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## SELF-ASSEMBLY OF LOW-DIMENSIONAL 3D TITANIUM SYSTEMS DURING QUASI-EQUILIBRIUM STEADY-STATE CONDENSATION

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*Structure formation mechanisms of low-dimensional porous systems are explained on the ground of different growth rates at local condensate areas and partial coalescence of the structural fragments. By means of scanning and transmission electron microscopy the formation mechanisms of porous Ti condensates on glass and KCl cleaved facets are studied. It is shown by the example of self-assembly of porous Ti layers that the factors underlying such process are self-organization of time-constant critically low effective supersaturation and continuous sequence of interdependent structure and morphology changes of the growth surface that cause the appearance of active centers for attaching adatoms.*

**Keywords:** SELF-ASSEMBLY, LOW-DIMENSIONAL STRUCTURES, POROSITY, SELF-ORGANIZATION, SUPERSATURATION.

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### 1. INTRODUCTION

Prospects of self-assembly of porous micro- and nanosystems can make qualitative changes in the development of many high technologies. A number of existing methods for the formation of such structures, as a rule, is based on the involvement of multi-stage rather complex technologies [1-5]. At the same time, 3D porous architecture can be formed on the ground of different growth rates of the adjacent local condensate areas [6, 7]. Such spatially distributed selectivity of the condensate growth is observed during the processes in the vicinity of the thermodynamic equilibrium. The porous water frost formation occurring at the slow air temperature reduction and appearance of critically small supersaturations is the well-known example. However, realization of such structure formation mechanism for metals, due to their low volatility, is a rather complex problem. We will consider one of the alternate solutions. For plane as well as isotropic in the temperature and structural respects growth surface, a small value of supersaturation

$$\xi = (n - n_e)/n_e, \quad (1)$$

where  $n$  and  $n_e$  are the current and the equilibrium concentrations of condensed atoms above the growth surface, can be the criterion of proximity to the phase equilibrium. In this case, for the vapor-condensate system

$$n_e = \frac{A(T)}{k_b T} \exp\left(-\frac{E_d}{k_b T}\right), \quad (2)$$

where  $E_d$  is the desorption energy;  $T$  is the growth surface temperature and  $A(T) = \exp(\alpha T + \beta/T + \gamma)$ ;  $\alpha, \beta, \gamma$  are the constants characterizing the matter [8, 9]. According to (1) and (2), in order to reduce supersaturation to the critical value in the vapor-condensate system one should increase the growth surface temperature and decrease  $n$  or condensed flux  $J_c$ . Because of small values of  $n_e$  for the majority of metals, their quasi-equilibrium condensation is possible under deposition of the extremely weak vapor fluxes in the range of sufficiently high temperatures. It is technically difficult to solve such problem for the majority of metals in the vapor-condensate system.

Considering plasma-condensate system, it is necessary to take into account a number of factors, which influence the process of approach to equilibrium. In connection with this we note, first of all, that under the action of plasma particles on the growth surface its additional heating takes place. Moreover, direct or indirect energy transfer to adatoms from plasma particles and incomplete thermal accommodation of adatoms, which initially have increased energy, lead to the decrease in  $E_d$  to the effective value [9]

$$E = E_d - \delta E, \quad (3)$$

where  $\delta E$  is the random subtrahend, which is characterized by mean value  $\bar{E}$  and dispersion  $\sigma^2 = \overline{(\delta E - \bar{E})^2}$ . In turn, increase in the growth surface temperature and decrease in  $E_d$  to the effective value, according to (1) and (2), promote the decrease in the supersaturation  $\xi$ . Therefore, at certain conditions, plasma-condensate system allows to realize quasi-equilibrium condensation even of such weakly volatile substances as metals.

