Formation of adsorbate structures induced by external electric field in plasma-condensate systems

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Abstract. We present a new model of plasma-condensate system, by taking into account an anisotropy of transference reactions of adatoms between neighbor layers of multi-layer system, caused by the strength of the electric field near substrate. We discuss an influence of the strength of the electric field onto first-order phase transitions and conditions for adsorbate patterning in plasma-condensate systems. It is shown that separated pyramidal-like multi-layer adsorbate islands can be formed in the plasma-condensate system if the strength of the electric field near substrate becomes larger than the critical value, which depends on the interaction energy of adsorbate and adsorption coefficient.

Key words. Plasma-condensate systems, nano-structured thin films, pattern formation, nano-structures.

PACS. 05.10.-a Statistical physics and nonlinear dynamics 89.75.Kd Pattern formation in complex systems 81.65.Cf Surface patterning 68.43.-h Adsorption on surfaces 81.07.-b Fabrication of nano-structures

1 Introduction

Nano-structured thin films attract increased attention in science and engineering due to their unique properties which make possible their usage in modern electronic devices [1-4]. Experimental studies and analytical treatment together with numerical simulations show that by using different techniques for thin films growth one can observe patterning on the growing surface. These patterns can be either transient or stationary. It depends on the system control parameters, which are usually related to: flux of adatoms toward growing surface; type of adsorbed particles (type of atoms/ions), that defines the activation energies of adsorption and desorption; temperature; etc. Moreover, in real experiments one always deals with multi-layer growth, where the minimization principle of the surface energy leads to an appearance of the vertical current of adatoms from top toward bottom layers. At the same time from the naive physical consideration one can state, that the concentration of adsorbate on the bottom layer is always larger then one on the top layer. This difference results in a bias in a standard vertical diffusion of adsorbate between layers. The competition of these two effects also affects the growing surface morphology [5-7].

Most of experimental studies and theoretical modeling and predictions of nano-sized adsorbate islands formation were done for high-vacuum and low-vacuum vapor deposition in gas-condensate systems. Here by varying the pressure in a chamber and temperature one can get either ordered pattern of vacancies inside adsorbate matrix [8], or elongated adsorbate structures [9,10] or nano-dots [11,12]. At the same time analytical studies and numerics show that real systems manifest self-organization processes with formation of stable complexes of adatoms in addition to equilibrium adsorption and desorption reactions [13,14]. It was shown that non-equilibrium reactions only govern realization of stable surface patterns in numerical simulations of pattern formation in one-layer gas-condensate model [15,16,17,18,19]. In Refs. [20,21] authors discussed controlling of the type of surface patterns and linear size of structures by varying adsorption coefficient, interaction energy of adsorbate, non-equilibrium reactions rate and intensity of internal fluctuations. In multi-layer low-vacuum gas-condensate systems with vertical anisotropic current of adsorbate, caused by gas phase pressure large-sized adsorbate islands on the upper layer are formed on the adsorbate matrix with separated vacancy cluster on bottom layers [7].

In order to produce separated adsorbate islands with small lateral linear size the plasma-condensate devices are used. In the framework of this technique ions, sputtered by magnetron, attain growing surface, located in a hollow cathode [22,23]. The electric field near substrate leads to desorption of a part of adatoms back to plasma, their additional ionization, and adsorption on the high levels of multi-layer growing surface [22]. Hence, the strength of the electric field controls the anisotropy strength of the vertical diffusion of adatoms between neighbor layers with preferential motion from lower layers to upper ones, in contrast to the case for gas phase pressure induced anisotropy in low-vacuum gas-condensate systems. Processes of surface patterning in plasma-condensate devices were considered mostly by experimental studying (see, for example, Refs. [23,24]). It was shown a possibility to get separated adsorbate islands with linear size around hundreds nanometers. In recent work [25] authors provided numerical study of adsorbate islands formation in multi-layer plasma-condensate system by varying anisotropy strength of vertical diffusion of adsorbate between neighbor layers, caused by the strength of the electric field near substrate.

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At the same time there is no any discussion about the range of the main control parameters responsible for ordering processes on the surface during deposition.

