DYMENSIONAL IMPURITY EFFECTS IN A CRYSTAL STRUCTURE OF THIN METAL FILMS

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In the present work it is established that under metal films condensation under rough vacuum conditions the formation of anomalous modifications, which are always observed in bulk samples, occurs. Based on the theoretical and experimental analysis of our and other authors results we concluded that these phases become stable due to the action of dimensional impurity effect and they are penetration phases of remaining atmosphere gases into metal lattice.

Keywords: *CRYSTAL STRUCTURE, DIMENSIONAL IMPURITY EFFECTS, CRITICAL THICKNESS, PHASE TRANSITIONS, ANOMALOUS PHASES.*

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1. INTRODUCTION

A question about anomalous phases initiation, their chemical composition and stabilization mechanism in thin layers of the transition and rare-earth metals was discussing in [1-5] for a long time. The assumed polymorphous metal modifications, which are not observed in bulk samples, the metastable amorphous phase, which is formed due to low diffusive mobility of atoms of condensed matter on a substrate, the high-temperature forms in bulk samples, which become stable in thin films at rather low temperatures, the impurity phases, which are formed because of the interaction between an atomic beam and atoms of remaining atmosphere, are related to a number of these phases. Correct interpretation of chemical composition of anomalous phases is complicated because of the lack of experimental results, and due to vicinity of lattice parameters and expected polymorphous modifications as well.

Such authors as D.I. Lainer and V.A. Kholmyanskii (Ta films), S.A. Semiletov and others (rare-earth metal and transition d-metal films), M. Gasgnier and A. Curzon (rare-earth metal films), Z.Z. Zyman (Ti films) and other authors (see the analysis of these works in Ref. [4]) concluded that experimental conditions, at which anomalous phases are formed, are far from the ideal ones for stabilization of polymorphous modifications, and therefore, if proceed from crystallographic analysis data, these phases, most likely, are the inter-stitial phases. At the same time, A.I. Bublik and B.Ya. Pines (Cr, V, and Ni films), P. Denbigh and R. Marcus (Ta and Mo films), K. Chopra and others (Zr, Hf, and Re films), E. Miske and M. Gillet, R. Marcus and S. Quigley (Ta films), N.T. Gladkih (rare-earth metal and transition d-metal films) had interpreted the anomalous phases as the polymorphous metal modifications, which are formed in accordance with the phase dimensional effect theory [1]. The authors of Ref. [6, 7] had interpreted the anomalous hexagonal phase in epitaxial Ni/(001)Au films [6] or in Ni films, which are

deposited by laser sputtering on the substrates (001)KCl or a-C/(001)KCl [7], as the metastable polymorphous modification, which becomes stable due to the phase dimensional effect. Note, that only authors of Ref [1, 4, 8-10] made an attempt of thermodynamical estimation of polymorphous transition critical thickness based on a theory of Ref. [1]. Thus, the conclusions of different authors about impurity or polymorphous nature of anomalous phases are mostly qualitative, since they based on the chemical analysis of crystals. At the same time both points of view have the right to life, because the first one is natural and logical, if one takes into account the high chemical activity of film materials on the basis of rare-earth metals and transition d-metals, and the second one does not contradict to general thermodynamic considerations of the work [1]. The analysis of anomalous phases nature, based on our own experimental results, is represented below.

We and the authors of cited works have obtained the film samples using the vacuum plants with oil pumping VUP-4 and VUP-5 (the residual gases pressure was $P \cong 2 \cdot 10^{-4}$ Pa) and, in individual cases, using ultrahigh-vacuum plant with oil-free pumping and minimal pressure $P \cong 10^{-7}$ Pa. Evaporation of refractory metals (Ti, Zr, Hf, V, Nb, Ta, Mo, W, Re, Co, and Ni) was done using an electron-beam gun. Relatively fusible metals (Sc, Y, and Cr) were evaporated by usual resistive method from Mo-, W-, and (Ta-Re)-boats. The freshly-deposited carbon films or NaCl single-crystal wafers (100) were used as substrates for films, meant for the further structural study. Thin films of Al (the accuracy is $\pm$ 0,001 nm) or NaCl ($\pm$ 0,0002 nm), deposited on observable metal film in this technological process, were the standards under interplanar spacing calculation.

