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EVOLUTION OF PHASE COMPOSITION AND ASSOCIATED PROPERTIES IN THE PROCESS OF GROWTH OF NANOSTRUCTURED FILMS

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1. Introduction

Nanostructured films are widely used in optics, microelectronics, laser engineering and many other fields of science and technology [1]. The materials must possess certain properties, for instance, mechanical or electrophysical depending on the application. The properties, as a rule, are determined by the composition of the growing films and also by the size of the crystalline grains forming the films [2]. Both systems can be studied in a similar way. Film systems are examined here only as an example since now they are widely used.

Irrespective of the preparation techniques, the films in the process of their growth pass a series of stages typical for a first-order phase transition [1, 3–9]. These stages are the nucleation of nano-clusters of a new phase [1, 10–17], their growth [10], Ostwald ripening [1, 3–8, 17], coagulation [11] and formation of a continuous film. When the nucleation process occurs under considerable supersaturation, the density of islands of new phase and the degree of substrate filling are high and the stages following nucleation may not take place [1]. In this case, both composition and structure are determined by the nucleation processes which have a complicated non-linear nature [12–16]. To control the process at this stage is not possible. Special methods such as nucleation process control are to be used. As shown in Refs [3–9], the growth parameters can be controlled only at the Ostwald ripening stage, where nucleation of new islands does not take place and a continuous film has still not formed. The possibility of composition and structure control is based on the fact that at this stage an ensemble of islands of new phase begins to interact with

generalized diffusion and thermal fields formed on the substrate's surface, and fluxes of atoms incident on it.

The aim of this work is to find out the dependence of the distribution function of nano-islands on their composition and, accordingly, the distribution functions with respect to one or another property (such as, conductivity, mobility and so on) dependent on the initial composition. It was shown previously that there is a great difference between evolution of nano-islands grown from substances forming a continuous series of solid solutions and stoichiometric substances formed as a result of chemical reactions. This leads to a significant difference in the growth processes of films both at the nucleation stage and the Ostwald ripening stage [3–9]. For this reason, these cases are analyzed separately.

2. Evolution of the phase composition of nano-islands at the Ostwald ripening stage.

2.1. EVOLUTION OF PHASE COMPOSITION IN SOLID SOLUTION

Let the equilibrium state diagram of a system for a growing film be the state diagram of a binary system with continuous solubility of components in a solid phase (see Fig 1). This means that both nucleation and Ostwald ripening processes are possible only when the system is supercooled to a temperature between the liquids line and the T_a line (see Fig 1). When the system is cooled in such a way that the temperature rapidly arrives at values lying between the T_a — line and the solidus curve, then the system readily solidifies without separation into phases and the composition of the solid phase corresponds to that of the liquid phase [18]. These processes are not discussed in this paper.

If a nano-island ensemble on the substrate surface is at the Ostwald ripening stage and is supercooled to a temperature in the interval between T_a and the liquidus line, then the composition of each island is related with its size, R, by the following equation [6, 7]:

$$C_{SR} = \frac{2\sigma w C_{L0}}{k_B T R} + C_{L0} + \psi \left(\frac{2\sigma w C_{L0}}{k_B T R} + C_{L0} \right), \qquad (1)$$

where σ is the surface tension on the island-vapor (solution) interface; k_B is the Boltzmann constant ; T is the absolute temperature; C_{L0} is the equilibrium concentration of a component, for instance, A on the liquidus line (Fig.1), i.e. in a liquid phase; w is the volume per atom in an island; ψ is the functional relationship for the solidus-liquidus line, i.e. $C_{S0} - C_{L0} = \psi(C_{L0})$, describing the diagram of state (Fig.1); C_S — is the equilibrium concentration of a component of a solid solution, for instance, A in the solid phase.
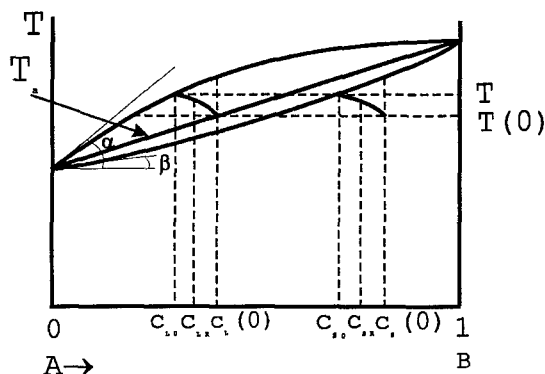
Figure 1: Diagram of states for a binary system with continuous solubility of components in a solid phase. Here C_{S0} and C_{L0} are equilibrium concentrations of a component in solid and liquid phases, respectively. C_{SR} is the composition of islands of radius R; T_a is the temperature below which an alloy solidifies without changes in composition; $\bar{T}(0)$ and $\bar{C}_L(0)$ are the initial temperature and concentration in melt and solid phase, respectively; α is the slope angle of the liquidus line for $C \to 0$; β is the slope angle of the solidus line for $C \to 0$.

