Transition from thermodynamically to kinetically controlled regime of nucleation in a materially open system

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Abstract
The nucleation of islands during the first order phase transition in a materially open system is studied. Expressions for the island size and density are obtained as functions of the temperature, material flux and the total concentration of material introduced into the system. It is shown that at a certain critical concentration the transition from the thermodynamically to the kinetically controlled regime of nucleation is observed. In the subcritical range the density of islands increases with temperature and the amount of material and is flux independent. In the overcritical range the density decreases with the temperature, increases with the flux and does not depend on the total concentration. The characteristic size of the islands decreases simultaneously with the increase of their density.

1. Introduction

The kinetics of nucleation constitutes an important part of the entire theory of the first order phase transitions [1, 2]. Condensation of supersaturated vapours, solidification of liquid alloys, growth of crystals from melts, aggregation of islands in dense adsorbates, nucleation of thin films and many other physical phenomena can be described within the frame of this theory. The number of applications of nucleation theory rapidly increases. In particular, it has been recently applied to studying the kinetics of formation of coherent islands in strained heteroepitaxial systems [3–5], a problem that has an important impact on the technology of quantum dot fabrication [6]. One of the main advantages of nucleation theory is the opportunity to describe the time evolution of a particular system with given material constants under strongly non-equilibrium conditions. The timescale hierarchy of different stages of phase transition enables us to distinguish the stage of arrangement of the steady state in the near-critical region [7],

the nucleation stage [2], the size relaxation stage [1], the stage of ripening [8] and the stage of direct coalescence of islands leading to the formation of a continuous condensed phase [9]. In many cases, in particular during the deposition of thin films and heteroepitaxial growth of quantum dots, the nucleation process is technologically controlled [6, 10]. This provides an opportunity to change the external parameters of the island formation process and to stop it at the desired stage of growth.

The most important structural characteristics of an island ensemble during the first order phase transition are the island density N and average size L. These quantities can be controlled experimentally with high accuracy and therefore are suitable for the verification of theoretical models. Also, the values of N and L in largest measure determine the physical properties of technologically fabricated structures, for example crystallites obtained by freezing transitions [11], thin films [10] and quantum dot heterostructures [6] grown on a solid surface by various deposition techniques. To control the process of island formation, we require an adequate theoretical description of the dependence of island size and density on the external parameters of the process. In many cases, the metastability of a condensing system is ensured by a material flux into the system of a certain intensity V. The source of this flux can be a chemical reaction in the system induced by some external factors, arrival of particles into the system from the surroundings, deposition of atoms onto a surface etc. The measure of the system metastability is supersaturation $\zeta = n/n_e - 1$, where n is the concentration of particles of a condensing phase and n_e is its equilibrium concentration, which is a known function of system temperature T. Below we consider the case of $T = \text{const}$ for a condensing phase and all islands of a new phase. The isothermal conditions of nucleation are normally ensured by the presence of a passive substance or substrate stabilized at temperature T and playing the role of a thermal reservoir. The classical nucleation theory [1, 2, 10] can be applied only to the case of sufficiently low temperatures, i.e. when T is well below the critical temperature T_c. For concreteness, we assume that the time dependence of V is given by $V(t) = V = \text{const}$ at $t < t_0$ and $V(t) = 0$ at $t > t_0$, where t_0 is the moment when the material flux is switched off. If the escape of particles from the system is not allowed (in the case of adsorbates and thin films, this means the effective absence of desorption on a timescale of interest, which is conventional for theoretical models of molecular beam epitaxy and related growth techniques [3–5]), the total concentration of particles in the system is given by $n_{tot} = Vt$ at $t \leqslant t_0$ and $n_{tot} = Vt_0 \equiv n_{max}$ at $t > t_0$. Here n_{max} is the total concentration of the material introduced into the system before the material flux is switched off. Under the described assumptions, the major control parameters of the nucleation process are the temperature T, the intensity of material flux V and the total amount of condensing substance n_{max}.

In this work we investigate the island formation kinetics at temperatures well below the critical temperature T_c. Only the initial stage of the process is studied, when there is no indirect or direct interaction between the islands (ripening [8], elastic interactions [6], coalescence [9] etc). The major goal of our study is to find theoretical dependences of the island density N and size L_R after the size relaxation stage on the external parameters of the nucleation process, $N(T, V, n_{max})$ and $L_R(T, V, n_{max})$. For the description of the condensing and new phases of the system we use the lattice gas (LG) model, which is widely used to study first order phase transitions [13] especially in adsorbates [14] and thin films [10]. A dilute condensing phase is described as a system with barrier jump diffusion between the LG sites. Two-dimensional (2D) and three-dimensional (3D) systems are considered simultaneously. The present study was partly stimulated by our recent work [4] devoted to the kinetics of coherent island formation in heteroepitaxial systems. There it was shown that if the concentration of material exceeds a certain critical value (the definition of this critical concentration will be given below), the density of islands increases and their size decreases on increasing the material