The microscope REMMA-4 was used for obtaining the electron-diffraction patterns and for carrying out the electron-microscopic study. An elemental composition of initial sample and thin films was studied by the method of the secondary ion mass-spectrometry using the device MS-7201M, and phase transformations in a process of films annealing were directly studied in a micro-scope column by sample heating with an electron beam or a special stove.

The dual-probe method based on the digital device V7-23 was applied for study of electrophysical properties of anomalous phases. Glass polished plates with fused molybdenum rods − the current leads − were used as substrates in this case.

2. CRYSTAL STRUCTURE, CHEMICAL COMPOSITION AND ELECTRICAL PROPERTIES OF ANOMALOUS PHASES

During the study of phase composition of films, obtained in rough vacuum, the anomalous phases formation with the face-centered cubic (fcc) lattice, the hexagonal close-packed (hcp) one, or much more rare, with more complex lattices was observed. The diffraction patterns of anomalous phases, which become stable in V (a), W (b), and Cr (c) films what correspond to the compositions VO_x (x $\cong$ 1), W_3O, and Cr_2O_3, are presented in Fig. 1. Typical diagram of the phase composition in T_s-d coordinates on the example of Nb films (T_s is the substrate temperature, d is the film thickness) is represented in Fig. 2.

The characteristic property of the given diagrams is that under decreases of condensation velocity and/or increase of residual gases pressure the transition points from an amorphous phase into a crystal one or from an anomalous phase into a phase, typical for bulk samples, are displaced to a region of greater

thickness and temperature. Under improvement of conden-sation conditions the stabilization region of anomalous phases is appreciably narrowed and in ultrahigh vacuum ($P \cong 10^{-5}$-10^{-8} Pa) anomalous phases are not fixed at all.
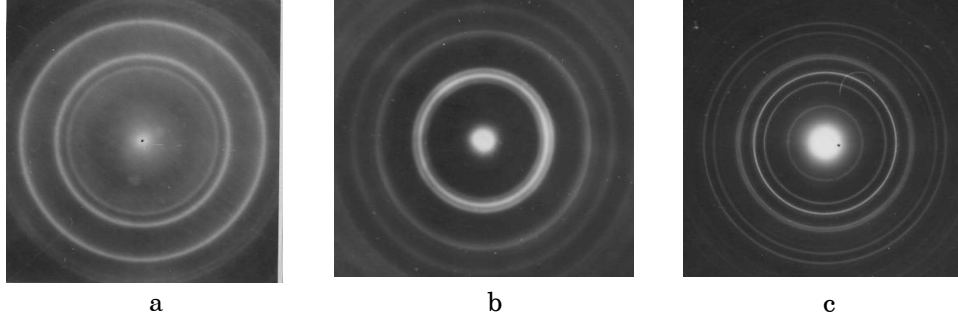
Fig. 1 − *Diffraction patterns of anomalous phases with the fcc lattice (a), the lattice of A-15 type (b), and the spinel type (c)*
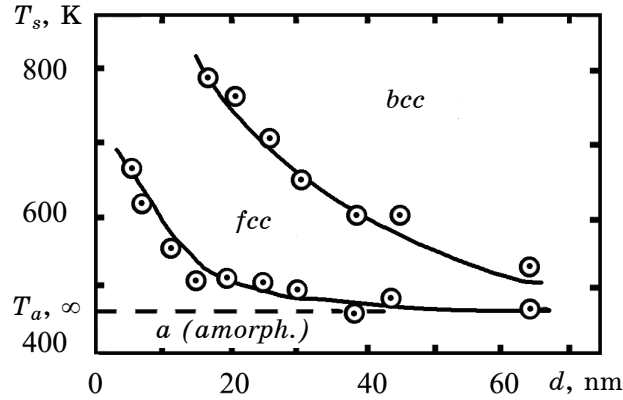
Fig. 2 − *Diagram of the phase composition for Nb films. T_a,∞ is the temperature, below which in films the amorphous phase becomes stable at $d \to \infty$. The interpretation of the fcc phase nature is presented in Table 2.*

