

Effect of diffusion on nucleation of two-dimensional nanoislands

M. V. Sorokin and A. E. Volkov*

Russian Research Centre Kurchatov Institute, Kurchatov Sq. 1, Moscow, 123182, Russia

(Received 5 July 2004; revised manuscript received 25 April 2005; published 30 November 2005)

Effect of diffusion on the steady-state nucleation of two-dimensional nanoislands is described analytically. New approach takes self-consistently into account coupling between the kinetics of adatoms near the island edge, their diffusion on the surface and annihilation at other islands. It was shown that due to this coupling the nucleation barrier can considerably differ from that predicted by the thermodynamics and can depend on the diffusion parameters of adatoms. This effect can be used for controlling of the kinetics of nanoisland nucleation.

DOI: [10.1103/PhysRevE.72.051603](https://doi.org/10.1103/PhysRevE.72.051603)

PACS number(s): 64.60.Qb, 82.60.Nh, 68.43.Hn, 68.43.Jk

I. INTRODUCTION

Advanced technologies of surface nanostructuring often have the physical origin in the decay kinetics of supersaturated surface solutions. Such solutions can be produced by deposition of monomers (adatoms) on the surface and/or specific heat treatments. Being the first order phase transformation, decomposition of a supersaturated surface solution results in creation of an ensemble of islands of either a chemical compound of deposited atoms with those of the substrate or pure islands built up by impurity atoms. The initial supersaturation forms the driving force for this decomposition. Tending to the equilibrium, such phase transformation passes through the well separated kinetic stages (nucleation [1–3], growth [4,5], Ostwald ripening [6–9]) reflecting considerable changes of the states of the solution and ensemble.

Analytical approaches describing decomposition of supersaturated solutions are based on the adiabatic principle [10,11]. This principle declares that diffusion currents of monomers in the vicinities of clusters adjust themselves to the actual cluster sizes. In this case the probabilities of absorption and desorption of atoms on the cluster interfaces depend only on these sizes and clustering is the Markovian stochastic process completely described by these probabilities [12,13]. For such process the temporal and spatial dependencies of the distribution function of the cluster sizes can be evaluated from the general Chapman-Kolmogorov equation.

Clustering starts from nucleation of small islands forming due to random walks and adhering of monomers. At small supersaturations initially unstable small clusters must overcome some critical size for the following stable growth. Being the smallest stable island, the critical nucleus can considerably exceed the interatomic distance when the supersaturation is low. This provides the continuous approximation of the sizes of islands close to the critical cluster when the Chapman-Kolmogorov equation can be sequentially reduced to the master equation and, further, to the Fokker-Planck one [12].

In the general case the absorption and desorption probabilities depend on both (i) the kinetics of adatoms in the vicinity of the island edge including their interaction with this edge, and (ii) the diffusion current of adatoms from the surface interior to the island so that the difference between the absorption and desorption rates of adatoms coincides with this current value at the island edge. The diffusion current results from spatial inhomogeneity of the adatom concentration induced by a forming island. Due to the adiabatic principle it can be determined from the solution of the steady-state diffusion problem in the vicinity of the selected island. The average concentration of monomers on the surface and their absorption by other islands form the boundary conditions for this problem. Thus, absorption and desorption mechanisms couple the kinetics of adatoms at the island edge with their diffusion on the surface depending on monomer annihilation at other islands. Because diffusion is not an equilibrium process this coupling can result in such forms of the parameters governing clusterization which can considerably differ [12–20] from those predicted by the thermodynamic approach assuming that forming clusters do not disturb the solution [3,21].

The following reasons motivate our choice of the steady-state nucleation mode [1–5,12,20–29] in the two-dimensional (2D) system for demonstration of the effect of coupling of the absorption and desorption probabilities with adatom diffusion near the island edge. First, in contrast to the three-dimensional (3D) case no finite solutions of the steady-state 2D diffusion problem exists in the vicinity of a selected island without taking into account the screening effect [4,5,22,23]. This screening results from absorption of monomers by all other islands which forms the boundary conditions for the diffusion problem. Therefore, in 2D systems the coupling between diffusion of monomers to the fixed cluster and the parameters of the island ensemble provides analytical realization of the fundamental adiabatic principle. Second, due to self-adjusting, the steady-state can be described by a small number of parameters that facilitates formulation of the model, its examination and comparison with results of experiments and computer simulations. Third, in contrast to the growth or Ostwald ripening stages, it is assumed traditionally that nucleating islands do not disturb the solution providing the thermodynamic forms of the parameters governing the nucleation. Because small modifications of the

*Electronic address: volkov@dni.polyn.kiae.su

forms of the absorption and desorption probabilities at the nucleation stage affect crucially [20] the evolution of the cluster ensemble even at the late kinetic stages the fundamental effect which can change these forms in comparison to those predicted by the thermodynamic is interesting from the fundamental point of view as well as a tool for a desirable controlling of nanoclustering.

II. GOVERNING EQUATIONS

The ensemble of 2D islands is assumed as that of monolayer disks having radiuses $R=(n\omega/\pi c_{is})^{1/2}$ determined by the numbers n of constituent impurity atoms. Here ω is the island area per atom and c_{is} is the atomic impurity concentration in islands. $c_{is} < 1$ is assumed when impurity adatoms tend to form chemical compounds with host atoms.