flux and decreasing the temperature of the system. This theoretical conclusion is confirmed by many experimental studies of quantum dot ensembles, in particular in the Ge/Si(100) and InAs/GaAs(100) heteroepitaxial systems [5]. In this work it will be shown that the described performance of island ensembles in the overcritical range has a general character and holds for all systems undergoing the first order phase transition in a materially open system. All overcritical island ensembles are essentially kinetically controlled. In the subcritical range of concentrations, the dependence of island size and density on the external parameters is totally different and is primarily determined by thermodynamics. This indicates the transition form a thermodynamically to a kinetically controlled regime of nucleation in a materially open system at a certain critical concentration, an effect which has been recently predicted in the case of islanding during heteroepitaxy in strained systems [15]. Our results can be summarized in the form of graphs of the relaxed island size and density as functions of the total concentration of material n_{max} at different values of T and V. These graphs provide a detailed characterization of the structural properties of island ensembles at the kinetic stage of phase transition.

2. The model

Concerning the theory of the first order phase transitions within the frame of the LG model, the mean field equation of state [13] at $T < (5/2)T_c$ gives the following result for the equilibrium concentration of a dilute phase at temperature T:

$$n_e(T) = n_0 \exp\left(-2\frac{T_c}{T}\right). \tag{1}$$

The equilibrium concentration of a dense phase is very close to the maximum density $n_0 = l_0^{-\alpha}$, where l_0 is the lattice spacing and α is the space dimension ($\alpha = 2$ for 2D and $\alpha = 3$ for 3D LG). A dilute phase can be assumed to be ideal. Here and below the lattice is assumed to be square or cubic; the islands of a new phase are also assumed to have the shape of squares or cubes for the 2D and 3D case respectively. The free energy of formation of an island with i particles (expressed in thermal units) in the case of homogeneous nucleation is given by [1]

$$\Delta F(i) = A i^{(\alpha-1)/\alpha} - \ln(\zeta + 1)i. \tag{2}$$

The first term gives the energy required to create the interface boundary between the island of a dense phase and a dilute phase, and the second term presents the difference in chemical potentials of dilute and dense phases. The parameter $A \equiv 2\alpha l_0^{\alpha-1}\gamma/k_B T$ is proportional to the specific interface energy γ per unit area in the 3D case or per unit length in the 2D case (surface tension for liquid drops, surface energy for crystals, interfacial boundary energy for monolayer islands); k_B is the Boltzmann constant. For modest variations in T, the temperature dependence of A in liquids and solids can be approximated in the form [16]

$$A(T) = \frac{T_A}{T} - B \tag{3}$$

where $T_A \equiv 2\alpha l_0^{\alpha-1}\Delta h/k_B$ and $B \equiv 2\alpha l_0^{\alpha-1}\Delta s$; Δh and Δs are the specific enthalpy and entropy of the boundary formation, respectively. The values of T_A and B can be assumed to be approximately constant. Obviously, the critical temperature T_c and the characteristic interface temperature T_A are entirely the equilibrium values. Using equation (1), the main parameters of the classical nucleation theory [1] are found in the form

$$i_c = \left[\frac{(\alpha - 1)}{\alpha}\frac{A}{\ln(\zeta + 1)}\right]^\alpha \tag{4}$$

$$F \equiv \Delta F(i_c) = \frac{(\alpha - 1)^{\alpha-1}}{\alpha^\alpha}\frac{A^\alpha}{\ln^{\alpha-1}(\zeta + 1)}. \tag{5}$$

Here i_c is the number of particles in the critical nuclei and F is the nucleation barrier in thermal units. As a function of supersaturation ζ, the nucleation barrier decreases with increasing ζ, i.e. the higher the supersaturation the lower is the barrier that must be surpassed by the nuclei due to thermodynamic fluctuations to undergo the phase transition. At fixed ζ, the nucleation barrier lowers at increasing temperature, because the intensity of fluctuations in the subcritical region increases.

