

Growth rate of a crystal facet of arbitrary size and growth kinetics of vertical nanowiresVladimir G. Dubrovskii^{1,*} and Nickolai V. Sibirev²¹*Ioffe Physical Technical Institute of the Russian Academy of Sciences, Politekhnikeskaya 26, 194021, St. Petersburg, Russia*²*Institute for Analytical Instrumentation of the Russian Academy of Sciences, 190083 Rizhsky prospekt 26, St. Petersburg, Russia*

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We present a modification of the Kolmogorov-Johnson-Mehl-Avrami crystallization model to the case of a finite size crystal facet growing layer by layer. A general expression for the facet growth rate is derived that provides an asymptotic matching to the known limit cases of very small and very large facets. The derived expression is applied to the study of the growth kinetics of vertical nanowires in the “vapor-liquid-solid” growth mechanism. The presented model generalizes the Givargizov-Chernov theory of whisker growth, shows why the whiskers grow much faster than the nonactivated surface, and gives the dependence of the growth rate of nanowires on the diameter of drop of liquid alloy and the growth conditions.

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I. INTRODUCTION

Crystal growth from vapors and liquid alloys has been studied extensively because of a key role of composite structures in modern microelectronics and optoelectronics. The growth process consists of many stages, including the nucleation of islands, their independent growth, coalescence, formation of a continuous film surface, and its further time evolution [1]. In many technologically important cases crystals grow layer by layer so that the islands are formed two dimensionally and the lateral growth of each layer starts only when the formation of a previous layer is fully completed [2]. The driving force for the growth process is the metastability of a condensing phase: the supersaturation of a two-dimensional “vapor” of adatoms or a liquid alloy. Applying classical nucleation theory to the description of two-dimensional island formation, one can find expressions for the island nucleation rate I and lateral growth rate of islands v as the functions of the supersaturation, the energetics of a particular deposit-substrate system and the kinetic parameters of elementary processes on the surface [1]. One of the most important characteristics of the growth process is the normal growth rate dH/dt , where H is the height of crystal. In layer-by-layer growth, dH/dt is a certain function of I , v , and facet linear size R [3]. When R is very large, the normal growth rate is R independent. In this case $dH/dt=f(I,v)$ can be found from the well known model proposed by Kolmogorov [4], Johnson and Mehl [5], and Avrami [6] (KJMA model), which has been used extensively in the theory of crystal growth [3,7–9], alloy solidification [10], monolayer film formation [11], and many other growth processes.

Recently, however, there has been an increasing interest towards the growth of crystals of nanometer lateral sizes, in particular vertical nanowires (VNW's) (or nanowhiskers) [12–14]. VNW's are grown by the “vapor-liquid-solid” (VLS) mechanism first described by Wagner and Ellis [15]. The lateral size of the whisker is usually determined by the diameter of a droplet of a liquid catalyst. Since typical lateral

size of a growing facet is only several tens of nanometers, the size dependent effects come into play and the R behavior of the vertical growth rate should be carefully investigated. It should be noted here that in the case of a very small facet the growth rate is also easily determined [3]. The purpose of this paper is to present a generalized expression for $dH/dt=f(I,v,R)$ that is valid for arbitrary values of I , v , and R and provides an asymptotic matching to the known results in the limit cases of very small and very large facet. The obtained results will be applied to studying the growth kinetics of VNW's. The presented kinetic model considerably generalizes the known Givargizov-Chernov (GC) theory [16] and answers a number of important questions concerning the mechanisms of whisker formation by the VLS mechanism.

II. GENERALIZED KJMA MODEL AND THE GROWTH RATE OF CRYSTAL FACET

Consider a crystal facet of radius R , growing due to the nucleation of two-dimensional disc-shaped islands of monolayer (ML) height and of radius r . If the consumption of atoms of a condensing phase goes through the island boundary [1,3,11,17], the lateral growth rate of overcritical islands $v=dr/dt$ does not depend on r . The nucleation theory shows that normally the critical size of islands is much smaller than the technologically interesting range [1,3,7–11,17]. Therefore the islands can be assumed to arise with zero size. If I and v are time independent, the characteristic time between two consecutive birth processes on the facet surface is given by $t_b=1/\pi R^2 I$, and the time required for a nuclei to cover the facet area is given by $t_g=R/v$. The ratio of these two characteristic times gives the nondimensional control parameter

$$\alpha \equiv \frac{\pi R^3}{v}. \quad (1)$$

At $\alpha \ll 1$ ($t_g \ll t_b$) a single nuclei covers the whole facet before the next nuclei is formed. This condition relates to the so-called monocenter regime of nucleation [3]. The normal growth rate (measured in the number of ML per unit time) $dH/dt=\pi R^2 I$ is v independent. In the opposite case of α