In order to elucidate the effect of monomer diffusion on the cluster kinetics we assume in this paper (a) homogeneous nucleation of 2D islands during decomposition of one-component supersaturated surface solution of impurity adatoms; (b) negligible amount of adatoms accumulated in islands in comparison to that contained in the surface solution and negligible rate of this accumulation. This suggestion provides the constant mean adatom concentration of the surface solution, the constant critical size and the steady-state nucleation (for details see Appendix); (c) low supersaturation resulting in the critical size which considerably exceeds the interatomic distance. This provides the continuous approximation of the island sizes in the vicinity of the critical cluster; (d) no lattice misfits between islands and the substrate. Thus, no elastic effects, which are often important, are taken into account. We suggest also that the surface fraction of nanoislands is negligible and distances between islands are much larger than their average radius. Nucleation in such dilute ensemble of islands can be described in terms of the ‘‘one cluster’’ distribution function $f_{1n}(n, t)$ so that $f_{1n}(n, t)dn = f_{1R}(R, t)dR$ is the surface density of islands with sizes $n \dots n+dn$ (radiuses $R \dots R+dR$) at time t [12]. This distribution function is normalized to the surface density of islands ρ so that $\int f_{1n}(n, t)dn = \int f_{1R}(R, t)dR = \rho = N/S$, where N is the total number of islands and S is the surface area.

Evolution of this distribution function in the vicinity of the critical size is described by the Fokker-Planck equation (FPE) [12,13],

$$\partial f_{1n}/\partial t = -\partial I/\partial n. \quad (1)$$

We choose the Ito form for FPE when the island current along the ‘‘size’’ axis n is defined as $I(n; t) = Af_{1n} - \partial(Bf_{1n})/\partial n$ [12–14]. The kinetic coefficients A and B are, respectively, the ‘‘hydrodynamic’’ rate and the ‘‘diffusion’’ coefficient of islands in the size space. These coefficients completely determine the evolution of the island ensemble. They depend on the probabilities of absorption P and desorption Q of an adatom at the island edge per unit time,

$$A(n) = P(n) - Q(n), \quad B(n) = [P(n) + Q(n)]/2. \quad (2)$$

In particular, A and B determine the form of the steady state island current into the growth region of the size axis (the steady-state nucleation rate) [1–3,12],

$$I_s = f_0(n_{\min})B(n_{\min})\sqrt{\frac{1}{2\pi}\left|\frac{d^2\varphi}{dn^2}\right|_{n=n_c}}\exp(-\varphi_c). \quad (3)$$

Here f_0 is the distribution function, which maintains the detailed balance in the island ensemble at the size axis $I(f_0) = Af_0 - \partial(Bf_0)/\partial n = 0$. n_c is the size of the critical island which is in equilibrium with the supersaturated solution, $\varphi_c = \varphi(n_c)$ is the nucleation (critical) barrier and the function $\varphi(n)$ is determined by the kinetics coefficients,

$$\varphi(n) = -\int_{n_{\min}}^n \frac{A(n')}{B(n')}dn'. \quad (4)$$

It should be noted that the forms of the kinetic coefficients and, respectively, the forms of $\varphi(n)$ and the nucleation barrier do not depend on the chosen Ito form of FPE [12–14].

Absorption and desorption rates: The probability Q of desorption of an adatom from an island per unit time (evaporation rate) depends on (1) the number of atoms at the edge layer which has the thickness l close to the diffusion jump length λ of adatoms, (2) Gibbs barriers for adatom evaporation, and (3) the rate of adatom diffusion outside the island (see Fig. 1 in Ref. [27]),

$$Q(n) = \frac{2\pi R l \xi}{\omega} c_{is} \exp\left(-\frac{\Psi + \delta F_s}{T}\right) \frac{\nu}{4} \exp\left(-\frac{\Phi_m + \varepsilon}{T}\right). \quad (5)$$

Here $\xi \ll 1$ takes into account the edge roughness; ν is the attempt frequency of atomic jumps, $1/4$ takes into account 2D geometry; Ψ is the Gibbs energy of dissolution of a monomer from a flat edge. $F_s(R) = 2\pi R \gamma = 2\gamma(\pi\omega n)^{1/2}$ is the Gibbs energy of the curved island edge and $\delta F_s(R) = -\partial F_s/\partial n = -\gamma\omega/R$ is its change due to evaporation of an adatom. The edge tension γ is assumed as constant. Φ_m is the barrier for diffusion of adatoms on the surface, and T is the temperature measured in the energy units. An additional barrier ε is taken into account in the edge vicinity [25,30–32]. This barrier can originate from possible distortion of diffusion energetic near the edge, or due to edge roughness [33], or peculiarities of adatom diffusion related to collective effects near the island edge [34]. Investigation of the specific microscopic mechanisms resulting in this barrier is beyond the scope of this paper.