Situation is considerably complicated for non-uniform in the structural and morphological respects growth surface. In this case desorption energy  $E_i$  will correspond to each local area of the growth surface. In accordance with this energy, one will observe local supersaturation  $\xi(E_i)$ . In the vicinity of the equilibrium  $\xi(E_i)$  can take different signs. Then the whole growth surface can be divided into two categories. The first one contains areas of the growth surface where condition  $\xi(E_i) > 0$  holds that allows the substance to condense. Otherwise ( $\xi(E_i) < 0$ ), condensation in local areas of the growth surface will not occur. In the following, we will call such variant of the preferential local growth as the structural selectivity.

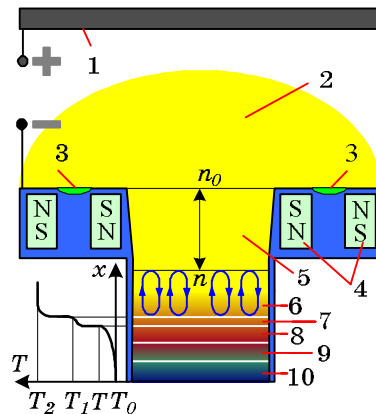
The growth surface curvature, which influences the local chemical potentials by the Gibbs-Thomson effect, is of a special interest in such processes. For example, the coalescence of two crystals leads to the appearance of the growth surface areas with negative curvature. In this case, one can speak about the appearance of the system of active centers, whom lower chemical potentials correspond to. Consequently, increase in the supersaturation  $\xi$  can occur in the region of crystal coalescence that stimulates secondary nucleation or, at least, attaching of separate adatoms [6].

The above listed mechanisms, which influence the local condensate growth, are intricately interdependent. Thus, effect of the structural selectivity on the condensate self-assembly will lead to the changes in the growth surface morphology that, in turn, influences the Gibbs-Thomson effect. Obviously, there is a feedback between these selective growth mechanisms. Therefore, infinite alternation of sequential interdependent changes in the selective processes determines the increase or decrease in the rate of condensate growth in its different areas that, finally, promotes the porous structure formation.

Thus, structure formation mechanisms of low-dimensional porous systems can be explained on the basis of different growth rates of the growth surface local areas and self-consistent changes of the structural and morphological characteristics. In addition, condensation in the vicinity of the equilibrium is the necessary condition of the selective processes. Realization of the stated working approach on the example of self-assembly of low-dimensional porous Ti layers is the main target of the present work.

**2. EXPERIMENTAL TECHNIQUE AT SELF-ORGANIZATION OF QUASI-EQUILIBRIUM CONDENSATION**

To obtain Ti condensates we have used the device whose operational principles were given in detail in [9]. Therefore, we will dwell on some main aspects of the device operation. Schematically it is represented as accumulative plasma-condensate system (APCS) in Fig. 1. This device consists of the magnetron sputterer and associated hollow cathode.



*Fig. 1 – Cross-section of the axially symmetric APCS: 1 – anode; 2 – zone of plasma propagation; 3 – erosion zone; 4 – system of magnets; 5 – hollow cathode; 6 – area of the annular mass transfer; 7 – layer of adatoms; 8 – condensate; 9 – substrate; 10 – cooler. Qualitative temperature distribution near the growth surface is represented on the left*

Substance is sputtered in the erosion zone 3 (see Fig. 1). Sputtered atoms are thermalized in the conditions of the increased working gas pressure. In the following, due to the diffusive movement sputtered atoms are accumulated in the vicinity of the substrate 9 (Fig. 1) [10]. Simultaneously with the substance accumulation, heating of the substrate 9 surface by plasma occurs. Because of such action, the majority of adatoms are re-evaporated again, then they are ionized, and under the action of electric field they are directed on the substrate ones more [11]. Such annular mass transfer mechanism additionally accumulates the substance near the substrate. Henceforth, under the action of plasma the substrate surface is heated up to the temperature, which is the maximum one for these conditions; and substance accumulation moves the system to the supersaturated state. Barrier nucleation, which appears in this case, occurs due to the accumulated near the substrate sputtered atoms. For this reason, concentration of sputtered atoms near the substrate decreases in the initial time of condensation. At the same time, growth surface tempera-

ture increases because of the complete thermal accommodation of adatoms. Therefore, accumulation of the deposited substance moves the system to the supersaturated state; and start of condensation automatically reduces supersaturation to the critical value. Self-consistent change of non-linearly interdependent supersaturation and growth surface temperature is the most important link of the self-organization of the steady-state quasi-equilibrium condensation.