Let us consider the ranges of values of the ψ function near small values of C_{L0} concentration of the component A, i.e. near the origin of coordinates. In this case the ψ function can be approximated by two straight lines. In this case

$$C_{SR} = \frac{2\sigma w C_{L0}}{k_B T R} + C_{L0} + \gamma \left(\frac{2\sigma w C_{L0}}{k_B T R} + C_{L0} \right) . \qquad (2)$$

Here $\gamma = \mathrm{tg}\,\alpha / \mathrm{tg}\,\beta - 1$; $\mathrm{tg}\,\alpha$ is the angle coefficient of the straight line binding liquidus line and $\mathrm{tg}\,\beta$ is the angle coefficient of the solidus line; $(1 + \gamma)$ is the distribution coefficient of liquid and solid phases within the equilibrium one, i.e. $1 + \gamma = C_{S0}/C_{L0}$. Note, that if $\gamma < 0$, concentration of the component in the liquid is higher than in the solid (i.e. an easily fusible component is analyzed). In the case when $(1 + \gamma) > 1$, i.e. $\gamma > 0$, concentration of this component is higher in the solid phase than in the liquid. The expression for the island radius R could be obtained from (2):

$$R = \frac{2\sigma w C_{L0}(1 + \gamma)}{k_B T \left[C_{SR} - C_{L0}(1 + \gamma) \right]}. \qquad (3)$$

Let us define $C_{SR} - C_{L0}(1 - \gamma)$ as ξ_R. It is seen from equation (3) that there is an unambiguous relation between the island radius, R, and composition. Thus, if $C_{SR} \to C_{L0}(1 + \gamma)$, i.e. $\xi_R \to 0$, then $R \to \infty$. If $\xi_R \to \infty$, then $R \to 0$. It was shown previously in Refs [6–8], that in order to find out the size distribution function of islands, $f(R,t)$ at the Ostwald ripening stage, it is necessary to solve the set of equations that involves the

continuity equation for the distribution function, the matter-and-heat balance equation, the equation describing relation between the flux of matter arriving at an island and the flux of heat released during the growth of the island; the coupling equation of the melting point for an island with radius, R, with the concentration of matter which is in equilibrium with it and the equation expressing the dependence of the growth rate of an island on its radius.

Since there is an unambiguous correlation between R and ξ_R, let us consider the distribution function $f(R,t)$ - the distribution function of island versus inverse composition values, i.e. $\varphi\left(\frac{1}{\xi_R}, t\right)$. In accordance with (3), for $t \to \infty$, and $R \to \infty$, $\xi_R \to 0$, it is more convenient to use the reciprocals of the compositions, i.e. $1/\xi_R \to \infty$ at $t \to \infty$. So, we pass from $f(R,t)$ to $\varphi(1/\xi_R, t)$, i.e. $f(R,t)dR = \varphi(1/\xi_R, t)d(1/\xi_R)$. In this case the set of equations describing the size distribution function $f(R,t)$, derived in Refs [6, 7] for the function $\varphi(1/\xi_R, t)$, could be written as:

$$\frac{\partial \varphi(1/\xi_R, t)}{\partial t} + \frac{\partial}{\partial (1/\xi_R)}\left[\varphi(\frac{1}{\xi_R}, t)\frac{d(1/\xi_R)}{dt}\right] = 0 \tag{4}$$

$$Q_D(t) = N_0 \Delta C(t) + \kappa \int_0^\infty \varphi(1/\xi_R, t)(1/\xi_R^3)d(1/\xi_R) \tag{5}$$

$$Q_T(t) = \lambda C_P \rho \Delta T(t) + \kappa^* \int_0^\infty \varphi(1/\xi_R, t)(1/\xi_R^3)d(1/\xi_R) \tag{6}$$

$$L J_{D,R} = J_{T,R} \tag{7}$$

$$T_R = \varphi(C_L, R) \tag{8}$$

$$\frac{d(1/\xi_R)}{dt} = \frac{A_P}{\alpha^P (1/\xi_R)^{p-1}}\left[\frac{\alpha(1/\xi_R)}{R_c} - 1\right]. \tag{9}$$