The equilibrium atomic concentration of monomers at the curved island edge $C_{\text{eq}}(R)$ is evaluated from the equality of the chemical potentials of adatoms at the edge and on the surface [35]:

$$C_{\text{eq}}(R) = c_{is} \exp\left(-\frac{\Psi + \delta F_s}{T}\right) = C_{\text{eq}}^0 \exp\left(\frac{\gamma\omega}{RT}\right). \quad (6)$$

Here $C_{\text{eq}}^0 = c_{is} \exp(-\Psi/T)$ is the equilibrium concentration of monomers near the flat edge. Taking into account Eq. (6) and the usual form of the diffusion coefficient of adatoms $D = (\lambda^2\nu/4)\exp(-\Phi_m/T)$ we can finally rewrite the desorption rate (5) as follows:

$$Q(n) = \frac{2\pi R l \xi}{\omega \lambda^2} D \exp(-\varepsilon/T) C_{\text{eq}}(R). \quad (7)$$

The absorption probability (absorption rate) $P(n)$ depends on the number of adatoms in the outside layer nearest to the island edge and the barrier Φ_m for diffusion jumps of adatoms between this layer and the edge:

$$P(n) = \frac{2\pi R l \xi}{\omega} C(\vec{r}_s) \frac{\nu}{4} \exp\left(-\frac{\Phi_m + \varepsilon}{T}\right) \\ = \frac{2\pi R l \xi}{\omega \lambda^2} D \exp(-\varepsilon/T) C(\vec{r}_s). \quad (8)$$

Here $C(\vec{r})$ is the local atomic concentration of adatoms on the surface, points \vec{r}_s belong to the island edge and $C(\vec{r}_s)$ is the concentration in the outside layer nearest to the edge.

In Eqs. (7) and (8) we assume $\lambda \ll R$ according to the continuous approximation about the island sizes, and neglect a difference between the chemical potentials of substrate atoms on the surface and in islands when $c_{is} < 1$.

III. DIFFUSION IN THE ISLAND VICINITY

Due to the adiabatic principle [10,11] diffusion currents of monomers in the vicinities of clusters adjust themselves to the actual cluster sizes and positions [27]. In this case the adatom concentration $C(\vec{r})$ between islands, which number, positions and sizes are considered as fixed, is described by the steady-state diffusion equation,

$$\nabla^2 C(\vec{r}|\Xi) = 0. \quad (9)$$

Here $\Xi = (\vec{r}_1, R_1; \vec{r}_2, R_2; \dots; \vec{r}_N, R_N)$ indicates positions \vec{r}_i and radii R_i of all N islands constituting the ensemble. The boundary conditions for Eq. (10) are formed by (i) absorption and desorption of monomers on the edges of all islands and (ii) coincidence of the adatom concentration far from the island edges with the mean concentration of adatoms on the surface C_0 :

$$\oint_{l_k} (\vec{j}(\vec{r}_s^k|\Xi), \vec{e}_k) dl_k = Q(n_k) - P(n_k) \\ = \frac{2\pi R_k l \xi}{\omega \lambda^2} D \exp\left(-\frac{\varepsilon}{T}\right) [C_{\text{eq}}(R_k) - C(\vec{r}_s^k|\Xi)]$$

$$C(\vec{r}|\Xi) = C_0 \quad (|\vec{r} - \vec{r}_k| \gg R_k).$$

Here $\vec{j} = -\omega^{-1} D \nabla C$ is the surface diffusion current of adatoms, \vec{e}_k is the unit normal vector at edge points \vec{r}_s^k of k th island and integration is performed over these points.

In order to determine the kinetic coefficients (2) describing evolution of the ‘‘one cluster’’ distribution function $f_{1n}(n, t)$ we should reduce the problem (9) by averaging over parameters of all islands excepting the selected one. Fixing the parameters of the island $k=m$ as $\vec{r}_m=0$ and $R_m=R$ we can modify the particular form of the diffusion problem (9) transferring the boundary conditions at the edges of residual islands into the diffusion equation,

$$D \nabla^2 C(\vec{r}|\Xi) + \omega \sum_{k=1, k \neq m}^{N-1} (\vec{j}(\vec{r}|\Xi), \vec{e}_k) \delta(l_k) = 0, \quad (10)$$

$$\omega^{-1} D \oint_{l_m} (\nabla C(\vec{r}|\Xi), \vec{e}_m) dl_m = P(n_m) - Q(n_m), \quad (11)$$

$$C(\vec{r}|\Xi) = C_0 \quad \text{when } |\vec{r} - \vec{r}_k| \gg R_k.$$

Here $\delta(l_k)$ is the edge delta function depending on edge coordinates \vec{r}_s^k of k th island so that $\int_S \chi(\vec{r}) \delta(l_k) d\vec{r} = \oint_{l_k} \chi(\vec{r}_s^k) dl_k$ for a surface function $\chi(\vec{r})$.