In order to calculate the growth rate of overcritical islands ($i \gg i_c$), we utilize the expression $di/dt = W^+(i)(1 - n_e/n)$ [1] where $W^+(i)$ is the rate of attachment of particles to the nuclei with i particles. Using the simplest approximation for the diffusion coefficient in condensed matter [16], the attachment rate can be presented as [10]

$$W^+(i) = S_i l_0 n \frac{\nu}{2\alpha} \exp\left(-\frac{T_D}{T}\right). \tag{6}$$

Here $S_i = 2\alpha l_0^{\alpha-1} i^{(\alpha-1)/\alpha}$ is the area (length) of the boundary of island with i particles, ν is the vibration frequency of atoms in the LG sites, 2α is the number of nearest neighbours for a diffusion jump, $T_D \equiv E_D/k_B$ is the characteristic diffusion temperature and E_D is the activation energy for a diffusion jump. Equation (6) holds, for example, for the crystallization of material A from a dilute liquid alloy A–B (including the case of crystallization on the solid surface of material A) and for 2D islanding of material A on the solid surface of material B, but is not valid in the case of vapour condensation. In terms of the variable $\rho \equiv L/l_0 = i^{1/\alpha}$, which equals the linear size of islands expressed in the units of lattice spacing, the island growth rate does not depend on the island size:

$$\frac{d\rho}{dt} = \frac{\zeta}{\tau}. \tag{7}$$

The characteristic time of island growth in view of equation (6) is given by

$$\tau = \alpha \frac{n_0}{\nu n_e} \exp\left(\frac{T_D}{T}\right). \tag{8}$$

The characteristic time τ strongly decreases with T, because the increase in temperature speeds up the diffusion processes. Obviously, the diffusion temperature T_D has an essentially kinetic origin.

The nucleation rate in classical condensation theory is found from the Zeldovich formula [2]

$$I = nW^+(i_c)\sqrt{-\frac{F''(i_c)}{2\pi}} e^{-F}. \tag{9}$$

The stationary size distribution $g_s = I\tau/\zeta$ is very quickly attained in the whole near-critical region [7]. Using equations (2), (4), (6) and (8), the expression for the stationary distribution expressed in the units of equilibrium concentration of particles, $f_s \equiv g_s/n_e$, takes the form

$$f_s(\zeta) = \frac{\alpha^{(3-\alpha)/2}(\alpha-1)^{\alpha/2-1}}{\sqrt{2\pi}} A^{\alpha/2-1} \ln^{(3-\alpha)/2}(\zeta+1) \frac{(\zeta+1)^2}{\zeta} e^{-F(\zeta)}. \tag{10}$$

The exponential dependence of f_s on $F(\zeta)$ given by equation (10) demonstrates that the stationary distribution is extremely sensitive to the changes in supersaturation (for a relatively small increase in ζ the stationary distribution increases in order of magnitude). Equation (10) is valid only at $F(\zeta) \gg 1$ [4, 10, 12].

The independence of the island growth rate from island size ρ enables us to write the following solution for the size distribution of islands $f(\rho, t)$ (expressed in the units of n_e) in the whole overcritical region [4, 10, 12]:

$$f(\rho, t) = f_s(\zeta(x)) \equiv f(x) \tag{11}$$

where $x(\rho, t) = z(t) - \rho$. The function $z(t)$ determines the time evolution of the island size distribution. The definition of $z(t)$ according to

$$\frac{dz}{dt} = \frac{\zeta}{\tau}; \qquad z(t = t_*) = 0 \tag{12}$$

where t_* is the moment at which the supersaturation reaches its maximum, selects $z(t)$ as the most representative linear size of islands that were nucleated at maximum supersaturation and therefore at maximum nucleation rate: $z(t) = L_*(t)/l_0$.

The equation of material balance in the materially open system with an incoming material flux can be presented in the form [3]

$$\Phi = \zeta + G. \tag{13}$$

Here $\Phi \equiv n_{tot}/n_e - 1$ is the ideal supersaturation, i.e. the supersaturation that would be established in the system in the absence of nucleation, and G is the total number of atoms in the islands in the units of n_e. Since the characteristic size $z(t)$ increases in time, equation (13) can be equally considered in terms of variables t or z. Under the assumptions on the form of material flux made in the introduction, the time dependence of ideal supersaturation is given by

$$\Phi(t) = \begin{cases} t/t_\infty, & 0 \leqslant t \leqslant t_0 \\ t_0/t_\infty \equiv \Phi_0, & t > t_0. \end{cases} \tag{14}$$

Here $t_\infty = n_e/V$ is the time required to reach the equilibrium concentration of a dilute phase from zero concentration at the material flux of intensity V and $\Phi_0 \equiv n_{max}/n_e - 1$ is the maximum ideal supersaturation reached by the moment of the interruption of material flux. The function G in terms of variable z can be presented in the form

$$G(z) = \int_{-\infty}^{z} dx \, (z - x)^\alpha f(x) \tag{15}$$

where $i = \rho^\alpha$ is taken into account. Equations (11)–(15) constitute the closed system of equations for the island size distribution and supersaturation and therefore enable us to find the island characteristic size and density as functions of time and the control parameters of the condensation process. As shown by Kuni [12], an extremely strong non-linearity of the problem allows us to construct a self-consistent analytical solution for the major characteristics of the condensation process.