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$\gg 1$ ($t_g \gg t_b$) many islands arise in one layer and then grow and coalesce to form a continuous ML. The normal growth rate in this case is found from the KJMA formula for the crystallized fraction of facet [3,7–11]

$$g(t) = 1 - \exp \left[-\pi \int_0^t d\tau I(\tau) r^2(\tau, t) \right], \quad r(\tau, t) = \int_\tau^t dt' v(t'), \quad (2)$$

where $r(\tau, t)$ is the current radius of nuclei born at time τ . The KJMA formula is valid under the following assumptions [4]: (a) Poissonian nucleation process, (b) nucleus growing with fixed geometrical shape and orientation, (c) nuclei growth rate $v(t)$ depending only on t , (d) solidlike coalescence, (e) space homogeneity of the system, and (f) the absence of boundaries. Since Eq. (2) applies to the case of an infinitely large facet, the resulting growth rate is R independent. At $I = \text{const}, v = \text{const}$ the coverage $g(t) = 1 - \exp(-\pi v^2 I t^3/3)$ and therefore $dH/dt = (\pi v^2 I/3)^{1/3}$. Summarizing, the expressions for dH/dt in the two known cases of monocenter and polycenter nucleation are given by [3]

$$dH/dt = \begin{cases} \pi R^2 I, & \alpha \ll 1, \\ (\pi v^2 I/3)^{1/3}, & \alpha \gg 1. \end{cases} \quad (3)$$

The simplest way to introduce the boundary effect into the KJMA scheme is to write Eq. (2) in the form

$$g(t) = 1 - \exp \left[-\int_0^t d\tau I(\tau) S(\tau, t, R) \right] \quad (4)$$

with the effective crystallized area of facet $S(\tau, t, R)$ defined as

$$S(\tau, t, R) = \frac{1}{\pi R^2} 2\pi \int_0^R d\rho \rho S(\tau, t, \rho, R). \quad (5)$$

Here $S(\tau, t, \rho, R)$ is the area of the facet covered by the time t by the nuclei formed at time τ at distance ρ from the facet

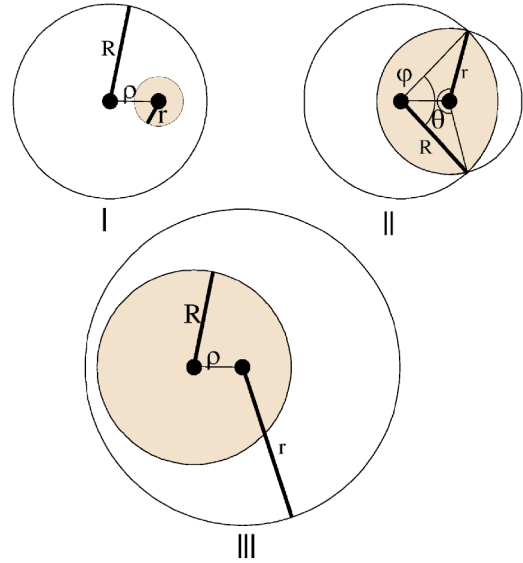


FIG. 1. Three possible geometrical situations for finding the transformed area $S(r, \rho, R)$ (shown dark). In case I the facet is considerably larger than the nuclei and the transformed area equals the nuclei area πr^2 irrespective of facet radius R and position ρ . In case III the facet area is small and the transformed area equals the total facet area πR^2 irrespective of nuclei radius r and position ρ . In case II the facet and island sizes are comparable to each other and the transformed area depends on r, ρ , and R .