Here Eqn. (4) is the continuity equation of the distribution function of islands versus island composition; Eqn. (5) is the equation of the matter conservation law expressed via the distribution function in terms of composition; Eqn. (6) is the equation of heat conservation law expressed through the distribution function in terms of composition; Eqn. (7) is the equation coupling heat and matter fluxes on the surface of an island of composition C_{SR}; Eqn. (8) is the equation coupling the melting point of an island of radius, R, and its composition; Eqn. (9) is the equation describing the change of an island composition in time; $Q_D(t)$ and $Q_T(t)$ are the power carried by the matter flux arriving at the substrate and the power in the heat flow, respectively; $\Delta C(t)$ and $\Delta T(t)$ are the supersaturation and supercooling on a substrate or in the melt, respectively [6, 7]; C_P and ρ are the heat capacity and density of a melt or substrate, respectively depending on where the ripening process takes place; λ is the thickness of the melt or substrate layer,

where the Ostwald ripening process takes place, λ is of the order of average island size, i.e. $\lambda \sim \bar{R}$ (more information about λ value and its calculation can be found in [1]); A_P and p are the coefficients dependent on the mechanism of island growth [1, 6, 7]; the coefficient p can take the values of $p = 2, 3, 4$ (in the case of evolution of faceted islands $p = 5$); R_c is the critical radius of islands; $\chi_{cr} = \frac{2\sigma w C_{L0}(1+\gamma)}{k_B T} \frac{2}{3} \frac{\pi}{w N_0} [\chi(\theta)]^{-1}$; $\kappa^* = \kappa/L$; L is the latent heat of crystallization per atom of the precipitated phase; N_0 is the number of adsorption sites on the substrate, $N_0 \sim 1/a^2$ (or the total number of atoms in solution, N_a depends on the kind of heat/mass transfer mechanism realized in a system [6, 7]; a is the lattice constant of the substrate; $\chi(\theta) = 2(2 - 3\cos\theta + \cos^3\theta)^{-1}$; θ is the wetting angle; $\alpha =\cdot 2\sigma w C_{L0}(1 + \gamma)$. Note, that in the general case, as shown in Refs [6, 7], the values of $Q_D(t)$ and $Q_T(t)$ can be represented in the form $Q_D(t) = Q_{0D} + g_{0D}t^n$, $Q_T(t) = Q_{0T} + g_{0T}t^n$, where Q_{0D} and Q_{0T} are the total amount of matter and heat on a substrate at the beginning of the Ostwald ripening, respectively; g_{0D} and g_{0T} are the strengths of sources (sinks) of matter and heat; n is an arbitrary number, $n \geq 0$ at the Ostwald ripening stage, i.e. when $t \to \infty$, $Q_D(t) \to g_{0D}t^n$ and $Q_T(t) \to g_{0T}t^n$.

Equations (4)–(9) were derived by substitution of variables from Eqn. (3) into the equations describing evolution of the size distribution function [6, 7]. Since $R_c(t) = \frac{\alpha'}{\Delta(t)}$, where $\alpha' = \frac{\alpha \cdot C_{L0}}{C_{L0}(1+\gamma)}$, then

$$\frac{\alpha/\xi_R}{R_c(t)} = \frac{(\bar{C}(t) - C_{L0})(1+\gamma)}{C_R - C_{L0}(1+\gamma)} \tag{10}$$

As $C_{L0}(1 + \gamma) = C_{S0}$, then

$$\frac{\alpha}{\xi_R R_c(t)} = \frac{(\bar{C}(t) - C_{L0})C_{S0}}{(C_R - C_{S0})C_{L0}} \tag{11}$$

In accordance with (11) we can rewrite (9), as

$$\frac{d(1/\xi_R)}{dt} = \frac{A'_p}{(1/\xi_R)^{p-1}} \left[\frac{(\bar{C}(t) - C_{L0})(1+\gamma)}{C_R - C_{S0}} - 1 \right], \tag{12}$$

where $A'_p = A_p/\alpha$.

