

---

---

LOW-DIMENSIONAL SYSTEMS  
AND SURFACE PHYSICS

---

---

# Regularities of Al Layer Structure Formation Near Phase Equilibrium in Plasma–Condensate System

V. I. Perekrestov, A. S. Korniyushchenko, and Yu. A. Kosminskaya

*Sumy State University, ul. Rimskogo-Korsakova 2, Sumy, 40007 Ukraine*

*e-mail: perv@phe.sumdu.edu.ua*

Received May 3, 2007; in final form, October 24, 2007

**Abstract**—A fundamentally new technological approach to creating porous metal structures on isotropic substrates during condensation of a reverse diffusion flow in a planar dc magnetron is proposed. The physical foundations of the operation of self-organized sputtering systems are analyzed. Conditions of the formation of main varieties of porous structures, such as weakly coupled micro- and nanocrystals, and three-dimensional labyrinth structures, are found using scanning electron microscopy. It is established that the main prerequisites for the formation of pores are the stationarity of the process and proximity to the phase equilibrium in the plasma–condensate system.

PACS numbers: 68.55.-a, 81.15.Ef

DOI: 10.1134/S1063783408070275

## 1. INTRODUCTION

Recently, the wide range of possible applications of porous nano- and microstructures has caused relentless research interest. Porous materials are most often formed by chemical etching or compacting of micro and nanoparticles. Certain progress has also been achieved in the direct formation of porous layers under conditions of fairly small constants of stationary deposition (less than 0.07) [1–4]. However, development of this very promising technology is impossible without finding the relation between the mechanisms of formation of pores and technological conditions. The objective of this study is to solve this problem.

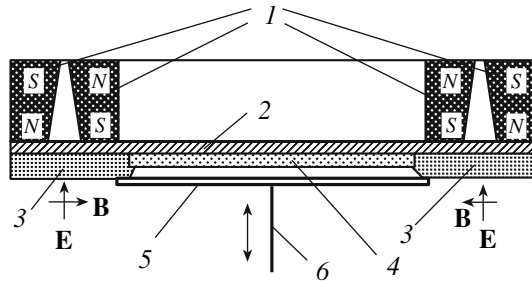
## 2. PHYSICAL FOUNDATIONS OF STRUCTURE FORMATION IN SELF-ORGANIZED SPUTTERING SYSTEMS

The mechanism of nucleation of a condensate under conditions of extremely small supersaturation is beyond the scope of equilibrium thermodynamics and involves barrier nucleation [5, 6]. Forming chemical bonds of maximum possible energy, atoms are built in, one by one, only on active centers of the growth surface, such as edges of monoatomic steps of the crystal growth, lattice defects, and grain boundaries. One example of this kind of condensation is the layer-by-layer growth of crystals. Because such centers are limited in number, the discrete character of the corresponding spectrum of chemical-bond energies becomes progressively more pronounced. At small supersaturation, all of these factors lead to a clearly defined critical energy  $E_c$  of chemical bonds between atoms and the growth surface below which the atom-by-atom forma-

tion of the condensate becomes unlikely. On the other hand, near the equilibrium, the layer formation mechanism is very sensitive to technological conditions [7], which imposes more stringent stationarity requirements on the condensation process. The criterion of stationarity can be the fixed position of  $E_c$  in the energy spectrum of chemical bonds on active growth centers. For example, if the Frank–van der Merve mechanism does not operate, then a necessary prerequisite to reproducible pore formation is the immutable position of  $E_c$  in the spectrum of chemical bond energies  $E_{ai}$  of atoms in the half-crystal positions. Indeed, under these conditions, atom-by-atom deposition at the edges of monoatomic growth steps occurs only when the condition  $E_{ai} > E_c$  is satisfied (neglecting the signs of  $E_{ai}$  and  $E_c$ ), i.e., on individual crystallographic planes. The number of such planes is decreased as the phase equilibrium in the environment–condensate system is approached. Therefore, the more rapid growth of the condensate in certain crystallographic directions on separate local sections can finally lead to the formation of a porous structure.

It is necessary to stress that the conditions of bulk pore formation can be satisfied using a volume diffusion field (characterized by equal probabilities of atoms arriving at various faces of the crystal), the efficiency of which increases with the working-gas pressure. Since the absorption of impurities by the growth surface can change the energy spectrum of chemical bonds, the condensation should take place under extremely low partial pressures of reactive gases.

Therefore, a necessary condition for porous metal layers to form is quasi-equilibrium stationary conden-



**Fig. 1.** Sputtering system (schematic): (1) permanent magnets, (2) target and substrate holder, (3) sputtering target, (4) substrate, (5) flap, and (6) flap rod.

sation in a very pure inert environment at an increased pressure.

