

Kinetics of the initial stage of coherent island formation in heteroepitaxial systems

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The stress-driven formation of coherent islands in heteroepitaxial systems is studied within the frame of the kinetic theory of nucleation under dynamical conditions. The kinetic model for a description of the time evolution of the island size distribution and wetting layer thickness in Stranski-Krastanow growth mode is developed. The time scale hierarchy of the nucleation stage, the size relaxation stage, and the stage of critical wetting layer formation enable us to construct analytical solutions to the model kinetic equations. The time dependence of the lateral size distribution, wetting layer thickness, and other characteristics of the island formation process are calculated. Analytical expressions for the substrate temperature and growth rate dependence of the mean lateral size and surface density of islands are obtained and analyzed.

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I. INTRODUCTION

The spontaneous formation of coherent islands in heteroepitaxial systems is of high technological relevance as it is a major method to produce dense arrays of nanoscale quantum dots.^{1,2} Carrier confinement in quantum dots makes the prospects for their use in novel optoelectronic devices very favorable.³ The optical properties of quantum dot arrays in particular systems are determined by the island shape and size distribution. Experimental results obtained for different deposit and substrate combinations⁴ demonstrate a strong dependence of surface morphology on growth conditions such as the growth rate and substrate temperature. A technological need for tuning the surface morphology by an appropriate choice of growth conditions requires further development of relevant theoretical models which could help in an understanding of the overall system performance at variable conditions.

An equilibrium model for the free energy of an array of coherent strained islands has been developed by Shchukin *et al.*⁵ It has been shown that the combined effect of strain-induced renormalization of surface energy and elastic relaxation on island edges may result in the minimum of free energy. This minimum relates to a particular energetically favorable size and a narrow lateral size distribution.⁶ The essentially equilibrium character of the model and the absence of flux and temperature dependence of island morphology have stimulated theoretical studies of island formation kinetics.^{7–9} As has been recently shown by Osipov *et al.*,^{10,11} the formation of coherent islands within a wide range of parameters can be well described within the frame of classical nucleation theory adopted to the case of molecular beam epitaxy and related growth techniques.

To develop the kinetic theory of coherent island formation, we need to find the driving force and the kinetic mechanism for the transition from two-dimensional to three-dimensional growth (2D–3D transition).¹² The driving force for coherent island formation in strained systems is always the relaxation of elastic energy in the islands.^{1,5,11} In Stranski-Krastanow growth mode, two kinetic mechanisms are principally possible: consumption of matter from a metastable “sea of adatoms” on the surface of the wetting

layer and consumption of matter directly from a metastable wetting layer.¹¹ The kinetics of coherent island formation from a metastable “sea of adatoms” has been studied recently in the case of self-limiting growth.^{8–10} However, experiments^{4,11} show that the wetting layer thickness considerably decreases in time as the islands grow. Therefore, stress-driven diffusion flux of particles from the wetting layer to islands constitutes the dominant kinetic mechanism for 2D–3D transitions. The role of adatoms is mainly restricted to a reiterative building of the 2D wetting layer.^{12,13} As long as the wetting layer thickness h is lower than the equilibrium thickness h_{eq} found from the Muller-Kern criterion,¹⁴ 2D layer-by-layer growth takes place. When the wetting layer thickness increases above the equilibrium value, a 2D–3D transition is observed. This transition results in the reduction of the free energy. Therefore, the parameter $\zeta = h/h_{\text{eq}} - 1$ is the measure of wetting layer metastability. By analogy with supersaturation in gas-vapor media, this parameter is termed as superstress.¹¹

This aim of this work is the construction and study of a kinetic model for the stress-driven formation of coherent strained islands in heteroepitaxial systems. The existence of a time scale hierarchy of different stages of the island formation process enables us to describe the process analytically. Time dependences of the island size distribution and wetting layer thickness are obtained. Simple analytical expressions for the mean lateral size of coherent islands, the size distribution width, the island surface density, and the wetting layer thickness are obtained and analyzed.

II. THEORY**A. Free energy of coherent island formation**

The free energy of the stress-driven coherent island formation in Stranski-Krastanow growth mode can be presented in the form¹¹

$$\Delta F(i) = \Delta F_{\text{elas}} + \Delta F_{\text{surf}} + \Delta F_{\text{attr}}. \quad (1)$$

Here ΔF_{elas} is the difference in elastic energy of i atoms in the island and in the wetting layer, ΔF_{surf} the difference in surface energy of the island and of the wetting layer surface

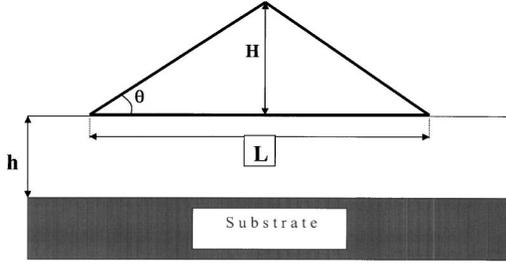


FIG. 1. Schematic representation of the system geometry in Stranski-Krastanow growth mode: L , lateral size of the island; H , island height; θ , contact angle; h , wetting layer thickness.