Finally the set of Eqns (4)–(8) and (12) completely describes the evolution of phase composition at the stage of the Ostwald ripening of a substance with the state diagram of a binary system with continuous solubility of components in a solid phase. Let us introduce the following variables: $U = \frac{(\bar{C}(t) - C_{L0})(1+\gamma)}{C_R - C_{S0}}$; $x = \frac{\Delta_0}{\Delta(t)}$; $\tau = \ln x^p$, where Δ_0 and $\Delta(t)$ are the supersaturation at the initial stage of ripening process n at time t. Equations (4)–(9) written with these variables are completely identical to the equations describing the process of non-isothermal Ostwald ripening [6–8]. Their solutions in variables u and τ will be the same. The solution of the equations are given in [6–8]. By passing from variables u and τ to variables $1/\xi_R$ and t and also to the function $\varphi(1/\xi_R, t)$, we shall

obtain the relationship of island distribution with respect to composition in time. This solution is essentially dependent on a technique of deposition of material on a substrate as well as on the intensity of cooling (or heating) of the substrate. It is well known, that the Ostwald ripening stage starts only in the presence of weak sources of matter at $0 \leq n < 3/p$. In this case, as analysis shows [6, 7].

$$\varphi(1/\xi_R, t) = \frac{2\sigma\omega C_{L0}(1+\gamma)N(t)}{k_B T R_C(t)} P_p(U). \qquad (13)$$

Here, $P_p(U)$ is the probability density for U to range between U and $(U + dU)$; the index p indicates the particular mechanism of heat/mass transfer realized in the system; $N(t)$ is the density of islands on a substrate at the time t, the analytical expressions of this value are given in [1, 3–8]; $R_C(t)$ is the critical size of islands at the time t. In Eqn. (13) instead of the critical radius $R_C(t)$ one can use the average radius, since they are related to each other by equation $\bar{R}(t) = R_C(t)C_{pn}$, (see Refs [1, 3–5]). Coefficient, C_{pn}, depend on the mechanism of heat/mass transfer and the power carried by sources of matter and heat. Numerical values of C_{pn} can be found in Refs [1, 3–5]. The value $\frac{2\sigma C_{L0}(1+\gamma)w}{k_B T R_C(t)} = \frac{2\sigma C_{S0}w}{k_B T R_C(t)} = \Delta(t)$ is supersaturation.

The value of supersaturation in accordance with [7] changes in time as:

$$\Delta(t) = \frac{2\sigma\omega C_{L0}}{k_B T C_{pn}} \left(\bar{R}_0^p + A_p^0 t\right)^{-1/p} \qquad (14)$$

Here, $\bar{R}_0$ is the average size of islands at the initial stage of the Ostwald ripening. Coefficient A_p^0 is the kinetic coefficient associated with the coefficient, A_p, derived above and it depends on the heat/mass transfer mechanism realized in the system. Values of these coefficients for all possible mechanism of heat/mass transfer are given in [6, 7]. In particular, when the islands are in the form of spherical segments and their growth occurs, as a rule, due to heat/mass transfer on the substrate surface with $\lambda_s \gg R_1$ $p = 4$

$$A_p^0 = \frac{27}{32} \frac{D_a \sigma w^2 N_0 C_{sb0} K_s \ell_{sb} \phi_1(\theta)}{(D_a N_0 C_{Lsb0} L^2 \ln(H/R_1) + K_s \ell_{sb} k_B T_0^2 \ln(\lambda_s/R_1))},$$

where λ_s is the free path length of adatoms; D_a is the Brownian diffusion coefficient of adatoms; σ is the surface tension at the old phase-island interface (solution, melt, vapor); $\phi_1(\theta)$ is the geometrical factor; K_s is the thermal conductivity of the substrate, $K_s[Jm^{-1-1}]$; ℓ_{sb} is the thickness of a substrate layer where the ripening process takes place [1, 7]; L is the latent heat of crystallization per atom of a precipitated phase; C_{Lsb0} is the equilibrium concentration of adatoms on a substrate; T_0 is the equilibrium temperature of crystallization (of solution, vapor or melt); H is the average distance between islands on a substrate [7]; $R_1 = R \cdot \sin\theta$; θ is the wetting angle.

Analytical expressions of $P_p(U)$ functions for all values of p are given in [1, 3–8], that is why in Fig 2 only the plots of $P_p(U)$ values for $p = 2, 3$ and 4 for $n = 0$ are presented.
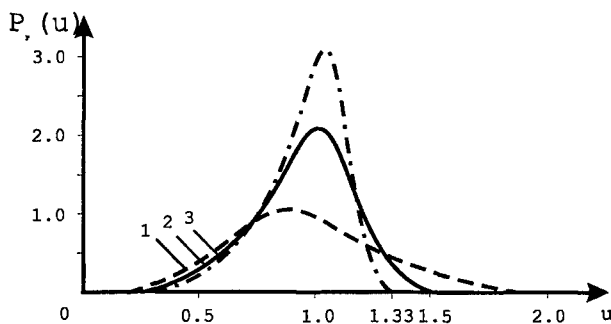
Figure 2: $P_2(U)$, $P_3(U)$ and $P_4(U)$ functions for nano-islands with the spherical shape.