For necessary averaging m -cluster distribution functions are introduced [36],

$$f_m(\vec{r}_{i_1}, R_{i_1}; \vec{r}_{i_2}, R_{i_2}; \dots; \vec{r}_{i_m}, R_{i_m}) = \int f_N(\Xi) d\Xi_{(i_1 \dots i_m)},$$

$$d\Xi_{(i_1 \dots i_m)} = \prod_{\substack{n=1 \\ n \neq i_1 \dots i_m}}^N dR_n d\vec{r}_n$$

Here $f_N(\Xi)$ is the surface distribution function of all N islands. It is normalized to the surface density of islands, $\int f_N(\Xi) d\Xi = \rho$. The conditional probabilities to find an island $m+1$ with parameters (\vec{r}_{m+1}, R_{m+1}) , when parameters of m other islands are fixed, are defined as following:

$$p_{m+1}(\vec{r}_{m+1}, R_{m+1} | \vec{r}_{i_1}, R_{i_1}; \vec{r}_{i_2}, R_{i_2}; \dots; \vec{r}_{i_m}, R_{i_m}) \\ = \frac{f_{m+1}(\vec{r}_{i_1}, R_{i_1}; \vec{r}_{i_2}, R_{i_2}; \dots; \vec{r}_{i_m}, R_{i_m}; \vec{r}_{m+1}, R_{m+1})}{f_m(\vec{r}_{i_1}, R_{i_1}; \vec{r}_{i_2}, R_{i_2}; \dots; \vec{r}_{i_m}, R_{i_m})}.$$

And finally, the m th concentration moment C_m depending on the parameters of $m < N$ fixed islands is introduced by averaging the concentration over parameters of residual $(N-m)$ islands,

$$C_m(\vec{r} | \vec{r}_{i_1}, R_{i_1}; \vec{r}_{i_2}, R_{i_2}; \dots; \vec{r}_{i_m}, R_{i_m}) \\ = \frac{\int C(\vec{r}|\Xi) f_N(\Xi) d\Xi_{(i_1 \dots i_m)}}{f_m(\vec{r}_{i_1}, R_{i_1}; \vec{r}_{i_2}, R_{i_2}; \dots; \vec{r}_{i_m}, R_{i_m})}.$$

The zero-order concentration moment coincides with C_0 .

For the dilute ensemble, when the mean distance between islands are much larger than the mean island size, averaging of Eq. (10) and boundary conditions (11) over the parameters of all islands excepting the selected one gives (see also Ref. [11]),

$$\nabla^2 C_1(\vec{r}|0, R) + \frac{2\pi l \xi N}{\lambda^2} \exp\left(-\frac{\varepsilon}{T}\right) \int R' p_2(\vec{r}, R' | 0, R) \\ \times [C_2(\vec{r}|0, R; \vec{r}, R') - C_{\text{eq}}(R')] dR' = 0, \\ dC_1/dr|_{r=R} = l \xi \lambda^{-2} \exp\left(-\frac{\varepsilon}{T}\right) [C(\vec{r}_s|0, R) - C_{\text{eq}}(R)], \\ C_1|_{r \rightarrow \infty} = C_0, \quad (12)$$

Here \vec{r}_s belongs to the edge of the fixed island. The second term in Eq. (12) is the loss intensity, which describes loss of monomers at residual islands of the ensemble. The index 2

indicates that during averaging already positions of two islands are fixed, the selected one $(0, R)$ in the origin of the coordinate system and the “probe” one having parameters (\vec{r}, R') . The coupling between the absorption and desorption rates and the diffusion current of adatoms at the edge of the probe island is taken into account in the second term of Eq. (12).

Generally, the second concentration moment $C_2(\vec{r}|0, R; \vec{r}, R')$ should be evaluated from the third concentration moment through the equations similar to Eq. (12) and so on. Thus, the diffusion equations for the concentration moments form the infinite coupled hierarchy originating from coupled hierarchy of the partial distribution functions [36]. Usually, this infinite hierarchy is truncated by the simple first-order additive or multiplicative approximations when the second concentration moment is replaced by the sum or product of the first moments [11]. In order to provide a self-consistent description of the screening effect in Eq. (12), a new approximation of the second concentration moment is used in this paper,

$$C_2(\vec{r}|0, R; \vec{r}, R') = C_1(\vec{r}|0, R) - \alpha(R') [C_1(\vec{r}|0, R) - C_{\text{eq}}(R')]. \quad (13)$$

Here $\alpha(R')$ depends on the radius of the probe island and will be determined later.

In the dilute ensemble the conditional distribution function p_2 can be approximated by the “one-cluster” distribution function,

$$p_2(\vec{r}, R'|0, R) = f_1(\vec{r}, R')/\rho \text{ or} \\ f_2(0, R; \vec{r}, R') = f_1(0, R)f_1(\vec{r}, R')/\rho.$$

Taking also into account spatial homogeneity of the system $[f_1(\vec{r}, R) = S^{-1}f_{1R}(R)]$ we reduce Eq. (12) to the following:

$$D(\nabla^2 - k^2)C_1 + G_{\text{eq}} = 0. \quad (14)$$

Here k is the sink strength

$$k^2 = l_s^{-2} = \frac{2\pi l \xi}{\lambda^2} \exp(-\varepsilon/T) \int_0^\infty R' [1 - \alpha(R')] f_{1R}(R') dR' \quad (15)$$

and l_s is the screening length [37]. The sink term in Eq. (14) provides the finite solution of the steady-state 2D diffusion problem in the vicinity of the selected island $(0, R)$. The last term in Eq. (14) is the averaged thermal adatom emission from islands,

$$G_{\text{eq}} = \frac{2\pi l \xi}{\lambda^2} \exp(-\varepsilon/T) \int_0^\infty R' [1 - \alpha(R')] C_{\text{eq}}(R') f_{1R}(R') dR'.$$

Averaging of Eq. (14) over the parameters of the selected island gives the relation between the values of the mean adatom concentration and the thermal emission, $Dk^2 C_0 = G_{\text{eq}}$.

