MATHEMATICAL AND COMPUTER MODELING OF INTERPHASE INTERACTION IN HETEROGENEOUS SOLID STRUCTURES

Volodymyr Yuzevych[1]
Bohdan Koman[2]

DOI: https://doi.org/10.30525/978-9934-26-195-4-14

Abstract. *The aim* of this work was to develop a mathematical model and computer modelling of interphase interaction, mechanical stresses and adhesion mechanisms between mechanically inhomogeneous media (different phases). *Methodology*. For the system "metal – dielectric" we use a macroscopic approach, which corresponds to the ratio of non-equilibrium thermodynamics and physics of solid surfaces. Let's consider the system of equations and boundary conditions for describing the change of energy parameters (σ_h, γ), which characterize the thermodynamic state of the system of contacting bodies. Method for calculating the main energy parameters (interfacial energy – γ_m, interfacial tension – σ_m, work of adhesion – A_{ad} and energy of adhesive bonds – γ_{ad}) in complex solid-state structures containing boundary phases is proposed. Based on the basic equations of nonequilibrium thermodynamics and surface physics a mathematical model of the interphase boundary is designed. A comparative analysis of the features of interphase interaction in the systems "metal-metal", "metal-semiconductor" and "metal-dielectric" on the example of interacting systems "Cu – Zn", "Cu – Si" and "Cu – quartz". It is established that the most sensitive parameter in the analysis of interphase interactions is the interphase energy γ_m.

A model of mechanical stress formation in the "condensate-substrate" system is proposed. In particular, internal stresses in metal condensates are caused by changes in the value of interphase energy parameters (primarily interfacial tension) in the substrate-nanocondensate system and due to

---

[1] Doctor of Physical and Mathematical Sciences, Professor,
Karpenko Physico-mechanical Institute of the NAS Ukraine, Ukraine

[2] Doctor of Physical and Mathematical Sciences, Professor,
Professor Department of System Design,
Lviv National Ivan Franko University, Ukraine

phase-forming processes accompanied by changes in surface energy in the condensate volume during its formation. The resulting internal stresses in metal condensates are an integral result of the action of statistically distributed on the plane of the film local stresses. Such phenomena are due to the anisotropy of the energy parameters of the interphase interaction in the condensate plane.

Behavior analysis of energy and adhesion parameters can be used to predict the results of interphase interaction in order to select contact pairs to create thermodynamically stable structures with predicted values of energy parameters of interphase interaction, a certain type of chemical bond and a given level of mechanical stresses.

1. Introduction

Modern functional materials are, as a rule, complex heterophasic systems with formed internal boundaries of the contact phase. In such systems, due to the physico-chemical, thermodynamic and mechanical incompatibility of the boundary phases, a complex interphase interaction occurs. Understanding the physical nature of such interaction opens the prospect of effective targeted change in the properties of materials and the creation of unique nanostructures.

These structures are also characterized by the evolution of phase formations in the process of formation, which is accompanied by a change in the surface energy of the system and, as a consequence, a change in its basic structurally sensitive parameters. Typical solid-state structures “semiconductor-metal”, “dielectric-metal”, “semiconductor (1) – semiconductor (2)” and graphene-based, as well as more complex compositions are used today as basic elements of modern micro- and nanoelectronics. They are characterized by the presence of interfacial boundaries, which are characterized by mechanical stresses, localized charges, linear defects, impurities and other imperfections. All this generally has a negative impact on the performance of such structures and their stability.

The greatest results in the study of interphase phenomena have been achieved for the systems “liquid (melt) – solid” and “liquid (melt) – vapor” [1–9]. However, the problem of interphase interaction in the system “solid body (1) – solid body (2)” (between mechanically inhomogeneous regions (E_1, E_2)) has not been studied today. The situation is complicated by the fact that modern experimental methods do not allow direct measurements to determine the interphase energy parameters, in particular the energy of the interphase interaction.

Thus, the ability to control surface processes at the interface is an important factor in solving the problem of obtaining materials with predictable physicochemical properties. Understanding the nature of mechanical stresses is also relevant, as their basic concepts were formulated in the in the middle of the last century mainly from a macroscopic standpoint. However, today they are no longer able to explain the peculiarities of their origin and evolution at the interphase boundaries of micro- and nanoobjects. Adhesion processes at the boundary of two media in modern literature are presented only descriptively and are fragmentary. However, the monograph [10] forms the general principles of such interaction for a number of structural materials according to which the main quantitative parameters are the energy of interfacial interaction γ_m and interfacial tension σ_m.

Thus, the outlined problem requires a comprehensive approach in the study of the interaction of two phases using the analysis of physicochemical, thermodynamic and mechanical compatibility of interacting phases.

2. Interfacial energy at the interface of solid media

Despite the significant amount of work devoted to the study of surface and interfacial properties of solids and melts, the theory and practice of these phenomena are still far from complete. It should be noted that the greatest progress in the study of interphase phenomena has been achieved today for the system of melt (liquid) – solid phase. Indicative in this aspect are the classical Jung equation, which is used to describe the interphase interaction in the system “ liquid medium – solid phase” for about 200 years and a significant number of works, including monographs [1; 7; 9] on this issue. In particular, Jung showed for the first time that the surface energies of the separation of solid and gas phases σsp, liquid and gas phases σ_{cp} are related by equation [1]:

$$2\,\sigma_{sp} = \sigma_{cp}\,(1+\cos\Phi_z) \qquad (1)$$

where Φ_z is the limiting angle of wetting of single-phase cast material. Therefore, by depositing a drop of liquid with known surface energy on the surface of a solid, it is possible to calculate the surface energy of the solid phase by the value of the critical wetting angle.

However, solving the problem of interphase interaction in the system “sol.st.(1) – sol.st.(2)”currently remains in its infancy. Nevertheless, knowledge of the energy parameters of such interaction is essential for modern nanotechnology and the creation of new structures for components of nano- and microelectronics. The problem is complicated by the fact that the existing modern experimental techniques do not allow direct measurements to determine the interfacial energy. In the literature there are only fragmentary data on the interfacial interaction of solid phases. In particular, in [11] surface phenomena during recrystallization of metals are considered, and interphase phenomena between solid metal phases. The influence of the substrate, thermodynamic supersaturation and stress mismatch between the emerging phase and the substrate are discussed in [12]. Based on the energy distribution of the nearest neighbors in [11] derived a formula and calculated the surface energy at the boundary of polymorphic α – and β – phases of tin, and in the Thomas-Fermi method was used to calculate the surface (in this case actually interfacial) energy at the boundary of two contacting dissimilar metals.

The calculated values in the order of magnitude coincide with the experimental data.