This data allows to suggest that they become stable due to the interaction of atoms of deposited metal with residual gases that is confirmed by indirect data. For example, approaching to the transition point fcc → bcc (body-centered cubic) a crystal lattice undergoes a very strong distortion, shown in that on the electron-diffraction patterns the line (113) is displaced towards the greater angles and the line (200) is displaced towards the smaller ones, and the others lines (220), (311), (222) are displaced very negligible. Distortion gradually reaches such degree, that it is impossible to interpret a lattice as the fcc one. At the same time it cannot be interpreted as the fcc lattice with stacking faults, since lines displacement does not correspond to the well-known Paterson scheme. Evidently, in this case the so-called concentration dimensional effect [5] (decrease of impurity atoms concentration while thickness increases due to a natural gas depletion of remaining medium) is shown. The impurity concentration decrease takes also place

under a substrate temperature increase (here a film thickness can be fixed), and in this case, not the dimensional effect, but the usual residual gases desorption from a substrate surface or a growing film is shown.

The reproduction of a films phase composition is possible in the case when holds the condition of some reduced parameter constancy

$$\alpha = AP \big/ \omega \sqrt{T_s} \ ,$$

which is, in fact, is the ratio of a number of residual gases molecules and a number of evaporable metal atoms (A is the certain constant coefficient, ω is the condensation rate). Varying P, ω, and T_s with other fixed condensation parameters (thickness, angle of molecular beam inflow, and others) it is possible to control a film phase composition and predict a probability of any anomalous phase formation. The aforesaid can be illustrated (see Table 1) by an example of thin Sc films, where at the parameter value $\alpha < 8,1\cdot10^{-7}$ Pa·sec/(m·K$^{1/2}$) the Sc hcp takes place, that is the phase proper to bulk samples, while at $\alpha > 2,4\cdot10^{-6}$ Pa·sec/(m·K$^{1/2}$) an anomalous phase in the form of ScH$_x$ hybrid ($x \cong 2$) is formed. In the range of intermediate values of α the disordered hexagonal Sc phase is observed. We note, that in [11] one more phase with the fcc lattice and parameter $\alpha = 0,492$ nm is described, and in the authors of [11] judgment it is the polymorphous modification, in contrast to the fcc phase that corresponds to ScH$_x$ [10]. Since the present work does not enclose the interpretation of this phase stabilizing mechanism, the conclusions of [11] seem to be unconvincing (significant error in characterization of lattice constant is non-exceptional). Also note, that in [12] the anomalous fcc phase in Sm films is hypothetically interpreted as a SmH$_x$ hybrid, which is oxidized to SmO$_3$.

Table 1 − *Experimantal data about the condensation conditions, parameter* α, *and the phase composition of Sc films obtained at T* = 300 K

№	d, nm	ω, nm/sec	P, Pa	α, Pa·sec/m·K$^{1/2}$	Phase composition
1	158,6	0,47	$1\cdot10^{-3}$	$1,2\cdot10^{-5}$	ScH$_x$ fcc
2	84,5	0,70	$5\cdot10^{-4}$	$4,1\cdot10^{-6}$	ScH$_x$ fcc
3	114,4	4,50	$2\cdot10^{-3}$	$2,0\cdot10^{-6}$	ScH$_x$ fcc
4	106,6	7,10	$3\cdot10^{-3}$	$2,4\cdot10^{-6}$	ScH$_x$ fcc
5	104,0	3,50	$8\cdot10^{-4}$	$1,3\cdot10^{-6}$	hcp disordered
6	110,5	4,40	$1\cdot10^{-3}$	$1,6\cdot10^{-6}$	hcp disordered
7	104,0	5,20	$2\cdot10^{-3}$	$1,9\cdot10^{-6}$	hcp disordered
8	117,0	7,80	$2\cdot10^{-3}$	$1,5\cdot10^{-6}$	ScH$_x$ fcc + Sc hcp
9	156,0	8,60	$1\cdot10^{-3}$	$8,1\cdot10^{-7}$	Sc hcp
10	201,5	15,5	$5\cdot10^{-4}$	$1,8\cdot10^{-7}$	Sc hcp
11	279,5	15,5	$8\cdot10^{-4}$	$3\cdot10^{-7}$	Sc hcp