We have established earlier [9] that in APCS non-linear interdependence of the supersaturation  $\xi_c$  and the growth surface temperature  $T$  during self-organization is described by the following system of equation:

$$c\dot{T} = \left[ \left( \chi\theta T_2 + \frac{\eta}{d} T_0 \right) + \frac{k_b n_e \delta}{\tau} T_2 \xi_e \right] - \left[ \left( \chi\theta + \frac{\eta}{d} \right) + \frac{k_b n_e \delta}{\tau} \xi_e \right] T, \quad (4)$$

$$\dot{\xi}_e = \frac{s}{S} \frac{D}{\lambda \delta} \left( \frac{n_0}{n_e} - 1 \right) - \left( \frac{1}{\tau} + \frac{s}{S} \frac{D}{\lambda \delta} \right) \xi_e - B(T) (1 + \xi_e) \dot{T}. \quad (5)$$

Here  $B(T) = \beta - 1/T + [(E/k_b)]/T^2$ ;  $c$  is the heat capacity of the growth surface;  $T_2$ ,  $T_1$  and  $T_0$  are the temperatures of plasma, adatoms, and cooler, respectively (see Fig. 1);  $\theta \equiv (T_2 - T_1)/(T_2 - T)$  is the coefficient of thermal accommodation of plasma atoms;  $\chi$  is the parameter defined by the product of the Boltzmann constant and plasma flux, which acts on the growth surface;  $\tau$  is the mean movement time of sputtered atoms along the mass transfer ring near the growth surface;  $\delta$  is the mean length of the annular mass transfer trajectory near the growth surface;  $d$  is the total thickness of the substrate and condensate;  $\eta$  is the effective heat conductivity coefficient of two-layer substrate-condensate system;  $S$  is the internal surface area of the hollow cathode 5;  $s$  is the inlet area of the hollow cathode 5;  $D$  is the coefficient of interdiffusion of sputtered atoms in plasma;  $\lambda$  is the characteristic distance on which atomic concentration changes from  $n$  to  $n_0$  (see Fig. 1);  $n_0$  is the atomic concentration of the sputtered substance on the hollow cathode inlet.