In general, it should be noted that the consistent theory of surface (interfacial) energy at the boundary “solid (1) – solid (2)” does not exist today. A significant breakthrough in this problem was the work [13], which obtained a general thermodynamic formula that allows us to estimate the surface energy at different interfacial boundaries, including at the boundary “solid phase – solid phase”.

However, the problem can also be considered from another angle. In particular, the authors [14] propose to solve it within the framework of the thermodynamic theory of the origin of a new phase in a solid. The kinetics of phase transformations in the solid phase is determined by the fluctuation of the centers of the new phase and their subsequent growth. Since the rate of nucleation and growth of the centers depend on the surface energy of the interface between the original and new phases, the volume of the transformed phase is directly related to the surface energy σtk at the solid-crystal nucleus boundary. It has been experimentally established that the formation of a crystalline nucleus on a solid-state substrate is easier than homogeneous nucleation, as follows from the general thermodynamic representations.

The action of the substrate can be associated with a decrease in the value of the interfacial energy of the interface “solid phase – crystalline nucleus” compared to the surface energy of the nucleus at the interface with steam or melt.

For surface energy at the boundary “solid – crystalline nucleus” the equation is obtained:

$$\sigma_{ТК} = \sigma_{РП} \cdot \left[\left(\frac{2 - 3\cos\theta + \cos^3\theta}{4} \right)^{2/3} + \left(\frac{2 - 3\cos\theta + \cos^3\theta}{4} \right)^{1/3} \cos\theta \right], \quad (2)$$

which is true for $0 < \theta > 180$. Here σрп is the surface energy at the liquid-vapor boundary, θ is the edge angle of wetting of a solid with liquid. The results of calculations based on this formula are in good agreement in order of magnitude with the data obtained by other methods [11].

The monograph [1] proposes a simple theoretical estimate of the surface energy of the separation of two solid phases. In particular, for typical metals it is evaluated:

$$\sigma_{\alpha\beta} = 0,268 \cdot \left[\frac{\Delta(H_{Mt})_{\alpha}}{(\alpha V_{Mt})^{2/3}} - \frac{\Delta(H_{Mt})_{\beta}}{(\beta V_{Mt})^{2/3}} \right],$$

where $\Delta(H_{Mt})_{\alpha}$, $\Delta(H_{Mt})_{\beta}$ is the molar heat of fusion of metals α and β, respectively, (αV_{Mt}), (βV_{Mt}) their atomic (molar) specific volumes.

It is established that, other things being equal, the interfacial energy of a solid at the boundary with a crystal is less than the corresponding value of the interfacial energy of the interface “solid phase – melt”, which is obviously due to the smaller difference in the binding energy of the solid phases.

3. Thermodynamic description of interphase interactions in composite systems

Research energy parameters (interfacial energy – γ_m, interfacial tension – σm, work of adhesion – A_{ad} and energy of adhesive bonds – γ_{ad}) of the interphase interaction is based on the considerations of the macroscopic approach, culminating in the model relations of nonequilibrium thermodynamics and solid state surface physics [2–4].

For the system “metal – dielectric” we use a macroscopic approach, which corresponds to the ratio of non-equilibrium thermodynamics and physics of solid surfaces. Let's consider the system of equations and boundary conditions for describing the change of energy parameters (σ_h, γ), which characterize the thermodynamic state of the system of contacting bodies [10; 15].

Relations for the thermodynamic model of the surface layer of metal (x > 0) (quasistatic situation) can be represented in Cartesian coordinates x, y, z (where x is perpendicular to the interface) in the form:

$$Div\,\hat{\sigma} + \rho \cdot \omega \cdot \vec{E} = 0, \quad \Delta\phi = \rho \cdot C_{\phi} \cdot \phi / \varepsilon_0 \,, \tag{3}$$

$$\phi = -\Phi_0; \quad \phi + \psi = const; \qquad \sigma_x = -\frac{\varepsilon_0}{2} \cdot \left(\frac{\partial \Psi}{\partial x}\right)^2 \text{ if x = 0}, \tag{4}$$

$$\sigma_{ij} = \left(\left(K - \frac{2}{3}G\right)e - \alpha_t K \cdot \Delta T - K(\beta\phi + \beta_c c)\right)\delta_{ij} + 2Ge_{ij}\,, \tag{5}$$

$$\omega_V = \rho\omega = \rho C_{\phi}(\phi - \gamma_t \cdot \Delta T) + \beta K e - \rho\eta_c c, \tag{6}$$

$$\mu_c = d_c c + d_t \cdot \Delta T + \beta_c K \frac{e}{\rho} - \eta_c \phi, \quad \Delta T = T - T_0, \tag{7}$$

$$\sigma_h = \int_0^h \sigma_y dx, \quad \sigma_y = \sigma_z, \;\; \gamma = \gamma_e + \xi\gamma_d, \tag{8}$$

$$\frac{\partial\gamma}{\partial k} = \frac{\partial(\gamma_e + \xi\gamma_d)}{\partial k} = 0, \quad k = \sqrt{\frac{\rho \cdot C_{\phi}}{\varepsilon_0}}\,, \tag{9}$$

$$\sigma_y + p = 0 \text{ (for } x = h) \tag{10}$$

Here γ, σ_h – surface energy (SE) and the surface tension in the case of contact of the metal with inert gas atmosphere (air) with the pressure p = 100 kPa; $\gamma_e = \int_0^h w_e dx$ – electric component of γ; $w_e = \frac{\varepsilon_0}{2}\left(\frac{\partial\Psi}{\partial x}\right)^2$ and $w_d = \frac{\sigma_x(\sigma_x - 4\nu\sigma_y)}{2E} + \frac{(1-\nu)\sigma_y^2}{E}$ – densities of the electrical and mechanical components of the SE; $\gamma_d = \int_0^h w_d dx$ – mechanical component of SE; h – effective thickness of the surface layer; σ_{ij}, e_{ij} – tensors of mechanical stress and strain (i, j = 1,2,3); $\sigma_{11} = \sigma_{xx} \equiv \sigma_x$; $\sigma 22 = \sigma_{yy} \equiv \sigma_y$;