The main goal of this work is to define conditions corresponding to formation of stationary separated (adsorbate or vacancy) structures on the growing surface in plasma-condensate systems. To that end we will derive the accurate model for adequate description of adsorbate concentration evolution in multi-layer plasma-condensate system by taking into account a decreasing of adsorbate concentration with number of layer and anisotropy in vertical diffusion of adatoms between neighbor layers induced by the electric field near substrate. The main attention in the article is paid to study an influence of the strength of diffusion of adatoms between neighbor layers induced by the electric field near substrate onto stability of surface structures.

The work is organized in the following manner. In the next section we construct the model for the adsorbate concentration evolution on the intermediate layer of multi-layer plasma-condensate system by deriving the functional dependence of the concentration of adsorbate on neighbor layers versus one on the current layer and discuss a physical limitation of the model. In Section 3 we perform analysis of the homogeneous system and discuss first-order phase transitions. In Section 4 we study stability of homogeneous stationary states to inhomogeneous perturbations and define conditions for stationary patterns formation in the system. We conclude in the last Section.

2 Model

Evolution of adsorbate concentration on the selected layer $n$ of N-layers system can be described by the reaction diffusion model of the standard form:

$$
\partial_t x_n = R(x_n) - \nabla J_n(x_n; \nabla),
$$

(1)

where $x_n \in [0, 1]$ defines through the ratio between adsorbed particles (adatoms) and total number of atomic sites in the fixed area of the layer lattice; $t$ is the time variable. Reaction term $R(x_n)$ defines quasi-chemical reactions between adsorbed particles. For the N-layer system one should take into account the following reactions: (i) adsorption, when particles attach the substrate and become adatoms; (ii) desorption, when adatoms can desorb back into plasma; (iii) isotropic vertical motion of adatoms between neighbor layers. Moreover, by considering plasma-condensate systems one should take into account additional anisotropic vertical diffusion, caused by the action of the electric field near substrate. This field will lead to preferential motion of adatoms from bottom layers to top ones. From the naive consideration adsorption processes on n-layer can be described by the term $f_a = k_a x_{n-1} (1 - x_n)(1 - x_{n+1})$, where $k_a$ is the adsorption coefficient, proportional to the pressure of the plasma (density of the plasma). We take into account that particle can become adatom if: (i) there is nonzero adsorbate concentration on the previous layer $(x_{n-1})$; (ii) there are free sites for adsorption on the current layer $1 - x_n$; (iii) there is free space on the next layer $(1 - x_{n+1})$. Substratum mediated desorption processes are described by the term $f_d = -k_d x_n x_{n-1} (1 - x_{n+1})$, where desorption coefficient $k_d = k_d \exp(U(r)/T)$ defines through desorption rate of non-interacting particles $k_d$ and interaction potential $U_n(r)$. Here we also admit that nonzero adsorbate concentration on the current layer $(x_n)$ can be desorb from existence previous layer $(x_{n-1})$ back to plasma through free space on the next layer $(1 - x_{n+1})$. For the isotropic transference reaction between layers, which define the standard vertical diffusion, we have the standard one-dimension expression $f_t = k_t (x_{n-1} + x_{n+1} - 2x_n)$ with the vertical diffusion coefficient $k_t$. To define the reaction rate for the electrical field induced anisotropic transference between layers let us proceed in the following way. The electric field is characterized by the strength $E = \nabla \phi$, where $\phi$ is the difference in electric potentials. Hence, the additional current of adatoms on the current $n$ layer caused by the electric field is defined as $J^E_n = (EZ \exp(Ez/T)x_n)$, where $Z$ is the valence of ion and $e$ is the electron charge. By taking into account that this transference is possible only on free sites on the corresponding layers for the reaction term, describing anisotropic transference, we get $f_a = u(x_{n-1} - x_n) - x_n (1 - x_{n+1})]$, where the rate $u = |E| Ze/T$, corresponds to the anisotropy strength defined through the strength of the electrical field near substrate.