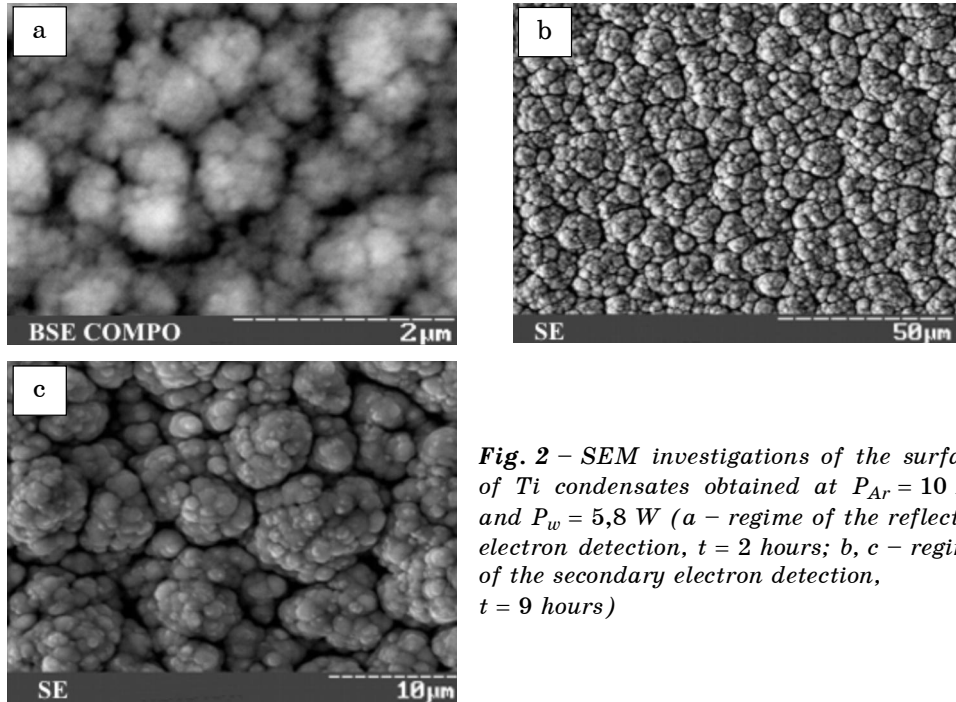
By the phase plane method, using the system of equations (4) and (5), and taking into account the substrate thickness and heat conductivity, we have determined the supersaturation and condensation temperature of titanium on glasses ( $T = 963$  K,  $\xi = 8,4 \cdot 10^{-4}$ ) and (001) KCl cleaved facets ( $T = 893$  K and  $\xi = 7,9 \cdot 10^{-2}$ ).

### 3. EXPERIMENTAL RESULTS AND DISCUSSION

Since during condensation titanium possesses high chemical activity, we have paid special attention to the limiting minimization of the partial pressures of chemically active residual gases. The necessary purity of the working gas Ar was achieved due to the preliminary and long-term (about 30 hours) Ti sputtering directly in the working chamber by two additional magnetrons [12]. Argon purification did not cease during the whole technological process that allowed to create the conditions for Ti condensation when the total partial pressure of chemically active gases was  $\sim 10^{-7}$ - $8 \cdot 10^{-8}$  Pa.

Now we will consider the structure formation mechanisms of porous low-dimensional 3D systems at Ti condensation on the glass substrates. The use of the SEM investigations allowed to reveal the appearance of the round-shaped clusters (see Fig. 2a), which are weakly coupled with each other, on the base

non-porous layer of condensed Ti. Since atomic-smooth growth surface always consists of the certain crystallographic plane, ball-shaped crystals imply the atomic-rough structure of the growth surface. Along with this, atomic-rough surface always contains a sufficient amount of active centers, which are uniformly distributed all over the surface. On these active centers atoms realize the chemical bounds, whose energy can exceed the chemical bond energy of atoms, which are in position of a semicrystal on the atomic-smooth surface. Incorporation of atoms into these active centers leads to the normal and uniform (in all directions) crystal growth [13]. Since in this case the surface-to-volume ratio takes the minimum value and maximally strong chemical bonds are realized, the limiting minimization of the free energy takes place. Such processes are possible at substance condensation near the equilibrium.

