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Thermodynamic Description of Interface Interaction in Nanolayers on the Metal Fe–Dielectric Al_2O_3 Boundary

S. V. Kniaz[1], O. J. Kotsiumbas[1], I. S. Kuz'[2], O. M. Bordun[2],
O. I. Moroz[1], O. N. Kuz'[1], and D. S. Leonov[3]

[1]*Lviv Polytechnic National University,*
12, Bandery Str.,
UA-79013 Lviv, Ukraine
[2]*Ivan Franko National University of Lviv,*
1, Universytets'ka Str.,
UA-79000 Lviv, Ukraine
[3]*Technical Centre, N.A.S. of Ukraine,*
13, Pokrovska Str.,
UA-04070 Kyiv, Ukraine

Using basic equations of surface physics and thermodynamics of nonequilibrium processes, a mathematical model is developed to determine the interfacial energy, interfacial tension, energy of adhesive bonds, work of adhesion and others physical quantities characterizing nanolayer on the 'metal Fe–insulator Al_2O_3' boundary. The developed technique can be used for evaluation of interfacial parameters of interaction between another physical-nature composite pairs with taking the nature of the double electrical layer into account.

За допомогою основних рівнянь фізики поверхні та термодинаміки нерівноважних процесів розроблено математичний модель для визначення міжфазної енергії, міжфазного натягу, енергії адгезійних зв'язків, роботи адгезії й інших фізичних величин, що характеризують наношар на межі «метал Fe–діелектрик Al_2O_3». Розроблену методику можна використати для оцінки міжфазних параметрів взаємодії між композиційними парами іншої фізичної природи з урахуванням природи подвійного електричного шару.

Key words: metal, insulator, nanolayer, electric charges, interfacial energy, energy of adhesive bonds, aluminium oxide.

Ключові слова: метал, діелектрик, наношар, електричні заряди, міжфазна енергія, енергія адгезійних зв'язків, оксид алюмінію.

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1. INTRODUCTION

The systems of 'metal oxide' are widely used as active and passive elements of micro- and nanoelectronics, elements of power sources, batteries capillary energy, corrosion-resistant materials and others [1, 2]. Such systems have a unique physical and mechanical properties and a high chemical inertness.

Due to diffusion, a transition layer is formed at the boundaries of such systems. The transition layers can be external and internal. At the same time, in the macromodel description of contacting 'metal–insulator' surfaces, it is necessary to have reliable information about changes in the physical characteristics of the metal as well as the dielectric.

Their values should not only adequately correspond to the basic energy characteristics of the interphase layers such as interphase energy of tension, the energy of adhesive bonding and the work of adhesion, but they also cannot violate the criterion of the strength of the transition layer material. With the use of alloying impurities, one can change and optimize the electrical and mechanical properties of the transition layer.

2. MATERIALS AND METHODS

It is a well-known example that aluminium oxide Al_2O_3 is used for metals' corrosion protections and for increase of hardness characteristics of aerospace devices buildings [3]. To improve composite ceramics performance, the structures like 'Al_2O_3–powder' with a higher strength parameter had found a widespread use [4]. By varying the concentrations and types of powders, one can produce the composite materials with a wide range of physical, mechanical and electrical parameters.

To obtain a thermodynamically stable composite of the 'metal oxide' type with the assumed physical and mechanical properties, it is required a deep understanding of the physical phenomenon on the interface 'nanolayer–metal oxide–nanolayer'. However, due to the complexity of the processes on the interface of two environments, their quantitative description is difficult. An empirical approach is usually used to describe an interfacial interaction of two materials. Therefore, the real situation of determining an electric charge on the 'metal oxide' interface is absent [5]. Some parameters of the free surfaces can be estimated by density functional theory (DFT)

[6, 7]. DFT is rather complicated and cumbersome for practical use; it is also uses the additional theoretical assumptions that simplifies the calculation process but reduces the accuracy and reliability of experimental data. In addition, DFT is not effective for interface energy calculations. For a macromodel description of contacting surfaces like 'metal–dielectric' one, it is important to have reliable information about the variation of their physical characteristics, which is included in the equation of state and is linked together with the state parameters. Their values must properly meet the basic energy characteristics of the interface layer, namely, interfacial energy γ_m and bounds' adhesion energy γ_{Ad} [6–9]. The positive results of such an approach for 'metal–semiconductor' were shown in Refs. [8, 10].