Studying electrophysical properties of anomalous phases their relatively high resistivity was discovered, and, basically, the semiconducting behavior of conduction. In individual cases electrophysical properties of anomalous phases have their own features. Thus, in the case of fcc phase with a lattice constant from $\alpha = 0,426$ nm to $\alpha = 0,438$ nm, which is observed in Nb films [13], on the temperature dependence of resistivity (ρ), that is 10^3-10^4 times

larger in comparison with resistivity of Nb bcc, two sections with different activation energy of electrical conduction $\Delta\varepsilon_1 = 0,30$ eV (at $T < 500$ K) and $\Delta\varepsilon_2 = 1,75$ eV (at $T > 500$ K) are fixed. Such a clearly defined semiconductor properties of this anomalous phase confirm an impurity mechanism of its stabilization. Analysis of lines strengths on the electron-diffraction patterns and values of a lattice constant allows to conclude that chemical composition of the present fcc phase is closed to NbN_xO_{1-x}, $x \cong 0,3$-$0,5$. Note, that during this phase annealing up to $T > 820$ K the NbO_x ($x \cong 1$) fcc formation with some other electrical properties occurs.

In thin Ti films two temperature intervals on the $\rho(T)$ dependence with activation energies of electrical conduction $\Delta\varepsilon_1 = 0,18 \cdot 10^{-2}$ eV and $\Delta\varepsilon_2 = (0,23$-$6,65) \cdot 10^{-2}$ eV, that corresponds to two different phases on the Ti basis − hcp (Ti, O) and fcc TiO_x ($x \cong 1$), − are fixed as well.

Such a large spread of $\Delta\varepsilon_2$ suggests that during the annealing process of TiO_x phase in rough vacuum ($\sim 10^{-3}$ Pa) its interaction with the atoms of remaining atmosphere occurs. This is in full confirmed during the TiO_x production and annealing in vacuum $\sim 10^{-5}$-10^{-6} Pa. In this case $\Delta\varepsilon_2$ had a fixed value $\Delta\varepsilon_2 = 14,6 \cdot 10^{-2}$ eV in the temperature range of $300 - 600$ K (at $T > 600$ K the TiO_x decay with formation of Ti hcp occurs).

The anomalous phases, observed under V films condensation, have their own features in electrophysical properties. The phase composition variety (amorphous (a) V or VO_x ($x \cong 1$), crystalline phases VO_x, V_2O_3, VO_2, V_2O_5, and others) gives an opportunity for their wide practical application as sensors of a critical temperature (VO_2 and V_2O_3 films) [14, 15]; resists for nanolithography (a-V) [16] with 70 nm resolution; precursors for nanolithography resist development (nano-V (grain size is 30-50 nm)) [16, 17] and so forth. According to the data of [14, 15] in VO_2 films in the temperature range of 340-350 K the phase transition from a low-temperature phase with monoclinic lattice and high resistivity to a high-temperature metal tetragonal phase occurs, which is accompanied by the simultaneous phase transition of type II metal-dielectric (semiconductor). As a result of transition the resistivity decreases by 3-4 orders at $d \cong 1000$ nm or by an order at $d \cong 100$ nm, although the critical transition temperature and its hysteresis do not depend on a thickness. Such resistivity behavior of VO_2 film allows to use it as a thermoresistor in the scheme of effective thermal protection during transitions or temperature increases. The obvious drawback of such a sensor is the relatively low work temperature. Therefore in [18] the electrophysical properties of $V_2O_3 + VO_x$ heterogeneous films have been studied from the point of view of their applicability as a high-temperature sensor of critical temperature, since the temperature of the phase transition of type II in bulk V_2O_3 is 430-520 K [19]. The researches of [18] showed that under annealing in vacuum $\sim 10^{-3}$ Pa the film with VO_x composition gradually passes into V_2O_3, although a small amount of VO_x remaines in samples. Consider in detail the $\rho(T)$ dependence behavior in this case. Starting from $T = 300$ K the value $\rho = 5 \cdot 10^{-6}$ Ohm·m remains sensibly constant until $T = 430$ K, and in the range of 430-500 K it is doubled. Then in the range of 500-570 K a growth rate of ρ decreases, but at $T = 570$-600 K it rises again up to value $\rho \cong 1,7 \cdot 10^{-5}$ Ohm·m. The authors of [18]