$P_p(U)$ functions can be experimentally found using the technique described in [1], i.e. by expressing U via the average radius of islands $U = R \cdot C_{pn}/\bar{R}$. This way is more convenient than to express U via concentrations $U = (\bar{C}(t) - C_{s0})/(C_R - C_{s0})$, which are hardly measurable values in the experiment. The distribution function in terms of composition (13) can be actually expressed through values independent of composition (except the C_{s0} value)–this is an advantage of our approach. Equilibrium concentrations C_{L0} and C_{s0} as well as equilibrium temperature T_0 are determined from the solution of Eqns (5)–(8) for $t \to \infty$. For $t \to \infty$ the equations transform into algebraic equations. The equations can be easily solved and, as a result, the values of C_{L0}, C_{s0} and T_0 can be obtained (for more details see [6, 7]).

The average composition of nano-islands is calculated from the equation

$$\bar{\xi}(t) = \left[\int\limits_0^\infty \frac{1}{\xi_R(t)} \cdot \varphi(1/\xi_R, t) d\left(\frac{1}{\xi_R}\right) \right]^{-1} . \qquad (15)$$

Taking into account Eqn. (3) and expressing $\varphi(1/\xi_R, t) d(1/\xi_R)$ via $f(R, t) dR$, as it is done before, we shall get

$$\bar{\xi}(t) = \frac{2\sigma\omega C_{L0}(1+\gamma)}{k_B T} \left[\bar{R}(t) \right]^{-1} . \qquad (16)$$

Finally we shall obtain:

$$\bar{\xi}(t) = \frac{2\sigma\omega C_{L0}(1+\gamma)}{k_B T} \left[\bar{R}_0^p + A_p^0 t \right]^{-1/p} . \qquad (17)$$

Comparing Eqn. (17) with (14), $\Delta(t) = \bar{\xi}(t)/(1+\gamma)$ is readily obtained. This result is associated with the fact that compositions of solid and liquid phases are related to each

C_R

a

C_R

b

C_{R0}

C_{S0}

0 $10^{-8} m$ R 0 t

$\bar{\xi}(t)$
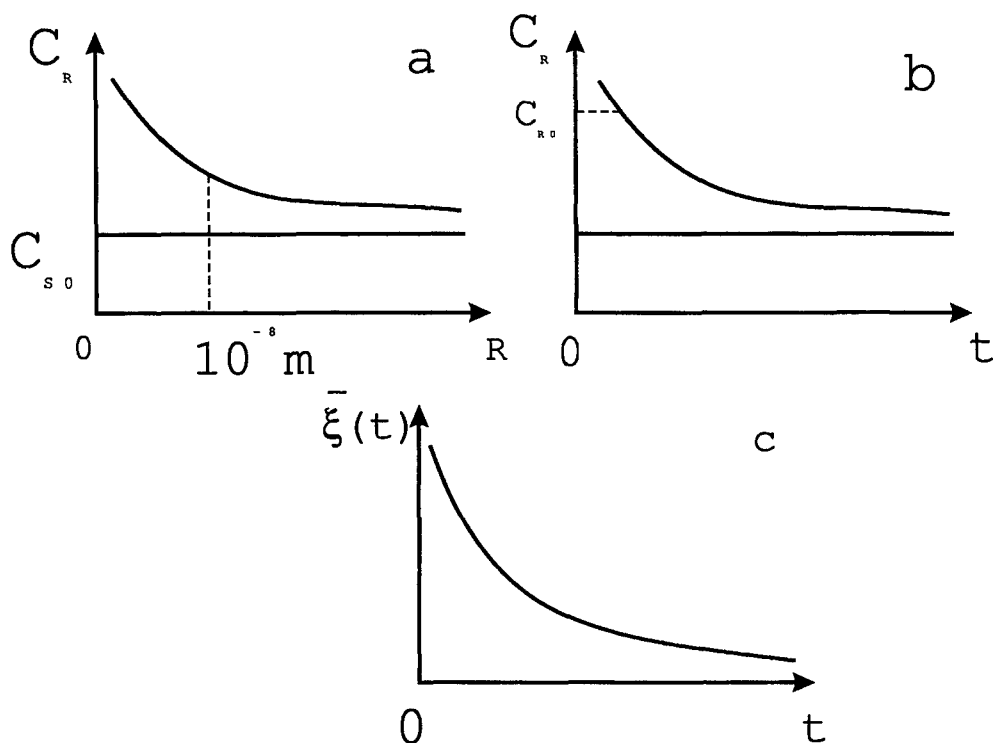
c

0 t

Figure 3: Dependence of composition of nano-islands on size (a) and composition of nano-island on time (b); time dependence of the mean composition of nano-islands (c).