covered by this island, and ΔF_{attr} the difference in energy of deposit-substrate interactions of i atoms in the island and in the wetting layer. The island is assumed as being the pyramid with a square base of length L and contact angle θ , as shown in Fig. 1. In this case $i = (L/\alpha l_0)^3$ with $\alpha = (6h_0 \cotan \theta / l_0)^{1/3}$, h_0 being the monolayer (ML) height and l_0 the average distance between atoms on the surface. The first term in Eq. (1) is given by

$$\Delta F_{\text{elas}} = -[1 - z(\theta)] \lambda \varepsilon_0^2 l_0^2 h_0 i, \quad (2)$$

where λ is the elastic modulus of deposit, ε_0 the misfit parameter, $l_0^2 h_0$ the average volume per atom in the film, and $z(\theta)$ the relative relaxation of elastic stress in the island. The function $z(\theta)$ has been found numerically from finite-element calculations¹⁵ and can also be estimated by the Ratsch-Zangwill approximation.¹⁶ The elastic contribution to the overall free energy of island formation is always negative and increases by an absolute value with θ . This means that the elastic energy per atom in the island is always lower than in the wetting layer and that taller islands have lower elastic energy than flatter ones.²

Surface energy contribution to $\Delta F(i)$ is determined by the difference

$$\Delta F_{\text{surf}} = \left[\frac{\sigma(\theta)}{\cos \theta} - \sigma(0) \right] L^2, \quad (3)$$

where $(1/\cos \theta - 1)L^2$ is the additional surface area created due to island formation, $\sigma(\varphi) = \gamma(\varphi) + \tau_{\alpha\beta} \varepsilon_{\alpha\beta} + \Lambda_{\alpha\beta\mu\nu} \varepsilon_{\alpha\beta} \varepsilon_{\mu\nu}$ is the renormalized surface energy per unit area, $\varepsilon_{\alpha\beta}$ the surface deformation tensor, and γ the surface energy at zero lattice misfit.^{1,2,5} The orientations $\varphi=0$ and $\varphi=\theta$ correspond to the substrate surface and four equivalent pyramid facets. For simplicity, it is assumed that the contact angle θ is determined by a cusped local minimum of the quantity $\sigma(\varphi)/\cos \varphi$ at $\varphi=\theta$ and that all islands have constant aspect ratio $\beta = \tan \theta / 2$. In contrast to the model of cube-shaped islands of Ref. 11, in this case the free energy of island formation is the function of only one independent variable i . Shchukin *et al.*⁵ suggested that the strain-induced renormalization of the surface energy may result in a negative difference ΔF_{surf} despite an obvious inequality $\gamma(\varphi)/\cos \varphi - \gamma(0) > 0$ (initial surface is stable against faceting). In this work we consider an alternative mechanism of

3D islanding at $\Delta F_{\text{surf}} > 0$ —i.e., when the formation of an additional surface area of the island remains energetically unfavorable under strain.

The third term in Eq. (1) arises due to the attraction of atoms to the substrate. According to the Muller-Kern model,¹⁴ the energy of this attraction per unit surface area in layer $k+1$ is $\Psi_0 \exp(-k/k_0)$, where Ψ_0 is the wetting energy on the substrate surface and k_0 the relaxation coefficient. Exponential relaxation of the wetting energy is typical for semiconductors. The coefficient k_0 is normally of order of unity. It can be shown¹¹ that for sufficiently tall islands the absolute value of the attraction energy in the wetting layer is much higher than in the island. Therefore, ΔF_{attr} can be simplified to

$$\Delta F_{\text{attr}} \cong -F_{\text{attr}}^{\text{WL}} = \frac{\Psi}{h_0} \exp\left(-\frac{h}{k_0 h_0}\right) l_0^2 h_0 i, \quad (4)$$

where h/h_0 is the wetting layer thickness in ML.

Combining Eqs. (2)–(4) in Eq. (1) and expressing ΔF in the units of thermal energy, the island formation energy $F \equiv \Delta F/k_B T$ takes the form¹¹

$$\begin{aligned} \frac{\Delta F}{k_B T} \equiv F = & \frac{\sigma(\theta)/\cos \theta - \sigma(0)}{k_B T} L^2 \\ & - \frac{1}{k_B T} \left[(1-z) \lambda \varepsilon_0^2 - \frac{\Psi_0}{h_0} \exp\left(-\frac{h}{k_0 h_0}\right) \right] l_0^2 h_0 i, \end{aligned} \quad (5)$$

where k_B is the Boltzmann constant and T the substrate temperature. The expression in the square brackets in Eq. (5) represents the difference of chemical potentials of atoms in the wetting layer and in the island. The negative difference of chemical potentials relates to a *stable* wetting layer with thickness $h < h_{\text{eq}}$. The positive difference of chemical potentials relates to a *metastable* wetting layer with thickness $h > h_{\text{eq}}$. The equilibrium wetting layer thickness

$$h_{\text{eq}} = h_0 k_0 \ln \left(\frac{\Psi_0}{h_0 (1-z) \lambda \varepsilon_0^2} \right) \quad (6)$$

is determined by the ratio between characteristic wetting and elastic forces.¹⁴ At $h > h_{\text{eq}}$, a 2D-3D transition is possible because the gain in elastic energy is higher than the energy required to overcome attraction forces and to create additional surface area of the island. Introducing superstress $\zeta = h/h_{\text{eq}} - 1$ and linearizing Eq. (5) in ζ , the dependence of the island formation energy on the number of atoms in the island takes conventional form

$$F(i) = A i^{2/3} - B \zeta i. \quad (7)$$

The constants A and B , defined as

$$A \equiv \frac{[\sigma(\theta)/\cos \theta - \sigma(0)]}{k_B T} \alpha^2 l_0^2, \quad B \equiv \frac{h_{\text{eq}}}{h_0 k_0} \frac{(1-z) \lambda \varepsilon_0^2 l_0^2 h_0}{k_B T}, \quad (8)$$

are determined by the ratio of surface energy to thermal energy and of elastic energy to thermal energy, respectively.

