

INTERNAL MECHANICAL STRESSES AND SELF-ORGANIZING PROCESSES ON "SILICON-METAL CONDENSATE" INTERFACE

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We investigate regularities of internal stresses formation in metal condensates (Cu, Al, Cr, Au) and the peculiarities of self-organization processes in monocrystalline silicon substrates. The behavior of interphase interaction parameters on "metal film (Cu, Al, Cr, Au) - silicon" and during the phase transition in "melt (metal) - solid phase (metal)" on the investigated substrate were analyzed. The evaluation method of time formation of maximum internal stresses in metal condensates on solid substrates and mechanism of their formation were proposed. On "Si - metal (Cr, Cu, Au, Al)" interface, the energy parameters values of interfacial interaction: interfacial tension, interfacial energy, adhesion work and adhesive bonds energy were evaluated.

Keywords: interphase, interfacial tension, interfacial energy, adhesion work, adhesive bonds energy.

Introduction.

Without commonality detracting, it can be stated that mechanical stresses arise at the "solid substrate - metal condensate" boundary because of the intense energy dissipation of the condensed atoms high-energy flow that is balanced by the interaction with the substrate. It is believed that the total amount of mechanical stress is equal to additive sum of internal (intrinsic) σ_i and thermal σ_{temp} stresses values: $\sigma = \sigma_i + \sigma_{temp}$ [1, 2]. The nature of the thermal stress component σ_{temp} has been well studied for many metallic condensates [3, 4]. Thanks to complex studies of many metal condensates, the problem of its minimization is solved today (mostly by technological methods) even in quite complex systems - modern structures of microelectronics (e.g., [5-8]). However, the nature of σ_i intrinsic (internal) component of mechanical stress is still debatable. There is also no physical vision of mechanical stresses nature in nanocondensates. Basic structural factor to interpret their nature is used. In general, it is believed that the internal stresses are caused by peculiarities of film formation process, the disequilibrium of the condensation process, recrystallization and interaction of condensates with residual gases [1, 9–11].

The accumulation of huge amount of experimental material in the physics field and technology of thin films today made it possible to formulate some empirical regularities (mostly of the technological plan) of intrinsic stresses evolution in thin films [1,2, 12-14]. However, the mechanism of grain boundaries growth in thin films and physical formation mechanisms of internal stresses based on thermodynamic approach, taking into account changes in surface and interfacial energies have not substantiated. Today, there is no such

theory for explanation of mechanism of initial condensate growth in the form of island-nanodispersion state. The understanding of macro- and micro-processes responsible for the internal stresses formation will provide the possibility of metal condensates deposition with improved characteristics by means of systematic changes in their internal structure and interphase interaction on "condensate-substrate" boundary.

This work purposes to clarify the growth regularities of internal (inherent) stresses in metal condensates on monocrystalline silicon. Which reflect the dynamics of interphase interaction from the stage of island-nanodisperse condensate to continuous film, and to substantiate their formation mechanisms from the standpoint of thermodynamics.

Experiment

Internal stresses $\sigma_i(d)$ kinetics in Cr, Cu, Au and Al metal condensates during their deposition on unheated (111) surface silicon substrates were experimentally investigated. Thin metal films were grown in VUP-5A at vacuum condition not worse than 10^{-5} Pa by the condensating thermally evaporated metal vapor on substrate surface. As substrates, chemically polished surfaces obtained by scribing monocrystalline silicon plates of KEF - 4.5 (111) were used. After the final etching in standard CP-4 polishing etch, the substrates had dimensions of $70 \times 4 \times 0,25$ mm³. To remove residual mechanical stresses caused by previous mechanical processing, the plates were annealed in a vacuum at temperature of 1000°C ($\pm 1^\circ\text{C}$). The technique of synchronous control of internal mechanical stresses $\sigma_i(d)$ in metal condensates on solid substrates is described in detail [15].

Results

The general regularity of $\sigma_i(d)$ dependencies for Cu, Cr, Al and Au films is two-stage nature in internal stresses evolution during the vacuum condensates growth on monocrystalline silicon substrates [15, 16]. In particular, there is sharp increase in σ at first stage to the maximum value σ_{max} at given condensation rate ω and their further decrease with increasing film thickness in the second stage. Schematically, such dependence is shown in fig. 1. The obtained regularities are typical for studied metals.