Since the equilibrium aluminum vapor pressure at the melting temperature is very low ( $\sim 10^{-7}$  Pa [8]), the conditions close to equilibrium cannot be provided only by depositing extremely weak vapor flows at the maximum possible growth surface temperature  $T_c$ . In other words, classical molecular beam epitaxy is unsuitable in this case. The problem can be overcome by employing electrolytic deposition, condensation from supersaturated solutions, CVD methods, or decomposition of metalorganic compounds. In these well-known technologies, the proximity to equilibrium is mainly achieved by temperature-dependent chemical processes favoring the transfer of adatoms of the condensate back into the solution or gas mixture. In comparison to molecular beam epitaxy, such processes are less sensitive to variations in  $T_c$  and, therefore, can be easily controlled. For this reason, designing analogous more universal systems based upon physical principles seems to be promising.

First systems of this kind have been created using hollow cathode and have been employed to perform atom-by-atom deposition of layers with different porous structures [3] and even to synthesize individual microcrystals of diamond [4]. In this case, the close-to-equilibrium conditions are created by intensive transitions of adatoms into the gaseous phase under the influence of a low-temperature plasma, which is in contact with the growth surface. Under these conditions, it is convenient to employ, instead of  $E_{ai}$ , effective chemical

bond energies  $E_{ei} = -E_{ai} + (E_s \pm \Delta E)$ , where  $\Delta E$  is the deviation of the energy transferred to adatoms by bombarding particles from the mean value  $E_s$ . Since the magnitude of  $E_{ai}$  is reduced to the effective values, close-to-equilibrium conditions can be achieved at lower, fairly accessible values of  $T_c$ . By minimizing the value of  $\Delta E$ , one can attain a high degree of stationarity of the condensation process.

In this paper, we use reverse diffusion flows in a planar dc magnetron. In this case, the substrate holder and the sputtering target (Fig. 1) are at the same potential, which provides a synchronous variation and adjustment of the technological parameters important for the proximity to equilibrium, such as  $T_c$ , deposition flux, and the energy and flux of particles bombarding the growth surface. This technological procedure also favors self-organization of the stationary process. Indeed, when the power of a discharge is varied within certain limits, the deposition flux and the energy of particles bombarding the growth surface are changed simultaneously, which can preserve the position of  $E_c$ . Another special feature of the self-organized ion sputtering is that, after repeated evaporation, the probability of atoms being ionized and deposited again until a sufficiently strong chemical bond is formed is high [9]. This cyclic mechanism of mass transfer augments the volume diffusion field and makes it possible to utilize the condensing material more effectively. It should be noted that multiple ion collisions at a higher pressure of the working gas not only cause a reverse diffusion flow but also average the energy of the particles bombarding the growth surface [10], which is an important condition for enhancing the spatially distributed growth of the condensate. The stationary close-to-equilibrium condensation can also be controlled by varying the discharge power and pressure of the working gas. Since these parameters can be controlled quite well, it is easy to achieve reproducible results of condensation.

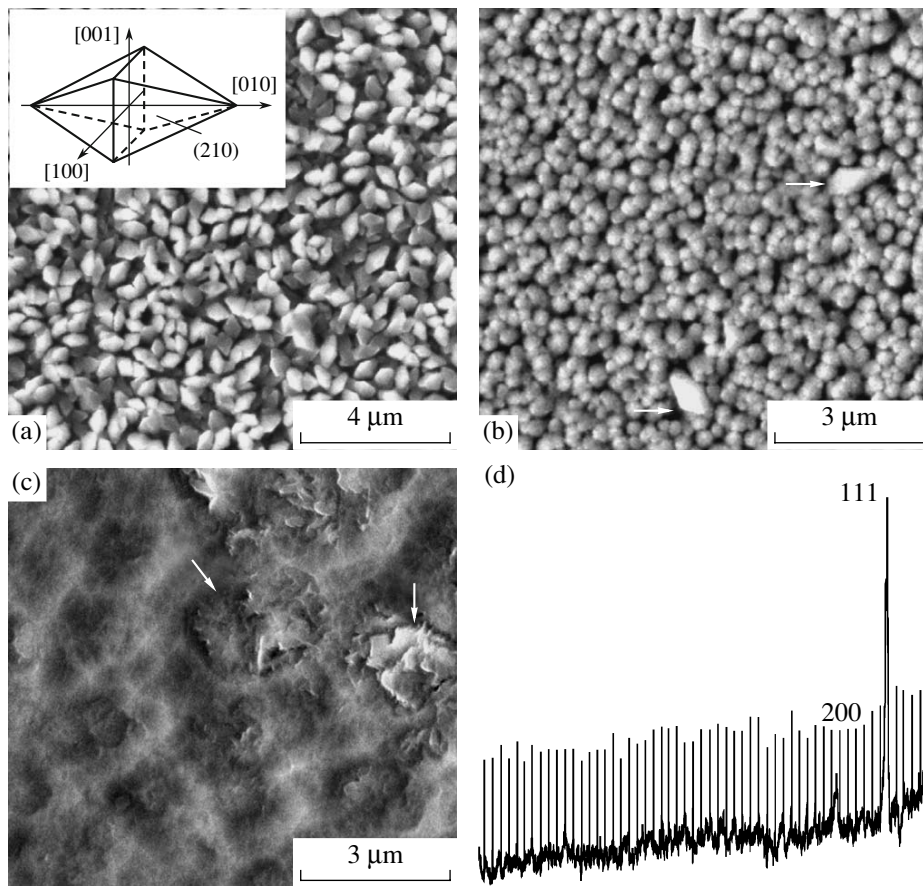
In this work, aluminum was condensed on a glass substrate at an argon pressure  $P_{Ar} = 15\text{--}25$  Pa, with the partial pressure of reactive gases being only  $8 \times 10^{-8}$  Pa. The latter condition was achieved by titanium sputtering using the method described in [11].