3. Solutions for critical supersaturation, island size and density

The exponential dependence of the stationary distribution on the supersaturation enables us to use the following approximation for $f(x)$ near the point of maximum supersaturation [4, 12]:

$$f(x) = f_s(\Phi_*) \exp\left[-\frac{\Gamma}{\Phi_*}(\Phi_* - \zeta(x))\right] \tag{16}$$

where the assumption $\zeta_* \approx \Phi_*$ means that at the point of maximum supersaturation the total number of particles in the islands is negligibly small. The parameter

$$\Gamma = -\Phi_* \frac{dF}{d\zeta}\bigg|_{\zeta = \Phi_*} = \frac{\Phi_*}{\Phi_* + 1} i_c(\Phi_*) \tag{17}$$

is of the order of the number of atoms in the critical nuclei at supersaturation Φ_* and therefore can be considered as the large parameter of the theory [12]. The last relationship in

equation (17) is obtained by using equations (4) and (5). In view of equation (14) and $\zeta_* \approx \Phi_*$, the ideal supersaturation near Φ_* can be presented in the form

$$\Phi(x) = \begin{cases} \Phi_* + (\Phi_*/\Gamma)cx, & x \leqslant z_0 \\ \Phi_* + (\Phi_*/\Gamma)z_0, & x > z_0. \end{cases} \tag{18}$$

Here the parameter c is given by

$$c = \frac{\Gamma}{\Phi_*} \frac{\mathrm{d}\Phi}{\mathrm{d}x}\bigg|_{x=0} = \frac{\Gamma}{\Phi_*^2 Q}. \tag{19}$$

It should be remembered that according to equations (19) and (17) the parameters Γ and c depend on Φ_*. The kinetic control parameter Q introduced in [4] is determined by the ratio between the characteristic time of ideal supersaturation growth t_∞ and the characteristic time of island growth τ, $Q \equiv t_\infty/\tau$. As the ratio of timescales of macroscopic and microscopic processes, the parameter Q is very large (normally $Q > 100$). Employing the above definitions for t_∞ and τ and making use of equation (1), the resulting dependence of Q on the temperature and material flux reads

$$Q(T, V) = \frac{V_0}{V} \exp\left(-\frac{T_D + 4T_c}{T}\right) \tag{20}$$

with $V_0 \equiv v n_0/\alpha$. Thus, the kinetic control parameter is inversely proportional to the intensity of material flux and increases with temperature as the Arrhenius exponent [4].

The parameter z_0 in equation (18) is determined by the total concentration of material introduced into the system (maximum ideal supersaturation Φ_0) and the maximum supersaturation Φ_*:

$$z_0 = \frac{\Gamma}{c}\left(\frac{\Phi_0}{\Phi_*} - 1\right). \tag{21}$$

Equations (18) and (21) demonstrate an important difference between the following two cases [12]:

$$\text{Overcritical range:} \qquad \Phi_0 > \Phi_c; \qquad \Phi_* = \Phi_c; \qquad z_0 > 0 \qquad (22)$$
$$\text{Subcritical range:} \qquad \Phi_0 < \Phi_c; \qquad \Phi_* = \Phi_0; \qquad z_0 = 0. \qquad (23)$$

At the overcritical value of the total amount of material introduced into the system ($\Phi_0 > \Phi_c$), the maximum of supersaturation is reached due to a kinetic balance between the arrival of particles into the system from a material flux and the consumption of particles by the growing islands. In the subcritical range of Φ_0 ($\Phi_0 < \Phi_c$), the maximum supersaturation is reached simply as the result of the interruption of a material flux. In this case the maximum supersaturation equals Φ_0. The critical supersaturation Φ_c should be determined from the equation of material balance at $\mathrm{d}\zeta/\mathrm{d}z|_{z=0} = 0$ and at this stage is unknown.

The scheme of further calculations is fairly straightforward and in the overcritical range in the case of quantum dot formation in strained heteroepitaxial systems is described in detail in [4]. According to equations (13), (16) and (18), the distribution $f(x)$ near its maximum can be presented in the form

$$f(x) = f_s(\Phi_*) \begin{cases} \exp[cx - (\Gamma/\Phi_*)G(x)], & x \leqslant z_0 \\ \exp[cz_0 - (\Gamma/\Phi_*)G(x)], & x > z_0. \end{cases} \tag{24}$$

Substitution of these expressions into equation (15) gives the closed integral equation for $G(z)$. This equation is solved by iterations. It can be shown [12] that the first approximation of the solution corresponding to substitution of $G(x) = 0$ into the integral term ensures a high relative

accuracy of the results. In particular, in the essentially overcritical range (at sufficiently large z_0) $G(z)$ is found in the form

$$G(z) = f_s(\Phi_c) \int_{-\infty}^{z} \mathrm{d}x \, (z - x)^{\alpha} \mathrm{e}^{cx} = \frac{\alpha!}{c^{\alpha+1}} f_s(\Phi_c) \mathrm{e}^{cz}. \tag{25}$$

