However, the Dul'nev method does not allow determination of the exact value of the effective conductivity, it only points to the limits, within which its actual value must lie [6]. It should be noted that the authors of the mentioned works have not investigated the problem of formation of polytherms of resistance of different types and have not established conditions for the occurrence of states with zero values of the TCRs. This has been the task Vasilenko et al. have set themselves in [7], where the domain of existence of a zero TCR is determined in the approximation of a matrix-statistical structure and it is shown that a resistive material with a zero TCR can be obtained only for $0.1 < A \cdot B < 10$, where A is the specific conductivity of the semiconductor at an infinitely high temperature and B is the specific conductivity of the

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Ural State Technical University, Ekaterinburg, Russia. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 74, No. 1, pp. 153–155, January–February, 2001. Original article submitted June 23, 2000.

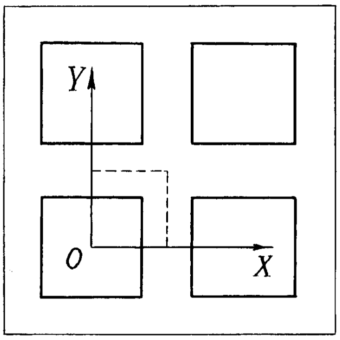


Fig. 1. Scheme of the cross section of a heterogeneous structure.

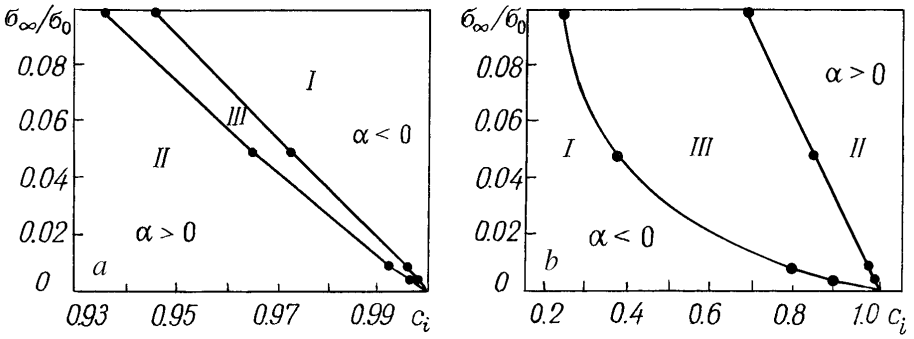


Fig. 2. Conditions for realization of states with negative (I) and positive (II) TCRs and with a U-shaped polytherm $\rho(T)$ (III): a) system with semiconducting inclusions; b) with metal inclusions. The temperature range investigated is 0–400°C.

metal at 273 K. One result of this work is the fact that the temperature T_c at which the TCR vanishes is independent of the concentration of the conducting phase, which contradicts the results of numerous experiments [1, 2].

In the present work with the aid of the method of finite elements [8] numerical modeling of two-phase metal–semiconductor systems has been carried out with the aim of revealing the values of the material parameters at which minimum TCR values are realized. Numerical calculations of resistance polytherms $\rho(T)$ have been done for two-phase metal–semiconductor systems characterized by a matrix structure with square inclusions, the centers of which form a square grid. Consideration is given to the cases of a semiconductor matrix with metal inclusions and a metal matrix with semiconductor inclusions. A cross section of the heterogeneous structure discussed is shown schematically in Fig. 1.

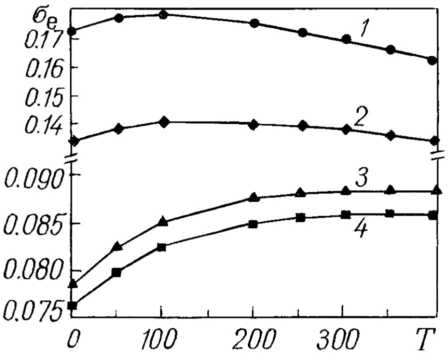
To calculate the effective conductivity of the system, we single out an elementary cell that is a square with one of its vertices being at the center of a square inclusion. In Fig. 1 the cell is bounded by the dashed line. We choose the origin of the rectangular coordinate system (X, Y) at a cell vertex and direct the axes along its sides.

We apply an electric field along the axis OY. The spatial distribution of the current density in this system was established from the functional extremum condition:

$$\chi = \int_V J^2/\sigma dV .$$

The effective conductivity of the heterogeneous system is

$$\sigma_e = \langle J \rangle / \langle J/\sigma \rangle ,$$



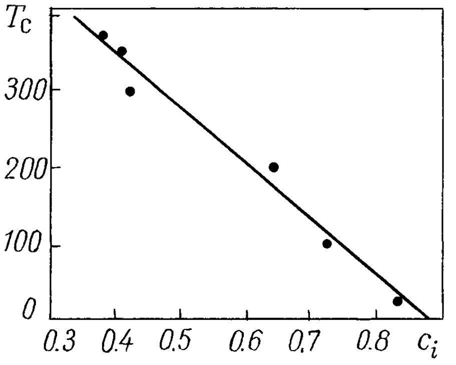


Fig. 3. Effective conductivity σ_e as a function of the temperature T for a semiconducting matrix with metal inclusions, $\sigma_\infty/\sigma_0 = 0.05$, and inclusion concentrations c_i equal to 0.3844, 0.4225, 0.64, 0.7225 for curves 1–4, respectively. σ_e, arbitrary units; T, °C.