### 3. RESULTS AND DISCUSSION

Atoms located in half-crystal positions on different crystal planes are surrounded by different number of first-, second-, and third-nearest neighbors. Evidently, the value of  $E_{ai}$  of atoms in such positions is proportional to the numbers of  $j$ th neighbors ( $Z_j$ ), which we designate as  $|Z_1Z_2Z_3|$ . The numbers  $|Z_1Z_2Z_3|$  for fcc aluminum are shown in the table in descending order. It follows that, if the conditions are sufficiently close to equilibrium, the structure will form exclusively on the (210) planes. In other words, if the energy  $E_c$  is located between the  $|6\ 2\ 10|$  and  $|6\ 3\ 0|$  energies (see table), then the (210) plane is basal for the formation of the

Numbers  $|Z_1Z_2Z_3|$  for various facets of the fcc crystal [7]

Facet	$ Z_1Z_2Z_3 $
(210)	$ 6\ 2\ 10 $
(531)	$ 6\ 3\ 0 $
(311)	$ 5\ 3\ 10 $
(110)	$ 5\ 2\ 10 $
(100)	$ 4\ 1\ 2 $
(111)	$ 3\ 3\ 9 $



**Fig. 2.** (a–c) Variation in the structure of Al condensates with decreasing degree of saturation: (a)  $P_w = 1.8$  W and  $P_{Ar} = 20$  Pa; (b)  $P_w = 1.8$  W and  $P_{Ar} = 15$  Pa; and (c)  $P_w = 1.8$  W and  $P_{Ar} = 15$  Pa, without water-cooling of the substrate holder. (d) X-ray diffraction pattern showing the nucleation texture.

corresponding crystal habitus. For this reason, we select from the entire experimental material the structure that is obtained with a water-cooled substrate holder, a discharge power  $P_w = 1.8$  W, and  $P_{Ar} = 20$  Pa. An important feature of this structure (Fig. 2a) is that it is composed of weakly linked crystals whose equilibrium shape confirms the above prediction. This fact indicates a high degree of stationarity of the technological process, and the structure itself can be used to estimate the position of  $E_c$ . Note that the statistical uniformity of the structure (Fig. 2a) in thickness can reach tens of micrometers, which can be explained by repeated nucleation on active centers on the growth surface.