This equation allows us to find the critical supersaturation Φ_c and the normalization constant of the island size distribution $f_s(\Phi_c)$. Differentiating equation (13) with respect to z, using equations (25), (18) and the condition $\mathrm{d}\zeta/\mathrm{d}z/_{z=0} = 0$ at the point of maximum supersaturation, one obtains

$$f_s(\Phi_c) = \frac{\Phi_c}{\alpha! \Gamma} c^{\alpha+1}. \tag{26}$$

Comparing equation (10) at $\zeta = \Phi_*$ and equation (19) it is seen that the only two terms that can compete with each other in equation (26) are very large quantities $\exp[F(\Phi_c)]$ and $Q^{\alpha+1}$. Therefore, in a logarithmical scale equation (26) gives the relationship between the thermodynamic and kinetic parameters in the form

$$F(\Phi_c) = (\alpha + 1) \ln Q. \tag{27}$$

Making use of equations (1), (3), (5) and (20), the final expression for the critical supersaturation is obtained as

$$\Phi_c(T, V) = \exp\left[\left(C_\alpha \frac{(T_A/T - B)^\alpha}{\ln(V_0/V) - (T_D + 4T_c)/T}\right)^{1/(\alpha-1)}\right] - 1 \tag{28}$$

where $C_\alpha \equiv (\alpha - 1)^{\alpha-1}/\alpha^\alpha(\alpha + 1) = 1/27$ for $\alpha = 3$ and $1/12$ for $\alpha = 2$. Critical supersaturation rapidly decreases with the temperature and less rapidly increases with the material flux. The critical concentration according to the definition for Φ_c is given by $n_c = (\Phi_c + 1)n_e$ and the time to reach the critical concentration from zero concentration amounts to $t_c = n_c/V$.

Substitution of the obtained result for $G(x)$ into equations (24) gives the self-consistent expressions for the island size distribution $f(x)$. In particular, for the essentially overcritical range form equations (24)–(26) it follows that the size distribution $f(x) = f_s(\Phi_*) \exp[cx - \exp(cx)]$ and therefore is approximately Gaussian. The density of islands N is then found from

$$N = n_e \int_{-\infty}^{\infty} \mathrm{d}x \, f(x). \tag{29}$$

The characteristic size of islands at the end of the size relaxation stage ($\zeta \to 0$, $\Phi \to \Phi_0$, $L_* \to L_R$) is found from the equation of material balance by using the mono-disperse approximation for the size distribution [4]: $\Phi_0 = G(z) \approx (N/n_e)(L_R/l_0)^\alpha$. The characteristic size at the end of the size relaxation stage is therefore determined by the density of islands and by the total concentration of material in the system n_{max}

$$L_R = l_0 \left(\frac{n_e}{N} \Phi_0\right)^{1/\alpha} = l_0 \left(\frac{n_{max} - n_e}{N}\right)^{1/\alpha}. \tag{30}$$

Obviously, the island size relaxation takes a longer time for subcritical islands.

Omitting the results of calculations, the final equation for the island density is obtained in the form

$$N = K N_{max} (1 - \mathrm{e}^{-f} + G(f)) \tag{31}$$

where

$$K = \begin{cases} (\Phi_c/\Phi_0)^\alpha [(\Phi_c + 1) \ln(\Phi_c + 1)/(\Phi_0 + 1) \ln(\Phi_0 + 1)]^{\alpha-1} & \\ 1, \Phi_0 > \Phi_c, & \end{cases} \quad \Phi_0 \leqslant \Phi_c \qquad (32)$$

$$f = \begin{cases} [\ln(\Phi_0 + 1)/\ln(\Phi_c + 1)]^{\alpha^2+(3-\alpha)/2}(\Phi_0/\Phi_c)^\alpha [(\Phi_0 + 1)/(\Phi_c + 1)]^{\alpha+2} & \\ \quad \times \exp[-(F(\Phi_0) - F(\Phi_c))], & \Phi_0 \leqslant \Phi_c \\ \exp[\Gamma_c(\Phi_0/\Phi_c - 1)], & \Phi_0 > \Phi_c \end{cases}$$
$$(33)$$

$$G(f) = f \int_0^\infty d\mu \, \exp\left[-f \sum_{i=0}^{\alpha+1} \frac{\mu^i}{i!}\right] \qquad (34)$$

and $\Gamma_c \equiv \Gamma(\Phi_c)$. The maximum density N_{max} reached in the overcritical concentration range is given by

$$N_{max} = \frac{n_e}{\alpha!} \left[\frac{\alpha(\alpha + 1)}{A}\right]^\alpha \frac{1}{\Phi_c^\alpha (\Phi_c + 1)^{\alpha-1}} \left(\frac{\ln Q}{Q}\right)^\alpha. \qquad (35)$$