suggest that the second resistivity jump is connected with the total film oxidation to the V_2O_3 composition. They also note a hysteresis of the $\rho(T)$ dependence at $T < 600$ K and its irreversible behavior, if hold V_2O_3 film at $T = 570\text{-}600$ K, that first of all is connected with the further V_2O_3 oxidation to $VO_{1,75}$-VO_2 and V_2O_5 composition.

As to the conclusions of [6, 7] about polymorphous nature of the hcp phase in Ni films it is necessary to make such a remark. According to our data [8] this phase is generated because of the interaction of Ni and N atoms what is confirmed by the other authors conclusions (see papers cited in [8]). If in the case of [6] the stabilization of metastable hcp modification can take place that conclusions of [7] are doubtful, since the experimental values of the lattice constants, calculated in [7] on the basis of electron-diffraction patterns, have quantities $a = 0,266$ nm and $c = 0,433$ nm, that corresponds to the data of [8], and they considerably differ from the theoretical values $a_t = 0,249$ nm and $c_t = 0,406$ nm for a conjectural Ni hcp phase.

Based on the obtained results we prejudiced the feasibility of the phase dimensional effect [1] in rare-earth and d-metal films. In this connection the research of chemical composition of anomalous phases was carried out. In Fig. 3 the typical mass-spectrums of secondary ions from anomalous fcc phases, observed in Mo and W films, are presented, which confirm the conclusion about impurity stabilization mechanism of anomalous fcc phases in these films. The same results are obtained based on the example of anomalous phases in V and Nb films as well.
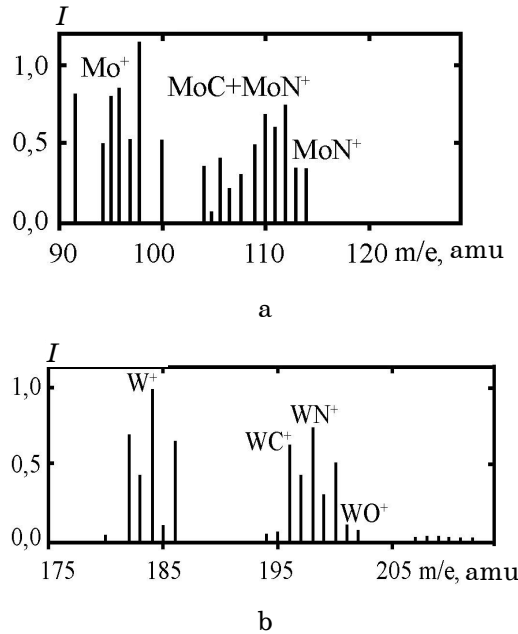
Fig. 3 − Mass-spectrum of secondary ions from anomalous fcc phases in Mo (a) and W (b) films

The known results about anomalous phases in thin films are colligated in Table 2. Data about type and lattice constants, formation conditions and supposed chemical composition is presented here. Taking into account the presented results it is necessary to discuss a question of principle − the stabilization reason in thin and island films of polymorphous modifications, which are not observed in bulk samples.