Solving Eq. (14) we obtain the concentration of adatoms at the edge of the fixed island,

$$C_1(R) = C_0 + \frac{u}{1+u} [C_{\text{eq}}(R) - C_0], \quad (16)$$

$$u(R) = \frac{l \xi \exp(-\varepsilon/T) K_0(kR)}{\lambda^2 k K_1(kR)}. \quad (17)$$

Here K_0, K_1 are the modified Bessel functions of the zeroth and first order, respectively.

Averaging Eq. (13) over the parameters of the selected island we obtain the value of the first moment at the edge of the probe island,

$$C_1(R') = C_0 - \alpha(R') [C_0 - C_{\text{eq}}(R')]. \quad (18)$$

Taking into account the equivalence of all islands of the ensemble and comparing Eqs. (16) and (18) we determine the relationship between the functions $\alpha(R)$ and $u(R)$,

$$\alpha(R) = \frac{u(\alpha, R)}{1 + u(\alpha, R)}. \quad (19)$$

Equation (19) self-consistently closes our hypothesis (13) about truncating of the hierarchy of the concentration moments.

The parameter $u(R)$ [Eq. (17)] couples the effective length of diffusion jumps of adatoms in the vicinity of the island edge $\lambda^* = \lambda \exp(\varepsilon/T)/\xi$ with the effective length $l_{\text{eff}}(R) = l_s K_0(R/l_s)/K_1(R/l_s)$. $l_{\text{eff}}(R)$ can be treated as the dimension of the affected zone of the island of size R on adatom diffusion. Two limit cases for the forms of $l_{\text{eff}}(R)$ and parameter $u(R)$ can be extracted (below $\lambda = l$ for simplicity).

(i) At weak screening, when $R/l_s \ll 1$, the effective length l_{eff} is reduced to $l_{\text{eff}}(R) \approx R \ln(R/l_s)$. Neglecting a weak logarithmic dependence, we obtain that in this case the effective length coincides with the island size $l_{\text{eff}}(R) \approx R$ resulting in the following form of the parameter $u(R)$:

$$u(R) \approx R/\lambda^*. \quad (20)$$

(ii) At strong screening ($R/l_s \gg 1$) $l_{\text{eff}}(R)$ coincides with the screening length $[l_{\text{eff}}(R) \approx l_s]$. The parameter $u(R)$ does not depend on the island size in this case,

$$u(R) \approx l_s/\lambda^* = u_s. \quad (21)$$

Comparing λ^* with $l_{\text{eff}}(R)$ we can also extract two limit cases for the radial dependence of the adatom concentration (16) in the vicinity of the selected island.

(1) The concentration radial “step” realizes in the vicinity of the fixed island when $l_{\text{eff}}(R) \ll \lambda^*$ and $u(R) \ll 1$ [see Fig. 1(a)],

$$C^{(r)}(R) \approx C_0. \quad (22)$$

Such island does not disturb the solution and the microscopic kinetics of monomers in the vicinity of the island edge is determined by their reaction with the edge (reaction controlled case, rcc). Diffusion affects negligibly the island energetic and nucleation of such islands can be described in the framework of the thermodynamic approach [35]. Well-known form of the sink strengths can be obtained in this case, $k^2 = 2\pi l \xi \exp(-\varepsilon/T) \lambda^{-2} \langle R \rangle (N/S)$, where $\langle R \rangle$ is the mean radius of islands.

(2) A large affected zone $[l_{\text{eff}}(R) \gg \lambda^*, u(R) \gg 1]$ gives gradual modification of the monomer concentration in the vicinity of the island [diffusion “clouds,” see Fig. 1(b)],

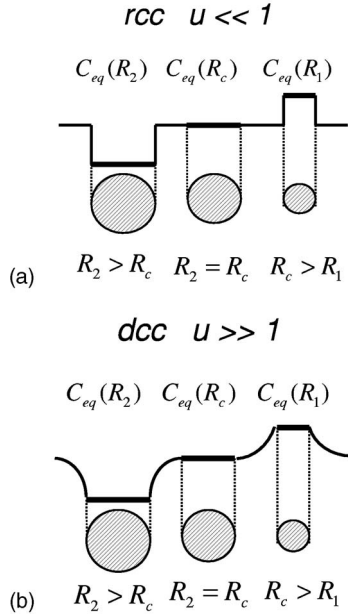


FIG. 1. Spatial profiles of the adatom concentration in the island vicinity in rcc (a) and dcc (b) cases. The average concentration C_0 coincides with the equilibrium one at the edge of the critical island $C_0 = C_{eq}(R_c)$. Islands larger than the critical one tend to growth [$C_0 > C_{eq}(R_2)$]. Smaller islands ($R < R_c$) tend to be dissolved [$C_0 < C_{eq}(R_1)$].

$$C^{(d)}(R) \approx C_{eq}(R) \neq C_0. \quad (23)$$

Perturbation of the adatom concentration by such island results in diffusion currents affecting absorption of adatoms by the island (diffusion controlled case, dcc). Because diffusion is not an equilibrium process the kinetics of such islands cannot be described under thermodynamic assumptions about their energy.