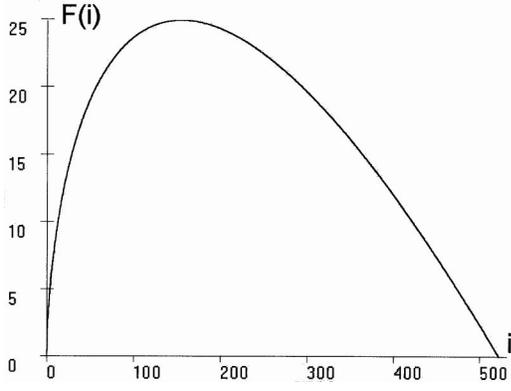


FIG. 2. Dependence of island formation energy on the number of atoms in the island $F(i)$ for the parameters described in the text.

The obtained expression for the free energy provides the following results for the main inputs of classical nucleation theory:¹⁷

$$i_c(\zeta) = \left(\frac{2A}{3B\zeta} \right)^3, \quad F(\zeta) = \frac{4}{27} \frac{A^3}{B^2 \zeta^2}, \quad -F''(i_c) = \frac{9}{8} \frac{B^4 \zeta^4}{A^3}. \quad (9)$$

Here i_c is the number of atoms in critical nuclei, $F(\zeta) = F(i_c(\zeta))$ the nucleation barrier, and $-F''(i_c)$ the reverse width of formation energy in near-critical region. As follows from Eqs. (6) and (8), the equilibrium wetting layer thickness and critical size only slightly depend on temperature and the nucleation barrier is proportional to $1/T$. For the parameters of the Ge/Si(100) system ($\lambda = 1.27 \times 10^{12}$ dyn/cm², $\varepsilon_0 = 0.042$, $h_0 = 0.145$ nm, $l_0 = 0.395$ nm, $\Psi_0 = 450$ erg/cm², $\sigma(\theta) \approx \sigma(0) = 800$ erg/cm²) at $T = 470$ °C, taking $\theta = 20^\circ$ ($z = 0.59$) and putting $k_0 = 0.9$, we obtain the following estimates: $h_{\text{eq}}/h_0 = 3.35$ ML, $A = 2.59$, and $B = 0.617$. With $\zeta = 0.53$ corresponding to a wetting layer thickness of 5.1 ML this gives $i_c = 155$ atoms and $F = 25$. The dependence of the island formation energy on the number of atoms in the island is presented in Fig. 2.

B. Evolution equation and equation of material balance

In classical nucleation theory, the nucleation rate is found from the Zeldovich formula¹⁷

$$I = \frac{W^+(i_c)}{l_0^2} \sqrt{-\frac{F''(i_c)}{2\pi}} e^{-F}, \quad (10)$$

where $W^+(i_c)$ is the number of atoms attached to the critical nuclei per unit time. The island growth function di/dt is given by $W^+(i)dF(i)/di$. In the overcritical region, in view of Eq. (7), this yields $di/dt = W^+(i)B\zeta$. As stated in the Introduction, the dominant growth mechanism is assumed as being the diffusion of atoms from the wetting layer to the island under the influence of the elastic stress field around the island. In this case the attachment rate $W^+(i)$ can be estimated as

$$W^+(i) = \frac{4D}{\nu l_0^2} \alpha i^{1/3}, \quad (11)$$

where D is the coefficient of the stress-driven diffusion from the wetting layer to islands and ν the cutoff parameter for the elastic stress field. Normally, $\nu \gg 1$ and we will consider $\nu = 10$ for our further numerical estimates.

As has been shown by Kuni,¹⁸ the study of the evolution of the island size distribution is considerably simplified by introducing a new variable for which the growth function is no longer size dependent. As follows from Eq. (11), the growth function does not depend on size in terms of the variable

$$\rho = i^{2/3} = \left(\frac{L}{\alpha l_0} \right)^2, \quad (12)$$

which equals the island base area in units of $(\alpha l_0)^2$. In terms of size ρ , the growth function is simply proportional to superstress:

$$\frac{d\rho}{dt} = \frac{\zeta}{\tau}. \quad (13)$$

The characteristic time

$$\tau = \frac{3l_0^2 \nu}{8\alpha BD} \quad (14)$$

is of the order of the averaged diffusion time of atoms in the wetting layer. Using Eqs. (11) and (14) in Eq. (10), the nucleation rate can be presented in the form

$$I(\zeta) = \frac{a}{\pi l_0^2} \zeta \exp[-F(\zeta)], \quad (15)$$

with $a \equiv \frac{3}{4}(\pi A)^{1/2}$. Under the condition $F \gg 1$, providing the applicability of the macroscopic description of the nucleation process, the evolution equation for the island size distribution $g(\rho, t)$ in terms of the variable ρ reads^{10,12,18}

$$\frac{\partial g}{\partial t} = -\frac{\zeta}{\tau} \frac{\partial g}{\partial \rho},$$

$$g(\rho, t=0) = 0, \quad g(\rho=0, t) = g_s(\zeta(t)). \quad (16)$$

This equation is written for the overcritical region: the moment $t=0$ corresponds to $\zeta=0$ and $h=h_{\text{eq}}$. The stationary distribution $g_s(\zeta)$ does not depend on ρ :

$$g_s(\zeta) = \frac{\tau}{\zeta} I(\zeta) = \frac{a}{l_0^2} \exp[-F(\zeta)]. \quad (17)$$

Since island formation at $h < h_{\text{eq}}$ is *a priori* impossible, the initial condition to Eq. (16) is obvious. The boundary condition is transferred from the boundary of the near-critical and overcritical regions to the point $\rho=0$ because near-critical islands are small in size and effectively unimportant in the material balance.¹²