Table 2 − *Experimental data about anomalous phases in transition d-metal films*

Film material	Lattice type	Lattice parameter, nm	Electrical properties	Formation conditions	Chemical composition
1	2	3	4	5	6
Sc	fcc CaF_2 type	0,478	Metallic conduction	During the condensation in vacuum $\sim 10^{-4}$ Pa	ScH_x, $x \cong 2$
	bcc Mn_2O_3 type	0,989	Dielectric	During the ScH_x annealing in vacuum	Sc_2O_3
Y	fcc CaF_2 type	0,529	Metallic conduction	During the condensation	YH_x, $x \cong 2$
	bcc Mn_2O_3 type	1,0697	Dielectric	During the YH_x annealing in vacuum	Y_2O_3
Gd	fcc CaF_2 type	0,528	–	–	GdH_x, $x \cong 2$
	bcc Mn_2O_3 type	–	–	During the GdH_x annealing in vacuum	Gd_2O_3
Ti	fcc NaCl type	0,422	Semiconductor conduction with activation energy $\Delta\varepsilon_2 = (0,23\text{-}14,6)\times \times 10^{-2}$ eV	During the condensation	TiO_x, $x \cong 1$
	fcc Al type	0,432	–	During the condensation	$TiC_xO_{x\text{-}1}$
Zr	fcc Al type	0,504	Dielectric	During the amorph. films annealing in vacuum $\sim 10^{-3}$ Pa	ZrO_x, $x \cong 2$
Hf	fcc Al type	0,501-0,506	–	During the amorph. films annealing in vacuum $\sim 10^{-3}$ Pa	HfO_x, $x \cong 2$
V	fcc NaCl type	0,406-0,411	Semiconductor conduction with $\Delta\varepsilon = 0,07$ eV	During the condensation	VO_x, $x \cong 1$

1	2	3	4	5	6
Nb	fcc Al type	0,426-0,438	Semiconductor conduction with $\Delta\varepsilon_1 = 0,3$ eV ($T < 500$ K) and $\Delta\varepsilon_2 = 1,75$ eV ($T > 500$ K)	During the condensation	NbN_xO_{1-x}
Ta	fcc Al type	0,445	Very high resistivity	During the condensation	TaC_x, $x \cong 1$
Cr	sc Al5 type	0,458	Resistance can not be measured, as it's impossible to obtain a pure phase	During the condensation	Cr_3O
Mo	sc Al5 type	0,499	-"-	During the condensation	Mo_3O
W	sc Al5 type	0,504	-"-	During the condensation	W_3O
Mo	fcc Al type	0,415-0,417	-"-	During the condensation	MoC_xN_{1-x}
W	fcc Al type	0,416	-"-	During the condensation	WC_xN_{1-x}
	fcc Al type	0,425	–	During the annealing of W/C bcc film system up to $T = 970$ K	WC_x, $x \cong 1$
Pd	fcc CaF_2 type	0,405	–	During the annealing up to $T \cong 900$ K	PdH_x
Re	sc Al5 type	0,329	Dielectric	During the condensation	ReO_3
	hcp Ti_3O type	$a = 0,323$ $c = 0,508$	Metallic conduction	During the amorph. or cryst. Re films annealing	Re_3O
Ni	hexagonal	$a = 0,264$ $c = 0,444$	Semiconductor conduction	During the Ni fcc annealing	Ni_3N

3. ANALYSIS OF POLYMORPHIC TRANSFORMATIONS POSIBILITY IN SAMPLES

The Table 2 data prejudices an idea about the feasibility of polymorphous transitions by the A.I. Bublik and B.Ya. Pines [1] mechanism. According to numerous authors data, in thin films and fine particles the following types of polymorphic transformations can be observed: decrease of a phase transition pressure [20]; stabilization of high-temperature crystalline phases at substrate temperature $T_s < T_0$ (T_0 is the phase transition temperature in bulky crystal); formation of crystalline phases with smaller surface energy,

which is not observed in bulk samples. The two first cases are confirmed experimentally. Thus, in thin InSb films the phases of high pressure InSb II and IV [20] are found and the temperature decrease of hcp → fcc transition in Tl [21] and Co [22] films is fixed. As to the last case, just using it the mechanism of anomalous phases stabilization, described in the previous section, can be explained. We will show, that even within the phenomeno-logical theory [1] one can conclude about the formation impossibility of the pointed polymorphous modifications in the form of equilibrium phases in transition d-metal films. For this we use the thermodynamic considerations, developed in [1], for estimation of the phase transition critical thickness d^* in a free polycrystalline film.