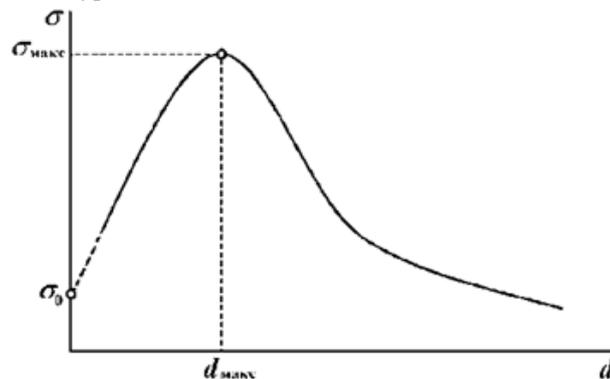


Fig. 1. Schematic dependence of internal stresses kinetics of metal condensates on silicon.

The analysis of experimental dependences confirms the positions of characteristic maxima $\sigma_{m\omega}$ for given sedimentation rate fit on straight line $d_{n\omega} = k\omega_n$ in the coordinates $d_{n\omega}(\omega_n)$ (fig. 2).

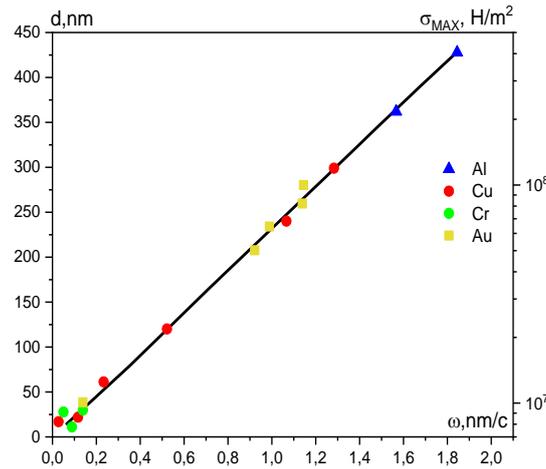


Fig. 2. Dependence of $\sigma_{m\omega}$ maximum stresses position on the experimental dependences of $\sigma(d)$ by thickness in metal condensates on their deposition rate ω .

Note that, in addition to Cu and Al, maximum stress coordinates for Cr and Au films are also superimposed on the same line. Therefore, for silicon substrate, the angular coefficient of slope dependence is the same for all studied condensates: Cr, Cu, Au, Al. Since parameter $k = \Delta\sigma_{m\omega} / \Delta\omega$ (fig. 2) specifies angular coefficient of straight line slope has the dimension of time. It is logical to assume that it determines the condensates transition time from highly dispersed (island) structure to continuous film with spatial framework over the entire area of substrate at different rates of their deposition in relation to the given substrate crystallographic orientation. For the listed metals this time is the same, is about 220 s. It's correspond to the time of condensate Ostwald ripening. Pointing the characteristic points of different metals on one line, proves the dominant role of substrate in mechanical stresses evolution at initial stage of Cr, Cu, Au, Al condensates growth. Therefore, internal mechanical stresses formation in copper, gold, aluminum and chromium nanocondensates on silicon surface self-organization processes on the part of the silicon substrate exert dominant influence. That provides equivalent conditions for spreading of non-equilibrium island in to disperse structure.

Let us analyze the role of substrate in mechanism of σ_{max} stresses evolution in metal condensates according to data on fig. 2. In this regard, it should be emphasized that maximum values of σ_{max} for studied metals are reached at the smallest thicknesses in Cr condensates (≈ 50 nm). As we can see, Al condensates have the greatest thickness to achieve the maximum stress level. In this context, it is appropriate to consider the interface interaction in "metal condensate - silicon" at the atomic level, taking into account the potential ability of the substrate atoms, on the one hand, and the metal condensate, on the other hand, to form chemical bonds.

Silicon have relatively high electronegativity ($\sim 1,8$ according to Pauling [17]), is capable of greater electron attachment than condensed metals (Cr $-1,56$; Cu $- 1,76$; Au $-1,42$; Al $- 1,47$). Therefore, such interaction will be accompanied with electrons transfer to silicon.