center (the transformed area) [4]. The integration in Eq. (5) is taken over the whole facet area. Equations (4) and (5) are certainly approximate, because we use the averaged value of $S(\tau, t, \rho, R)$ instead of the direct introduction of the boundary effect into Eq. (4) [18]. The function $S(\tau, t, \rho, R)$ depends on τ and t via the radius of nuclei $r(\tau, t)$ which remains the same as defined in Eq. (2). Three possible geometrical situations for finding $S(r, \rho, R)$ at different values of r, ρ , and R are illustrated by Fig. 1. The formulas for $S(r, \rho, R)$ in these three cases are given by

$$S(r, \rho, R) = \begin{cases} \pi r^2, & r \leq R - \rho, \\ R^2(\theta/2 - \sin \theta/2) + r^2(\varphi/2 - \sin \varphi/2), & R - \rho < r < R + \rho, \\ \pi R^2, & r \geq R + \rho, \end{cases} \quad (6)$$

where $\theta = 2 \arccos[(R^2 + \rho^2 - r^2)/2R\rho]$ and $\varphi = 2 \arccos[(r^2 + \rho^2 - R^2)/2r\rho]$. Obviously, case I in Fig. 1 corresponds to polycenter and case III to monocenter nucleation while case II describes the transition between the two limit regimes.

In principle, the substitution of Eq. (6) into Eq. (5), further integration of Eq. (5), and using the result in Eq. (4) allows us to find the characteristic time of ML formation and therefore the normal growth rate of the facet. However, the presented expressions are not of friendly form due to the presence of reverse trigonometric functions. A detailed analysis of Eqs. (5) and (6) shows that the numerical result

for $S(\tau, t, R) = S[r(\tau, t), R]$ can be approximated with high accuracy by the power function of the form

$$S(y, R) = \begin{cases} \pi R^2 [y^2 - (3/8)y^3 - (1/16)y^4 + (1/32)y^5], & y \leq 2, \\ \pi R^2, & y > 2, \end{cases} \quad (7)$$

where $y(\tau, t) = r(\tau, t)/R$. The comparison between the numerical result for $S(y, R)$ obtained from Eqs. (5) and (6) and

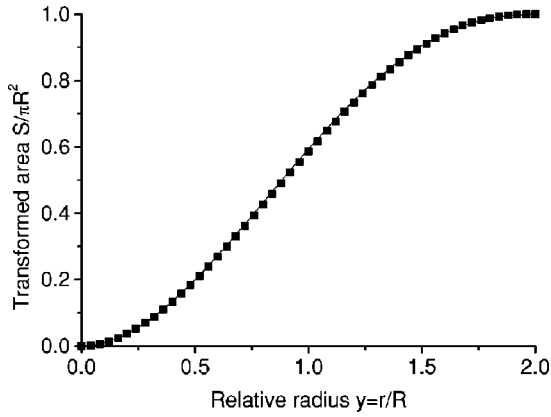


FIG. 2. Comparison between the numerical solution for the transformed area obtained from Eqs. (5) and (6) (black squares) and the power function defined by Eq. (7) (solid line).

the approximation given by Eq. (7) is shown in Fig. 2.

At constant I and v the use of Eq. (7) in Eq. (4) gives the generalized KJMA exponent

$$g(t) = g(y) = 1 - \exp[-\alpha f(y)]. \quad (8)$$

Here $y(t) = r(0, t)/R = vt/R$, $\alpha = \text{const}$ is defined in Eq. (1) and

$$f(y) = \begin{cases} (1/3)y^3 - (3/32)y^4 - (1/80)y^5 + (1/192)y^6, & y \leq 2, \\ y - 0.9, & y > 2. \end{cases} \quad (9)$$

The time dependencies of coverage g obtained from Eqs. (8) and (9) at fixed I and v and different values of facet radius R are presented in Fig. 3. The curve at $\alpha = 10^5$ presents the usual Kolmogorov exponent in the polycenter mode, the curve at $\alpha = 1$ corresponds to an intermediate mode, and the curve at $\alpha = 0.125$ presents the situation when the size associated effects become dominating. Figure 3 demonstrates that at the same growth conditions (I and v) smaller facets grow considerably slower than the larger ones.