other by the state diagram presented in Fig.1.

The changes in composition in an island can be obtained from the following relationship

$$C_R = C_{S0} + \frac{\Delta(t)}{U}, \qquad (18)$$

where $\Delta(t)$ is determined from Eqn. (14), whereas $U = R/R_c$.

The dependence of island compositions on their sizes are shown in Figures $3a,b,c$ (for composition of the particular island dependent on its growth time and dependence of the average composition of islands on time).

Let us do some estimates. As follows from Eqn. (18). $C_R = C_{S0} + \frac{2\sigma\omega C_{S0}}{k_B T R}$. Let us assume, σ to be $\sim 10^{-1} \div 10 J/m^2$, and $k\,T \sim 10^{-19} J$, we shall get for: $C_R \sim C_{S0}\left(1 + \frac{10^{-10}}{R}\right)$. For this reason, the main change in composition of islands takes place for $R \leq 10^{-8} m$. In this case, the change of composition will be within a few tens of atomic percents and this fact

is of particular importance for the measurement electrophysical properties.

2.2. EVOLUTION OF THE COMPOSITION OF A NANO-ISLANDS OF STOICHIO-METRIC COMPOSITION.

When islands are of strictly stoichiometric composition, as it is shown in Refs [1, 3–5, 8], the regions of phase coexistence and accordingly, the composition of island films are determined from the solution of the system of equations derived in [1, 5]. Detailed analysis of the set of equations is performed in Ref. [1, 3–5, 8] and some particular solutions for specific systems are given. Now we shall pass to the description of phase composition evolution at the nucleation stage.

3. Evolution of phase composition in new phase islands at the nucleation stage

3.1. EVOLUTION OF PHASE COMPOSITION IN SOLID SOLUTION ISLANDS.

At the nucleation stage there is no unambiguous relation between size and composition as compared to the Ostwald ripening stage. Note, that new phase nucleation processes in such systems were investigated by many authors [12, 14, 15, 20, 21]. It turned out that fluctuations of components involved in a nucleus happen independently of each other. The control of the composition is impossible at this stage.

3.2. EVOLUTION OF PHASE COMPOSITION IN ISLANDS OF STOICHIOMETRIC COMPOSITION.

When islands of new phase are stoichiometric compounds, the nucleation process can occur in several stages (see Ref. [20]). It is shown that the nucleation process is essentially dependent on whether or not chemical reactions in multicomponent adsorbed gas occur simultaneously with the formation of the end reaction product. We have shown in [20] that for specific conditions it is possible to observe self-oscillations of the number of nuclei and self-organization phenomena are possible.

4. Evolution of the composition–dependent properties of growing nanostructured films

It is well know that many properties of solids are essentially dependent on their chemical and phase composition. The properties can be the concentration of charge carriers in semiconductors, their mobility, conductivity of metals and alloys, absorption and electro-magnetic wave scattering, strength properties [2, 18], etc. Without claiming any consistent investigation of the properties, we show here merely the main principle for calculation of their evolution in the process of nanostructured film growth.

4.1. EVOLUTION OF PROPERTIES IN SOLID SOLUTION NANO-ISLANDS.

Let $F(C, t)$ be the function describing the relation between certain properties of the solid (in this case, an island) on composition. Let us find the distribution function of properties of different composition. To do this we shall pass from the function $\phi(1/\xi_R)$, expressing distribution function of island in terms of composition to the distribution function with respect to properties, $\Theta(F, t)$:

$$\Theta(F, t) \, d(F) = \varphi\left(\frac{1}{\xi_R}, t\right) d\left(\frac{1}{\xi_R}\right), \tag{19}$$