μ_c, c – chemical potential and the concentration of impurities; δ_{ij} – Kronecker symbols; e – the first invariant of the strain tensor; ρ – density of the material; ω_v, ω – volumetric and mass charge density, respectively; $\varphi = \Phi - \Phi_0$ – deviation of the modified chemical potential Φ of the electrical charges from its equilibrium value Φ_0 in the volume of the body at a distance x > 30 nm from the surface ($\Phi = M_e/z_e$, M_e – chemical potential of the conduction electron of the metal; ze – electric charge per unit mass of the conduction electrons ($[M_e]$ = J/kg, $[z_e]$ = C/kg, $[\Phi]$ = C)); Ψ – the potential of the electric field ($[\Psi]$ = V); $\psi = \Psi - \Psi_0$ – deviation of the potential Ψ from its equilibrium value Ψ_0; $\vec{E} = \nabla\Psi = grad\Psi$ – the amplitude of the electrical field; $\varepsilon_0 = 8{,}85 \cdot 10^{-12}$ F/m – electric constant; $\Delta T = T - T_0$ – temperature change; K, G – the bulk modulus and shear modulus; E, ν – Young's modulus and Poisson's ratio; $C\varphi$– capacitance; k – the inverse value of the distance, at which the volume charge in the surface layer varies by a factor e; β – electrostrictive coefficient of thermal expansion; ξ – coefficient (dimensionless) that characterizes the change in γ when changing the mechanical component γd, for condition when the electric component γe remains unchanged $\left(\frac{\partial\gamma}{\partial\gamma_d} |_{\gamma_e = const} = \xi \right)$; α_t, β_c, γ_t, η_c, d_c, d_t – physical characteristics of the material (metal) which are included in the equation of state (4), (5) and (6) [10]. For more adequate fit of the model given by eq. (3–10) to the modern physical notions, it is necessary to take into account the offset Z_b of the electron double layer with respect to the boundary of the solid (metal). For this purpose we use a well-known formula [10]:

$$Z_b = \frac{3}{4k_F}\left(\frac{\pi}{2} + \left(\frac{5E_V}{3E_F} - 1 \right) \arcsin\sqrt{\frac{3E_F}{3E_F + 5E_V}} - \sqrt{\frac{5E_V}{3E_F}} \right), \qquad (11)$$

where E_F – Fermi energy, E_V – the work function of the conduction electron and k_F – Fermi wave vector. By setting the values of γ and σ_h (SE and tension) in eq. (8) – (10) (taking into account eq. (3) – (7), (11)), we obtain a system of 4 equations. In this case we can determine the values of ξ, k, β and geometrical characteristics h of the surface layer for the metal, which is in contact with an inert gas atmosphere (air) at a pressure p = 100 kPa. Using the value of k, we can find $C\varphi$ and Φ_0 with the help of the eq. (9) and (11):

$$C_{\phi} = \frac{\varepsilon_0 \cdot k^2}{\rho}, \quad \Phi_0 = \frac{q_0 W_e}{2\varepsilon_0 k^2} \cdot \left(2 - \exp\left(-kZ_b\right)\right), \tag{12}$$

where W_e – the bulk density of the conduction electrons of the metal away from the surface (at a distance of more than 30 nm, $[W_e] = 1/\mathrm{m}^3$).

For most of metals values of the surface tension σ_h are determined experimentally [11]. The surface energies γ of the metals are determined both experimentally and theoretically. Among the theoretical studies one should note partial results obtained for a number of metals using the method of density functional [16; 17]. According to the authors, the empirical formula for γ in steel [18] has good consistency with the experimental data. Hence it has been applied for a number of other metals:

$$\gamma = a_R \cdot \frac{E_V}{R^2} - a_C, \tag{13}$$

where R – atomic radius, a_R, a_C – empirical constants ($a_R = 7128$; $a_C = 110$ J/m^2).

Surface tension σh and surface energy γ are connected by Hering's relation [19]:

$$\sigma_h = K_R \left(\gamma + \Xi \left(\frac{\partial \gamma}{\partial \Xi} \right)_T \right), \tag{14}$$

where K_R – factor for matching dimensions ($[K_R] = \frac{N \cdot m^2}{m \cdot J}$), since $[\sigma_h] = \frac{N}{m}$; $[\gamma] = \frac{J}{m^2}$; Ξ – surface area and $\left(\frac{\partial \gamma}{\partial \Xi} \right)_T$ represents the change of the surface energy during surface layer deformation at a constant temperature.

Based on the model, wherein the interfacial layer consists of two parts, the interfacial energy γm and interfacial tension σm at the interface between the substrate (semiconductor or insulator) – metal are defined by the following relations:

$$\sigma_m = \int_{-H}^{H} \sigma_y dx, \quad \sigma_y = \sigma_z, \tag{15}$$

$$\gamma_m = \gamma_e + \xi_m \gamma_d, \ \gamma_e = \int_{-H}^{H} w_e dx, \ \gamma_d = \int_{-H}^{H} w_d dx. \tag{16}$$

Here ξ_m-physical characteristics of the interfacial layer (dimensionless)

$\left(\frac{\partial\gamma_m}{\partial\gamma_d}|_{\gamma_e=const}=\xi_m\right)$; $2H$ – its effective thickness; γ_e, γ_d – electrical and mechanical components of the interfacial energy γ_m respectively, as in eq. (8).

Finally, by the analogy to the equilibrium condition of the surface layer we can write the equilibrium condition for the interfacial layer as in [15]:

$$\frac{\partial\gamma_m}{\partial k}=\frac{\partial(\gamma_e+\xi_m\gamma_d)}{\partial k}=0. \tag{17}$$

Boundary conditions. Let us formulate boundary conditions for metal – insulator (or semiconductor) interface (at x = 0) which corresponds to the electrical double layer. This interface is formed by conduction electrons from the side of metal and by bounded electrical charges from the side of dielectric [10]:

$$\phi_+=-\Phi_0;\quad z_-=-Z_e;\quad j_x^+=j_{xe}^-;\quad \sigma_y^+=\sigma_y^-;\qquad \sigma_x^+=\sigma_x^-;$$

$$\Psi^+=\Psi^-;\quad \vec{u}^+=\vec{u}^-;\quad E_\tau^+=E_\tau^-;\quad D_x^+-D_x^-=\Omega, \tag{18}$$

where $\sigma_x^\pm$, $\sigma_y^\pm=\sigma_z^\pm$ – mechanical stresses along directions which are perpendicular to the interface between two media respectively; $\vec{u}^\pm$ displacement; $E_\tau^\pm$ – tangential component of the electrical field; $D_x^\pm, P_x^\pm$ – components of the electrical field induction and polarization vectors respectively are directed along the normal (axis x) towards the plane of interface (x = 0); Ω – density of the surface (excess, uncompensated) charges (created by free electrons). If the metal surface is not charged from the outside, then Ω = 0.

The work of adhesion A_{ad} and adhesive bonds energy γ_{ad} are defined based on the known relations [15]:

$$A_{ad}=\sigma_h+\sigma_{ph}-\sigma_m,\quad \gamma_{ad}=\gamma+\gamma_p-\gamma_m, \tag{19}$$

where σ_{ph} and γ_p – surface tension and energy of a dielectric which contacts with an inert gas medium (air) in which the pressure is 100 kPa.