The time evolution of superstress is driven by two major processes: consumption of atoms from the wetting layer by

growing islands and arrival of atoms onto the surface from the material flux of deposit. Theoretical models of molecular beam epitaxy¹⁹ assume the effective absence of desorption on the time scale of interest. In the absence of desorption and at low coverage of the surface, the equation of material balance is given by

$$h_{\text{eq}} + h_0 \int_0^t dt' V(t') = h + h_0 l_0^2 \int_0^\infty d\rho \rho^{3/2} g(\rho, t), \quad (18)$$

where $i = \rho^{3/2}$ is taken into account. The growth rate V in ML/s is assumed below as being constant at $t \leq t_0$ and zero at $t > t_0$, where t_0 is the moment of growth interruption. Integral term in the right hand side of Eq. (18) gives the total volume of islands per unit surface area at time t . The equation of material balance can be rewritten in terms of superstress as follows:

$$\Phi = \zeta + G \quad (19)$$

where G is the total volume of islands divided into h_{eq} and

$$\Phi(t) = \begin{cases} t/t_\infty, & 0 \leq t \leq t_0, \\ t_0/t_\infty, & t > t_0. \end{cases} \quad (20)$$

The time constant $t_\infty = h_{\text{eq}}/h_0 V$ is the time required to grow an equilibrium wetting layer on a bare substrate. The total amount of deposited material per unit surface area $h_{\text{tot}}(t) = [\Phi(t) + 1]h_{\text{eq}}$. Obviously, the function $\Phi(t)$ presents the superstress in the absence of nucleation (“ideal superstress”).

Equations (19) and (20) together with Eqs. (16) constitute the closed system of equations for the island size distribution $g(\rho, t)$ and superstress $\zeta(t)$. An extremely strong exponential dependence of the nucleation rate and stationary size distribution on superstress and the independence of the growth function on island size allows an analytical treatment of the system.

C. Analytical solution for the island size distribution

The solution to the evolution equation for the island size distribution can be written in the form^{10,18}

$$g(\rho, t) = g_s(\zeta[\zeta(z(t)) - \rho]), \quad (21)$$

where $z(t)$ determines the position of the size spectrum in the ρ axis at time t . As follows from the equation of material balance, superstress reaches its maximum at time t_* when the nucleation rate and stationary size distribution are also maximum. Islands nucleated at time t_* will remain the most representative in the size spectrum moving along the ρ axis with rate ζ/τ . Time t_* represents the moment of 2D-3D transition onset at which the wetting layer has maximum thickness, also referred to as the critical thickness.⁴ The definition for $z(t)$ according to

$$\frac{dz}{dt} = \frac{\zeta}{\tau}, \quad z(t = t_*) = 0, \quad (22)$$

selects $z(t)$ as the most representative size of islands nucleated at the critical wetting layer thickness. This definition

implies $z < 0$ at $t < t_*$ and $z > 0$ at $t > t_*$. Introducing the new variable $x = z - \rho$ ($x \leq z$), the island size distribution takes the form $g(\rho, t) = g(x) \vartheta(z - x)$, where $\vartheta(z - x)$ is the step function and $g(x) \equiv g_s(\zeta(x))$. Following the method of Ref. 18, the problem of studying the time evolution of the island size distribution and superstress is divided into two separate problems: (i) finding the island size spectrum $g(x)$ and $\zeta(z)$ in terms of the variables x and z and (ii) finding the time dependence $z(t)$.

According to Eq. (12), the mean lateral size of islands at time t is given by

$$L_*(t) = \alpha l_0 \sqrt{z(t)}. \quad (23)$$

The total volume of islands in terms of the variable z takes the form

$$G(z) = \frac{h_0 l_0^2}{h_{\text{eq}}} \int_{-\infty}^z dx (z - x)^{3/2} g(x). \quad (24)$$

The exponential dependence of the stationary distribution on superstress enables us to use the following approximations for $g(x)$ and $\Phi(x)$ near the point of maximum superstress:¹⁸

$$g(x) = g_s(\Phi_*) \exp\left[-\frac{\Gamma}{\Phi_*} [\Phi_* - \zeta(x)]\right], \quad (25)$$

$$\Phi(x) = \Phi_* + \frac{\Phi_*}{\Gamma} c x. \quad (26)$$

The parameter

$$\Gamma = -\Phi_* \left. \frac{dF}{d\zeta} \right|_{\zeta = \Phi_*} \quad (27)$$

will be considered below as the large parameter of the theory. The parameter $c = (\Gamma/\Phi_*) (d\Phi/dx)_{x=0}$ in view of Eq. (22) and $\zeta_* \approx \Phi_*$ is given by

$$c = \frac{\Gamma}{\Phi_*^2} \frac{\tau}{t_\infty}. \quad (28)$$

The assumption $\zeta_* \approx \Phi_*$ will be proved below. At this step, the characteristics at the point of maximum superstress and therefore the numerical values of the parameters Γ and c are undetermined.