For the studied systems, the value of $X_{\text{Si-Me}}$ is always less than 0,4, which, according to [17] is accompanied by covalent bond action by partial electrons transfer from atoms with lower electronegativity (metals) to atoms with higher electronegativity (Si). The share of the ionic component will not exceed $\sim 10\%$.

The adhesive properties of "silicon-condensate" interphase will determined precisely by such interaction. A decrease in the electronegativity of the metals in the given series (Cr, Cu, Au, Al) relative to electronegativity of the substrate should accompanied by increase in the level of intrinsic stresses on interface boundary, since the role of the substrate in the formation of bonds with adsorbed atoms increases. Copper stands out here, which has an abnormally high electronegativity value among the listed metals. By the way, we note that this metal also has abnormal parameters in terms of other properties, in particular, a high diffusion coefficient, great plasticity, as well as the ability to twin and recrystallize even at room temperatures.

Note that ability to reconstruct, in which the surface structure changes within wide limits during the deposition of submonolayer adsorbate coatings, is one of the characteristic properties of covalent crystals surface (in particular, silicon) [18]. More than 300 such structures - atomic reconstructions on a silicon substrate of various orientations have been found [19].

Such surface modification changes many of its properties and can be used as process control parameter of nanostructures self-organized growth. We emphasize that we are not talking about buffer layers, which actually replace the material of the substrate, forcing the growth of "sandwiches". Surface modification by sub-monolayer reconstruction is designed to ensure the self-assembly process, while preserving such characteristics as low roughness, high crystal perfection, and low defect density.

From this point of view, the described self-organizing processes are those that take place, most of all, not in the deposited film, as is realized in molecular-beam epitaxy of the "semiconductor-semiconductor" type by creating certain spatial-periodic structures on the surface of the substrate, but by means of silicon surface reconstruction under the deposited metal with $\Delta X < 0,4$. Later in the deposition process, this reconstructed surface will provide the same rheological properties of condensed drops and close conditions of thermalization of the molecular beam of Cr, Cu, Au, Al deposited metals on the silicon surface. The last factor determines the original dependence shown in fig. 2. The given differences for σ_{max} in number of studied metals can be explained, obviously, only from the point of view of the peculiarities of the adhesive properties of metals on silicon substrates.

Thermodynamic description of interphase interaction in "silicon - metal". Energy and adhesion parameters

The basis of the mathematical model for describing the interphase interaction in the studied systems is the ratio of non-equilibrium thermodynamics and physics of the surface of a solid body. We will investigate the change in energy and adhesive parameters of the thermodynamic state at "metal film - silicon substrate" interface by equations that describe mechanical and electrical processes on surface layers [20].

A structurally sensitive parameter on "substrate-film" interface is interphase energy [21]. To evaluate, we will utilize the procedure of transition from surface energy to interphase

energy [20]. Consider the macroscopic model of solid body surface layer (fig. 3, a), in which the region $x > 0$ (V_1) occupies the solid body, and $x < 0$ (V_2) – air (x, y, z – cartesian coordinates). The surface layer is conventionally represented by deformed ions, the electric charge of which is balanced by a spatial electron cloud. As a result of the reconstruction of the surface layer, mechanical stresses arise: compressive σ_x along the x -axis and tensile - along the y axis. The corresponding distributions charges and mechanical stresses are presented on fig. 3 (b,c,d).