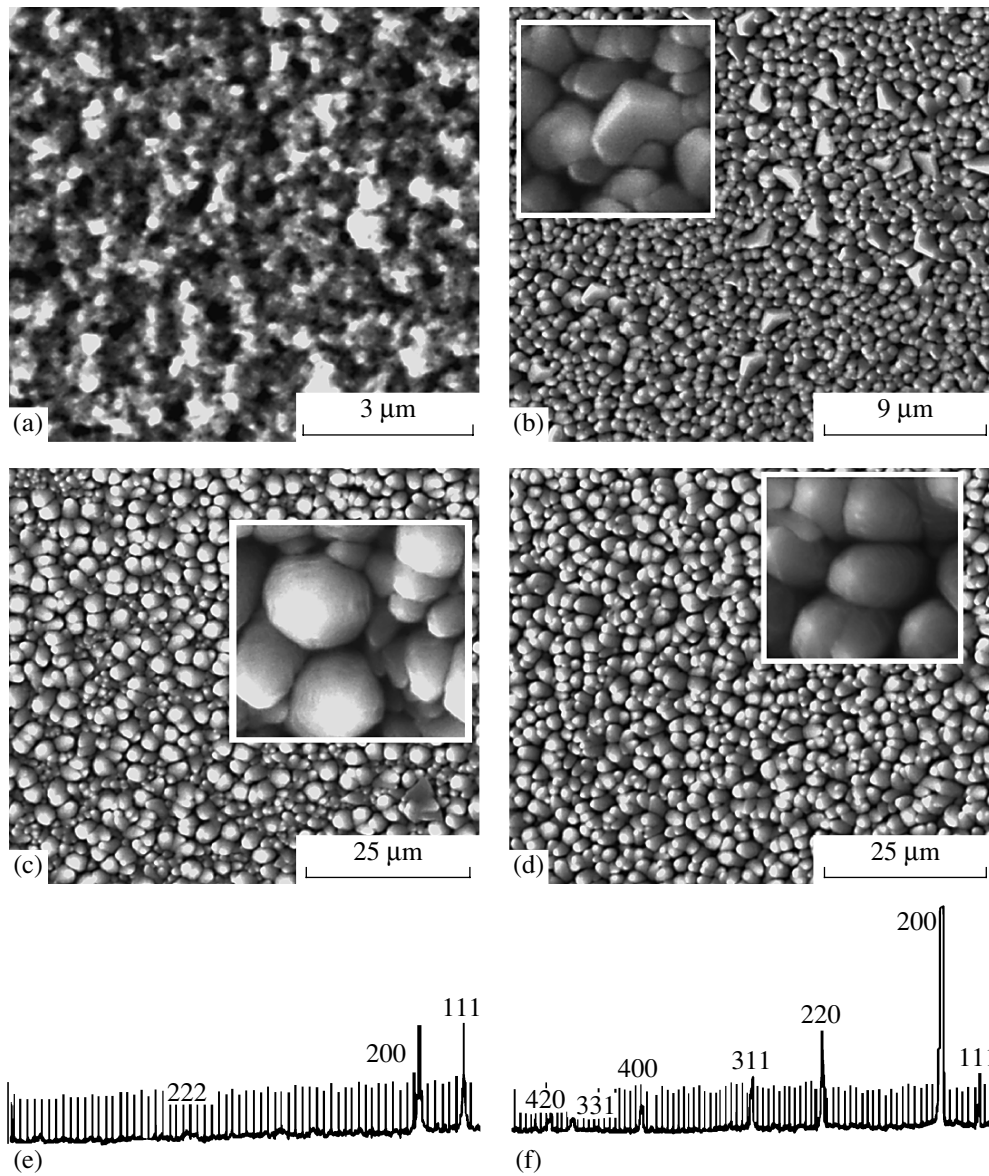
The validity of the above ideas concerning the mechanism of structure formation is also supported by the fact that further approach to equilibrium (increase in  $E_c$ ) by lowering the working gas pressure to 15 Pa (with all other technological parameters remaining the same) leads to the transition from the tangential to normal growth of crystals (Fig. 2b). In this case, equilibrium is approached because the decreased working-gas pressure leads, on the one hand, to a decreased reverse

diffusion flow of the condensation material and, on the other hand, to increased energies of the particles bombarding the growth surface. Since the  $[6\ 2\ 10]$  energy is maximum possible for fcc crystals (see table), a further increase in  $E_c$  should inevitably cause reduction in the free surface energy through a change in the shape of the crystals. The proximity to the transition from the tangential to normal growth is confirmed by the fact that some crystals (indicated by arrows in Fig. 2b) preserve faceting of the previous structure. A more rigorous explanation of the change of the structure formation mechanism can be given in terms of the variation in the free energy  $\alpha_i$  of a monatomic step. In the simplest case, we have [7]

$$\alpha_i = nE_{ai} - nkT_c \ln(1 + 2\chi),$$

where  $\chi = \exp(-E_{ai}/kT_c)$  and  $n$  is the density of atoms on the end face of the monatomic step.

As already mentioned, an increase in the energy of particles bombarding the growth surface leads to a decrease in  $E_{ai}$  down to effective energies, which, together with a possible increase in  $T_c$ , inevitably



**Fig. 3.** (a–d) Variation in the structure of Al condensates with increasing discharge power:  $P_w =$  (a) 1.4, (b) 2.7, (c) 3.24, and (d) 4 W. (e, f) X-ray diffraction patterns for (e) porous and (f) columnar structures.

causes  $\alpha_i$  to become zero. Under these conditions, smoothing of monatomic steps is so strong that, in effect, the growth surface turns into a structurally uniform atomically rough system. In contrast to atomically smooth surfaces, condensation on such surfaces can occur at any point with an equal probability, which leads to normal growth, which depends on the local temperature of the growth surface, the intensity of its bombardment by particles, and condensation flux. The transition from faceted to rounded crystal shapes has a sharp boundary in our case because the initial crystals are formed on a single plane with a maximum value of  $E_{ai}$ . It should be stressed that, in contrast to the tangential growth, conditions closer to equilibrium preclude

repeated nucleation. This conclusion is suggested by the constant density of crystals on the growth surface, which is a prerequisite to the formation of columnar structures.