Substitution of Eqs. (25) and (26) into Eq. (24) results in the integral equation for the total volume of islands per unit surface area:

$$G(z) = \frac{h_0 l_0^2}{h_{\text{eq}}} g_s(\Phi_*) \int_{-\infty}^z dx (z - x)^{3/2} \exp\left[c x - \frac{\Gamma}{\Phi_*} G(x) \right]. \quad (29)$$

This equation is valid during the whole nucleation stage. Substitution of Eq. (26) into Eq. (19) at $z = x$ yields

$$\zeta(x) - \Phi_* = \frac{\Phi_*}{\Gamma} c x - G(x), \quad (30)$$

which is also valid during the whole nucleation stage. Equation (29) is solved by iterations. In the first approximation, substitution of $G(x)=0$ into the right-hand side of Eq. (29) gives the following self-consistent expressions for $g(x)$ and $g_s(\Phi_*)$:

$$g(x) = g_s(\Phi_*) \exp(cx - e^{cx}), \quad (31)$$

$$g_s(\Phi_*) = \frac{4}{3\sqrt{\pi}} \frac{h_{\text{eq}}}{h_0 l_0^2} \frac{\Phi_*}{\Gamma} c^{5/2}. \quad (32)$$

The normalization constant $g_s(\Phi_*)$ is found from comparing the results of the differentiation of Eqs. (29) and (30) at $z=0$ with employing $\zeta'(0)=0$. The dependence of the superstress on z at the nucleation stage is given by

$$\zeta(z) = \Phi_* + \frac{\Phi_*}{\Gamma} (cz - e^{cz}), \quad (33)$$

providing $\zeta_* = \Phi_* (1 - 1/\Gamma) \approx \Phi_*$ at $\Gamma \gg 1$.

The surface density of islands is determined by

$$n(z) = \int_{-\infty}^z dx g(x). \quad (34)$$

Integration of the size distribution given by Eq. (31) results in

$$n(z) = N [1 - \exp(-e^{cz})], \quad (35)$$

where $N = g_s(\Phi_*)/c$ is the surface density of islands in the end of the nucleation stage. As follows from Eqs. (33) and (35), nucleation of islands takes place on a very short time scale and is practically finished at $cz \sim 1$. At the nucleation stage, the change in superstress and wetting layer thickness remains relatively small.

The island size distribution given by Eq. (31) is approximately symmetric near $x=0$ and can be presented in the form of a Gaussian

$$g(x) = g_s(\Phi_*) \exp\left(-\frac{x^2}{\Delta x^2}\right), \quad (36)$$

where $\Delta x = \sqrt{2}/c$ is the distribution half-width. The nucleation time Δt is the time to form the essential part of the size spectrum of width $2\Delta x$ —i.e., the time required for z to travel from point $-\Delta x$ to Δx . Using Eq. (22), the nucleation time is obtained in the form

$$\Delta t = \frac{2\sqrt{2}}{\Gamma} t_*, \quad (37)$$

which shows that at large Γ the nucleation process is much faster than the process of the formation of the critical wetting layer.

The characteristics at maximum superstress are found from comparing Eqs. (32) and (17) at $\zeta = \Phi_*$, which results in the algebraic equation for Φ_* . In view of $F(\Phi_*) \gg 1$, the solution to this equation can be approximated by

$$\Gamma = 5 \ln Q, \quad Q \equiv \frac{t_\infty}{\tau}. \quad (38)$$

The parameter Q is determined by the ratio of the time of wetting layer formation and characteristic diffusion time in the wetting layer under the influence of stress field. This parameter is very large and normally ranges from 10^3 to 10^6 , providing the validity of the strong inequality $\Gamma \gg 1$. As will be shown below, all characteristics of the island formation process and island array morphology depend on the system energetic constants, growth rate, and temperature mainly via Q . Therefore, the parameter Q serves as the control parameter of the model. The definitions for t_∞ and τ together with Eqs. (6) and (8) provide the following expression for Q :

$$Q = \frac{8}{3} \alpha k_0 \ln^2 \left[\frac{\Psi_0}{(1-z)\lambda \varepsilon_0^2 h_0} \right] \frac{(1-z)\lambda \varepsilon_0^2 h_0}{k_B T} \frac{D(T)}{\nu V}. \quad (39)$$

The parameter Q depends on the elastic and wetting energy of the heteroepitaxial system ($\lambda \varepsilon_0^2$ and Ψ_0), geometrical shape of islands [$\alpha(\theta)$ and $z(\theta)$], growth rate, and temperature approximately as $Q \propto D(T)/VT$.

Using Eq. (38), all characteristics of the nucleation stage are expressed in terms of the parameters Q , A , and B . In particular,

$$\Phi_* = 0.24 \frac{A^{3/2}}{B \ln^{1/2} Q}, \quad (40)$$

$$\Delta t = \frac{0.57}{\ln Q} t_*, \quad (41)$$

$$N = \frac{30}{l_0^2} \frac{h_{\text{eq}}}{h_0} \frac{B^2}{A^3} \frac{\ln^{3/2} Q}{Q^{3/2}}. \quad (42)$$

The time t_* of the 2D-3D transition onset equals $\Phi_* t_\infty$. The time required to grow a wetting layer of critical thickness on bare substrate equals $(\Phi_* + 1)t_\infty$. All analytical expressions presented in this section apply to the case when growth interruption takes place after the end of the nucleation stage ($t_0 > t_* + \Delta t$). Equations (40)–(42) together with Eq. (31) for the island size distribution complete the analytical description of the nucleation stage in terms of the variables z and x .