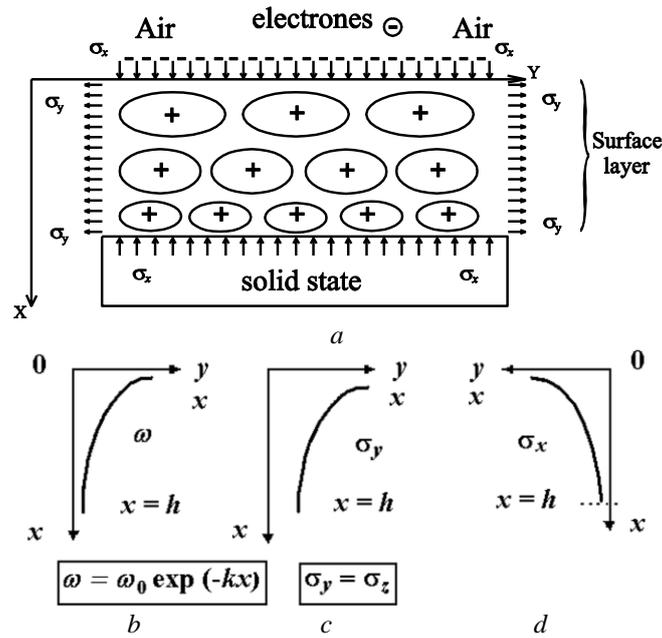


Fig. 3. Model of surface layer, electrical charges distributions and mechanical stresses.

We present the correlation of surface layer thermodynamic model in metal region ($x > 0$) in coordinates x, y, z in the form of four equations system according to [16, 20]:

$$\text{div} \vec{\sigma} + \rho \omega E = 0; \Delta \varphi = \rho C \varphi / \varepsilon_0; \quad (1)$$

$$\sigma_{ij} = [(K - 2G/3)e - \alpha_t K \Delta T - K \beta \varphi] \delta_{ij} + 2G e_{ij};$$

$$\omega_\nu = \rho \omega = \rho C_\varphi (\varphi - \gamma_t \Delta T) + \beta K e; \quad (2)$$

$$\sigma_y + p = 0 \text{ for } x = h, \varphi = -\Phi_0; \varphi + \psi = \text{const}; \sigma_x = -\frac{\varepsilon_0}{2} \left(\frac{\partial \Psi}{\partial x} \right)^2 \text{ at } x = 0; \quad (3)$$

$$\sigma_h = \int_0^h \sigma_y dx, \sigma_y = \sigma_z, \gamma = \gamma_1 + \xi \gamma_2, \frac{\partial \gamma}{\partial k} = \frac{\partial (\gamma_1 + \xi \gamma_2)}{\partial k} = 0. \quad (4)$$

where σ_h – surface tension; γ – surface energy (SE); σ_{ij} , e_{ij} – components of stress tensors $\hat{\sigma}$, deformation \hat{e} ($i, j = 1, 2, 3$); $\sigma_{11} = \sigma_x$; $\sigma_{22} = \sigma_y$; δ_{ij} – Kronecker symbols; e_{ij} is the first strain tensor invariant; ρ – density of material; $p = 100$ kPa - atmospheric pressure; ω_v, ω – spatial and mass densities of electric charge respectively; $\varphi = \Phi - \Phi_0$ – deviation of the Φ modified potential of the electric charge from its equilibrium value Φ_0 in the volume of body; Ψ – scalar potential of electric field intensity; $\psi = \Psi - \Psi_0$ – deviation of Ψ from its equilibrium value Ψ_0 ; $E = grad\Psi$ – electric field strength; $\gamma_1 = \int_0^h w_1 dx$, $\gamma_2 = \int_0^h w_2 dx$ – electrical and mechanical components of SE; $w_1 = \frac{\varepsilon_0}{2} \left(\frac{\partial \Psi}{\partial x} \right)^2$, $w_2 = \frac{\sigma_x(\sigma_x - 4\nu\sigma_y)}{2E} - \frac{(1-\nu)\sigma_y^2}{E}$ – density of electrical and mechanical components SE; h – effective thickness of the surface layer; $\Delta T = T - T_0$ – temperature change; K , G – comprehensive compression and shear coefficients; C_i is the specific electrical capacity of unit mass of continuous medium; $k = \sqrt{\rho C_\varphi / \varepsilon_0}$; ξ , k , α_t , β , γ_t – physical characteristics of the material, which are included in the equation (3.2) [10]; $\Psi + \Phi$, $\psi + \varphi$ – electrochemical potential of conduction electrons and it's changes (increase).

The distribution of electric charges ω and mechanical stresses σ_{ij} in the vicinity of surface layer can be found with relations (1) – (3), utilize method of σ_{ij} and e_{ij} series expansion by a small parameter $b_M = \beta\Phi_0$. Surface tension σ_h and γ energy are determined with (4), utilize distribution of electric charges and mechanical stresses with (1) – (3) and taking into account the condition of equilibrium (quasi-equilibrium) of the surface layer (the third equation from (4)).