The mechanism of structure formation in the immediate vicinity of equilibrium is of certain interest. In our case, such conditions are achieved by switching off water cooling of the substrate holder, with all other technological parameters of the previous experiment remaining unchanged. From the microstructure presented in Fig. 2c, it can be seen that the condensation under conditions extremely close to equilibrium prevents pore formation. According to the above discussion, the mechanism of structure formation under such

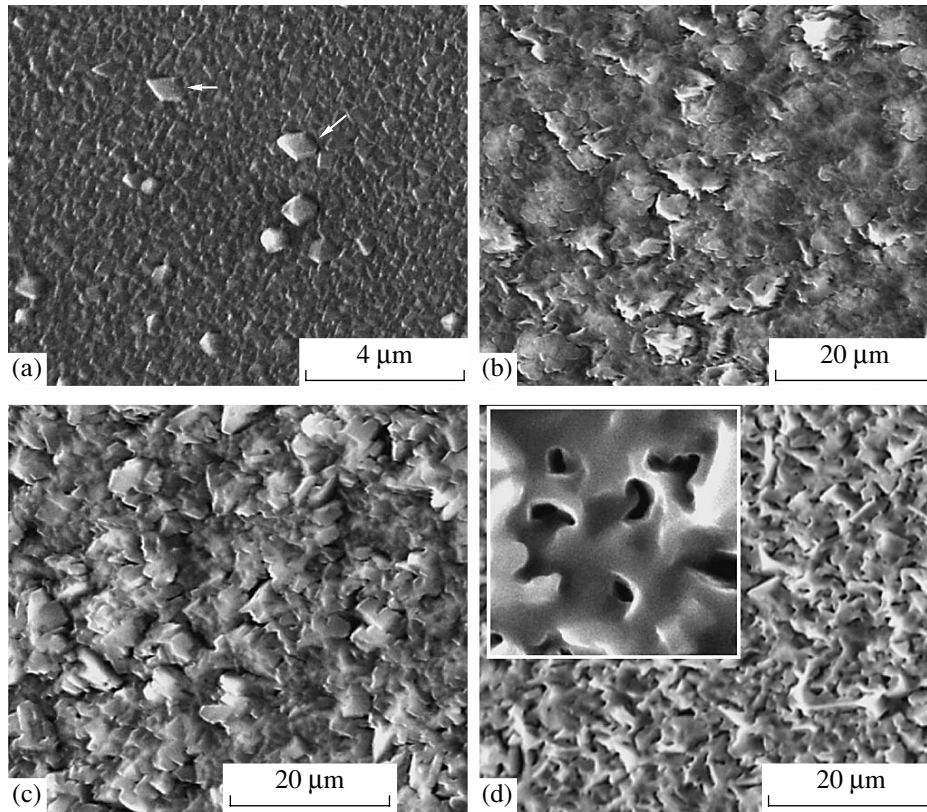


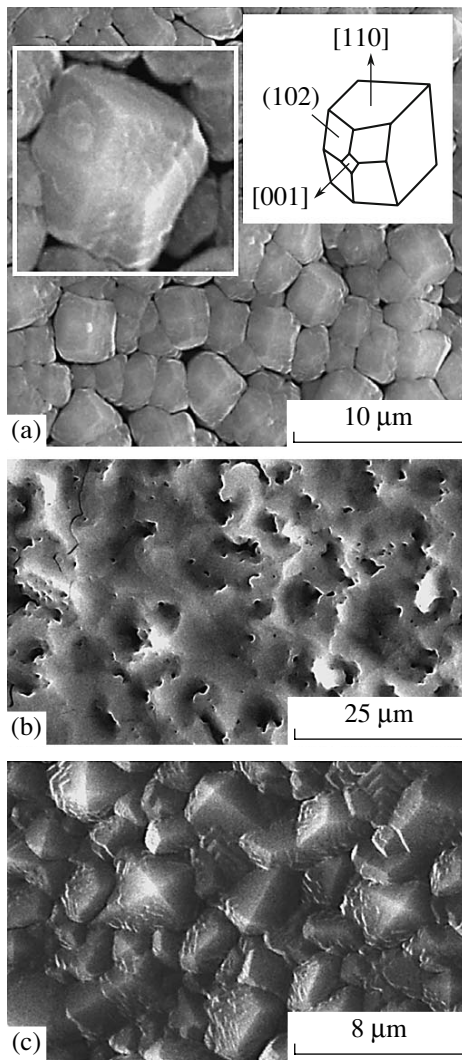
Fig. 4. Nucleation of (a) columnar and (b–d) labyrinth structures.