To define the diffusion term $J_n$ in Eq. (1) we will use the approach, proposed in Refs. [15,16,17,26,27]. We assume that the total lateral diffusion flux is described by the ordinary diffusion $-D_0 \nabla x_n$ and diffusion caused by the interactions between adatoms on $n$ layer. The last one is defined through the force $F_n = -\nabla U_n$ and induces speed $v_n = (D_0/T) F_n$. The corresponding flux $v_n x_n$ is possible onto free $(1 - x_n)$ sites, only. Hence, the lateral diffusion flux of adsorbate on $n$ layer reads:

$$
J_n = -D_0 \nabla x_n - (D_0/T) \mu(x_n) \nabla U_n,
$$

(2)

where the mobility of adatoms $\mu(x_n) = x_n (1 - x_n)$ is introduced. The unknown adsorbate interaction potential $U_n$ can be defined in the framework of self-consistent approximation, which frequently used by studying pattern formation in reaction-diffusion systems [11,15,16,17,18,19,20,25,26,27,30,31,32,33,34], etc. In the framework of this procedure the interaction potential $U_n(r)$ can be represented in the form: $U_n(r) = x_n(r) - x_n(r) \exp(-r^2/4r_0^2)$, where $r$ is the interaction energy and $r_0$ is the interaction radius. By assuming that the adsorbate concentration varies slow within the interaction radius we expand the integral

$$
\int u_1(r - r') x_1(r') dr' \approx \int u_1(r') \sum_n \frac{(r - r')^n}{n!} \nabla^n x_1(r) dr'
$$

and retain only three non-vanishing terms. Finally, we get:

$$
\int u(r - r') x(r') dr' \approx \epsilon x(r) + \epsilon(1 + r_0^2 \nabla^2)^2 x(r).
$$

(3)
Hence, the substratum mediated interaction potential $U_n$ on $n$ layer becomes the form \[ U_n(r) \simeq -\epsilon x_n-1(r) [x_n(r) + \mathcal{L}_{SH} x_n(r)] , \] where $\mathcal{L}_{SH} = (1 + \frac{r^2}{\alpha^2})^2$ is the Swift-Hohenberg operator and $\nabla U_n$ in Eq. (3) is defined as follows: $\nabla U_n = -\epsilon x_n-1(r) \nabla [x_n(r) + (1 + \frac{r^2}{\alpha^2})^2 x_n(r)]$.

The main goal of this work is to define the conditions of pattern formation on a surface during adsorption in plasma-condensate system with anisotropic vertical diffusion of adatoms between layers. In Ref. [7] for two- and three-layers gas-condensate system authors shows the corresponding phase diagram illustrating domains of main system parameters when the growing surface can be structured with formation of separated adsorbate islands or separated vacancy islands inside adsorbate matrix on each layer. In this article we are aimed to define the system parameters domains responsible for pattern formation on any layer of $N$-layers plasma-condensate system. To this end we will derive the functional dependencies of the adsorbate concentration on the previous $(n-1)$ and the next $(n+1)$ layers through the adsorbate concentration on the current layer $n$ by taking into account that the concentration of adsorbate on each next layer is less than one on the current layer.

By considering the multi-layer system the adsorbate concentration on each layer can be defined according to the fraction $x_n = S_n / S_0$ where $S_0 \propto R_0^2$ is the square of the substrate with linear size $R_0$ and $S_n \propto R_n^2$ is the coverage square of $n$ layer by adsorbate. According to the principle of minimization of surface energy the adsorbate concentration on each next layer is less than one on the current layer. Hence, considering multi-layer adsorbate island as a pyramidal structure, we assume, that the linear size of the multi-layer adsorbate structure on each layer decreases by the small value $d$ with the layer number growth, $R_n = R_0 - nd$. In the framework of this description the parameter $d$ defines the terrace width of the multi-layer pyramidal structure of adsorbate. Hence, the adsorbate concentration on any $n$ layer is defined as: $x_n \simeq (1 - nd/R_0)^2$. Next by using simple algebra one finds that the concentration of adsorbate on nearest layers to $n$ one is defined through $x_n$, as: $x_{n-1} = (\sqrt{x_n} + 1/2\beta_0)^2$, $x_{n+1} = (\sqrt{x_n} - 1/2\beta_0)^2$ with $\beta_0 = 2d/R_0 < 1$. In this case for the isotropic vertical diffusion described by $f_z$ one gets $1/2\beta_0^2$. It means, that according to condition that the concentration of adsorbate decreases with number of the layer the standard vertical diffusion is characterized by bias which tends to zero only for the layer by layer growth. Parameter $\beta_0$ defines the number $N$ layers in multilayer plasma-condensate system through the relation $x_{N+1} = 0$, as $N = 2/\beta_0 - 1$, with $x_N = \beta_0^2/4$.