4. Peculiarities of interphase interaction in the systems “copper – metal (Zn)”, “copper – semiconductor (Si)” and “copper – dielectric (quartz)”

As an example of the application of the above thermodynamic description and quantitative comparison, we analyze the interphase interaction in “alternative” and at the same time typical systems: “copper – metal (Zn)”, “copper – semiconductor (Si)” and “copper – dielectric (quartz)”. have an excellent nature of the near-surface layers (bound charges – metal and dipole complexes – dielectric, semiconductor). This comparison will allow to analyze the features of the interfacial layers between solids with significantly different surface charge and different mechanical parameters without using complex information about the specifics of the band surface structure of each of the contacting solids.

In the calculations we use the following numerical values of physical constants for copper (indices (+)), zinc (indices (-)), silicon (-), quartz (-):

E + = 118 GPa; $\nu_+ = 0.372$; $\omega_+ = 8.45 \cdot 1028$ 1/m^3;
$\sigma h_+ = 2.125$ N/m, $\gamma_+ = 1.623$ J/m^2 (Cu);

E– = 81 GPa; $\nu_- = 0.25$; $\omega_- = 13.1 \cdot 1028$ 1/m^3;
$\sigma_{h-} = 0.9$ N/m, $\gamma_- = 1.01$ J/m^2 (Zn);

E– = 70 GPa; $\nu_- = 0.25$; $\omega_- = 7.92 \cdot 1028$ 1/m^3;
$\sigma_{h-} = 1$ N/m, $\gamma_- = 0.737$ J/m^2 (quartz).

Here, the values of surface energies γ_+, γ_- were obtained using the method of atomic interactions and relations (16).

According to calculations using the method of decomposition by a small parameter (small parameter for metal – $b_м = b\Phi_0$; for semiconductor or dielectric – $b_{мс} = b_c \cdot Z_c$) within the system of equations (3–11) due to the solution of contact and contact-boundary value problems for room temperature values of energy and adhesion characteristics of the material of the interfacial layer:

a) “Cu – Zn” system – $\gamma_m = 0.089$ J/m^2; $\sigma_m = 0.112$ N/m; $A_{ad} = 3.023$ N/m;

$z_a = A_{ad} / \sigma_m = 27.0$; $W_{ad} = 2.434$ J/m^2; $z_{ad} = W_{ad} / W_m = 27.3$; $z_e = \gamma_3 / W_m = 0,0376$. (2.12)

b) “Cu – quartz” system – $\gamma_m = 0.307$ J/m^2; $\sigma_m = = 0.44$ N/m; $A_{ad} = 2.685$ N/m;

$z_a = A_{ad} / \sigma_m = 6.1$; $W_{ad} = 2.053$ J/m^2; $z_{ad} = W_{ad} / W_m = 6.68$; ze = $\gamma_3 / W_m = 0.133$. (2.13)

The electrical components of the interphase energy in the contact metals “Cu – Zn” ($z_{ea} = 0.0376$) and in the systems “Cu – Si” (zeb = 0.111), “Cu – quartz” ($z_{ec} = 0.133$) differ significantly, respectively, by 2.95 and 3.54 times ($z_{eb}/z_{ea} = 0.111 / 0.0376 = 2.95$; $z_{ec}/z_{ea} = 0.133 / 0.0376 = 3.54$).

It was found that the energy of γad adhesion bonds in the systems "Cu – Zn", "Cu – Si", "Cu – quartz" does not differ much in absolute value (W_{ada} = 2.43 J/m^2, W_{adb} = 2, 55 J/m^2, W_{adc} = 2.05 J/m^2). However, the ratio z$_{ada}$ = W_{ada}/W_m for the system of two metals (z_{ada} = 27.3) is several times greater than that in the system "metal – nonmetal" ($z_{adb} = W_{adb}/W_m$ = 9,9; $z_{adc} = W_{adc}/W_m$ = 6,68),), ie z_{ada}/z_{adb} = 2,76; z_{ada}/z_{adc} = 4,09.

For the systems "Cu – Zn", "Cu – Si", "Cu – quartz" specific numerical values of interphase tension σ_m, interphase energy W_m, adhesion work Aad and new energy characteristic of the interfacial layer – energy of adhesion bonds W_{ad}, which exceeds the interfacial energy W_m. Approximately the same number of times the work of adhesion A_{ad} is greater than the interfacial tension σ_m. In particular, for systems: "Cu – Zn" – $z_{ada} = W_{ada}/W_m$ = 27,3, $z_{aa} = A_{ada}/\sigma_m$ = 27,0; "Cu – Si" – $z_{adb} = W_{adb}/W_m$ = 9,9, $z_{ab} = A_{adb}/\sigma_m$ = 8,87; "Cu – quartz" – $z_{adc} = W_{adc}/W_m$ = 6,68, $z_{ac} = A_{adc}/\sigma_m$ = 6,10).

In order to compare with $z_e = \gamma_3/W_m$ (z_{ea} = 0,0376, z_{eb} = 0,111, z_{eb} = 0,133) we write the data of the ratio $z1 = \gamma_1/\gamma$, obtained on the basis of (3– 9) $z_1 = \gamma_1/\gamma$ = 0,221 (Cu), z_1 = 0,209 (Zn), z_1 = 0,241 (Si), z_1 = 0,242 (quartz). (20)

We can conclude that the contact of the two media causes both absolute and relative reduction of the power of the electric double layer near the interface, which follows from the differences between the relative components of energy characteristics z_e and z_1.

Of practical interest for real systems are the temperature dependences of interphase energy γm, interphase tension σ_m and interphase electric charge Q. For example, for the system "Cu – Zn" such dependences are calculated within the temperature range [0; 1 000oC], presented in Figure 1.

We emphasize that the experimental dependences of the surface tension σ_h on the temperature in the range [0; 1 000°C] for copper, zinc, quartz, silicon are linear. They are test for estimating temperature changes of energy values γ_+, γ_- using the method of atomic interactions and taking into account the centrally symmetric potential of the central forces of Born-Mayer [10]:

$$u_{\alpha\beta} = \frac{q^2}{R_{\alpha\beta}} - \frac{c_{\alpha\beta}}{R_{\alpha\beta}^6} - \frac{d_{\alpha\beta}}{R_{\alpha\beta}^8} + b_{\alpha\beta} \cdot \exp\left(\frac{R_{\alpha\beta}}{\rho_q}\right), \tag{21}$$

where q is the electric charge of the particles; $R_{\alpha\beta}$ is the distance between the particles α and β; cαβ, $c_{\alpha\beta}$, $d_{\alpha\beta}$, $b_{\alpha\beta}$ – constants (for materials); ρ_q is the "stiffness" parameter.