extreme conditions should indeed lead to further reduction in the free surface energy through decreasing the growth surface. Evidently, the creation of such nonporous structures is largely defined by the texture of condensate nucleation. X-ray diffraction data indicate that, during nucleation, the (111) plane of aluminum is parallel to the substrate surface (Fig. 2d). Taking into account the Volmer–Weber nucleation conditions for the aluminum–glass pair and the fact that the (111) plane has the closest packing, we can conclude that such nucleation texture corresponds to a minimum of the free energy of the condensate–substrate interface. Moreover, the (111) plane also has a minimum value of  $E_{ai}$  (see table). All of these conditions, on the one hand, favor the formation of a thin condensate layer over the entire substrate surface and, on the other hand, specify the normal growth of crystals. The formation of a corrugated surface (Fig. 2c) is also due to small values of  $E_{ai}$  for the basal (111) plane. This fact and the extreme proximity to equilibrium should inevitably lead to a predominant growth direction different from [111] and, therefore, to a curvature of the condensate surface.

It is interesting to note that recurring nucleation occurs at depressions of the growth surface (the corresponding spots are marked by arrows in Fig. 2c), which indicates that the degree of supersaturation depends on the curvature of the growth surface. Apparently, such

leveling of the surface is possible only near equilibrium and is accompanied by a decrease in the surface energy.

In the method of magnetron sputtering suggested in this paper, an increase in the discharge power causes  $E_c$  to decrease not only through an increase in the flux of ions bombarding the erosion zone but also through the enhancement of the sputtering factor. However, both the energy and flux of particles affecting the growth surface at increased values of  $P_{Ar}$  are changed only slightly with increasing discharge power [10]. Therefore, combined changes in the technological conditions with increasing discharge power within certain limits (with the working gas pressure remaining unchanged) should lead to supersaturation of the deposition flux. Our further studies are based on this fact. Figure 3 shows several microstructures obtained during cooling the substrate holder and varying the discharge power from 1.4 to 4.0 W at  $P_{Ar} = 15$  Pa. From analyzing the microstructure in terms of the effect of the increased discharge power within these limits, it follows that the size of fragmentary formations increases approximately from 300 nm to 2  $\mu$ m. This process is accompanied by the transition from three-dimensional labyrinth structures (Fig. 3a) to columnar formations due to the normal growth of crystals (Figs 3b–3d). In the case of extremely small values of the applied power, the increasing adsorption of impurities by crystallographic

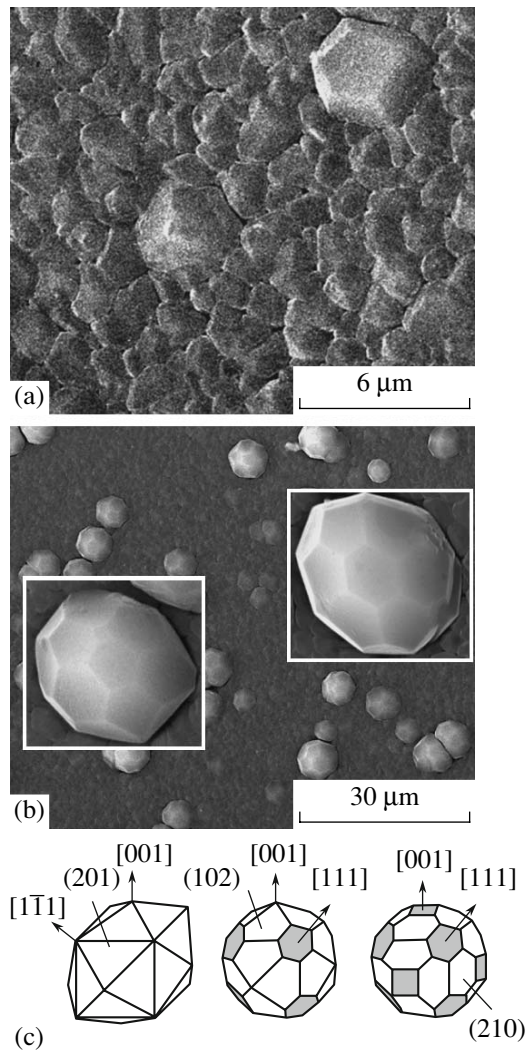


**Fig. 5.** Structure of Al condensates obtained with a water-cooled substrate holder: (a)  $P_w = 9$  W and  $P_{Ar} = 20$  Pa, (b)  $P_w = 70$  W and  $P_{Ar} = 25$  Pa, and (c)  $P_w = 2.4$  W and  $P_{Ar} = 25$  Pa. The insets show the magnified image of a microcrystal (left) and a diagram of the positions of some of its facets and the [110] direction (right).