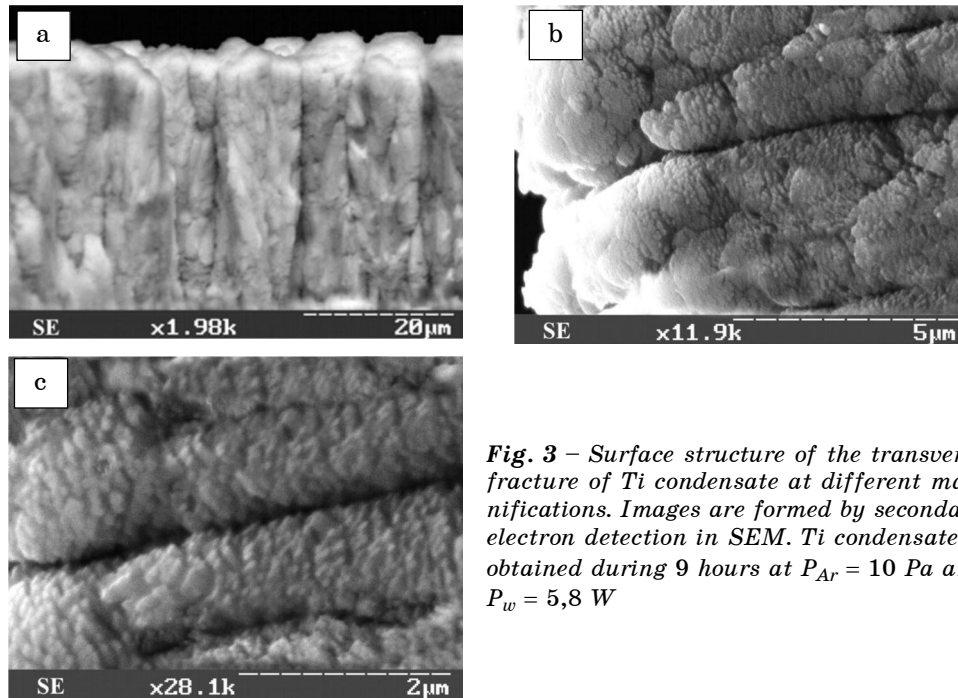


*Fig. 2 – SEM investigations of the surface of Ti condensates obtained at  $P_{Ar} = 10$  Pa and  $P_w = 5,8$  W (a – regime of the reflected electron detection,  $t = 2$  hours; b, c – regime of the secondary electron detection,  $t = 9$  hours)*

Processes occurring in the places of mutual contact of the weakly coupled uncut clusters have determinative value in the self-assembly. Thus, we have established before [6] that usual type of coalescence, which, as a rule, is observed during the condensation of highly supersaturated vapors [14-16], is excluded in our case. This is explained by the fact that self-assembly in the vicinity of the equilibrium occurs with the realization of maximally strong chemical bonds. Therefore, surface diffusion of condensed atoms defining the coalescence kinetics [14-16] is weakly expressed. In this case, difference in the chemical potentials  $\Delta\mu_r$  in the places of cluster coalescence is determined by the Herring relation

$$\Delta\mu_r = \frac{\Omega_c}{R_1} \left( \alpha + \frac{\partial^2 \alpha}{\partial \beta_1^2} \right) - \frac{\Omega_c}{R_2} \left( \alpha + \frac{\partial^2 \alpha}{\partial \beta_2^2} \right). \quad (6)$$

Here  $R_1$ ,  $R_2$ ,  $\beta_1$  and  $\beta_2$  are the corresponding main radiuses of negative and positive curvature and the angles determining the surface energy anisotropy  $\alpha$ ;  $\Omega_c$  is the specific volume per one atom in the crystal. It follows from the analysis of the relation (6) that at certain structural and morphological characteristics of the cluster coalescence area  $\Delta\mu_r$  can take increased values.

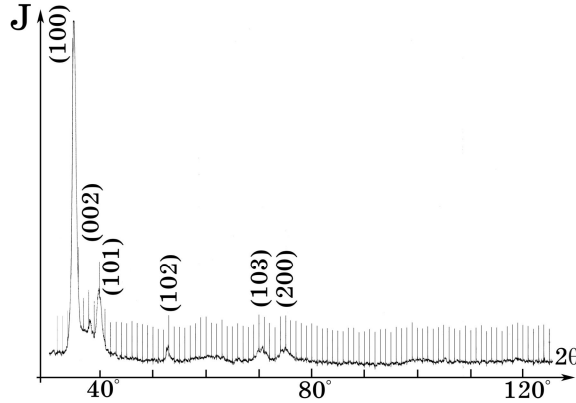


**Fig. 3** – Surface structure of the transverse fracture of Ti condensate at different magnifications. Images are formed by secondary electron detection in SEM. Ti condensate is obtained during 9 hours at  $P_{Ar} = 10$  Pa and  $P_w = 5,8$  W