By introducing the dimensionless constants $\epsilon \equiv \epsilon/\gamma$, $\alpha \equiv k_a/k_g$, $\beta_0 \equiv k_{f_z}^2$, $\nu' \equiv u/k_g^2$ and dropping all primes the reaction term $R(x)$ in Eq. (4) for $x_n = x$ becomes the form:

\[
R(x) = \alpha (1 - x) \nu(x) - \nu(x) e^{-2\epsilon x (\sqrt{\gamma + \beta_0})^2} + u \beta_0 \sqrt{\gamma (1 - 2x)} + \frac{1}{4} \beta_0^2 (u + 2),
\] (5)

where $\nu(x) = (\sqrt{\gamma + 1/2\beta_0})^2 \left[ 1 - (\sqrt{\gamma + 1/2\beta_0})^2 \right]$. Next it is more convenient to measure time in units $t' \equiv t k_g^4$, distance in units $r' = r/L_d$, and by introducing diffusion length $L_d = \sqrt{D_0/k_g^2}$ the evolution equation for the adsorbate concentration Eq. (1) reads:

\[
\partial_t x = R(x) + D_0 \nabla^2 [\gamma (x + \mathcal{L}_{SH} x)] + \xi(t),
\] (6)

where $\gamma(x) = \mu(x) (\sqrt{\gamma + 1/2\beta_0})^2$ and $\xi(t)$ is the delta-correlated Gaussian zero-mean noise with intensity $\sigma^2$ proportional to the bath temperature.

The derived model for evolution of the adsorbate concentration on the intermediate layer of multilayer system has one physical limitation, related to the limit value of the adsorbate concentration on the previous $(n-1)$ layer, $x_{n-1} = 1$, corresponding to the substrate. In such a case one gets the limit value for the adsorbate concentration on the current (first) layer, $x_{max} = (1 - 1/2\beta_0)^2$. This limit value allows one to define the minimal value of the anisotropy strength $u$ or the maximal value of the parameter $\beta_0$, when $x \leq x_{max}$. In Fig. (1) we plot the dependence of the minimal value of the anisotropy strength $u_{min}(\beta_0)$ on the parameter $\beta_0$. Here the dependence $u_{min}(\beta_0)$ bounds the domain I of system parameters, when the concentration of adsorbate on the current layer does not exceed value $x_{max}$. Insertion shows the dependence $u_{min}(\alpha)$ at $\beta_0 = 0.1$. From Fig. (1) it is seen that even infinitely small value of $\beta_0$, which defines the difference in the adsorbate concentration on neighbor layers, requires non-zero value of the anisotropy strength $u_{min}$ for holding the relation $x_{n-1} \leq 1$. At $\beta_0 \to 0$ the adsorbate concentration on any layer remains constant, defined by adsorption coefficient $\alpha$ and interaction strength $\epsilon$. In such a case equation (6) describes evolution of adsorbate concentration in one-layerlike model with $f_z = f_{u} \to 0$. It follows, that an increase in ether adsorption coefficient $\alpha$ or interaction strength $\epsilon$ decreases the domain I corresponding to to multilayer growth. In the insertion in Fig. (1) we show dependencies...
\( u_{\text{min}}(\alpha) \) at fixed \( \beta_0 = 0.1 \). It is seen, that in the case of small pressure \((\alpha \to 0)\) \( N \)-layer growth is possible at non-zero anisotropy strength \( u \) only (electric field induced transference of adatoms between neighbor layers).