IV. THE CRITICAL SIZE AND NUCLEATION BARRIER

In order to obtain the kinetic coefficients $A(n)$ and $B(n)$ we substitute Eq. (16) into Eqs. (2), (7), and (8) ($\lambda = l$),

$$A = \frac{2\pi R \xi}{\omega \lambda} D \exp\left(-\frac{\varepsilon}{T}\right) \frac{C_0 - C_{eq}(R)}{1 + u},$$

$$B = \frac{\pi R \xi}{\omega \lambda} D \exp\left(-\frac{\varepsilon}{T}\right) \frac{C_0 + (1 + 2u)C_{eq}(R)}{1 + u}.$$

Being in equilibrium with the solution the critical island does not disturb it, $C_{eq}(R_c) = C_0$. This leads to zero “hydrodynamic” rate at the critical size $A(n_c) = 0$ and gives the radius of the critical cluster, $R_c = \gamma \omega [\Psi - T \ln(c_{is}/C_0)]^{-1}$. In the important vicinity of the critical size, where $|C_0 - C_{eq}(R)| \ll C_0$, the ratio A/B is reduced to

$$\frac{A}{B} \approx \frac{C_0 - C_{eq}(R)}{C_0} \frac{1}{1 + u(R)}. \quad (24)$$

Equation (24) results in the following form of the nucleation barrier [see Eq. (4), $n_{\min} = 0$]:

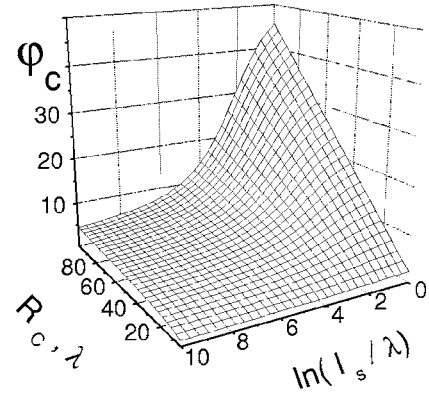


FIG. 2. The dependence of the nucleation barrier φ_c on the critical radius R_c and screening length l_s . Calculations were made for the system parameters providing $2\pi\gamma/T = 1$ and $\exp(-\varepsilon/T) = 0.1$.

$$\varphi_c = -\frac{2\pi\gamma}{T} \int_0^{R_c} \left(\frac{R}{R_c} - 1\right) \frac{dR}{1 + u(R)}. \quad (25)$$

This form (25) of the nucleation barrier considerably differs (see Fig. 2) from $\varphi_c^T = \pi\gamma R_c/T$ predicted by the thermodynamic approach from the minimum work $\Delta R_{\min}(n)$ of island creation in 2D supersaturated solutions [35] [$\Delta R_{\min}(n) = -n\Psi + Tn \ln(c_{is}/C_0) + 2\pi\gamma(n\omega/\pi c_{is})^{1/2}$, $\partial\Delta R_{\min}/\partial n|_{n_c} = 0$, $\Delta R_{\min}(n_c) = \varphi_c^T \cdot T$].

V. EFFECT OF DIFFUSION ON THE NUCLEATION BARRIER

Taking into account that Eq. (25) is integrated in the interval $(0, R_c)$ we can conclude that the thermodynamic form of the nucleation barrier cannot be applied when $u(R_c) = l_{\text{eff}}(R_c)/\lambda^* \gg 1$ because a part of the undercritical island sizes in Eq. (25) belongs to the dcc domain. Otherwise, when $u(R_c) = l_{\text{eff}}(R_c)/\lambda^* \ll 1$ the thermodynamic forms can be applied because all undercritical islands belong to the rcc domain.

The parameter $u(R_c) = l_{\text{eff}}(R_c)/\lambda^*$ couples three length parameters, (i) the critical size R_c characterizing the thermodynamic stability of the supersaturated solution, (ii) the screening length l_s which has the kinetic nature originated from the absorption abilities of the all islands of the ensemble, and (iii) the effective diffusion length $\lambda^* = \lambda \exp(\varepsilon/T)/\xi$. It is important that the parameters R_c and l_s cannot be reduced to those of some selected group of islands. They reflect the general thermal and kinetic properties of the total system consisting from the supersaturated solution of adatoms and all islands of the ensemble. The third parameter λ^* also has the general meaning describing conditions of adatom absorption at the island edges for the particular system.