The aim of this paper is to introduce the evaluation methods of thermodynamic and adhesive parameters (interface energy γ_m, interface tension σ_m, interfacial electric charge Ω, and electrocapacity of double electrical layer C_m, electrical component γ_{mE} of interface energy of interface nanolayers in 'metal–dielectric') by using macroscopic surface physics and thermodynamics of nonequilibrium processes. The proposed methodology must be tested for calculating the typical parameters of interfacial interaction in (Ag, Au, Cu, Fe)–Al_2O_3. It is necessary to find the variations of interfacial tension and energy, electric component of the surface energy, specific surface charge and contact potential difference (CPD) according to changes in the basic parameters of the dielectric layer. The main information parameters of the interface are the interface tension and energy (characteristics of the interfacial interaction).

3. RESULTS AND DISCUSSION

The proposed model for estimating the interface phenomenon between two materials is based on the assumption of connections between mechanical and electrical processes on the solid-state surface [1]. Let us consider the interface between two mediums: 'metal–insulator' or 'metal–inert-gas environment'. Metal and dielectric are multielemental continuous medium. Inside the metal, we have the following components: ions of the basic substance (*e.g.*, copper Cu^{++}), conduction electrons, impurities, point defects. In dielectric, we have components such as atoms of the basic substance, which are considered as dipoles and which characterize a bound electric charge, impurities and point defects. In an inert gas environment, the composition components are not considered. In the vicinity of the medium boundaries, we can observe the separation of electric charges. The double electric layer (DEL) is formed (nanolayer, which corresponds to 'surface condenser'), and an electric potential difference $\Delta\Psi_m$ is appeared [2]. Let us consider the stationary position of the contact media in the form 'metal–inert gas environment' (such as air), 'dielectric–air' and 'metal–insulator'. The surface tension (ST) σ_h and surface energy (SE) γ, which are basic energy parameters of DEL, are proportional to each other and given by Herring–Shuttleworth relation [8]:

$$(\sigma_h)_{ij} = K_R\left(\gamma\delta_{ij} + \left(\frac{\partial\gamma}{\partial e_{ij}}\right)_T\right),\ \sigma_h = K_R\left(\gamma + \left(\frac{\partial\gamma}{\partial e}\right)_T\right),$$
$$\sigma_h = K_R\left(\gamma + S_b\left(\frac{\partial\gamma}{\partial S_b}\right)_T\right), \tag{1}$$

where S_b is the body surface area, $\partial\gamma/\partial S_b$ is the expression of the characteristic of change on the energy surface γ during a deformation (because the derivative in surface area S_b at the constant temperature T is a deformation), $K_R = 1\ \mathrm{N\cdot m^2/(m\cdot J)}$ is the dimension-matching parameter, δ_{ij} is the Kronecker symbol, e_{ij} are components of the deformation tensor $\hat{e}$ (i, $j = 1$, 2 for two-dimensional surface phases in Cartesian co-ordinates x, y).

The components of the deformation tensor $\hat{e}$ with the components of the displacement vector $\mathbf{u}$ in Cartesian coordinates (x, y, z) are related by the following equations [8, 10]:

$$\hat{e} = Def\mathbf{e},\ \left(e_{xx} = \frac{\partial u_x}{\partial x},\ e_{yy} = \frac{\partial u_y}{\partial y},\ e_{zz} = \frac{\partial u_z}{\partial z}\right),\ \mathbf{u} \Rightarrow (u_x,\ u_y,\ u_z). \tag{2}$$

The deformation tensor $\hat{e}$ is related with the components of stress tensor $\hat{\sigma}$ by the equation of state, which is the defining equation of the generalized Hooke's law [8, 10]:

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

where K is a bulk modulus, G is a shear modulus, c_k is the variation of the concentration of impurity C_k ($k = 1$, 2,..., n, $c_k = C_k - C_{k0}$), $\Delta T = T - T_0$ is the temperature variation, $\varphi = \Phi - \Phi_0$ is the deviation of the modified chemical potential of electron conductivity (MCPCE), Φ_0 is the value of MCPCE metal at a considerable distance from the surface, where the effect of DEL on the conduction electron is not manifested, β is the electrostrictive coefficient of thermal expansion, α_t is the temperature coefficient of thermal expansion, β_{ck} is the concentration coefficient of thermal expansion.