### 3 Stability of the stationary homogeneous states

It is known that gas-condensate systems undergo first-order phase transitions (see, for example, Refs. [18,5,19,20,21]). In this section we will study homogeneous system and discuss dependencies of the stationary adsorbate concentration on control parameters and phase transitions in plasma-condensate system, described by Eq.(6). To proceed we assume \( \nabla \cdot \mathbf{J} = 0 \) and consider stationary limit with \( \beta_0 x = 0 \), leading to the equation \( R(x) = 0 \). Typical dependencies of the stationary adsorbate concentration on the intermediate layer \( x_{st} \) versus adsorption coefficient \( \alpha \) are shown in Fig. 2 for different values of the anisotropy strength \( u \). It follows, that at small values of the anisotropy strength (see solid curve for \( u = 0.1 \)) the plasma-condensate system undergoes first-order phase transition with increase in the adsorption coefficient \( \alpha \) from low-density state (plasma) to high-density state (adsorbate) at \( \alpha = \alpha_1 \). With a decrease in the adsorption coefficient one has transition from high- to low-density state at \( \alpha = \alpha_2 \). Hence if the adsorption coefficient takes values inside the interval \((\alpha_1, \alpha_2)\), then the system becomes bi-stable. A decrease in the interaction strength \( \varepsilon \) requires larger values for adsorption coefficient \( \alpha \) when the studied system is bi-stable; the width of the interval \((\alpha_1, \alpha_2)\) becomes smaller (compare solid and dash-dot curves in Fig. 2). An increase in the anisotropy strength \( u \) leads to a degeneration of the interval for adsorption coefficient values, responsible for bi-stability of the system (compare dash-dot and dash curves in Fig. 2). Hence, at large \( u \) system is always mono-stable. In Fig. 3 we present dependencies of the stationary adsorbate concentration \( x_{st} \) versus anisotropy strength \( u \) at different values of adsorption coefficient \( \alpha \). Here values of the homogeneous stationary adsorbate concentration are limited by the value \( x_{\text{max}} \) which corresponds to the minimal value of the interaction strength \( u_{\text{min}}(\alpha, \varepsilon, \beta_0) \). From Fig. 3 it follows that at small values of adsorption coefficient with increase in the anisotropy strength one gets first-order phase transition from high-density state toward low-density state at \( u = u_1 \) (see panel for \( \alpha = 0.04 \)). An increase in adsorption coefficient results in more complicated picture of phase transformations (see panel for \( \alpha = 0.06 \) in Fig. 3). Here at small \( u \) one has the similar to the previous case picture with increased value \( u_1 \). For the case \( u > u_1 \) one gets additional first-order phase transition from low- to high-density state and the width of the hysteresis loop \((u_2, u_3)\) depends on both adsorption coefficient \( \alpha \) and interaction energy \( \varepsilon \). This effect is caused by the competition between adsorption and anisotropic transference. Further growth in \( \alpha \) leads to transformation of the dependence \( x_{st}(u) \) and an increase in anisotropy strength leads to first-order phase transition from low-density state to high-density state at \( u = u_4 \) (see panel for \( \alpha = 0.15 \)). At large values of \( \alpha \) explicit decreasing dependence \( x_{st}(u) \) is realized in the high-density phase.

![Fig. 2. Dependencies of the stationary adsorbate concentration on the intermediate layer \( x_{st} \) on adsorption coefficient \( \alpha \).](image)

![Fig. 3. Dependencies of the stationary adsorbate concentration on the intermediate layer \( x_{st} \) versus anisotropy strength \( u \) at \( \varepsilon = 4.0 \), \( \beta_0 = 0.1 \) and different values of the adsorption coefficient \( \alpha \).](image)
For detailed analysis of system states we calculate the effective potential $V(x) = -\int R(x)$ in each domain and at values $\alpha$ and $u$, corresponding to binodals and spinodal. Minimums of $V(x)$ in Fig. 5 define stable states. In domain II the system is characterized by one stable and one unstable state. Domain III and IV correspond to the system parameters when the system is characterized by the single stationary low- and high-density state, accordingly (see panels b and c in Fig. 5). By fixing the anisotropy strength $u < u_3$ with decrease in the adsorption coefficient $\alpha$ we move from domain IV of single high-density state (point c) to bistability domain V (point e) through the binodal (point d). In this case the additional minimum of the potential $V(x)$ appears and system is in high-density state (the minimum at large $x$ is deeper). The two minima of the potential $V(x)$ becomes equivalent at values of the system parameters from the spinodal (dash curve) (see panel f in Fig. 5). Further decrease in the adsorption coefficient leads to transition of the system toward low-density state (see panel g in Fig. 5).