Evaluation of silicon surface energy. The parameters ratios of mechanical and electric fields in silicon are similar to (1)–(4). Since the polarization of atoms in silicon near the metal surface is quite large, we will use the approach according to which the surface energy $\gamma_d = \gamma_{d_1} + \xi_d \gamma_{d_2}$, along with the mechanical γ_{d_2} , the component γ_{d_1} is taken into account, which characterizes the bound electric charges distributed in thin layer (the approach of I.E. Tamm) [22].

For silicon, the state parameter will be the modified chemical potential of the bound electric charges Z_d and the density of bound electric charges ω_d [22]. At the same time,

$w_1 = \frac{\varepsilon_0}{2} \left(\frac{\partial \Psi}{\partial x} \right)^2$ is specific energy of bound electric charges field; $z_d = Z_d - Z_{d_0}$ potential change (deviation of potential Z_d to its equilibrium value Z_{d_0} far from the surface of the body); $b_{md} = \beta_d Z_d$ is a small parameter that we utilize similarly to the case of metal since the pondemotive force in metal is nonlinear.

Evaluation of interfacial energy and tension. The interfacial energy γ_m and the tension σ_m at the metal-silicon interface are determined similarly to relations (3), taking into account

that the interfacial layer consists of two parts and its effective thickness is $h_1 + h_2$ ($-h_2 < x < h_1$):

$$\gamma_m = \gamma_4 + \xi_m \gamma_5, \quad \gamma_4 = \int_{-h_2}^{h_1} w_1 dx; \quad \gamma_5 = \int_{-h_2}^{h_1} w_2 dx, \quad \sigma_m = \int_{-h_2}^{h_1} \sigma_y dx, \quad \sigma_y = \sigma_z, \quad (5)$$

where ξ_m is an empirical parameter found by solving problem.

To estimate σ_m and charge density Q_m of double electric layer in the metal region, we use relationship:

$$\sigma_m = \sigma_h - \sigma_{dh}, \quad Q_m = \int_0^{h_1} \rho \omega dx \quad (6)$$

where σ_{dh} is the surface tension of silicon in contact with air.

The equilibrium condition of the interphase layer (that is, for γ_m) and the approximate relations on the conditional boundaries that limit the area of the interphase layer (at $x = h$ and $x = -h$) are written in the form (analogous to (3) for γ):

$$\frac{\partial \gamma_m}{\partial k} = \frac{\partial(\gamma_4 + \xi \gamma_5)}{\partial k}; \quad \sigma_y^+ + p = 0 \quad (x = +h_1); \quad \sigma_y^- + p = 0 \quad (x = -h_2). \quad (7)$$

Here, the index (+) corresponds to the metal parameters, and (-) to silicon; $p = 100$ MPa – hydrostatic pressure.

Boundary (marginal) relations. The boundary conditions for interface between media (at $x = 0$) corresponding to the electric double layer can be written as:

$$\Phi_+ = -\Phi_0; \quad z_- = -Z_e; \quad j_x^- = -j_{xe}^-; \quad \sigma_y^+ = \sigma_y^-; \quad \sigma_x^+ = \sigma_x^-, \quad (8)$$

$$\bar{u}^+ = \bar{u}^-; \quad E_\tau^+ = E_\tau^-; \quad D_x^+ - D_x^- = \Omega,$$

where σ_x^\pm , $\sigma_y^\pm = \sigma_z^\pm$ - mechanical stresses along the normals, \bar{u}^\pm - displacement; E_τ^\pm - tangential component of intensity electric field; D_x^\pm , P_x^\pm - components of induction electric field and polarization vectors, which are directed along the normal (along the x -axis) to the interface between the media ($x=0$); Ω is the charges (excess, uncompensated) surface density created by free electrons. If the metal surface is not externally charged, then $\Omega=0$.

Adhesion work and adhesive bonds energy. The work of adhesion A_{ad} and the excess energy γ_{ad} of the "metal - silicon" interface that concentrated in the neighbourhood of interface are determined based on relations [20]:

$$A_{ad} = \sigma_h + \sigma_{dh} - \sigma_m; \quad \gamma_{ad} = \gamma_h + \gamma_{dh} - \gamma_m, \quad (9)$$

where γ_d - surface silicon energy on air interface. The first expression for A_{ad} (9) is well-known ratio of physical chemistry, second expression γ_{ad} (9) is entered in the same way as for A_{ad} – “adhesive bonds energy”.