Then, the equation of state (constitutive relation) has the following form [8, 10]:

$$\sigma_{ij} = \left(\left(K - \frac{2}{3}G\right)e - K\beta\phi\right)\delta_{ij} + 2Ge_{ij}, \tag{4}$$

$$\omega_V = \rho\omega = \rho C_\phi \phi + \beta K e = k^2 \varepsilon_0 \phi + \beta K e, \; k = \sqrt{\rho C_\phi / \varepsilon_0}. \tag{5}$$

In this case, the electrostrictive parameter of thermal expansion is written as $\beta = \frac{3(1+\nu)}{E}\frac{\partial\omega}{\partial e}\Big|_{\phi=\mathrm{const}}$.

The redistribution of conduction electrons and the generation of mechanical stresses are described by the two balance ratios, namely, the equation of balance momentum (the equation of the equilibrium of deformable bodies) and the equation that links electric vector field **E** with density of electric charges ω (state parameters) [8, 10, 11]:

$$Div\,\hat{\sigma} + \rho\omega\mathbf{E} = \mathbf{0}, \quad \varepsilon_0 \nabla\mathbf{E} = \rho\omega = \omega_V, \tag{6}$$

where ε_0 is the electric constant and $\rho\omega\mathbf{E}$ is the ponderomotive force in the balance equation of a local body element. The second Eq. (6) is one of the Maxwell's equations.

Let us consider the surface tension σ_h, surface energy (SE) γ, equilibrium condition of the surface layer and effective thickness h of the surface layer in the equation of state for determining the physical parameters β and k of the metal [8, 10, 11]:

$$\int_0^h \sigma_{yy}dx = \sigma_h, \; \sigma_{yy} = \sigma_{zz}, \tag{7}$$

$$\gamma_e + \xi\gamma_p = \gamma, \tag{8}$$

$$\frac{\partial\gamma}{\partial k} = \frac{\partial\left(\gamma_e + \xi\gamma_p\right)}{\partial k} = 0, \tag{9}$$

$$\sigma_{yy} + p = 0 \; (x = h), \tag{10}$$

where $\gamma_e = \int_0^h w_e dx$ is the electric component of the surface energy (SE), $\gamma_p = \int_0^h w_p dx$ is the mechanical (elastic) component of SE, $w_e = \frac{\varepsilon_0}{2}\left(\frac{\partial\Psi}{\partial x}\right)^2$ and $w_p = \frac{\sigma_{xx}\left(\sigma_{xx} - 4\nu\sigma_{yy}\right)}{2E} + \frac{(1-\nu)\sigma_{yy}^2}{E}$ are the densities of electrical and mechanical components of SE, respectively,

$p = 100$ kPa is the atmospheric pressure, h is the effective thickness of the surface layer, $E = G\dfrac{3K+4G}{3K+G}$ is the longitudinal elastic modulus (Young's one), $\nu = \dfrac{3K-2G}{2(3K+G)}$ is the Poisson's ratio, and k is the variational parameter. Expression (10) gives the value of the surface tension, and expression (8) gives the value of surface energy γ in the form of two components $\gamma = \gamma_e + \gamma_{dft}$. The first component γ_e describes electrostatic components, and the second one γ_{dft} describes kinetic, exchange, correlation components and energy of inhomogeneity of electron gas (based of density functional theory (DFT)).

The interfacial tension $\gamma_{\rm int}$, interfacial energy $\sigma_{\rm int}$, energy of adhesive bonds γ_{Ad} and work of adhesion A_{Ad} in the nanolayer at the 'metal–cover' interface are evaluated as follow [8, 10, 11]:

$$\gamma_{\rm int} = \gamma_{me} + \xi_m\gamma_{mp}\,,\ \gamma_{me} = \int_{-H_1}^{H_2} w_e dx\,,\ \gamma_{mp} = \int_{-H_1}^{H_2} w_p dx\,,\ \sigma_{\rm int} = \int_{-H_1}^{H_2} \sigma_{yy} dx\,, \quad (11)$$

$$\gamma_{Ad} = \gamma + \gamma_P - \gamma_{\rm int}\,,\ A_{Ad} = \sigma_h + \sigma_P - \sigma_{\rm int}, \quad (12)$$

where ξ_m is the ratio of the surface energy components on the 'metal–covering' interface; γ_{me}, $\gamma_{mech} = \xi_m\gamma_{mp}$ are electrical and mechanical (elastic) components of the interfacial energy, respectively; $H_1 + H_2$ is the effective thickness of the interfacial layer ($-H_1 < x < H_2$); σ_P and γ_P is the surface tension and the energy of the surface covering, respectively, of insulator or semiconductor on the interface of an inert gas environment (IGE) (or a physical vacuum).