In the general case, the average value of properties in nano-islands changes in time as

$$\bar{F}(t) = \int_0^\infty F(t)\Theta(F(t), t) \, d(F) . \tag{20}$$

Note, that Eqns (4)–(9) describe not only the evolution of composition and, accordingly, properties in nano-island films but the meaning of these values in continuous films as well. For this purpose it is necessary to estimate the time of coalescence of islands into a solid layer using the equations given in Ref. [3] and the distribution functions of islands in terms of composition in time. In this case, it is necessary to take into account that Eqn. (4)–(9) and, accordingly, (13)–(18) are valid, strictly speaking, only for total coverage close to zero. In the case when the total coverage essentially exceeds zero, the collision integral is to be introduced into Eqns (4)–(9), [22]. However, as it follows from calculations [22], the function values are only slightly changed. Therefore, Eqns (13)–(18) provide an adequate approximation.

When some property of islands depends both on their size and composition, i.e. $\Theta = \Theta(C, R, t)$, it is necessary to pass from variable R in the terms for $\Theta(C, R, t)$ to variable C_{SR} by means of Eqn. (3). In a consequence, we again get the function $\Theta(C, t)$. In the case, when the property, in question, is only the distribution function, i.e. $\Theta(R)$,

conditions for its evolution can be expressed through the size distribution function $f(R, t)$ [1].

4.2. EVOLUTION OF PROPERTIES IN NANO-ISLANDS OF STOICHIOMETRIC COMPOSITION.

The nano-islands of stoichiometric composition are homogeneous. Therefore, the property function depends on the islands' size only. The properties of a nano-film are determined by the number of islands of one or another phase and by the size distribution of islands colliding with each other. The technique for the phase coexistence regions determination is described in detail in Ref. [1, 3–5]. The diagram of phase coexistence regions for a three-component two-phase system (where one of the components is simultaneously included in both phases) is constructed therein. If there is an unambiguous relation between the distribution function of property values F for s-phases, $\Theta^s(F, t)$, and size of particles, then the distribution function for $n < 3/p$ can be derived in a similar way as in (13):

$$\Theta^s(F, t) = \frac{N^s(t)}{R_c^s(t)} \frac{dR}{dF^s} P_p^s(U), \tag{21}$$

where $N^s(t)$, $P_p^s(U)$, $R_c^s(t)$ are the functions of the number of islands $N^s(t)$, probability density $P_p^s(U)$ and critical radius of islands of s-phase [1, 3–5]; dF^s/dR is the derivative of relation between the properties and radius of an island of s-phase; $p = 2, 3, 4$ in accordance with the island growth mechanism. Evolution of the average value of a property can be described by an equation similar to Eqns (15).

Consequently, all conclusions on influence of heating or cooling of a substrate and the power of component sources presented in Refs [1, 3–5] for the size distribution function $f^s(R, t)$ of islands of phase s over a substrate can be extended for the function $\Theta^s(F, t)$. When islands of different phases (chemical compounds) have regions of mutual solubility, i.e. they can be solid solutions, evolution of their properties can be described in a similar way as in section 2.

On the contrary, when properties depend on sizes of islands and the function $\Theta(F, t)$ is known, the relative number of s-phase can be expressed as $J^s = \frac{1}{V_m^s N_0} \frac{\kappa(\theta)4}{3}\pi \int_0^\infty f^s(R, t)R^3 dR$; (here V_m^s is the volume of molecules of phase s; N_0 is the number of adsorption sites on the substrate surface $N_0 \sim 1/a^2$; a is the lattice constant of a substrate) can be expressed as follows:

$$J^s = \frac{1}{V_m^s N_0}\kappa(\theta) \int_0^\infty \Theta^s(F, t)Z^3(F)d(F), \tag{22}$$

taking into account the condition $f^s(R, t)dR = \Theta^s(F, t)dF^s$. $R = Z(F)$ is the inverse function from the function $F = Z(R)$. Thus, the coexistence region of different compo-
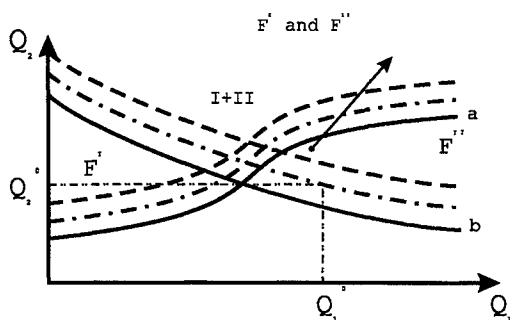
Figure 4: Values diagram of properties in the space of components Q_i and temperature (in projection on the Q_1, Q_2) plane. Boundaries of the values of properties in a system are indicated with the continuous line; displacement of the boundaries due to temperature change is indicated with dashed and chain-dotted line. Q_1^0 and Q_2^0 are certain initial quantities of components; I and II are the regions of different phases; F^I and F^II are the values of a property in islands of different chemical composition. The trajectory of a system in the presence of sources of components is indicated with arrow.