planes may become important. Since different crystal planes can differ in terms of the amount of absorbed impurities, not only the growth of individual crystals is suppressed but also condensation becomes more selective, which in the end governs the formation of three-dimensional labyrinth nanostructures (Fig. 3a). On the other hand, neglecting the difference in the size of crystals, we can conclude that the structures of condensates shown in Figs. 3b–3d are in many respects similar. This fact indicates that the condensation process remains stationary as the discharge power is varied. Note that the transition from labyrinth formations to columnar ones significantly changes the texture of condensates (see x-ray diffraction patterns in Figs. 3e, 3f).

At a discharge power of 4.7 W (at  $P_{Ar} = 15$  Pa), the mechanism of structure formation is changed qualitatively, which leads to the transition from columnar structures (Fig. 3d) to three-dimensional labyrinths (Fig. 4d). In order to further investigate such important changes in the structure formation, we performed additional studies of the surface morphology and texture of condensates and isolated two stages of formation of both columnar and labyrinth structures. During the first stage in both cases, a layer covering the entire substrate is formed. The nucleation texture for this layer is usually determined by the fact that the (111)Al plane is parallel to the substrate surface. The thickness of the basal layer can be 200–1500 nm, and it increases with growing discharge power. The beginning of the second stage is associated with increasing spatial selectivity of condensation, which is manifested either by individual faceted crystals on the growth surface (see Fig. 4a for the case of columnar structures) or by the enhanced growth of oblong crystals almost parallel to the substrate surface (Fig. 4b). Apparently, these two kinds of transitions have common reasons and are determined by the gradual decrease in the degree of supersaturation during the condensation and by the dominant growth of local areas where the energies of atomic bonds are larger than  $E_c$ . For example, the transition to columnar structures is due to the dominating growth of crystals on the (210) plane (see crystals indicated by arrows in Fig. 4a). The transition to labyrinth structures typically occurs at higher discharge powers, and the degree of supersaturation immediately above the growth surface in this case is modulated by the more pronounced relief of the basal nonporous layer (Fig. 4b). The later effect can increase the number of crystallographic planes on which the growth of the condensate is enhanced, which, in the end, leads to the gradual transition to labyrinth formation (Figs. 4b–4d). Note that three-dimensional labyrinth structures similar to that shown in Fig. 4d are observed when the discharge power is increased to 10.9 W.

Therefore, the pore formation begins because the supersaturation decreases gradually during the condensate growth. This decrease is probably related to the increased heating of the growth surface, because the heat dissipation is hindered by the increasing thickness of layers. Evidently, the nucleation of condensate on water-cooled substrates takes place at higher values of the difference ( $\Delta\mu$ ) between the chemical potentials of the environment and condensate. However, the influence of a plasma on the growth surface increases the condensation temperature and, hence, the value of  $E_c$ . As a result, the process ceases to be stationary, which is most clearly manifested at higher discharge powers and during cooling of the substrate holder. The creation of highly porous structures having low thermal conductivity favors the onset of stationarity of the process, which in the end leads to the formation of statistically uniform layers, whose thickness is only limited by the deposition time.



**Fig. 6.** (a, b) Formation stages of rounded Al crystals obtained without cooling of the substrate holder at  $P_{Ar} = 25$  Pa and discharge powers of 12.8–16.7 W and (c) the respective models.

By varying the discharge power at higher pressures of the working gas ( $P_{Ar} = 20$ – $25$  Pa), we obtained a wide range of structures in the form of loosely coupled three-dimensional layers of microcrystals (Fig. 5a), labyrinth structures (Fig. 5b), and nonporous layers containing relatively large facet crystals (Fig. 5c). This succession of structural changes can be explained in terms of increased supersaturation. For example, from the crystal habitus characterizing the structure in Fig. 5a, it follows that the condensate grows mainly on the (210) plane, i.e., at a relatively small degree of supersaturation. In contrast, the formation of nonporous structures, whose surfaces consist of well-cut crystals (Fig. 5c), occurs in the case of increased supersaturation, where many crystallographic planes are involved in the formation of the structures. Evidently, the jump in the degree of supersaturation is exclusively due to the

increase in  $P_{Ar}$ . The formation of a three-dimensional labyrinth structure in the case of a simultaneous increase in  $P_{Ar}$  and the discharge power (Fig. 5b) is apparently due to slowing down of the increase in the sputtering factor and the corresponding deposition flux at a relatively large discharge power [10].