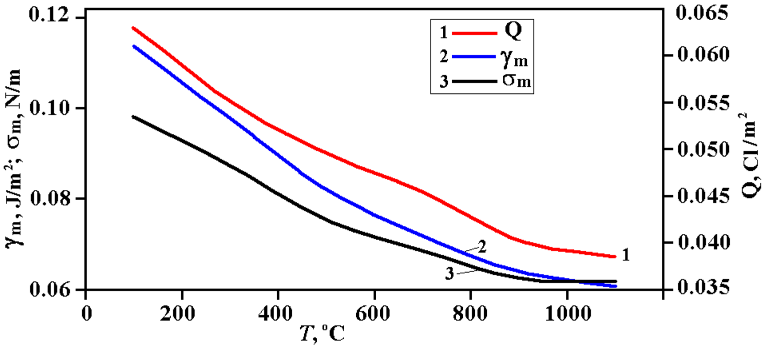

Figure 1. Temperature dependences of interphase energy γ_m, = f_1 (T), interphase tension σ_m = f_2 (T) and interphase electric charge Q = f_3 (T) for the system "Cu – Zn"

From the calculations it is established that the energy values γ_+, γ_- for copper and zinc are in the range [0; 1 000°C] have a temperature dependence close to linear.

Dependences of interphase energy γm, interphase tension σm, interphase electric charge Q on temperature in the range T = [0; 1 000°C] for "copper-quartz" and "copper-silicon" systems are similar to those for "Cu – Zn" and differ only quantitatively.

As we can see from the corresponding graphs (Figure 1), the dependences of the interphase physical quantities $\gamma_m = f_1(T)$, $\sigma_m = f_2(T)$, $Q = f_3(T)$ are nonlinear and their relative changes in the range [0; 1 000°C] can be quantified using the ratios:

$$\Delta w = 2(W_{m0} - W_{m1000}))/(W_{m0} + W_{m1000}) = 0{,}457;$$

$$\Delta\sigma = 2(\sigma_{m0} - \sigma_{m1000})/(\sigma_{m0} + \sigma_{m1000}) = 0{,}657;$$

$$\Delta \mathrm{Q} = 2(Q_0 - Q_{1000})/(Q_0 + Q_{1000}) = 0{,}484. \qquad (22)$$

Here the indices (0), (1000) correspond to the limit temperatures $T = 0$°C and $T = 1\ 000$°C.

According to (22) it can be stated that of the analyzed parameters W_m, σ_m, Q undergoes the most significant temperature changes.

Similar dependences are shown in Figure 2, in particular: adhesion energy $W_{ad} = f_4(T)$, adhesion work $A_{ad} = f_5(T)$, the ratio of the electrostatic

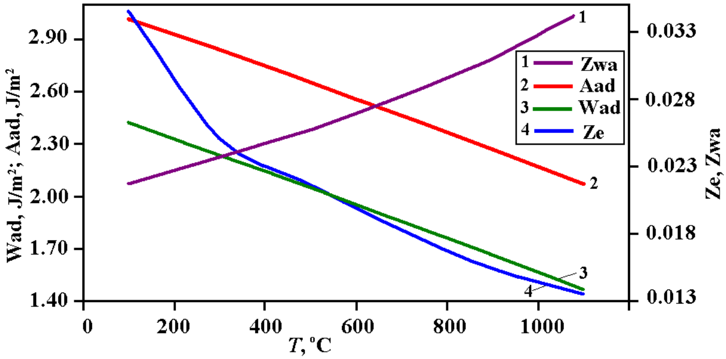

Figure 2. Temperature dependences of the energy of adhesive bonds $W_{ad} = f_4(T)$, adhesion work $A_{ad} = f_5(T)$, the ratio of the electrostatic component to the total interfacial energy $z_e = Z_e = f_6(T)$ ($z_e = \gamma_3/W_m$), as well as the ratio $Z_{wa} = 0,12\ (A_{ad} - W_{ad})/(A_{ad} + W_{ad})$ in the temperature range $T = [0;\ 1\ 000°C]$ for the "Cu – Zn" system

component to the total interfacial energy $z_e = Z_e = f_6(T)$ ($ze = \gamma_3/W_m$), and also the ratio $z_{wa} = Z_{wa} = 0{,}1 \cdot 2 \cdot (A_{ad} - W_{ad})/(A_{ad} + W_{ad})$ in the temperature range [0; 1000°C] for the "Cu – Zn" system.

Relative changes in physical quantities $W_{ad} = f_4(T)$, $A_{ad} = f_5(T)$, $z_e = f_6(T)$, $z_{wa} = f_7(\mathrm{T})$ для $T = [0;\ 1000°C]$ can be estimated using the relations of type (22):

$$\Delta W_{ad} = 0{,}495;\ \Delta A_{ad} = 0{,}370;\ \Delta z_e = 0{,}875;$$
$$\Delta z_{wa} = 0{,}458\ (z_{wa} = [0{,}217;\ 0{,}346]). \qquad (23)$$

Based on (23) we can conclude that among W_{ad}, A_{ad}, z_e, z_{wa} the most significant temperature changes belong to the parameter z_e ($\Delta_{ze} = 0{,}875$) and exceed the corresponding changes in the parameter σ_m ($\Delta\sigma = 0{,}657$).

5. Modeling of metal condensate growth processes taking into account interphase interaction

Let us analyze the growth of a copper film on a silicon substrate taking into account changes in surface and interfacial energies in the process of its condensation.

When describing the kinetics of metal film formation on the substrate, we will be based on the fact that the formation of condensate in the deposition process is not correct to describe a simple model with successive layers that structurally repeat each other and differ only in the set of corresponding modules $E_1 \dots E_n$. The most expedient is the model of chaotically placed microregions, arranged in deformation relative to the substrate (at the stage of nanocondensate) or subsequent layers of condensate unfolded, respectively, relative to each other during deposition.

In particular, the kinetics of the deposition process assumes that each subsequent layer due to condensation is formed on a pre-directed deformed sublayer, which includes chaotically placed microdeformations in the grain volumes carried out in light sliding directions characteristic of this crystal structure of the film.

For the initial stage of condensation, taking into account the orientation dependence of the Young's modulus on the angle θ between the directions of pre-deformation and the resulting stresses, the system "silicon – copper condensate" demonstrates a significant orientation dependence of energy parameters of interphase interaction. In particular, the interphase energy within the disorientation angle (0–90°) has a "bell-shaped" appearance, reaching a maximum value at an angle of 45° (Figure 3).

The energy of the adhesive bonds changes antisymmetrically, reaching a minimum at $\theta = 45°$.The behavior of other energy parameters – σ_m, A_{ad} is also characterized by the described laws [11].