sitions can be determined by known values of F. The diagram of values of the property function for a two-phase tree-component system where one of the components is simultaneously included into both phases, is given in Fig.4. The diagram is calculated in accordance with the technique described in [1, 3–5]. Fig. 4 shows that in the case when islands form a continuous film, the structure with a number of properties determined only by its dependence on the size of islands exists in regions I and II. Within the region $I + II$, islands of mixed composition, i.e. with a different value of properties F^I and F^{II} will grow. In the process of growth, the islands give rise to non-homogeneous properties of thin films. The regions of F values can be varied in the presence of sources of components (or through cooling heating of the substrate). For this purpose, it is necessary to choose a certain value of the decay degree of sources, n, in accordance with the island growth mechanism [1, 3–5].

Now, we pass to the nucleation of new phase islands in multicomponent systems during chemical reactions. It is shown in Ref. [21] that for some specific relation between chemical components and islands of different phases complex non-linear interactions occur. This causes periodic change of the number of islands in space and time. As a result periodic changes in thin films properties are observed. The value will change periodically in space and time as well (see Fig. 5a and 5b).

In the case of the formation of islands of several phases (chemical compounds), the behavior of properties is more complicated. However, when self-organization or self-induced oscillations occur in a system, appropriate properties will also periodically change either in space, or in time.
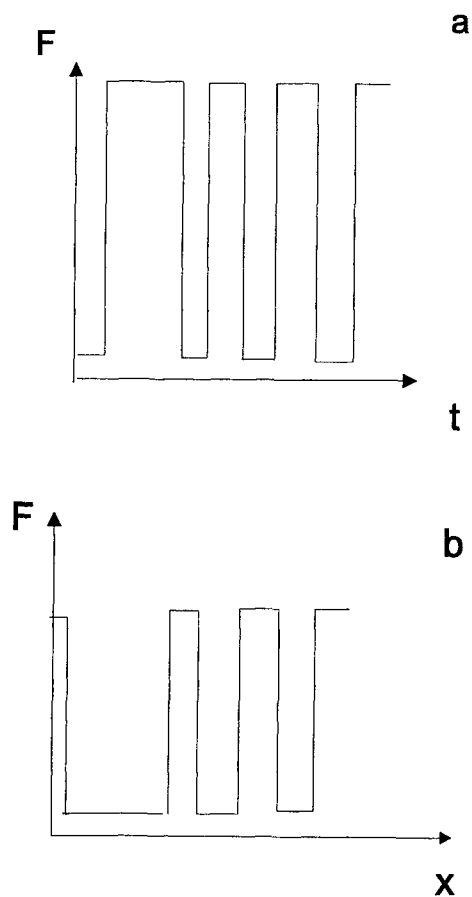
Figure 5: The scheme of the change in the values of properties for the case of new phase nucleation in multi-component systems in the presence of self-induced oscillations of composition — (a) or self-organization — (b).

5. Discussion

The relationship between size and composition of new phase nano-islands formed in the course of condensation of solid solution films is elucidated in the work. Analysis shows that the most favorable ways to control the composition of the nanostructured films are at the Ostwald ripening stage. At this stage there is an unambiguous relation between the size distribution function of islands and distribution function in their properties. This allows to pass from equations describing evolution of the size distribution function to equations of evolution of distribution function of properties in solid solution nano-islands. The analysis shows that considerable changes in composition occur for sizes less than $10^{-8}m$. In this case, their composition can be changed by tens of atomic percent that corresponds to $10^{12} \div 10^{13}m^{-3}$. For values of island radius $R > 10^{-8}m$ the composition of islands is independent of size actually regardless of substance.

It is shown that the coexistence diagrams can be constructed for stoichiometric compounds, and by means of change of atomic fluxes and controlling the degree of cooling or heating of a substrate one can pass from one property to another.

It is found that the control of properties at the nucleation stage is restricted. Only in the case with nucleation of stoichiometric compounds the structures with given properties may be obtained, provided that self-induced oscillations and self-organization take place. However, in this case it is necessary either to calculate beforehand the oscillation period of the composition [21], or to determine it experimentally and to stop the growth when the desired composition is achieved.

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