Using equation (28) for Φ_c, equation (17) and (4) at $\Phi_* = \Phi_c$ for Γ_c, equation (5) for $F(\Phi_0)$ and $F(\Phi_c)$, equation (1) for $n_e(T)$, equation (3) for $A(T)$ and equation (20) for $Q(T, V)$ and taking into account that $\Phi_0 \equiv n_{max}/n_e - 1$, the obtained equations (30)–(35) provide the description of island size and density depending on the thermodynamic parameters T_c, T_A, B, the characteristic diffusion temperature T_D and the control parameters of nucleation process T, V and n_{max}. The kinetics of average size $L_*(t)$ at the size relaxation stage can be described by an equation similar to that given in [4].

4. Transition from thermodynamically to kinetically controlled regime of nucleation

The asymptotic analysis of the obtained equations for N and L_R enables us to find analytically the leading dependence of the island size and density on the temperature, material flux and ideal supersaturation in essentially overcritical ($f \gg 1$) and essentially subcritical ($f \ll 1$) ranges of total concentration of material. Obviously, at $f \gg 1$ $K = 1$, $G(f) \to 0$ and $N \to N_{max}$. The leading TV dependence of N_{max} determined by equation (35) at $\Phi_c \sim 1$ is therefore $N \propto Q^{-\alpha}$. In view of equations (1), (20) and (30), the density and size of islands depend on the control parameters T, V and Φ_0 as follows:

$$N = N_{max} \propto n_0 V^\alpha \exp\left[\frac{\alpha T_D + (4\alpha - 2)T_c}{T}\right] \qquad (36)$$

$$L_R \propto l_0 \frac{\Phi_0^{1/\alpha}}{V} \exp\left(-\frac{T_D + 4T_c}{T}\right). \qquad (37)$$

At very small or large Φ_c the exponential dependence $\Phi_c(T, V)$ determined by equation (28) should be taken into account and equations (36), (37) will be modified. At $\Phi_c \sim 1$ the density increases with the material flux as V^α, decreases with the temperature as the Arrhenius exponent and is independent of the total concentration. The island size decreases with the flux as $1/V$, increases with the temperature and slowly increases with the ideal supersaturation Φ_0. The temperature dependence contains the kinetic diffusion temperature T_D. Therefore, the structure of the overcritical ensembles of islands is essentially *kinetically controlled*.

At $f \ll 1$, $1 - \exp(-f) \approx f$ and the asymptotic behaviour of $G(f)$ is given by $G(f) \approx [(\alpha + 1)!]^{1/(\alpha+1)} f^{\alpha/(\alpha+1)} \Gamma[1/(\alpha + 1)]/(\alpha + 1)$ (Γ here denotes the gamma function). Therefore, the leading asymptotic of N at $f \ll 1$ is $K N_{max} G(f) \sim N_{max} f^{\alpha/(\alpha+1)} \sim$

$N_{max} \exp[(\alpha/(\alpha + 1)(F(\Phi_c) - F(\Phi_0))]$. Using equation (27) for $F(\Phi_c)$, equaton (35) for N_{max} and equation (30) for L_R, the leading dependences of island density and size on the control parameters are obtained in the form

$$N \propto n_e \exp\left[-\frac{\alpha}{\alpha + 1} F(\Phi_0)\right] \propto n_0 \exp\left[-\frac{2T_c}{T} - \frac{(\alpha - 1)^{\alpha-1}}{(\alpha + 1)\alpha^{\alpha-1}} \frac{(T_A/T - B)^\alpha}{\ln^{\alpha-1}(\Phi_0 + 1)}\right] \quad (38)$$

$$L_R \propto l_0 \exp\left[\frac{F(\Phi_0)}{\alpha + 1}\right] \propto l_0 \exp\left[\frac{(\alpha - 1)^{\alpha-1}}{(\alpha + 1)\alpha^\alpha} \frac{(T_A/T - B)^\alpha}{\ln^{\alpha-1}(\Phi_0 + 1)}\right]. \quad (39)$$

In 3D space, the island density and size in the subcritical concentration range depend on the nucleation barrier at maximum supersaturation Φ_0 as $\exp[-(3/4)F(\Phi_0)]$ and $\exp[F(\Phi_0)/4]$, respectively (the result previously obtained in [12] for the case of condensation of a supersaturated vapour). In 2D space these dependences are given by $\exp[-(2/3)(\Phi_0)]$ and $\exp[F(\Phi_0)/3]$, respectively. The explicit dependence on T and Φ_0 in equations (38) and (39) is obtained from equations (3) and (5). Equations (38) and (39) show that the density of islands strongly increases and their size decreases on increasing the ideal supersaturation and temperature. All subcritical structures are flux independent. The relaxed islands are considerably larger and their density is much lower than in the overcritical range. The dependence of N and L_R on T and Φ_0 contains no kinetic parameters. Therefore, the structure of subcritical ensembles of islands is *controlled by thermodynamics*. The density of subcritical islands is considerably lower and their size is larger than in the overcritical concentration range.