In the insertion in Fig. 4 we show a change in the bi-stability domain by varying interaction strength $\varepsilon$ and adsorbate difference on neighbor layers $\beta_0$. Here solid curves correspond to $\varepsilon = 4$, $\beta_0 = 0.1$; dash-dot lines relate to $\varepsilon = 3$, $\beta_0 = 0.1$ and dash ones are obtained at $\varepsilon = 3$, $\beta_0 = 0.15$. It follows, that with an increase in $\beta_0$ the bi-stability domain shrinks in both $\alpha$ and $u$ (compare dash-dot and dash curves). An increase in the interaction strength leads to extension of the bi-stability domain in values of anisotropy strength, shrink in adsorption coefficient and appearance of the interval $(\alpha_{c1}, \alpha_{c2})$ of re-entrant first-order phase transitions (see Fig. 5 at $\alpha = 0.06$).

4 Stability analysis and pattern formation

To define the conditions for adsorbate structures formation during condensation in studied plasma-condensate system in this section we will provide the linear stability analysis of homogeneous stationary states $x_{st}$ to inhomogeneous perturbations. To that end in the framework of the standard linear stability analysis we will consider the deviation of the adsorbate concentration from the stationary value: $\delta x = x - x_{st} \propto e^{\lambda(k)t}e^{ikx}$, where $k$ is the wave number, $\lambda(k)$ is the stability exponent. Next, by expanding the reaction term $R(x)$ in the vicinity of the stationary state $x_{st}$ with $R(x_{st}) = 0$ from the evolution equation for the deviation $\delta x$, obtained from Eq. (6) one gets the stability exponent $\lambda(k)$ in the form:

$$\lambda(k) = d_k R(x)_{x=x_{st}}$$

$$-D_0k^2 \left[1 - \varepsilon \gamma(x_{st}) \left(1 + (1 - \rho_0^2k^2)^2 \right) \right],$$

where $\rho_0 = r_0/L_d$ and $k = kL_d$. The stability exponent $\lambda(k)$ can be used to characterize the stationary mor-

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1 For most of metals and semi-conductors the interaction radius $r_0 \sim 10^{-9}$m, and the diffusion length $L_d \sim 10^{-7} - 10^{-8}$m.
phology of the surface during condensation processes. If $\lambda(\kappa) < 0$ for all wave numbers $\kappa$ then any spatial perturbation degenerates in time and no spatial instabilities are possible in the stationary regime. Here any adsorbate structures, which can be formed at initial stages of the system evolution disappear at large time scales and adsorbate will cover the substrate homogeneously. In the case $\lambda(\kappa) > 0$ at $\kappa \in (0, \kappa_0)$ one gets picture typical for phase separation. For the case $\lambda(\kappa) > 0$ at $\kappa \in (\kappa_1, \kappa_2)$ one can expect formation of separated structures on the surface with the period of spatial modulations (mean distance between structures) $\kappa_0$ defined from $d_0 \lambda(\kappa) = 0$. By taking into account that $\rho_0 \rightarrow 0$ the analysis of Eq. (7) shows, that in the limit of large wave numbers $\kappa$ the stability exponent $\lambda(\kappa)$ is negative. Hence, to ensure the conditions of pattern formation in the studied plasma-condensate system one needs: (i) $d_0 R(x) |_{x=x_{st}} < 0$, which defines that the corresponding stationary state $x_{st}$ is stable; (ii) $\lambda(\kappa_0) > 0$. These two conditions allow one to compute the phase diagram, which define domain of control parameters values when during adsorption processes in plasma-condensate system one gets stationary separated adsorbate structures or vacancy clusters inside adsorbate matrix. The corresponding phase diagram in a plane $(\alpha, \beta)$ is shown in Fig. 6 for different values of interaction energy $\varepsilon$ and the coefficient $\beta_0$. Here for the system parameters taken from the bounded domain I stationary structures will be form on the growing surface at the condensation in multi-layer plasma-condensate system. In the domain II no patterns can be observed. The corresponding dependencies of the stability exponent $\lambda(\kappa)$ obtained in points A and B are shown in Figs. 6a and 6b, respectively. From Fig. 6 it is seen, that in the domain II the stability exponent takes negative values in the whole interval of the re-normalized wave numbers $\kappa$. In the domain I the dependence $\lambda(\kappa)$ crosses zero value twice and takes positive values inside the bounded interval of the wave numbers $(\kappa_1, \kappa_2)$. The mean period of them stationary structures location (mean distance between separated structures) is defined by the value $\kappa_0 \propto 1/\kappa_{st}$ in the $\kappa$-space.