For the 'metal–inert gas environment', we can write [11]

$$\gamma_e = (\Omega)^2/(2C) = C(\Delta\psi)^2/2\,,\quad C = \varepsilon_0 k/2\,,\ d_\xi = 2/k\,. \quad (13)$$

For the 'metal–insulator', we can write [8, 11, 12]:

$$\gamma_{mp} = (\Omega_m)^2/(2C_m) = C_m(\Delta\psi_m)^2/2,\ C_m = \varepsilon_0 k_m/2,\ d_{\xi m} = 2/k_m\,, (14)$$

where C_m and Q_m is the electrocapacity and the interface charge of DEL, respectively; $\Delta\psi_m$ is the contact potential difference of DEL; $d_{\xi m}$ is the effective thickness of DEL; k_m is the DEL variational parameters.

Our calculations show that the quantitative values of the energy parameters of interfacial interactions ($\gamma_{\rm int}$, $\sigma_{\rm int}$, γ_e, γ_{Ad}) in Fe–Al_2O_3 are slightly higher than the studied metals Ag, Cu, Au [8, 10–12]. In particular, values $\gamma_{\rm int}$, $\sigma_{\rm int}$, γ_e, γ_{Ad} determined by us for the system Fe–Al_2O_3 are the following:

$\gamma_{\text{int}} = 1.51$ J·m^{-2}, $\sigma_{\text{int}} = 1.23$ N·m^{-1}, $\gamma_{Ad} = 3.02$ J·m^{-2}, $A_{Ad} = 2.45$ J·m^{-2}.

The values obtained earlier in [10] for a number of metals (Cr, Cu, Au, Al) on Si, Ge, or Ni generally have slightly lower values than the values obtained by us. For example, for the Si–Cu system they are as follow:

$\gamma_{\text{int}} = 0.27$ J·m^{-2}, $\sigma_{\text{int}} = 0.61$ N·m^{-1}, $\gamma_{Ad} = 2.90$ J·m^{-2}, $A_{Ad} = 2.88$ J·m^{-2}.

For the Cu–Ge system, the same values are correspondingly:

$\gamma_{\text{int}} = 0.20$ J·m^{-2}, $\sigma_{\text{int}} = 0.46$ N·m^{-1}, $\gamma_{Ad} = 2.71$ J·m^{-2}, $A_{Ad} = 2.73$ J·m^{-2}.

In general, based on the results of [10], one can argue that the adhesion and higher levels of mechanical stresses at the Fe–Al_2O_3 boundary are better compared to a number of systems (Si, Ge, Ni)–(Cr, Cu, Au, Al). Based on this, there is a possibility of practical use of Al_2O_3 as a stable protective and anticorrosion coating for Fe.

The obtained theoretical results show the presence of a certain difference in the physical parameters of the studied electric double layer of a metal and semiconductor in the corrosion-resistant (Au, Ag, Cu) and both a metal and a dielectric in the non-corrosion-resistant (Fe) metals.

The quantitative values of the certain parameters can be used in the planning of the nanotechnological research and the quantitative description of the surface properties and interfacial interactions of metals and dielectrics.

4. CONCLUSIONS

Based on the results of this study, the following conclusions and recommendations have been formulated.

1. The quantitative values of the energy parameters of interfacial interactions (γ_{int}, σ_{int}, γ_e, γ_{Ad}) in Fe–Al_2O_3 are significantly higher than in the studied earlier systems (Si, Ge, Ni)–(Cr, Cu, Au, Al). This shows a greater adherence and higher levels of mechanical stress in the nanolayer on the boundary of Fe–Al_2O_3. Based on this, there are prospects of practical use of Al_2O_3 as a stable protective and anticorrosion coating for Fe.

2. The high value of electric component γ_e and the specific electrical charge Ω_m on the interface of DEL in Fe–Al_2O_3 nanolayer testify to dipole-electronic nature of the concentrated electric field. This also confirms the high value of the specific electrocapacity C_m, due to specific electronic configuration of Fe atoms compared to Ag, Cu, Au. Thus, the electronic configuration of the metal is im-

portant in the formation of interactions in the nanolayer on 'insulator–metal' interface.

3. The developed technique can be used to estimate the interfacial energy, interfacial tension, energy of adhesive bonds, work of adhesion and other parameters, which characterize the interaction between other pairs of different physical nature, taking into account the nature of the electric double electrical layer.

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