Because of these circumstances, coalescence area of two clusters (with the prevalent negative curvature) can represent the totality of the energy-efficient for condensation active centers, which condensed fluxes are focused at. Such reorientation of the limited condensed fluxes leads to the stabilization of the cluster shape and dimensions. In this case, in the cluster coalescence area two types of self-assembly [6] are possible. The first one is connected with the fact that gradual thickening of the isthmus, which binds clusters, occurs during condensation. Realization of the second type consists in the following: secondary nucleation is observed on the formed active centers. Here, irrespective of the stated types of self-assembly, further formation of the condensate is accompanied by pore initiation. This conclusion is confirmed by the study of the structure of Ti layers obtained during 9 hours at  $P_{Ar} = 10$  Pa and  $P_w = 5,8$  W. Thus, surface investigation of these layers using different magnifications and SEM operating modes implies that scale of structure formations is changed during self-assembly with the conservation of the growth surface general morphology (Fig. 2a, c). Along with this, comparative analysis of the condensate surface structure at different magnifications (see Fig. 2) allows to reveal its structural features, which resemble the fractal self-similarity principle. To a certain extent, the made assumption is confirmed by the structure of transverse fractures of these layers. Thus, represented in Fig. 3 fracture images at

different magnifications imply that they also consist of weakly coupled nano-sized clusters, which are combined into larger structural elements. We have to note that the authors of [17] have theoretically confirmed fractal structure of Ti condensates that is shown in Fig. 3.

Based on the X-ray diffraction investigations of titanium layers and the comparative analysis of the diffraction maximum intensities and the known data (Fig. 4) we have discovered that nucleation texture, at which (100) Ti || to the substrate surface, is observed regardless of the substrate material.



**Fig. 4** – X-ray diffraction patterns from Ti condensates obtained on glass substrates at  $P_w = 5,8 \text{ W}$  and  $P_{Ar} = 10 \text{ Pa}$

Now we consider the structure formation mechanisms of Ti condensates on KCl cleaved facets. First of all, we note that the initial stage of Ti condensation on KCl cleaved facets does not differ in essence from the initial stage of the layer structure formation on a glass. However, further growth of the condensate on KCl has a qualitatively different behavior connected with the layer growth of the faceted weakly coupled microcrystals, which, for the most part, have the same habits (see Fig. 5a). In this case, sufficiently long-term technological process leads to the secondary nucleation that defines the formation of 3D porous structure in the form of pile-up of the weakly coupled microcrystals (see Fig. 5b).

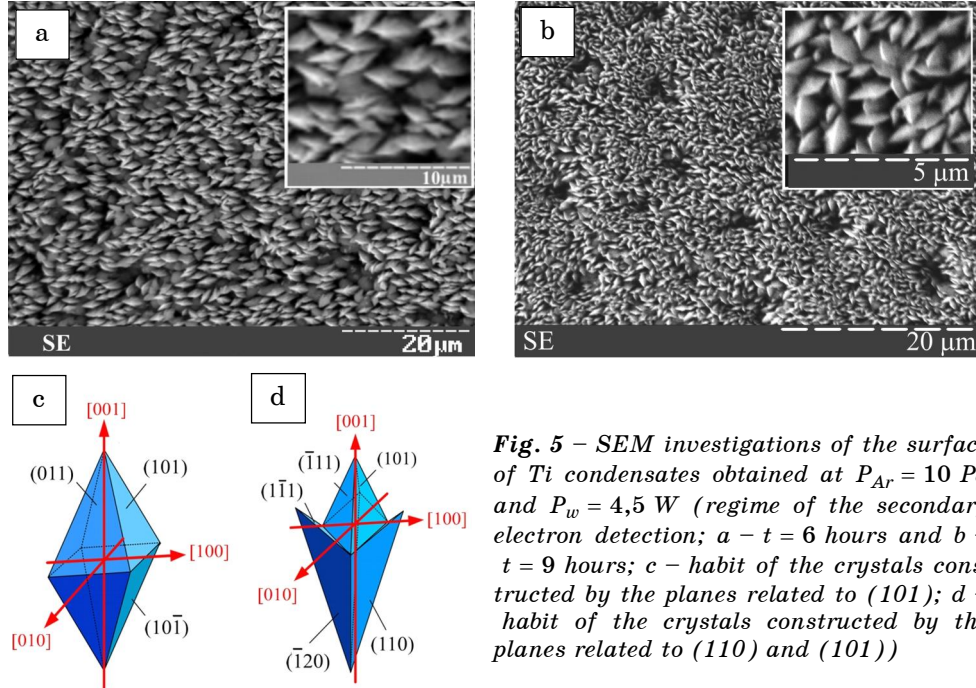
Such changes in the self-assembly are determined by the growth surface temperature reduction and the corresponding increase in the supersaturation  $\xi$ , which we have established earlier by solving equations (4) and (5). Therefore, transition from the atomic-rough to the atomic-smooth growth surface with the change of the substrates is explained by the transition from the normal to the layer crystal growth.