One should mentioned, that in the case of isotropic transference reactions (at $u = 0$) no stationary spatial instability can be possible for any values of adsorption coefficient $\alpha$, interaction energy $\varepsilon$ and coefficient $\beta_0$. Let us discuss dependence $\alpha(u)$ in Fig. 6 at $\beta_0 = 0.1$ and $\varepsilon = 3.3$ in details (see solid curve). The domain of pattern formation (domain I) is bounded by the minimal value of the adsorption coefficient $\alpha(u_{min})$ and the maximal values $\alpha_{max}$ and $u_{max}$. Hence, by fixing the anisotropy strength $u$ (fixing the strength of the electric field near substrate) and by increasing the adsorption coefficient we get the following transformations in the surface morphology. At low values of $\alpha$ (domain II under the solid curve) there is no enough adsorbate concentration on the layer to induce pattern formation and adsorbate with small concentration covers the layer homogeneously. With increase in the adsorption coefficient inside the domain I one gets separated adsorbate island on the current layer, meaning formation of pyramidal-like multi-layer adsorbate islands. At $\alpha > \alpha_{max}$ the large pressure produces large adsorbate concentration and neither desorption no interaction no anisotropic transference can stabilize adsorbate structures, formed at initial stages of the system evolution and adsorbate covers whole the layer, meaning growing of the surface in layer-by-layer scenario. Hence, an increase in adsorption coefficient leads to re-entrant patterning in the multi-layer plasma-condensate system. The same effect can be seen by varying the strength of the electric field, described by $u$, at fixed values of adsorption coefficient $\alpha$: small anisotropy can not induce pattern formation processes; at $u > u_{max}$ the strong anisotropy in vertical diffusion leads to a decrease in the adsorbate concentration and we get process analogous to the case with small $\alpha$. From obtained results it follows, that a decrease in both the adsorbate interaction energy and the difference in the adsorbate concentration on neighbor layers leads to shrink in the size of the domain of pattern formation.

Next, we will consider dependencies of the wave numbers $\kappa_1$ and $\kappa_2$, bounding domain of positive values of the stability exponent $\lambda(\kappa)$ and the value $\kappa_{st}$, defining the mean distance between structures, shown in Fig. 6. From

![Phase diagram for the plasma-condensate system illustrating domain of system parameters relevant to formation of stationary separated adsorbate structures (domain I). In domain II during exposing time adsorbate will homogeneously cover the substrate. Dependencies of the stability exponent obtained in points A and B are shown in panels (b) and (c) respectively.](image)
Fig. 7. Dependencies of the wave numbers $\kappa_1$ and $\kappa_2$, which define the interval of the positive values of the stability exponent $\lambda(\kappa)$, and $\kappa_0$, corresponds to the mean period of adsorbate structures location, versus: (a) anisotropy strength $u$; (b) adsorption coefficient $\alpha$; (c) adsorbate interaction energy $\varepsilon$.

Fig. 8. Numerical simulations of the evolution of the morphology of the intermediate layer of multi-layer system at $\alpha = 0.2$, $\varepsilon = 3.5$, $\beta = 0.1$, $u = 1$ and $\sigma^2 = 0.01$.

Fig. 7, it follows, that at $u < u_0^\varepsilon$ the whole dependence $\lambda(\kappa)$ lies under the line $\lambda = 0$. At $u > u_0^\varepsilon$ the stability exponent becomes positive in the interval $(\kappa_1, \kappa_2)$, which extends with growth in $u$. Here $\kappa_0$ increases with $u$ meaning formation of new adsorbate islands on the layer, that leads to a decrease in the mean distance between them in r-space. At $u = u_0^\varepsilon$, which is defined by the condition $d_u \kappa_0 = 0$ the interval for the positive values of the stability exponent becomes shrink and the distance between adsorbate clusters falls down, meaning formation of smaller number of adsorbate islands with larger period of their location due to anisotropy in transference reactions between layers. For the case $u > u_0^\varepsilon$ the stability exponent becomes negative and strong anisotropy leads to adsorbate structures disappear in the stationary regime. The dependence of the wave numbers $\kappa_1$, $\kappa_2$ and $\kappa_0$ on the adsorption coefficient $\alpha$ shown in Fig. 7b is similar to the previous case. A decrease dependence $\kappa_0(\alpha)$ here means an increase of the linear size of adsorbate islands. From the dependence of wave numbers on the interaction energy $\varepsilon$ (see Fig. 7c) it follows, that if the condition $\varepsilon > \varepsilon_1^\beta$ holds then the stability exponent becomes positive similar to the case shown in Fig. 7. An increase in $\varepsilon$ extends the interval $(\kappa_1, \kappa_2)$ and leads to growth in $\kappa_0$, meaning formation of large number of adsorbate structures with small averaged distance between them in r-space.