The calculations were performed using equations (17) and (30)–(35) in the case of formation of 2D islands on the solid surface from supersaturated 'vapour' of adatoms ($\alpha = 2$) for the following model parameters: $l_0 = 0.4$ nm, $T_c = 2200$ K, $T_A = 4200$ K, $B = 1$, $T_D = 10\,500$ K ($E_D \approx 0.9$ eV), $\nu = 10^{12}$ s^{-1}. For these parameters $n_0 = 6.25 \times 10^{14}$ cm^{-2} and $V_0 = 1.56 \times 10^{26}$ cm^{-2} s^{-1}. At $T = 600$ K and $V = 2 \times 10^{10}$ cm^{-2} s^{-1} we get $n_e = 6.5 \times 10^{-4} n_0 = 4.1 \times 10^{11}$ cm^{-2}, $\Phi_c = 0.797$, $F(\Phi_c) = 15.4$, $\Gamma_c = 12$ and $Q = 167$. The time to reach the equilibrium concentration $t_\infty = 20.5$ s, and the critical time $t_c = 37$ s. After the end of the nucleation stage in the overcritical concentration range the adatoms reach the surface density $N_{max} = 1.7 \times 10^8$ cm^{-2}. The average size of overcritical islands at $\Phi_0 = 1.5\Phi_c$ is 21.6 nm. The dependences of island size and density on the maximum ideal supersaturation in the system at different values of temperature and material flux for these parameters are presented in figures 1–4.

Figure 1 illustrates the typical temperature behaviour of island density. It is seen that at higher temperatures the nucleation under the material flux starts at lower critical supersaturation and the resulting density of overcritical islands is quite low. At lower temperatures the nucleation process requires higher critical supersaturation while the density of islands rapidly increases. Graphs of figure 2 present the dependence of average island size on ideal supersaturation at different temperatures. The size of relaxed islands rapidly decreases with the concentration of material in the system in the subcritical range, reaches its minimum at the critical concentration and then slowly increases with further increase in concentration. The size of overcritical islands strongly increases with the temperature.

The dependences of island size on ideal supersaturation at fixed growth rate and different temperatures *convert* in the near-critical range, indicating the transition from the thermodynamically to the kinetically controlled regime of nucleation in a materially open system.

As illustrated by the graphs in figure 3, at lower material flux into the system the nucleation starts earlier; however, the density of overcritical islands is smaller. With increasing flux the $N(\Phi_0)$ curves become steeper, the nucleation starts at higher critical concentration and the resulting density in the overcritical concentration range is larger.
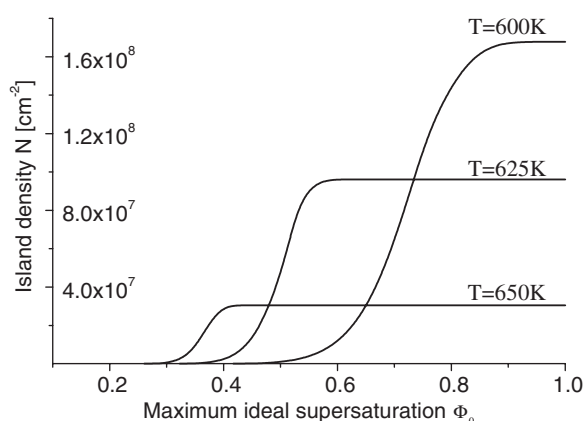
Figure 1. Dependences of island density on the ideal supersaturation at constant material flux $V = 2 \times 10^{10}$ cm^{-2} s^{-1} and three different temperatures for the model parameters described in the text. The critical concentration Φ_c amounts to 0.797, 0.531 and 0.387 at $T = 600$, 625 and 650 K respectively.
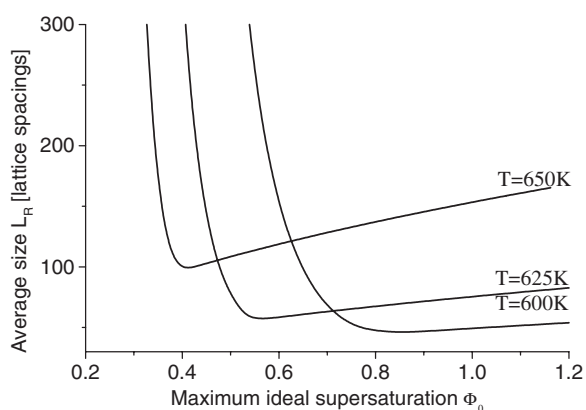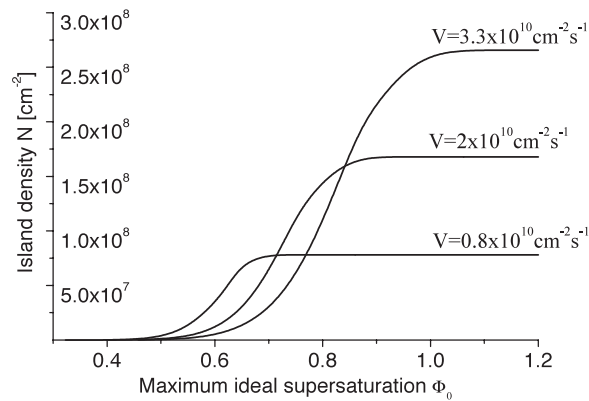