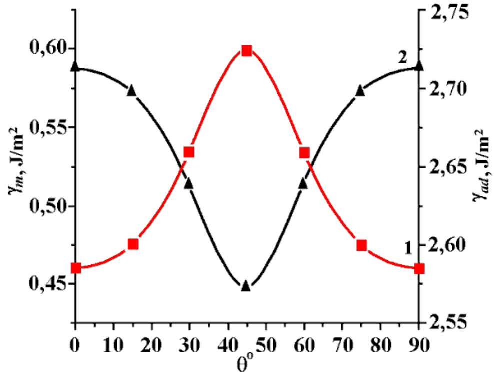

Figure 3. Anisotropy of interphase energy (1) and the energy of adhesive bonds (2) in copper-silicon condensates

To quantitatively describe the mechanical stresses in a thin film from the standpoint of interphase interaction, we formulate a mathematical model of the system "film – substrate". To do this, we use the equilibrium equation for the element of a continuous medium [20; 21] and the well-known equation of electrostatics, which connects the electric potential $\Psi = \psi + \Psi_0$ with the electric charge ω, (follows from Maxwell's equations). Thus, the main balance relations and equations of the model will look like:

$$Div\ \hat{\sigma} + \rho\cdot\omega\cdot\vec{E} = 0, \tag{24}$$

$$\varepsilon_0\Delta\Psi = \varepsilon_0\Delta\phi = -\rho\omega = -\omega_V\ , \tag{25}$$

Here $\hat{\sigma}$ the tensor of mechanical stresses with components σij; $\vec{E} = -grad\psi = -grad\Psi$; $\rho\cdot\omega\cdot\vec{E}$ – ponderomotor force; ρ – specific density of the material.

The system of equations (24–25) is supplemented by linear equations of state for the components of the tensor of mechanical stresses σ_{ij} and the density of electric charge ω, in which the temperature T is taken into account as a parameter:

$$\sigma_{ij} = \left(\left(K - \frac{2}{3}G\right)e - \alpha_t K\cdot\Delta T - Kb\phi\right)\delta_{ij} + 2Ge_{ij}\ , \tag{26}$$

$$\omega_V = \rho\omega = \rho C_\phi(\phi - \gamma_t\cdot\Delta T) + bKe\ . \tag{27}$$

Here δ_{ij} are Kronecker symbols; $e = e_{ii}/3$ – the first invariant of the strain tensor; $\Delta T = T - T_0$ – temperature change; K, G – coefficients of comprehensive compression and shear; C_φ – specific capacitance; b – electrostriction coefficient of volume expansion; α_t – is the temperature coefficient of volumetric expansion; γ_t – is the temperature coefficient of change of the modified chemical potential of conduction electrons Φ.

To complete the picture, we add the equation of the mechanics of a deformed solid, which connects the strain tensor $\hat{e}$ with the displacement vector $\vec{u}$:

$$\hat{e} = Def\ \vec{u}\ . \tag{28}$$

Thus, equations (24, 25) can be solved in displacements.

Using the relationship E_x = $-\partial\psi/\partial x = \partial\phi/\partial x$ (since the change in the electrochemical potential of electrons ($\psi + \varphi$) = const in contact media) and substituting the value of $\rho\omega$ from (27) to (24) on the boundary x=0, we obtain the boundary condition for the component of mechanical stresses (that is perpendicular to the boundary):

$$\sigma_x \equiv \sigma_{xx} = -\frac{\varepsilon_0}{2}\cdot\left(\frac{\partial\psi}{\partial x}\right)^2 = \frac{\varepsilon_0}{2}\cdot\left(\frac{\partial\phi}{\partial x}\right)^2 \tag{29}$$

The second boundary condition is obtained from the continuity of electrochemical potentials at the boundary of the media

$\Psi + \Phi = \psi + \Psi_0 + \varphi + \Phi_0 = \text{const}$. Here $\Psi = \psi + \Psi_0$, $\Phi = \varphi + \Phi_0$. At the boundary metal – non-conductive gaseous medium (or vacuum) $\Psi + \Phi = \text{const} = 0$ and get $\varphi = -\Phi_0$, $\psi = -\Psi_0$. Therefore, the second boundary condition on the boundary x=0:

$$\varphi = -\Phi_0 \qquad (30)$$

Solve the one-dimensional problem (24), (25) for the potential $\varphi$and the displacement components u_x. To do this, there are two equations and the two required values of φ, u_x. Mechanical stresses and components of the electric field of the type $E_x = -\partial\psi / \partial x = \partial\phi / \partial x$ in the near-surface layer are fed through φ, u_x.

Since (24) has a ponderomotor force, problem (24) and (25) are nonlinear. To solve it, we use the method of decomposition by a small parameter $b_* = b\times\Phi_0$ [23]. The boundary of the media is considered homogeneous along the y and z axes (no defects on the surface); x is perpendicular to the boundary.

As a result of solving this one-dimensional problem for the metal region, the relations for calculating the potential φ(x) and two relations for σ_x and σy are obtained:

$$\phi(x,k,\Phi_0) = -\Phi_0 \cdot \exp(-kx); \qquad k = \sqrt{\frac{\rho C_\phi}{\varepsilon_0}};$$

$$\sigma_x(x,b,k,\Phi_0) \approx -\frac{1}{2}\varepsilon_0 \cdot k^2 \cdot \Phi_o^2 \cdot e^{-2kx} - \frac{1}{2} b \cdot \Phi_0 \cdot K \cdot \Phi_* \cdot e^{-3kx} -$$

$$-(b\cdot\Phi_0)^4 \cdot \frac{9K^4}{8(3K+4G)^3} e^{-4kx}\left(1 + \frac{1}{10}\Phi_* e^{-2kx}\right) + C_x, \qquad (31)$$

$\sigma_y(x,b,k,\Phi_0)$ expressed similarly σ_x,

where $\Phi_0 = \frac{q_0 W_e}{2\varepsilon_0 k^2}\cdot\left(2 - \exp(-kZ_b)\right)$; $\Phi_* = \frac{\varepsilon_0 \cdot k^2 \cdot \Phi_o^2}{3K+4G}$;

$$Z_b = \frac{3}{4k_F}\left(\frac{\pi}{2} + \left(\frac{5E_V}{3E_F} - 1\right)\arcsin\sqrt{\frac{3E_F}{3E_F + 5E_V}} - \sqrt{\frac{5E_V}{3E_F}}\right);$$

$$C_x = \frac{b}{2} K \cdot \Phi_0 \cdot \Phi_* + (b\cdot\Phi_0)^2 \frac{3K^2}{2(3K+4G)}\left(1 + \frac{\Phi_*}{4}\right) +$$

$$+(b\cdot\Phi_0)^3 \frac{9K^3}{2(3K+4G)^2}\left(\frac{1}{3} + \frac{\Phi_*}{20}\right) + (b\cdot\Phi_0)^4 \cdot \frac{9K^4}{8(3K+4G)^3}\left(1 + \frac{1}{10}\Phi_*\right);$$

E_F and k_F – Fermi energy and wave vector; E_V – the work of the electron out of the metal; W_e [1/м^3] – bulk density of electrons of conductivity of metal far from the surface (approximately at a distance greater than 30 nm); q_0 – electron charge; Z_b is the displacement of the electric double layer relative to the body boundary.