D. Evolution of the mean lateral size of islands

In order to find analytical expressions for the evolution of the island size distribution and superstress, consider Eq. (19) under the assumptions $\Phi(t) \approx \Phi_*$ and

$$G(t) = \frac{h_0 l_0^2}{h_{\text{eq}}} N z^{3/2}(t), \quad (43)$$

where N is the surface density of islands defined in Eq. (42). The approximation $\Phi(t) \approx \Phi_*$ is valid at the initial stage of growth if the characteristic time of island size relaxation is much smaller than t_* . Equation (43) corresponds to a δ -shaped size distribution which is a reasonable approxima-

tion after the end of the nucleation stage. A simplified equation of material balance in view of Eq. (22) reads

$$\tau \frac{dz}{dt} + \frac{h_0 l_0^2}{h_{\text{eq}}} N z^{3/2}(t) = \Phi_* . \quad (44)$$

The solution to this equation is obtained in the form of the reverse dependence of time t on the relative lateral size $l = L_*/L_R$:

$$\frac{t-t_*}{t_R} = \ln \left[\frac{(1+l+l^2)^{1/2}}{1-l} \right] - \sqrt{3} \arctan \left(\frac{2l+1}{\sqrt{3}} \right) + \frac{\pi}{2\sqrt{3}} . \quad (45)$$

The mean lateral sizes at the end of the relaxation stage L_R and relaxation time t_R are given by

$$L_R = 0.2 \alpha l_0 \frac{A^{3/2}}{B} \frac{Q^{1/2}}{\ln^{2/3} Q} , \quad (46)$$

$$t_R = \frac{0.47}{\ln^{1/3} Q} t_* = 0.82 \ln^{2/3} Q \Delta t . \quad (47)$$

The time scale hierarchy of nucleation stage, size relaxation stage, and stage of critical wetting layer formation $\Delta t \ll t_R \ll t_*$ follows from Eq. (47) at sufficiently large Q .

The mean lateral size L_R given by Eq. (46) represents the characteristic size of coherent islands formed at the initial stage of growth. As the nucleation of islands and their further size relaxation are fast processes compared to the stage of critical wetting layer formation, L_R gives a numerical estimate for the typical lateral size of islands, in particular heteroepitaxial systems at given growth conditions. Equations (46) and (42) show that the quantity $N L_R^3$ weakly depends on the growth conditions. Therefore, an increase in the lateral size of islands leads to a decreasing island surface density approximately as $1/L_R^3$.

Further evolution of the mean lateral size is determined by the moment of growth interruption t_0 . If the growth is interrupted during or soon after the size relaxation stage, Eq. (46) gives a final lateral size upon growth interruption. If the exposure time is much longer than the moment of growth interruption, the stage of Ostwald ripening¹² would begin, resulting in the growth of bigger islands due to the decay of smaller ones. From the equation of material balance at $\Phi(t) \approx \Phi_*$ it follows that

$$\zeta(t) = \Phi_* (1 - l^3(t)) , \quad t \geq t_* . \quad (48)$$

At the end of the relaxation stage, the superstress goes to zero and the wetting layer thickness to its equilibrium value. All additional amount of deposit material corresponding to the metastable range of the wetting layer thickness $h_* - h_{\text{eq}}$ is adsorbed by the islands. If the deposition is continued long after the end of the relaxation stage ($t_0 \gg t_*$), the value of L_R may be interpreted as the initial condition to Eq. (19) at the next stage of growth with $\zeta \approx 0$. The solution for the time evolution of lateral size at this stage is

$$L_*(t) = L_R \begin{cases} (t/t_*)^{1/3}, & t \leq t_0, \\ (t_0/t_*)^{1/3}, & t > t_0. \end{cases} \quad (49)$$

It should be noted that the island growth law given by Eq. (49) may be broken at some stage due to the influence of the elastic stress field around big islands on the island growth rate,^{8–10} dipole-dipole elastic interactions between islands,⁵ relaxation of island shape [e.g., pyramid-to-dome transition in the case of Ge/Si(100) clusters²⁰], and coalescence processes. As these effects are not taken into account in the present model of the initial stage of island formation, islands simply continue to grow, consuming all additional amount of deposit to maintain the equilibrium wetting layer thickness. Secondary nucleation is not allowed by the equation of material balance. The surface density of the islands remains constant after the end of the nucleation stage. The lateral size continues increasing in time as $(t/t_*)^{1/3}$ until the growth is interrupted.

The lateral size distribution $f(L, t)$ is found from $g(x)$ upon returning to the old variables ρ and t and using Eq. (12):

$$f(L, t) = \frac{2L}{(\alpha l_0)^2} g(L, t) ,$$

$$g(L, t) = cN \exp[cx(L, t) - e^{cx(L, t)}] , \quad (50)$$

where

$$x(L, t) = \frac{L_*^2(t) - L^2}{(\alpha l^0)^2} . \quad (51)$$

The half-width of the lateral size distribution at the end of the relaxation stage $\Delta L_R = (0.4/\ln^{2/3} Q) L_R$. Therefore, the relative half-width $\Delta L/L_R$ is rather small at large Q .

E. Substrate temperature and growth rate dependence of the surface morphology

The obtained analytical expressions enable us to find the dependence of island size and surface density on the growth rate and substrate temperature. Below it is assumed for simplicity that islands have similar geometrical shape at different values of the growth rate and temperature—i.e., $\theta = \text{const}$. In fact, this restriction is not essential and the value of the contact angle can be adjusted to the experimental data at different V and T , in particular to access the experimentally observed effect of decreasing the aspect ratio at a rising lateral size in InAs/GaAs (Refs. 1 and 2) and island shape transformations in Ge/Si (Ref. 20) heteroepitaxial systems.

The temperature dependence of the diffusion coefficient can be approximated in Arrhenius form $D(T) = D_0 \exp(-T_D/T)$, where $T_D \equiv E_D/k_B$ is the characteristic diffusion temperature and E_D the activation energy for the stress-driven diffusion. For the control parameter this implies $Q \sim \exp(-T_D/T)/VT$. For the mean lateral size and surface density of islands in view of Eqs. (42) and (46), $A \propto 1/T$ and $B \propto 1/T$, the resulting VT dependence is given by

TABLE I. Numerical characteristics of the island formation process.