The normal growth rate of facet is given by

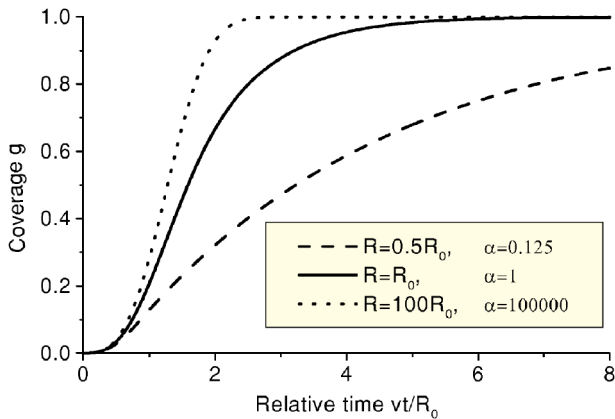


FIG. 3. Dependencies of coverage g on the relative time vt/R_0 , $R_0 = (v/\pi I)^{1/3}$ at three different facet radii R relating to different values of parameter α .

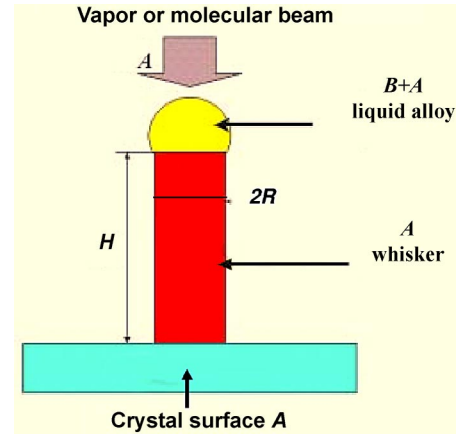


FIG. 4. Cylindrical whisker of material A of radius R and height H grown on the crystal surface of material A activated by the drops of liquid alloy $B+A$.

$$dH/dt = \frac{v}{Ry_*(\alpha)}. \quad (10)$$

Quantity $y_*(\alpha)$ is the solution to the transcendent equation

$$\alpha f(y) = 1 \quad (11)$$

that determines the characteristic time of ML formation.

The asymptotic matching of the obtained results to the known limit regimes [3] is obvious. At small $\alpha f(y) \approx y \gg 1$ and therefore $y_* \approx 1/\alpha$, while at large $\alpha f(y) \approx y^3/3 \ll 1$ and $y_* \approx (3/\alpha)^{1/3}$. From here Eq. (10) is immediately reduced to Eqs. (3) in both limit cases. It can be shown that Eqs. (7)–(11) remain valid for an arbitrary convex geometry of islands if we replace πR^2 to cR^2 , where R is a certain linear size of island and c the shape constant such that the island area $S = cR^2$.

III. KINETIC MODEL OF VNW GROWTH

The typical procedure of the VLS growth [12–16] of whiskers is shown schematically in Fig. 4. First, the catalyst B (e.g., Au) is deposited onto a crystal substrate of material A (e.g., Si, GaAs), then the substrate is transferred to a growth chamber and annealed before the whiskers are grown. Annealing leads to the formation of drops of eutectic liquid alloy $B+A$ (e.g., Au+Si or Au+GaAs) on the substrate. The deposition of material A from the vapor phase or molecular beam makes the alloy supersaturated. The whisker grows due to the crystallization of supersaturated alloy on the crystal surface under the drop.

Experiments [3,12–16] show that Si, GaAs, and InP whiskers at typical growth temperatures grow layer by layer. Since the initial eutectic drops usually have a broad size distribution and the whisker lateral size is usually of the order of the size of drop, the size dependence of whisker growth rate has been studied experimentally in many systems [3,12,16]. The known GC model provides the following expression for the whisker growth rate [16]:

$$dH/dt = K \left[\Delta\mu_v^0 - \frac{2\Omega_s\gamma_{sv}}{k_B T R} \right]^2 \equiv K\Delta\mu_v^2. \quad (12)$$