At weak screening and/or largest supersaturations, when $R_c/l_s \ll 1$, the parameter $u(R_c)$ is reduced to [see Eq. (20)],

$$u(R_c) = R_c/l_s^* = u_c. \quad (26)$$

At strong screening and/or smallest supersaturations, when $R_c/l_s \gg 1$, the parameter $u(R_c)$ is reduced to $u_s = l_s/\lambda^*$ [see

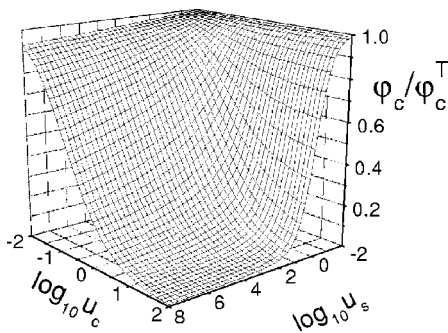


FIG. 3. Deviation of the nucleation barrier φ_c from its thermodynamic limit φ_c^T as the function of the dimensionless parameters $u_c = R_c/l_s^*$ and $u_s = l_s/\lambda^*$.

Eq. (21)]. The nucleation barrier (25) can be expressed as the function of these dimensionless parameters u_c and u_s ,

$$\varphi_c = \varphi_c^T \frac{2}{u_c} \int_0^{u_c} \frac{(1-x/u_c)dx}{1+u_s K_0(x/u_s)/K_1(x/u_s)}. \quad (27)$$

Equation (27) obviously demonstrates considerable deviations of the barrier φ_c from its thermodynamic limit φ_c^T . It is shown in Fig. 3 that the ratio φ_c/φ_c^T variates up to the order of magnitude in the parameter plane (u_c, u_s) . This plane can be divided into three domains corresponding different behaviors of the nucleation barrier (see Fig. 4).

In the first domain located in the close vicinities of axes $0u_c$ and $0u_s$, the values of the parameters u_c and u_s are small ($u_c \ll 1, u_s \ll 1$). In this region minor disturbance of the solution by nucleating islands leads to negligible deviations of the nucleation barrier φ_c from its thermal limit φ_c^T . The origins of the cases when subcritical islands does not disturb the solution are different for the different regions of the first domain. In the area along the axis $0u_s$, where $u_c \ll 1$, small critical nucleus or high barrier ε provide the thermal barrier φ_c^T . In the region along the axis $0u_c$, where $u_s \ll 1$, extremely strong screening neutralizes the abilities of islands to disturb

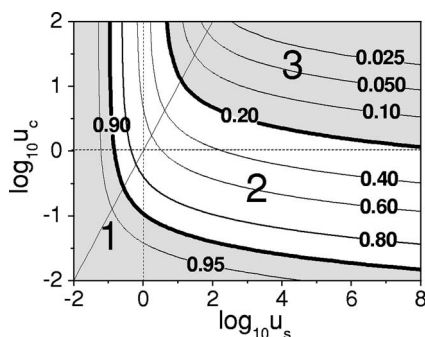


FIG. 4. The counter plot illustrates deviation of the ratio φ_c/φ_c^T from the unity in the plane (u_c, u_s) . The straight solid line corresponds to $u_c = u_s$. The dashed lines indicate $u_c = 1$ and $u_s = 1$. In the first domain (1) the thermodynamic form of the nucleation barrier is expected. In the second (2) and third domains (3) considerable deviation of the nucleation barrier from its thermal limit occurs. The dependence of the nucleation barrier on the screening length appears in the third domain (see the text for details).

the solution. It is interesting that in the second case the non-equilibrium adatom diffusion provides the thermodynamic form of the nucleation barrier. However, it is hard to imagine a system having the parameter values corresponding to the first domain. Indeed, only adatom absorption by a dense ensemble of large islands can provide necessary strong screening. Similar ensembles appear at the late kinetic stages at high supersaturations or on surfaces under continuous intensive generation of monomers. The thermodynamic approach cannot be applied to such systems. Also, the critical nuclei with sizes closed to the interatomic distance occurs at high supersaturations when application of the approach based on the nucleation barrier and steady-state nucleation is questionable. Therefore, we may conclude that the thermodynamic form of the nucleation barrier may be valid only in a very restricted domain of the system parameters where ε is extremely high ($\varepsilon/T \gg 1$).

In the second domain subcritical islands disturb the solution. As a result the ratio φ_c/φ_c^T decreases considerably demonstrating pronounced dependence on the screening length and critical radius. In contrast to the thermodynamic, the parameters of adatom diffusion and island ensemble appear in the nucleation barrier via its dependence on the screening length.

In the third domain the ratio φ_c/φ_c^T is of the order of magnitude smaller than the unity. Considerable perturbations of the solution by subcritical islands contained in this domain provide large deviations of the nucleation barrier from its thermal limit. Two limit cases can be separated in the third domain. At weak screening and/or largest supersaturations ($R_c/l_s \ll 1$) the dimensions of the regions where the subcritical nuclei affect adatom diffusion are determined by the sizes of these nuclei. In this case ($u_c \ll u_s; u_c \gg 1, u_s \gg 1$) the nucleation barrier depends only on the critical size and the screening length does not appear in its form, $\varphi_c \approx 2\varphi_c^T u_c^{-1} \ln u_c$. At strong screening and/or smallest supersaturations ($R_c/l_s \gg 1$) the dimension of the region where the subcritical nuclei affect adatom diffusion is determined by the screening length. In this case ($u_c \gg u_s; u_c \gg 1, u_s \gg 1$) the nucleation barrier is reduced to the following: $\varphi_c \approx \varphi_c^T u_s^{-1} (1 + 2u_s u_c^{-1} \ln u_s)$. The dependence of the barrier on the screening length is pronounced in the last form.