Stage	Characteristic time (s)	Wetting layer thickness (ML)	Surface density (cm ⁻²)	Lateral size (nm)	Size distribution width (nm)
Growth of equilibrium wetting layer	47.9	3.35			
Growth of critical wetting layer	73.5	5.1			
Nucleation stage	1.52	5.1	2.4×10^{10}		
Size relaxation stage	5.7	3.35	2.4×10^{10}	25	2.3

$$L_R \propto \frac{\exp(-T_D/2T)}{V^{1/2} T [\ln(\Lambda/VT) - T_D/T]^{2/3}}, \quad (52)$$

$$N \propto \frac{L_R^{-3}}{T^{1/2} [\ln(\Lambda/VT) - T_D/T]^{1/2}}. \quad (53)$$

The constant Λ is determined by the relationship $\ln Q_0 = \ln(\Lambda/V_0 T_0) - T_D/T_0$ at particular reference values of T_0 and V_0 . Therefore, the lateral size decreases with rising growth rate approximately as $1/V^{1/2}$ and increases exponentially with rising substrate temperature. Such a temperature behavior of the lateral size is in agreement with the conclusions of the microscopic model for the diffusion-induced islanding of Ref. 21. The surface density of islands relates to the lateral

size approximately as $1/L_R^3$ and therefore increases with growth rate and decreases with temperature.

III. RESULTS AND DISCUSSION

The characteristics of the island formation process were calculated for the values of parameters presented in Sec. II A. The growth rate V was fixed to 0.07 ML/s, cutoff parameter for the elastic stress $\nu = 10$, and diffusion coefficient in the wetting layer $D = 1.5 \times 10^{-12}$ cm²/s. The characteristic times of the different stages of growth, equilibrium, and critical wetting layer thickness, island surface density at the end of the nucleation stage, mean lateral size of islands, and size distribution width at the end of the size relaxation stage are summarized in Table I. The presented results demonstrate the existence of a time scale hierarchy of different stages of the island formation process. For the quoted material constants and substrate temperature, the parameter $\Gamma = 50$. The obtained numbers for the mean lateral size and surface density are in agreement with typically observed values for “hut” clusters in the Ge/Si(100) heteroepitaxial system.²⁰

The time dependences of the nucleation rate and island surface density at the nucleation stage are shown in Fig. 3. As seen from these figures, the nucleation of islands takes place during the short time interval ($\Delta t = 1.52$ s); the surface density goes to its maximum value $N = 2.4 \times 10^{10}$ cm⁻² at

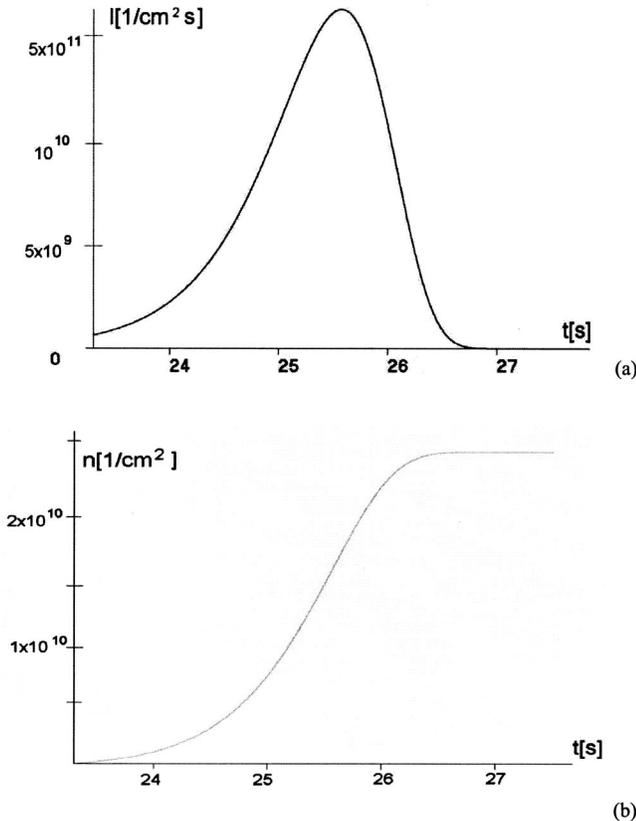


FIG. 3. Time dependences of the nucleation rate $I(t)$ (a) and island surface density $n(t)$ (b) for the parameters described in the text.

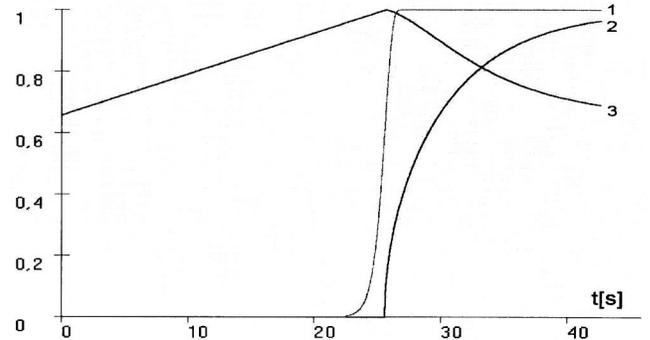


FIG. 4. Time dependences of the relative island surface density $n(t)/N$ (1), mean lateral size $l(t)$ (2), and wetting layer thickness $h(t)/h_*$ (3) at the size relaxation stage. Critical wetting layer thickness $h_* = 5.1$ ML, surface density at the end of the nucleation stage $N = 2.4 \times 10^{10}$ cm⁻², and mean lateral size at the end of the relaxation stage $L_R = 25$ nm.