Using relations (31) and numerical values of constants for silicon and copper (Young's modulus E, Poisson's ratio v, surface tension σ_h and energy γ, concentration of free electrons in the metal or particles of bound charges q: $E_{–}$= 154 GPa; $v_{–}$ = 0.34; $q_{–}$= 8.38 · 1028 1/m^3; $\sigma_{h–}$= 2.16 N/m, $\gamma_{–}$= 1.85 J/m^2 (Cu); $E_{–}$ = 138 GPa; $v_{–}$ = 0,27; $q_{–}$= 5,0 · 1028 1/m^3; $\sigma_{h–}$= 1,829 N/m, $\gamma_{–}$ = 1,623 J/m^2 (Si), calculated normal parallel limits of stress σyy and strain εy the first boundary layer of copper:

$$\sigma_{yy} = 5.8 \text{ GPa}; \varepsilon_y = \sigma_{yy}/E_1 = 0.05. \qquad (32)$$

After spraying the next layer, the previous layer becomes internal. Under these conditions, the σ_{yy} tension relaxes. Deformations to εy = 0,05 decrease, respectively. In the second layer, the concentration of vacancies begins to grow and goes to the ultimate possible value – 5%. However, the concentration of vacancies will not reach the limit, because in the process of stress relaxation vacancies are annealed and migrate parallel to the interface.

Therefore, depending on the spray rate, a certain type of substructure with the appropriate grain size is set. The corresponding grain sizes and film thicknesses correspond to a certain level of internal stresses and, according to the Hall-Patch ratios, also determined values of σ_{n1}.

It was found experimentally that the most interesting in terms of changes in physical and mechanical properties is the range of spray rates:

$$w_n = [w_{n1}; v_{n2}] = [0.2 \text{ nm/s}; 0.5 \text{ nm/s}], \qquad (33)$$

which corresponds to the following parameters of the copper film:

$$D_n = [D_{n1}; D_{n2}] = [400 \text{ nm}; 1600 \text{ nm}]; \sigma_{yn} = [\sigma_{yn1}; \sigma_{yn2}] = [17 \text{ MPa}; 51 \text{ M Pa}];$$
$$h_n = [h_{n1}; h_{n2}] = = [56 \text{ nm}; 110 \text{ nm}]. \qquad (34)$$

Here D_n is the grain size, σ_{yn} is the maximum normal tensile stresses in the film (acting parallel to the boundary and inside the thickness), which correspond to the film thickness [h_{n1}; h_{n2}]. Analysis of changes in mechanical stresses σ_{yn} in the film revealed that the numerical values decrease from values slightly smaller than σ_{yy} = 5.8 GPa to σ_{yn1}, σ_{yn2} continuously without maxima. However, the method based on the Stone formula does not allow such stresses to be recorded. There is a transition period during which the stresses in the film decrease to a certain value (for example, to σ_{yn1}, σ_{yn2}), and the displacements of the console δ, increase to some maximum values (they correspond to σ_{yn1}, σ_{yn2}). Therefore, stresses of type σyn (in particular, σ_{yn1}, σ_{yn2}) correspond to the end of the transition period of increasing console displacements δ, and also determine the stresses from which their values in the film can be monitored using a capacitive recorder.

We emphasize that at velocities $w_n < w_{n1}$ and $w_n < w_{n2}$ the maximum stresses σ_{yn} decrease with increasing velocity. In the range (33) the opposite pattern is observed: σ_{yn} = [17 MPa; 51 MPa], which obviously corresponds to changes in mechanical modules and grain size.

According to the applied experimental method for the range (33) it was found out:

$E = [E_1; E_2]$ = [118 GPa; 128 GPa]; $w = [w_1; w_2] = =$ [0.372; 0.347]. (35)

The experimentally obtained values of the yield strength σ_m for films, depending on the grain size D, are smaller, compared to polycrystalline copper, from 5 to 20%.

D_a = 200 nm – σ_{ma} = 450 MPa; D_b = 400 nm – σ_{mb} = 370 MPa;
D_c = 600 nm – σ_{mc} = 310 MPa; D_d = 800 nm – σ_{md} = 270 MPa. (36)

Let us estimate the change in the interfacial energy of the boundary “copper film – silicon substrate” with respect to silicon PE, using the method [15; 24]. Calculations, in particular, show that the relative change in interfacial energy during the deposition of the first layer of copper film with a grain size of 200 nm is 58%. During the deposition of the next layer with a grain diameter of 800 nm, the change in interfacial energy is 35%. Thus, the internal dimensional effect is accompanied by a change in the energy parameters of the interphase interaction between the interacting grains of the film.

Conclusion

1. A mathematical model of interphase interaction and adhesion mechanisms in heterophase systems is developed, taking into account the basic relations of surface physics and nonequilibrium thermodynamics. On the proposed model, a method for quantifying the relationship between electrical and mechanical components of the interphase energy of the

interacting phases (solid (1) – solid (2)) has been developed. 2. Based on the equations of nonequilibrium thermodynamics and surface physics, a mathematical model was developed that describes the physical and mechanical processes in the surface layers. The definition of surface energy, interphase energy, interphase tension is introduced and a new method for estimating changes in these physical quantities is proposed, which takes into account the distribution of electric charges in the surface layers. The division of surface energy into electrostatic and mechanical (elastic) components is proposed. Due to this, a method for determining changes in surface tension and energy in nonequilibrium conditions (eg external mechanical load) has been developed.

3. For systems "Cu – Zn", "Cu – Si" and "Cu – quartz" shows: a) electrical components of interphase energy in contact "Cu – Zn" metals and "Cu – Si" and "Cu – quartz" systems are significantly different (2.95 and 3.54 times, respectively), which indicates a much lower value of the power of the electric double layer near the interface two "Cu – Zn" metals in relation to the "Cu – Si" semiconductor or "Cu – quartz" dielectric metal; b) the energies of W_{ad} adhesion bonds in the systems "Cu – Zn", "Cu – Si", "Cu – quartz" differ slightly in absolute value, but the value of the ratio $z_{ad} = W_{ad} / W_m$ for the system of two metals is several times higher, than similar in the system "metal – non-metal"($z_{ada}/z_{adb} = 2{,}76$; $z_{ada}/z_{adc} = 4{,}09$.