If in the bulky crystal one of two phases has smaller free energy (for example, $F_{01} < F_{02}$) then in a thin film, taking into account the surface energy σ, this inequality can be the inverse one:

$$F_{01} + \left(\frac{\sigma A}{V}\right)_1 + \left(\frac{\sum\limits_{i,k} \sigma_{i,k} A_{i,k}}{V}\right)_1 > F_{02} + \left(\frac{\sigma A}{V}\right)_2 + \left(\frac{\sum\limits_{i,k} \sigma_{i,k} A_{i,k}}{V}\right)_2, \qquad (1)$$

where σ, σA, and σ_{ik} are the specific, the total surface, and the grain boundary specific energies, respectively; A and A_{ik} are the surface area of a film or a small particle and the contact area of the i-th and k-th grains, respectively; V is the film (or small particle) volume.

For a polycrystalline film of unit thickness, in assumption that during the phase transformation $2 \rightarrow 1$ the grain boundary area remains, we can obtain an expression for the critical thickness, below which the phase 2 and above which the phase 1 become stable

$$d^* = \frac{2(\sigma_1 - \sigma_2)}{F_{02} - F_{01}} + \frac{\sum\limits_{i,k} A_{ik}(\sigma_{ik}^{(1)} - \sigma_{ik}^{(2)})}{F_{02} - F_{01}}, \qquad (2)$$

where the first term corresponds to the critical thickness of the single-crystal film, and the second one gives some addition to d^* of the single-crystal film. Because of the small difference ($\sigma_{ik}^{(1)} - \sigma_{ik}^{(2)}$) this addition will be insignificant. In connection with this the estimation and calculation of d^* will be carried out for a single-crystal film using relation (1), transformed to the following type:

$$d^* = \frac{d_2(1 + \varepsilon)(1 - z_{n2} / z_{02}) - d_1(1 - z_{n1} / z_{01})}{\varepsilon(1 - T / T_0)}, \qquad (3)$$

where z_n and z_0 are the surface and the bulk coordination numbers, d_i is the interplanar spacing between layers parallel to a film surface, and $\varepsilon = (U_1 - U_2)/U_1 = \lambda_{1\rightarrow 2}/U_1$ ($\lambda_{1\rightarrow 2}$ is the phase transition heat).

Applying relation (3) to the specific, the more energetically efficient, equilibrium phase transitions

(111) fcc (2) → (110) bcc (1),
(100) hcp (2) → (111) fcc (1),
(111) fcc (2) → (100) hcp (1),

one can obtain the following relation for d^*:

$$d* = \frac{0,01 - 0,242 \frac{\Delta v}{v_1}(1+\varepsilon) + 0,364\varepsilon}{\varepsilon(1 - T/T_0)} a_1; \ d* = \frac{c_2(1+\varepsilon) - 2a_1/\sqrt{3}}{4\varepsilon(1 - T/T_0)};$$

$$d* = \frac{0,288(1+\varepsilon)a_2 - 0,250c_1}{\varepsilon(1 - T/T_0)},$$

where $\Delta v/v_1$ is the relative change of the lattice volume, a and c are the lattice parameters (c is calculated from relations $c_2 = 1,63 \ a_2$ and $a_2 = a_1/\sqrt{2}$).

The same relations can be obtained (see [4] in detail) for the meta-stable transitions, that is such conjectural transitions, when both phases orientate relative to a substrate by the planes, which have non-minimal surface energy (for example, transitions (111) fcc (2) → (100) bcc (1), (100) fcc (2) → (110) bcc (1), and others). Note that under condensation on amorphous substrates in equilibrium conditions only transitions of the type (4) must be realized. Other transitions can take place under condensation on a single-crystal substrate in quasi-equilibrium conditions and on amorphous substrates in non-equilibrium conditions. We should also emphasize that the phenomeno-logical thermodynamics has limits of applicability and, surely, the less film thickness, the worse results accuracy. Studying phase transitions in Co particles [22] a good quantitative agreement with calculation of the relative temperature decrease of the fcc → hcp phase transition, realized within relation (2), is obtained. This shows that sometimes suggested a priori opinion about theory inapplicability [1] to thin films is not quite right. The final result essentially depends on how reasonable values of ε and T_0 will be the basis for calculations. Obviously, it is reasonable to assume that in monomorphic (in a bulky state) metals $T << T_0$, since in this case T_0 at least is above the melting temperature, and T does not exceed the melting temperature of a thin film. The estimation of ε can be done, using values of the phase transition heat and the internal energy for bulk samples, which undergo any phase transitions. For example, for the fcc → bcc transition one can use the specified values for Mn, La, Ce, Yb, and Fe, and in this case $\varepsilon_{min} = 1,63 \cdot 10^{-3}$, $\varepsilon_{max} = 10,6 \cdot 10^{-3}$, and $\varepsilon_{av} = 6,1 \cdot 10^{-3}$. For the fcc → hcp transition using data for Co, La, and Ti the corresponding values of ε are: $0,9 \cdot 10^{-3}$; $2,8 \cdot 10^{-3}$, and $1,8 \cdot 10^{-3}$. Since transition d-metals do not generally possess polymorphism, it is necessary to calculate the lattice parameter value of anomalous phase (for example, calculated values of a_2 for Mo and W are 0,397 nm and 0,399 nm, respectively, while the experimentally observed values are 0,411-0,420 nm and 0,415-0,425 nm).