Fig. 4. Temperature T_c at which the TCR becomes zero as a function of the inclusion concentration c_i. The matrix is a semiconductor, the inclusions are a metal, $\sigma_\infty/\sigma_0 = 0.05$.

where $\langle\ \rangle$ indicates averaging over the sample volume V.

The dependences of the specific conductivities of the metal and semiconductor phases were established using the conventional expressions

$$\sigma_m = \sigma_0/[1 + \alpha\,(T - 273)]\,, \quad \sigma_s = \sigma_\infty \exp\,(-E/kT)\,.$$

In calculations we used the following values of the parameters: $E = 0.01$ eV, $\alpha = 1/273\ \mathrm{K}^{-1}$. The influence of the constants σ_0 and σ_∞ on the TCR of the heterogeneous system can be characterized by the ratio σ_∞/σ_0. This ratio represents a dimensionless parameter that was varied within the limits of 0.05–0.1.

The relative error of the effective conductivity calculated by the method of finite elements was determined from the Dykhne reciprocity relation [9]: $\sigma_e\sigma_e^D = \sigma_m\sigma_s$, where σ_e^D is the effective conductivity of a dual system obtained from the initial one by cyclic substitution of the materials of the matrix and the inclusions, and did not exceed 1–2%.

As a result of the numerical analysis carried out, it was found that with change in the concentration of the inclusions and the ratio σ_∞/σ_0 three qualitatively different situations are realized (see Fig. 2): 1) negative TCRs, 2) positive TCRs, 3) a transient region in which the resistance polytherm is U-shaped. In the latter region conditions for realization of a zero-TCR state appear. As is seen from the figure, a change in the topology of the particles of the semiconducting phase exerts a substantial influence on the shape of the diagrams presented. In the case of a semiconducting matrix, the transient region is substantially broader than in the metal phase. Moreover, in the case of a semiconducting matrix with metal inclusions, a zero TCR is formed only for high concentrations of the inclusions. The diagrams presented in Fig. 2 make it possible to predict the electrical properties of a heterogeneous system.

In the formation of a U-shaped resistance polytherm, there exists a temperature region in which the TCR acquires values approaching zero. For this case Fig. 3 provides characteristic curves describing the dependence of the effective conductivity of a heterogeneous system on the temperature $\sigma(T)$.

The temperature T_c of the maximum of the dependence $\sigma(T)$ decreases with increase in the concentration of the metal component, which completely agrees with experimental results [1, 2]. As is shown in Fig. 4, the dependence of the temperature T_c at which the TCR becomes zero on the concentration of the inclusions is linear. Consequently, the temperature in the vicinity of which the TCR acquires its minimum values for different concentrations of the inclusions can be predicted using the linear approximation $T_c(c_i)$.

Thus, the analysis of the domain of existence of a zero TCR carried out in the present work has shown that for development of composite resistors it is preferable to synthesize materials with a semiconducting matrix and metal inclusions.

Our numerical calculations make it possible to determine the necessary characteristics in the properties of the initial components (concentration, σ, TCR) for obtaining resistor materials with optimum characteristics. Furthermore, it should be noted that the employed method of finite elements makes it possible to take into account the size and shape of the inclusions. This provides the possibility of predicting the physical characteristics of experimental samples and giving recommendations on optimization of the composition and structure of resistive materials.

In conclusion, we note that use of the numerical modeling suggested in the present work can turn out to be very useful from the practical viewpoint as well since it allows one to reduce the range of experimental studies carried out so far only by the method of empirical search.

NOTATION

$\rho(T)$, polytherm of specific resistance; T, temperature; T_c, temperature of the maximum conductivity of the heterophase medium; χ, functional; J, local current density of the heterophase medium; V, volume of the elementary cell; σ_e, effective conductivity of the heterogeneous system; σ_m, conductivity of the metal phase; σ_{01}, specific electrical conductivity of the metal at the temperature $t = 0^oC$; α, temperature coefficient of resistance of the metal; σ_s, conductivity of the semiconducting phase; σ_∞, specific electrical conductivity of the semiconductor at $T \to \infty$; E, activation energy of the semiconductor; k, Boltzmann constant; c_i, concentration of the inclusions.

REFERENCES

1. K. I. Martyushov, *Obzory Élektron. Tekh., Ser. 5, Radiodetali Komponenty*, Issue 2 (1108), Moscow (1985).
2. K. I. Martyushov, *Obzory Élektron. Tekh., Ser. 5, Radiodetali Komponenty*, Issue 3 (683), Moscow (1979).
3. B. Shklovskii and A. Éfros, *Electronic Properties of Doped Semiconductors* [in Russian], Moscow (1979).
4. S. Kirkpatrick, *Phys. Rev. Lett.*, **27**, 1722–1725 (1971).
5. G. N. Dul'nev and V. V. Novikov, *Transport Processes in Inhomogeneous Media* [in Russian], Leningrad (1991).
6. I. N. Sachkov, *Zh. Tekh. Fiz.*, **66**, No. 2, 48–58 (1996).
7. O. A. Vasilenko, A. A. Maier, V. A. Chashchin, et al., *Inzh.-Fiz. Zh.*, **49**, No. 3, 477–481 (1985).
8. P. V. Gel'd, I. N. Sachkov, A. G. Gofman, and F. A. Sidorenko, *Dokl. Akad. Nauk SSSR*, **315**, No. 3, 604–607 (1990).
9. B. Ya. Balagurov, *Zh. Éksp. Teor. Fiz.*, **81**, No. 2, 665–671 (1981).