Among the results characterizing the functional capabilities of self-organized sputtering systems are also the data on condensation obtained without cooling the substrate heater at  $P_{Ar} = 25$  Pa and discharge power 12.8–16.7 W, which can also be explained in terms of the gradual decrease in the supersaturation with increasing layer thickness. A prominent feature of the initial stage of growth of a condensate obtained under these conditions is the formation of a porous structure in the form of loosely coupled microcrystals of arbitrary shape (Fig. 6a). From analyzing the crystal habitus, it is found that, in the subsequent stage of layer formation, the crystals grow predominantly with their facets based on the (210) plane (Figs. 6a–6c). These features of structure formation confirm once again that the degree of supersaturation decreases gradually during layer growth, and they also indicate that the transition to a selective growth of crystals occurs because of the increase in the critical energy. Apparently, the rounded shape of crystals (Fig. 6b) indicates an equal probability of matter arriving at different facets, which is a quite important property of self-organized ion sputtering systems.

In closing, we note that, in spite of the small discharge power, the growth rate of layers varies from 800 to 2000 nm/h, which is due to the focusing effect of a plasma flow favoring condensation of sputtered atoms on a limited area of the substrate surface. On the other hand, the increase in the growth rate is also due to the circular mass transfer near the growth surface [9].

#### 4. CONCLUSIONS

(1) For the first time, we have demonstrated that not only well-known crystal–solution, crystal–melt, and crystal–gas systems but also crystal–plasma systems can be effectively employed to achieve stationary conditions close to equilibrium. The last-mentioned variant can be realized using self-organized ion sputtering systems, which feature higher universality both in converting matter into the gaseous state and in providing conditions close to equilibrium.

(2) The stationarity criterion (the fixed position of the critical energy in the spectrum of chemical bond energies) can be satisfied even if the technological macroscopic parameters (such as the discharge power) are varied; and vice versa, it can be broken with these parameters being constant.

(3) Two main mechanisms of the formation of porous structures have been established. One of them leads to the formation of three-dimensional labyrinth layers due to anisotropic crystal growth rate, and the

other mechanism produces highly porous structures that consist of loosely coupled nano- and microcrystals formed through nucleation on active growth centers.

#### ACKNOWLEDGMENTS

This work was supported by the Ministry of Education and Science of Ukraine, project no. 71.03.03.07-08.

#### REFERENCES

1. V. I. Perekrestov, S. N. Kravchenko, and A. V. Pavlov, *Fiz. Met. Metalloved.* **88** (5), 72 (1999) [*Phys. Met. Metallogr.* **88** (5), 482 (1999)].
2. V. I. Perekrestov, A. V. Koropov, and S. N. Kravchenko, *Fiz. Tverd. Tela (St. Petersburg)* **44** (6), 1131 (2002) [*Phys. Solid State* **44** (6), 1181 (2002)].
3. V. I. Perekrestov, *Pis'ma Zh. Tekh. Fiz.* **31** (19), 41 (2005) [*Tech. Phys. Lett.* **31** (10), 830 (2005)].
4. V. I. Perekrestov and Yu. A. Kosminskaya, *Pis'ma Zh. Éksp. Teor. Fiz.* **78** (4), 258 (2003) [*JETP Lett.* **78** (4), 223 (2003)].
5. S. A. Kukushkin and A. V. Osipov, *Usp. Fiz. Nauk* **168** (10), 1083 (1998) [*Phys.-Usp.* **41** (10), 983 (1998)].
6. Ch. P., Poole, Jr. and F. J. Owens, *Introduction to Nanotechnology* (Wiley, New York, 2003; Tekhnosfera, Moscow, 2006).
7. *Modern Crystallography*, Ed. by B. K. Vainshtein, Vol. 3: A. A. Chernov, *Crystal Growth* (Nauka, Moscow, 1980; Springer, Berlin, 1984), p. 7.
8. *Handbook of Thin Film Technology*, Ed. by L. Maissel and R. Glang (McGraw-Hill, New York, 1970; Sovetskoe Radio, Moscow, 1977), Vol. 1.
9. A. G. Zhiglinskiĭ and V. V. Kuchinskiĭ, *Mass Transfer in the Course of Interaction of the Plasma with the Surface* (Énergoatomizdat, Moscow, 1991) [in Russian].
10. B. S. Danilin, *Application of Low-Temperature Plasma to the Deposition of Thin Films* (Énergoatomizdat, Moscow, 1989) [in Russian].
11. V. I. Perekrestov and S. N. Kravchenko, *Prib. Tekh. Éksp.*, No. 3, 123 (2002) [*Instrum. Exp. Tech.* **45** (3), 404 (2002)].

*Translated by G. Tsydynzhapov*