One should stress that the provided analysis of the stability of the homogeneous stationary state to inhomogeneous perturbation (see Fig. 7) allows one to determine conditions (values of the control parameters), when spatial instability will lead to formation of stationary multi-layer structures in the plasma-condensate system. At the same time this analysis does not give any information about the morphology of the layer defined by the type of structures, namely, either separated adsorbate structures on the layer, either separated holes in adsorbate matrix, or elongated percolating islands (typical for phase separation picture).

To illustrate the process of pattern formation during condensation in plasma-condensate system we perform numerical simulation. To this end we solve Eq. 6 numerically on two-dimension grid with size $L \times L$ with $L = 256$ sites, triangular symmetry (to provide formation of spherical structures) and periodic boundary conditions. We provide numerical integration with time-step $\Delta t = 10^{-3}$ and mesh size $\Delta x = 0.5$ by using relation $L_d/r_0 = 40$, that gives the relation $L = 12.8L_d$. We assume, that at initial time $t = 0$ the concentration of adsorbate on the intermediate layer equals zero. Snapshots of the system evolution at $\alpha = 0.2, \varepsilon = 3.5, \beta = 0.1, u = 1$ and $\sigma^2 = 0.01$ (inside domain I in Fig. 8a) are shown in Fig. 8. Here with the grey color we show the concentration of adsorbate counting from minimal (black) to maximal (white) color for each time instant. It follows, that at initial times the adsorbate starts to cover the current layer (see panel at $t = 10$). When the concentration of adsorbate attains supersaturation the small separated adsorbate clusters start to appear (see panel at $t = 30$). These clusters grow in time and rearrange (see panel at $t = 100$). At large time scales one gets the stationary picture of adsorbate clusters distribution on the current layer (see panel at $t = 600$), meaning formation of pyramidal-like islands of adsorbate during condensation in multi-layer plasma-condensate system. From numerical simulations we get the stationary mean adsorbate concentration, $\langle \rho_n \rangle \simeq 0.5943$, that gives the number of the current layer $n = 5$ with $N = 19$ is the total number of layers in adsorbate multi-layer structures. By using $L_d \simeq 5 \cdot 10^{-7} m$ we get the mean radius of stationary spherical structures $\langle R_n \rangle \simeq 0.18 \mu m$, the mean ra-
dium of adsorbate structures on the first layer \( \langle R_0 \rangle \simeq 0.24 \, \mu m \) and the terrace width for the adsorbate structures \( d \simeq 0.012 \, \mu m \).

5 Conclusions

In this article we present a new model of plasma-condensate system, by taking into account an anisotropy of transference reactions of adatoms between neighbor layers of multi-layer system, caused by the strength of the electric field near substrate. The derived model was used to describe pattern formation processes on an intermediate layer of multi-layer system. We focused our attention on detailed study of an influence of the anisotropy strength on the morphology change of the growing surface. We have discussed first-order phase transitions plasma-condensate and define the phase diagram illustrating the bounded domain of main system parameters when separated adsorbate cluster will be formed on the current layer of multi-layer system meaning growth of pyramidal-like adsorbate islands. It is shown that an increase in both adsorption coefficient proportional to the plasma pressure and strength of the anisotropy in transference of adatoms between neighbor layers, caused by the strength of the electric field near substrate, leads to re-entrant picture of pattern formation on the surface during adsorption/desorption processes in plasma-condensate systems. It is shown, that multi-layer nano-sized pyramidal-like adsorbate structures can be formed if the strength of the electric field near substrate exceeds the critical value.

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