For numerical calculations of energy and adhesion characteristics of the interphase layer of contacting interfaces according to above method, based on (1) – (9), the following values of physical constants were used for silicon (index “+”) and metals Cr, Cu, Au, Al (index “-”) [23,24]:

$$\begin{aligned}
E_+ &= 138 \text{ ГПа}; \nu_+ = 0,27; \omega_+ = 5 \cdot 10^{28} \text{ 1/M}^3; \sigma_{h_+} = 1,328 \text{ H/M}, \gamma_+ = 1,182 \text{ Дж/М}^2 \text{ (Si)}; \\
E_- &= 279 \text{ ГПа}; \nu_- = 0,21; \omega_- = 8,33 \cdot 10^{28} \text{ 1/M}^3; \sigma_{h_-} = 2,51 \text{ H/M}, \gamma_- = 1,854 \text{ Дж/М}^2 \text{ (Cr)}; \\
E_- &= 132 \text{ ГПа}; \nu_- = 0,34; \omega_- = 8,45 \cdot 10^{28} \text{ 1/M}^3; \sigma_{h_-} = 2,16 \text{ H/M}, \gamma_- = 1,992 \text{ Дж/М}^2 \text{ (Cu)}; \quad (10) \\
E_- &= 220 \text{ ГПа}; \nu_- = 0,44; \omega_- = 3,4 \cdot 10^{28} \text{ 1/M}^3; \sigma_{h_-} = 1,89 \text{ H/M}, \gamma_- = 1,18 \text{ Дж/М}^2 \text{ (Au)}; \\
E_- &= 70 \text{ ГПа}; \nu_- = 0,35; \omega_- = 18,6 \cdot 10^{28} \text{ 1/M}^3; \sigma_{h_-} = 1,22 \text{ H/M}, \gamma_- = 1,043 \text{ Дж/М}^2 \text{ (Al)}.
\end{aligned}$$

Surface energies γ_+ and γ_- were evaluated for "metal - silicon" interface by method of atomic interactions with Born-Mayer forces $u_{\alpha\beta}$ [20]:

$$u_{\alpha\beta} = \frac{q^2}{R_{\alpha\beta}} - \frac{c_{\alpha\beta}}{R_{\alpha\beta}^6} - \frac{d_{\alpha\beta}}{R_{\alpha\beta}^8} + b_{\alpha\beta} \exp\left(\frac{R_{\alpha\beta}}{\rho_q}\right), \quad (11)$$

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

Based on small-parameter expansion method [20, 25] (small parameter for metal is $b_M = b\Phi_0$, small parameter for semiconductor is $b_{MC} = b_C Z_C$) with equations (1)–(11) after solving contact-boundary problems at room temperature the value of material energies and adhesive characteristics of "Si - metals (Cr, Cu, Au, Al)" interphase layer were evaluated. The calculations are given in the table. 1 (contacting systems are placed in order of increasing maximum stress values $\sigma_y = \sigma_{\max}$).

Table 1. Thermodynamic parameters of interaction in the system of "metal condensate - single crystal semiconductor substrate (Si,Ge)"

(ΔX - electronegativity difference; γ_m - interphase energy, σ_m - interphase tension; A_{ad} - work of adhesion, γ_{ad} - energy of adhesive bonds, Q_m is the interphase charge). $Z_{ad} = A_{ad} / \gamma_{ad}$