Figure 2. Dependences of average size of relaxed islands on the ideal supersaturation at constant flux $V = 2 \times 10^{10}$ cm^{-2} s^{-1} and three different temperatures.

Figure 4 shows that the average size of relaxed islands is flux independent in the subcritical range and considerably decreases with increasing flux in the overcritical range. The dependence on ideal supersaturation is qualitatively the same as in figure 2. The size and density diagrams at fixed temperature and varying growth rate *split* in the near-critical range, thus indicating the transition to the kinetically controlled regime of nucleation at a larger concentration of material. The presented diagrams provide a characterization of island ensembles depending on the control parameters T, V and Φ_0 at the initial stage of nucleation and independent growth of islands.

5. Conclusions

The presented study shows an important difference in the behaviour of island ensembles below and above a certain critical concentration of material introduced into the system. It is shown that in the subcritical concentration range the structure of the island ensemble is thermodynamically

Figure 3. Dependences of island density on the ideal supersaturation at constant temperature $T = 600$ K and three different values of material flux. The critical concentration Φ_c amounts to 0.646, 0.797 and 0.916 at $V = 0.8$, 2 and 3.3×10^{10} cm^{-2} s^{-1} respectively.
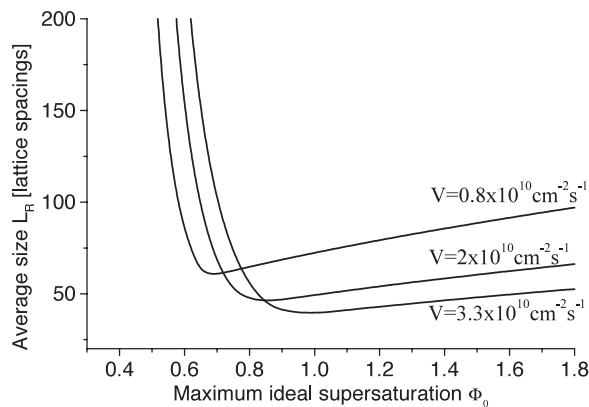
Figure 4. Dependences of average size of relaxed islands on the ideal supersaturation at constant temperature $T = 600$ K and three different values of material flux.

controlled, while in the overcritical range the structure is primarily determined by the growth kinetics. Therefore, the temperature, material flux and total concentration dependences of island size and density exhibit principally different behaviours at $n_{max} < n_c$ and $n_{max} > n_c$, as demonstrated by the obtained analytical formulae and the diagrams presented in figures 1 and 2. The use of a specific form of island formation energy and island growth function within the frame of the LG model is not critical for the general conclusions. Other choices of these functions will bring some new numbers in; however, the described behaviour of island ensembles will remain qualitatively the same. It is important that the presented approach also enables us to obtain the value of critical concentration as a function of the energetic parameters and temperature of the system. The presented approach can be modified to include the description of island size distribution [4, 12] and in particular to find the size distribution width at different conditions. One of the examples of critical concentration is the critical thickness of a wetting layer in strained heteroepitaxial systems relating to the transition from 2D to 3D growth [4], a value that can be controlled experimentally with high accuracy [6].

It should be pointed out that the described behaviour of the system is valid only for the initial stage of growth when the islands are small and the ensemble is dilute. Further evolution of the island ensemble during the first order phase transition in the materially open system will depend on the character of island–island interactions in the system. The obtained solutions for island size and density provide the relevant initial condition for the description of later stages of evolution towards the global equilibrium state of the system. Also, the presented results demonstrate the possibility of a kinetically controlled engineering of island ensembles with the desired structural properties by an appropriate choice of growth conditions (temperature and material flux) and the effective concentration of material introduced into the system.

Acknowledgments

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