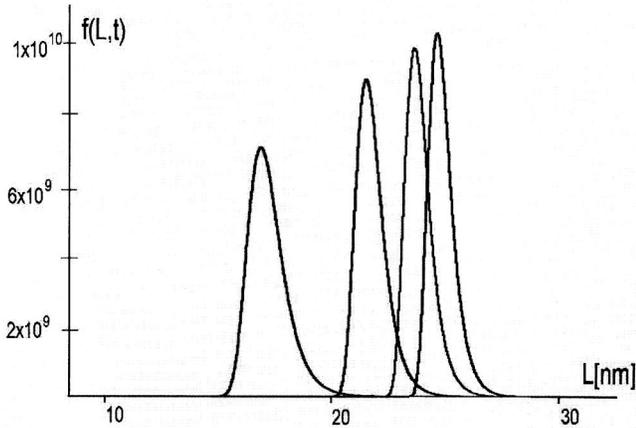


FIG. 5. Island lateral size distribution $f(L,t)$ in $\text{cm}^{-2} \times \text{nm}^{-1}$ at four different times $t = 29.9, 34.2, 38.5,$ and 42.8 s.

the end of the nucleation stage and remains constant during the size relaxation stage. In all figures, the time moment $t = 0$ relates to $h = h_{\text{eq}}$ so that the actual deposition time equals $t + t_{\infty}$ ($t_{\infty} = 47.9$ s is the time to grow the equilibrium wetting layer at a growth rate of 0.07 ML/s).

The time dependences of the wetting layer thickness and mean lateral size of islands obtained from Eqs. (45) and (48) are presented in Fig. 4. It is seen that the wetting layer thickness reaches a critical value at $t = t_*$ and then gradually decreases to its equilibrium value at the size relaxation stage. The mean lateral size of islands reaches its characteristic value $L_R = 25$ nm at the end of the size relaxation stage. The time dependence of the wetting layer thickness is in qualitative agreement with the experimental data and theoretical calculations of Ref. 11. The time evolution of the island size distribution is calculated by means of Eqs. (50), (51), and (48) and is demonstrated in Fig. 5. It is seen that the relative width of the size distribution decreases in time and is approximately 9% at the end of the size relaxation stage.

The theoretical substrate temperature dependence of the mean lateral size and island surface density given by Eqs. (52) and (53) was compared to the results of transmission electron microscopy observations of InAs quantum dots on a GaAs(100) surface grown at different temperatures.²²

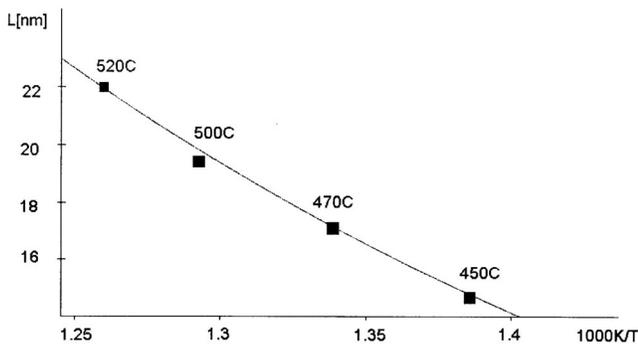


FIG. 6. Substrate temperature dependence of the mean lateral size of islands L_R at $T_D = 8000$ K. Solid squares are the experimental results of Ref. 22.

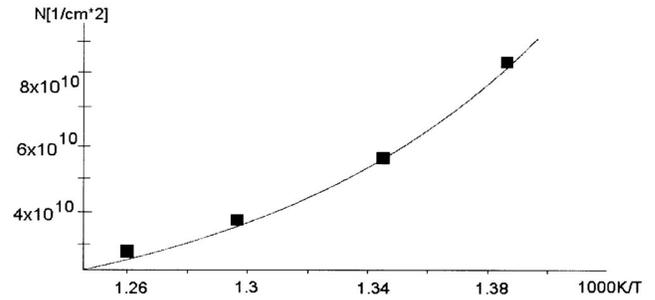


FIG. 7. Substrate temperature dependence of the island surface density N . Solid squares are the experimental results of Ref. 22 for the same temperatures as in Fig. 6.

Results presented in Figs. 6 and 7 show that the theoretical conclusions are in a fairly good agreement with the experimental data. Experimental dependences confirm the increase in lateral size with rising substrate temperature and corresponding decrease in island surface density approximately as $1/L_R^3$.

It should be noted that the presented model does not account for several important aspects that might have a considerable effect on the overall system performance. Among these, island shape relaxation,^{2,11} the contribution from a metastable “sea of adatoms” to island formation kinetics,¹⁰ dipole-dipole elastic interactions of coherent islands via the substrate,^{1,5} and the influence of elastic stress field on the island growth rate⁸⁻¹⁰ should be mentioned. However, neither of these effects excludes the possibility of a detailed kinetic description of the island formation process within the frame of classical nucleation theory. Generalization of the presented approach to include these effects constitutes the goal of our further studies.

To sum up, a kinetic model of the stress-driven formation of coherent islands in heteroepitaxial systems has been developed. The model allows a complete analytical description of the time evolution of the island size distribution and wetting layer thickness. It has been shown that the mean lateral size of islands increases with rising substrate temperature and decreases with rising growth rate. The surface density of islands decreases with rising lateral size. These theoretical conclusions agree well with the experimental data and previous theoretical findings. The model predicts realistic values for the lateral size and surface density which also do not conflict with the experimental results. Despite the simplicity of the obtained expressions, they might give a way for tuning the operating wavelength of optical devices based on quantum dot heterostructures by changing the technologically controlled parameters of the deposition process.

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