Surface	ΔX	γ_m , J/m ²	σ_m , N/m	A_{ad} , N/m	γ_{ad} , J/m ²	$Z_{ad} = A_{ad} / \gamma_{ad}$	Q_m , K/m ²
Si-Cr (sol.)	0,34	0,31	0,75	3,09	2,72	1,13	0,126
Si-Cr (liq.)	0,34	0,20	0,52	2,10	1,92	1,09	–
Si-Cu (sol.)	0,14	0,27	0,61	2,88	2,90	0,99	0,123
Si-Cu (liq.)	0,14	0,18	0,41	1,88	1,90	0,99	–
Si-Au (sol.)	0,38	0,12	0,37	2,84	2,24	1,27	0,093
Si-Au (liq.)	0,38	0,76	0,25	1,92	1,82	1,05	–
Si-Al (sol.)	0,33	0,08	0,10	2,24	2,15	1,08	0,099
Si-Al (p.)	0,33	0,05	0,07	1,62	1,70	0,95	–
Ge-Cr	0,45	0,41	0,89	2,25	2,06	0,26	0,150
Ge-Cu	0,25	0,20	0,46	2,73	2,71	0,37	0,110
Ge-Au	0,58	0,07	0,24	2,68	2,01	0,45	0,078
Ge-Al	0,54	0,22	0,46	1,79	1,74	0,34	0,125

The characteristic parameter of silicon-metal interfaces is value of interacting materials electronegativity difference, which does not exceed 0,4.

The evaluated data contain quantitative information about the features of interphase and adhesive interactions on "semiconductor - metal (Cr, Cu, Au, Al)" interface. In particular, in analyzed series of "Si – Me" interface, the σ_{\max} increase is accompanied with decrease of interfacial energy, interfacial tension, and adhesion work. A similar regularity is observed for new parameter γ_{ad} (adhesive bonds energy), evaluated with macroscopic parameters (it characterizes the level of particles energetic interaction in the near-surface layer). Exceptions was found only for copper, which is "anomalous", as already mentioned for other relation. Such tendency change can be characteristic for other systems as well, if it is necessary to predict changes in the level of maximum internal stresses and predict adhesive properties. Another feature in behaviour of interfacial interaction parameters is constancy of interfacial charge Q_m (the charge of the conventional covering of the electric double layer in the metal region) on "Si – Me (Cr, Cu, Au, Al)" (Q_m) interface.

Therefore, the self-organizing role of substrate during condensation of listed metals will be distinguished by values of electronegativity of substrate materials and condensate.

The difference in energy parameters of interphase interaction of deposited metals, indicates different adhesive abilities of such interfaces. In addition, it is precisely due to this factor that some differences in the morphology of the deposited metal condensates against the background of the self-organizing effect of the Si substrate should be expected, which is observed according to the results of AFM microscopy [26].

The determining factor (table 1) is jump in interphase interaction parameters γ_m , σ_m , A_{ad} and γ_{ad} , which is typical phenomenon for first kind phase transition of melt (Cu – substrate (Si) → melt (Cu) – substrate (Si)).

Such phenomenon is in all condensed metals and indicates the change in the alternative mechanism of interphase interaction in the dynamic transition in the "condensate - substrate" system when the nanodispersed liquid substance transmit to island structure.

For comparison, let's consider energy and adhesion parameters of Ge-based systems, which is similar in physical properties to Si, but has higher electronegativity ($\Delta X_{Ge} = 2,01$). The last factor determines the value of the electronegativity difference $\Delta X_{Ge-Me} > 0,4$ (except for Cu) for the selected metals, which ensures dominance in the interphase layer of contacting boundaries of the ionic-covalent bond type. Table 1 shows thermodynamic and adhesion parameters of the investigated Ge-based systems. It follows from the given data that these interphase do not have significant differences in the behaviour of the parameters, compared to the similar ones for the "Si – Me" systems, although they differ in absolute value. It's possibly this situation is the relatively insignificant contribution of the ionic component to the interphase interaction of such contacting systems. However, the interphase energy for such series of metals decreases, similarly as for Si-based substrate, but doubles these values for Si – Cr, Si – Al. A similar tendency is revealed by the interfacial tension and adhesion work. It is likely that better adhesion should be expected in contacting systems with dominance of covalent bonding. The interphase charge Q_m (coating charge of electric double layer) on "Ge – Me" boundary also does not undergo significant change.