VI. DISCUSSION

To be supplied with adatoms a forming island stimulates diffusion currents in its vicinity. Absorption and desorption rates of adatoms at the island edge are coupled with these currents. Such coupling occurs even in the case when no effect of other islands is taken into account. Tending to restore the equilibrium, diffusion, on the other hand, is not an equilibrium process. Diffusion clouds of adatoms modify the state of the supersaturated surface solution in the vicinity of the island edge changing the energetic of island formation. Due to the exponential dependence even small modifications of this energetic affect crucially the island kinetics. We demonstrate that modifications of the nucleation barrier are not small. It can be changed up to the order of magnitude when adatom diffusion in the island vicinity is taken into account.

We also demonstrate the fundamental coupling of the nucleation barrier with the parameters of the appearing island ensemble. Absorption of monomers by all islands forms the boundary condition for the general diffusion problem. This results in the screening effect. It manifests the decrease of the dimension of the region where a fixed island affects considerably diffusion of adatoms. This screening modifies the absorption and desorption rates of adatoms at the island edges. Finally, this results in appearance of the screening length in the form of the nucleation barrier.

Screening length depends on the diffusion coefficient of adatoms, the surface density of islands and the distribution of their sizes. Therefore, even at the early kinetic stage the system state cannot be reduced only to that of the supersaturated solution. Information about the island ensemble and diffusion parameters should be also taken into account. For the given supersaturation we can have a great variety of the initial system states depending on the specific parameters of the initial island ensemble instead of only the one state assumed by the thermodynamic. As a result, the nucleation barrier generally depends on these parameters originated from a history of specific treatments applied to the surface before (e.g., transient heating treatments). This dependence forms the basis for governing of the nucleation kinetics.

We conclude that mechanisms of fluctuation rise cannot be neglected in real systems. Moreover, knowledge about these mechanisms can give us additional tools for controlling of clustering. No such mechanisms are taken into account by the classical nucleation approach neglecting of disturbance of the supersaturated solution by forming nuclei.

ACKNOWLEDGMENTS

This research was supported by Grant No. 05-02-16994 from Russian Foundation for Basic Researches and Grant No. 16 (2005) for Junior Scientists from RRC KI. Support from Russian Scientific Schools Program (Grant No. 1795.2003.2) is also gratefully acknowledged.

APPENDIX: DURATION OF THE STEADY-STATE NUCLEATION

Starting from the average formation time t_c of the critical size n_c ,

$$t_c = \left(\frac{2}{\pi} \left| \frac{d^2\varphi}{dn^2} \right|_{n=n_c} \right)^{-1/2} \frac{\exp(\varphi_c)}{\omega f_0(n_{\min}) B(n_{\min})} = (2\omega I_s)^{-1} \quad (\text{A1})$$

the quasi-steady-state distribution of islands appears in the vicinity of the critical nuclei [12,38,39]. This distribution provides the steady-state current of islands into the growth region of the size axis forming an increasing number of growing islands. Due to absorption of adatoms by these islands the concentration of adatoms starts gradually decrease. Finally, such decrease results in the increase of the critical size suppressing nucleation of new islands. Thus, the steady-state conception is valid when the concentration decrease resulted from absorption of monomers by forming islands can be neglected,

$$|C_0(t_n) - C_0(t_c)| \approx |(dC_0/dt)_{t=t_c}(t_n - t_c)| \ll C_0(t_c). \quad (\text{A2})$$

Here t_n restricts the time scale of the steady-state nucleation.

The balance of monomers in the system is determined by their annihilation at islands,

$$\frac{1}{\omega} \frac{dC_0}{dt} = - \frac{d}{dt} \int_{n_{\min}}^{\infty} n f_{1n}(n, t) dn = - \int_{n_{\min}}^{\infty} n \frac{\partial f_{1n}(n, t)}{\partial t} dn. \quad (\text{A3})$$

Assuming that the island distribution in the growth region develops due to movement of the front $n_f(t)$ of the steady-state distribution $f_{1n}(n, t) = f_s \{1 - \Theta[n - n_f(t)]\}$ [27], where $\Theta(n)$ is the step function and $f_s(n)$ is the steady-state solution of FPE (1), we obtain from Eq. (A3):

$$\omega^{-1} dC_0/dt = -I_s n_f(t). \quad (\text{A4})$$

In Eq. (A4) $I_s = f_s(n_f) dn_f/dt = f_s(n_f) A(n_f)$ due to the negligible stochastic term in the steady-state island current at the steplike front of the distribution $[A f_s \gg \partial(B f_s)/\partial n$ for $n_f > n_c$ [21]].

Substituting Eq. (A1) into Eq. (A4) and taking into account Eq. (A2) we estimate the duration of the steady-state nucleation:

$$t_n - t_c \ll 2t_c C_0/n_f. \quad (\text{A5})$$

According to Eq. (A5) low supersaturations providing a large lag time t_c are favorable for appearance of the pronounced stage of the steady-state nucleation. Continuous generation of monomers at the surface (e.g., due to adatom deposition) also can considerably elongate this stage. This effect will be described in a separate paper.

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