4. On the basis of thermodynamic principles, taking into account changes in surface and interfacial energies, the process of copper film formation is analyzed. In the system "silicon-condensate of copper" the orientation dependence of energy parameters of interphase interaction (γ_m, γ_{ad}, σ_m, A_{ad}). is established. Quantitative estimates of mechanical stresses for the layered film growth model were performed. The resulting internal stresses in copper condensates recorded during cantilever deposition are an integral result of the action of statistically distributed local stresses in the film plane due to the anisotropy of the energy parameters of the interphase interaction in the condensate plane. The range of deposition rates ($0.2 \div 0.5$ nm $\cdot$ s^{-1}) of copper condensates on single-crystal Si substrates is characterized by anomalous changes in mechanical stresses due to changes in mechanical modules and grain sizes of copper condensate.

References:

1. Missol V. (1978). Poverkhnostnaya energiya razdela faz v metallakh [Surface energy of phase separation in metals] per. s polsk. Moscow: Metallurgya, 176 p. (in Russian)

2. Dzheykok M., Parfit Dzj. (1984). Khimiya poverchnostey razdela faz [Chemistry of interfaces] per. s angl. Moscow: Mir, 269 p. (in Russian)

3. Adamson A. (1979). Fizicheskaya khimiya poverchnostey [Physical chemistry of surfaces]. Moscow: Mir, 568 p. (in Russian)

4. Kuznetsov V. D. (1954). Poverckhnostnaya energiya tverdych tel [Surface energy of solid bodies]. Moscow: Gos. izd. techn. teor. lit., 220 p. (in Russian)

5. Rusanov A. I. (1967). Fazoviyye ravnovesiya I poverchnostnyye yavleniya [Phase equilibria and surface phenomena]. Leningrad: Khimiya, 388 p. (in Russian)

6. Nizhenko V. I., Floka L. I. (1981). Poverchnostnyye natyazheniye zhidkich metallov i splavov [Surface tension of liquid metals and alloys]. Moscow: Metallurgya, 208 p. (in Russian)

7. Kristian Dzh. (1978). Teoriya prevrashceniy v metallakh i splavakh [The theory of transformations in metals and alloys]. Moscow: Mir, 387 p. (in Russian)

8. Naydich Yu. V. (1972). Kontactnyye yavleniya v metallicheskich rasplavakh [Contact phenomena in metal melts]. Kyiv: Naukova Dumka, 196 p. (in Russian

9. Summ B. D., Goryunov Yu. V. (1976). Fiziko-khimicheskiye osnovy smachivaniya i rastekaniya [Physico-chemical bases of wetting and spreading]. Moscow: Khimiya, 486 p. (in Russian)

10. Soprunyuk P. M., Yuzevych V. M. (2005). Enerhetychni kharakterysty poverkkhnevych shariv: monohgrafiy. [Energy characteristics of surface layers]. Lviv: FMI. im. G. Karpenko NAN Ukrayiny, SPOLOM, 292 p. (in Ukrainian)

11.Koman B. P. (2017). Zakonomirnosti mizhfazovoyi vzayemodiyi u prypoverkhnevych sharakh structur tverdotilnoyi elektroniky: monohgrafiya [Regularities of interphase interaction in near-surface layers of solid-state electronics structures]. Lviv, 350 p. (in Ukrainian)

12. Sirota N. N. (1974). Vliyaniye termoddinaminamicheskogo peresysheniya pri poluchenii tonkich magnitnykh plenok. Magnitnyye plenki [Influence of thermodynamic supersaturation in the preparation of thin magnetic films]. Minsk: Vysheysha shkola, pp. 7–25. (in Russian)

13. Zadumkin S. N., Dokhov M. P. (1968). K voprosu poverkchnostnoy energii veshchestva na granitse razdela kristal-rasplav [To the question of the surface energy of a substance at the crystal-melt interface]. *Izv. AN SSSR Metally,* no. 1, pp. 91–95. (in Russian)

14. Dokhov M. P. (1983). Rasschet poverkhnostnoy energii granits razdela tverdykh faz [Calculation of the surface energy of solid phase boundaries]. *Zhurnal fizicheskoy khimii,* t. 57, pp. 1262–1269. (in Russian)

15. Koman B. P., Yuzevich V. N. (2012). Sobstvennyye mekhanicheskiye napryazheniya, termodynamicheskiye i adgezionnyye parametry v sisteme metallicheskiy kondensat-monocrystallicheskiy kremniy [Intrinsic mechanical stresses, thermodynamic and adhesive parameters in the system metal condensate – monocrystalline silicon]. *Fiz. tverd. tela*, t. 54, no. 7, pp. 1335–1341. (in Russian)

16. Gibs W. J. (1948). The collected works, V. 1. Thermodynamics. New Haven, Vale Univ. Press.

17. Oshcherin B. N. (1978). Poverkhnostnaya energiya poluprovodnikov tipa $A^2B^4C^5_2$ i steklovaniye ikh rasplava [Surface energy of $A^2B^4C^5_2$ semiconductors and glass transition of their melt]. *Fizika poverkhnostnykh yavleniy v rasplavakch,* ch. 2. Groznyy, pp. 22–26, (in Russian)

18. Osherin B. N. (1976). On surface energies of $A^N B^{8-N}$ semiconduction compounds. *Phys. Status solidi (a),* vol. 34, no. 1, pp. 181–187.

19. Shorkin V. S., Gorda M. A., Batranina M. A. (2005). Uchet nelokalnogo vzaimodeystviya chastic sredy vramkakh lokalnoy teorii uprugosti [Accounting for the nonlocal interaction of particles of the medium in the framework of the local theory of elasticity]. *Izvestiya Tulskogo GU. Seriya Matematika. Mekhanika,* t. 11, no. 2, pp. 160–173. (in Russian)

20. Tamm I. Ye. (2003). Osnovy teorii electrichestva [Fundamentals of the theory of electricity]: Ucheb. posobie dlya vuzov. 11-ye izd., ispr. i dop. M.: FIZMATLIT, p. 616. (in Russian)

21. Maugin G. A. (2011). Electromagnetics in Deformable Solids / *Mechanics and Electrodynamics of Magneto- and Electroelastic Materials*. Editors: R. W. Ogden, D. J. Steigmann, Publisher: Springer, vol. 527, pp. 57–105.

22. Yuzevich V., Koman B. (2014). Modeling the relationship of mechanical and electric parameters of surface of solids. *Phys. Sol. State*, vol. 56, no. 5, pp. 895–902.

23. Bogolyubov N. N., Mitropolskiy Yu. A. (1974). Asimptoticheskiye metody v teorrii nelineynykh kolebaniy [Asymptotic methods in the theory of nonlinear oscillations]. Moscow: Nauka, pp. 412. (in Russian)

24. Yuzevych V. M. (1984). Vplyv poverkchnevoyi enerhiyi na masstabnyy efekt pruzhno-plastychno deformivnoho tverdoho tila [Influence of surface energy on the scale effect of an elastically plastically deformable solid]. *Dop. AN URSR. Ser. A*, no. 8, pp. 60–63. (in Ukrainian)