In Table 3 the values of critical thickness for films of bcc and hcp metals are presented, and we have considered the examples of equilibrium and non-equilibrium planes interfacing (the values of d^*, obtained using the minimum value of a_{2exp}, are in the brackets). For Ni films ($a_1 = 0,352$ nm, $a_{2calc} = 0,249$ nm, and $c_{2calc} = 0,406$ nm) $d^* = 0,1$ nm.

We have already noted that the phenomenological theory, used by us, gives inexact value of d^*, though, probably, the basic error is connected not with the estimated relations, but with the approximate value of parameter ε. If this parameter is exactly known, the theory agrees well with the experiment. This takes place in the case of Co films [20]. Such agreement is also observed for Fe films: $d^*_{calc} = 9{,}6$ nm while $d^*_{exp} = 10{,}0$ nm ($T_s = 293$ K) and $d^*_{calc} = 16{,}8$ nm while $d^*_{exp} = 8{,}0$ nm ($T_s = 673$ K). Obtained results allow to assert that in the case of Cr, Mo, W, V, Nb, Ta, Ni, and Re films the formation of polymorphous modifications is impossible. As for Sc, Y, Ti, Zr, and Hf films the so definitive conclusion cannot be done, because the value of d^* in this case is not devoid of physical sense (it is equal some monolayers). Perhaps the cubic modification, observed by the authors of [11] in Sc films, is precisely the result of polymorphic transition. However, it seems that the conclusion of P.O. Panchekha [22] is more correct that the anomalous phases are not the metastable ones, conditioned by the deviation of crystallization conditions from the equilibrium ones, and are the result of realization of some specific impurity dimensional equilibrium states proper to fine samples.

Table 3 − *Critical thickness (in nm) of the fcc → bcc and fcc → hcp phase transitions*

Film material	$\varepsilon_{max} = 0{,}0106$		Film material	$\varepsilon_{max} = 0{,}0028$	
	(111) fcc → (110) bcc	(100) fcc → (110) bcc		(111) fcc → (001)hcp	(110) fcc→ (001) hcp
V	0,4 (0,4)	2,0 (2,0)	Sc	3,4	6,2
Nb	0,5 (1,8)	2,2 (3,7)	Y	5,8	8,9
Ta	0,5 (1,8)	2,2 (3,8)	Ti	3,5	6,0
Cr	0,4 (−)	1,9 (−)	Zr	3,4	6,1
Mo	0,4 (1,7)	2,1 (3,6)	Hf	4,3	6,0
W	0,4 (1,2)	2,1 (3,0)	Re	1,4	3,8

4. CONCLUSIONS

Based on the analysis of cited publications and our own experimental data we conclude that by now there is no any direct experiment, which confirms the formation of polymorphous modifications, not known in bulk samples. Moreover, under the films condensation in ultrahigh vacuum the formation of only those modifications occurs, which are proper to substance in a bulk state. Thus, the anomalous phases, which become stable under condensation in rough vacuum, are the penetration phases of the nitrogen, oxygen, hydrogen atoms and other residual gases into metal lattice.

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