Conclusions

The peculiarity of interphase interaction at the boundary of "metal nanocondensate (Cu, Al, Cr, Au) - solid substrate (Si)" is dominated with self-organization processes on silicon substrate surface, which provides equivalent conditions for wetting of non-equilibrium island-dispersed metal condensate. The degree of self-organizing role of substrate in nanocondensates formation process is determined by electronegativity difference ΔX value of substrate materials and the condensate (for silicon and deposited metals, the condition $\Delta X < 0,4$ is fulfilled, which ensures stable covalent bond in the "silicon - metal nanocondensate" system). The time of maximum level formation of internal stresses (time of Oswald ripening according to the two-stage dependence) at condensation of copper, gold, aluminum, and chromium on Si (111) substrates at speed 0,03–2,0 nm/s is constant (220 c) and is determined by self-organizing role of silicon surface crystallographic orientation (111). The jump in interphase interaction parameters γ_m , σ_m , A_{ad} and γ_{ad} , during phase transition at "melt (Cu) – substrate (Si)" → "solid phase (Cu) – substrate (Si)" was detected.

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ВНУТРІШНІ МЕХАНІЧНІ НАПРУЖЕННЯ ТА САМООРГАНІЗАЦІЙНІ ПРОЦЕСИ В СИСТЕМІ “КРЕМНІЙ –МЕТАЛІЧНИЙ КОНДЕНСАТ”**Б. П. Коман, В. М. Юзевич, Р. І. Бігун**

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Природу термічної компоненти механічних напружень $\sigma_{тер}$ вивчено на сьогодні достатньо добре для багатьох металічних конденсатів. Завдяки численным дослідженням проблему її мінімізації вирішують сьогодні навіть у доволі складних системах – реальних структурах сучасної мікроелектроніки (здебільшого технологічними методами). Однак, природа власної (внутрішньої) компоненти механічного напруження і досі має дискусійний характер. Існують лише певні модельні представлення механізмів виникнення таких напружень. Відсутнє також фізичне бачення природи механічних напружень у металевих наноконденсатах.

Унікальним результатом роботи є виявлена динаміка характерного максимуму напружень σ_{max} наноконденсатів від швидкості їх осадження. Встановлено, що максимум σ_{max} вкладаються на пряму лінію від швидкості конденсації. На цю ж лінію, крім Cu та Al, вкладаються також значення максимальних напружень для плівок Cr та Au. Таким чином, для кремневої підкладки, кутовий коефіцієнт нахилу такої залежності однаковий для досліджуваних металічних конденсатів: Cr, Cu, Au, Al. Кутовий коефіцієнт нахилу прямої, має розмірність часу - час переходу металічних конденсатів від острівкової системи до суцільної плівки з просторовим каркасом по всій площі підкладки за різних швидкостей їхнього осадження стосовно заданої кристалографічної орієнтації підкладки. Для досліджуваних металів, характеристичний час однаковий і становить близько 220 с. Він відповідає, часу оствальдівського дозрівання металевого конденсату на поверхні підкладки. Укладання на одну лінію характерних максимумів напружень для різних металів, засвідчує переважаючу роль підкладки у формуванні цих напружень на початковій стадії конденсації металу. Формуванню внутрішніх механічних напружень, у металічних наноконденсатах Cu, Au, Al та Cr, зумовлене впливом процесу самоорганізації з боку підкладки, що забезпечує однакові умови розтікання нерівноважної металічної острівцевої наноплівки по поверхні кремнію.

В роботі досліджено закономірності формування внутрішніх напружень в металічних конденсатах (Cu, Al, Cr, Au) та особливості самоорганізаційних процесів у підкладках монокристалічного кремнію. Проаналізовано поведінку параметрів міжфазової взаємодії в системах “металічна плівка (Cu, Al, Cr, Au) - кремній” та за фазового переходу “розплав (метал) - тверда фаза (метал)” на досліджуваній підкладці. Запропонована методика оцінювання часу формування максимальних внутрішніх напружень в металічних конденсатах на твердотільних підкладках та механізм їх формування. Для систем “Si – ме (Cr, Cu, Au, Al)” розраховані значення енергетичних параметрів міжфазової взаємодії: міжфазового натягу, міжфазової енергії, роботи адгезії та енергії адгезійних зв’язків.

Ключові слова: міжфазова границя, міжфазова взаємодія: сила міжфазового натягу, енергія міжфазової взаємодії, робота адгезії, енергія адгезійних зв’язків.

Стаття надійшла до редакції 09.02.2023

Прийнята до друку 15.02.2023