For atoms, which are in position of a semicrystal on the crystallographic (hkl) plane, the corresponding chemical bond energy  $E_{(hkl)}$  will be proportional to the number of neighboring atoms of the first, second and third orders ( $Z_1$ ,  $Z_2$  and  $Z_3$ ).

**Table 1** – Values of  $Z_1$ ,  $Z_2$  and  $Z_3$  for different faces of the hcp-crystal [13]

Plane	(001)	(100)	(012)	(101)	(110)
$Z_1, Z_2, Z_3$	3, 3, 1	4, 4, 0	4, 2, 1	5, 2, 0	5, 2, 1

Based on the values of  $Z_1$ ,  $Z_2$  and  $Z_3$  presented in Table 1 we can conclude that  $E_{(hkl)}$  takes maximum values on the crystallographic planes of the type of (101) or (110). Therefore, near the equilibrium the pointed types of crystallographic planes should be the basic ones at the formation of the condensate. This conclusion is confirmed by the identity of crystal habits obtained at self-assembly (see Fig. 5a, b) and based on the model approximation (Fig. 5c, d). Obviously, structural selectivity plays a main role in the formation of such condensates, and the same crystal habits are determined by the minimization of the free energy that is typical for sufficiently weak supersaturations.



**Fig. 5** – SEM investigations of the surface of Ti condensates obtained at  $P_{Ar} = 10$  Pa and  $P_w = 4,5$  W (regime of the secondary electron detection; a –  $t = 6$  hours and b –  $t = 9$  hours; c – habit of the crystals constructed by the planes related to (101); d – habit of the crystals constructed by the planes related to (110) and (101))

#### 4. CONCLUSIONS

1. The experimental and theoretical investigation results presented in the work indicate that the traditional concepts of the mechanism of metal condensation, existing up to now, were restricted only by sufficiently high supersaturations, and quasi-equilibrium self-assembly allows to obtain porous low-dimensional systems.

2. The processes, which take place in the cluster coalescence areas, play the defining role in the formation of porosity. These processes, on the one hand, exclude the coalescence, and, on the other hand, suppress the cluster growth and promote the secondary nucleation on the cluster interfaces. In this case, the pore formation is the result of reorientation of the bounded fluxes of condensed substance on the active centers, which allow to attach adatoms with the maximally strong chemical bonds.

3. The pore formation process during quasi-equilibrium condensation can be observed in two types. The first type is determined by the attachment of adatoms on the atomic-rough growth surface that results in the normal growth



of the clusters. The second type is observed during the layer growth of the weakly coupled crystals, which is caused by the growth surface temperature reduction and the corresponding transition to higher supersaturations.

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