Here $\Delta\mu_v^0$ is the difference of chemical potentials of atoms A in the vapor and solid phases (in $k_B T$ units, T is the substrate temperature during the whisker growth and k_B the Boltzmann constant) for the planar interfacial boundary, γ_{sv} is the surface energy of the solid - vapor boundary (per unit area), Ω_s is the volume per atom in the crystal, and K is an unknown coefficient of crystallization from the liquid alloy. The second term in the square brackets on the right-hand side of Eq. (12) arises due to the curvature of the whisker surface. Equation (12) qualitatively explains the experimentally observed increase in the whisker growth rate with an increase of the size of the droplet and the existence of a certain minimum size of droplet R_{\min} below which the whiskers cannot grow [3,12–14,16]. However, the GC model was proposed to describe the case of polycenter nucleation ($\alpha \gg 1$). This assumption looks quite reasonable for the typical whiskers of several microns width of the 1970's but is not necessarily true for modern VNW's with about 100 times smaller widths. Also, the GC model is not capable of explaining the quadratic dependence of the growth rate on the effective metastability of the vapor phase $\Delta\mu_v = \Delta\mu_v^0 - 2\Omega_s\gamma_{vs}/k_B T R$ [this dependence in Eq. (12) is simply the expression fitting the experimental curves [3,16]] and of finding the crystallization coefficient K . In particular, it is still unclear exactly why whiskers grow much faster than the nonactivated parts of surface. This question for the VNW is even more urgent because the results of the previous section show that the whisker growth rate decreases with decreasing lateral size. In order to study these questions, below we develop a self-consistent kinetic model of VNW growth.

The free energy of formation of a two-dimensional disc-shaped island of i atoms A from the supersaturated alloy (in $k_B T$ units) reads [1,3]

$$F_i = 2(ai)^{1/2} - \Delta\mu_i i. \quad (13)$$

Here $a \equiv \pi\sigma(\varepsilon_{ls}/k_B T)^2$, ε_{ls} is the interfacial energy of the liquid-solid boundary per unit length and σ is the surface area per atom in a ML. The difference of chemical potentials of atoms A in the alloy and in the crystal $\Delta\mu_l$ depends on the radius of droplet R due to the Gibbs-Thomson effect [16] similarly to Eq. (12)

$$\Delta\mu_l = \ln(1 + \zeta) - \frac{R_c}{R}. \quad (14)$$

Here $R_c = 2(\Omega_s\gamma_{sv} - \Omega_l\gamma_{lv})/k_B T$ is the characteristic radius determined by the difference of surface energies of solid-vapor (γ_{sv}) and liquid-vapor (γ_{lv}) boundaries and Ω_l is the volumes per atom in the liquid phase. For simplicity we assume that the whisker is a cylinder with the radius of droplet R and that the contact angle of drop amounts to 90° . In this case the curvature of the drop surface equals the curvature of the whisker. The supersaturation of liquid alloy ζ depends on the volume concentration C of atoms A in the alloy. In the case of a dilute alloy $\zeta = C/C_{\text{eq}} - 1$, C_{eq} being the equilibrium concentration of alloy. In fact, Eqs. (13) and (14) have a slightly

different physical sense than the corresponding Eq. (12) of the GC model. First, the driving force of the phase transition in Eq. (13) is the supersaturation of the liquid alloy, not the vapor supersaturation as in Eq. (12), because the condensing phase in the VLS growth mechanism is definitely the liquid. Second, Eq. (14) accounts for the curvature of the whisker and drop surface, while Eq. (12) only accounts for the curvature of the whisker surface (since γ_{sv} is normally 5–6 times larger than γ_{lv} and $\Omega_s \approx \Omega_l$, the difference here is not dramatic). From Eq. (13) follows the expressions of the classical nucleation theory [1] for the critical size i_c , nucleation barrier F , and the reverse width of formation energy in the near-critical range $i_c = a/\Delta\mu_l^2$, $F \equiv F(i_c) = a/\Delta\mu_l$, $-F''(i_c) = \Delta\mu_l^3/2a$. Following the standard procedure [1,3,11,17], assuming that the atoms from the liquid phase are attached by the monoatomic step of the island boundary, utilizing the Zeldovich formula for the nucleation rate and the balance equation for the growth rate of overcritical islands, one obtains

$$v = \frac{l_s}{\tau_D} \zeta, \quad I = \frac{1}{\pi l_s^2 \tau_D} (1 + \zeta) \sqrt{\frac{a}{\pi} \Delta\mu_l} \exp\left[-\frac{a}{\Delta\mu_l}\right]. \quad (15)$$

Here $l_s = (\sigma/\pi)^{1/2}$ is the linear size of the adsorption site and $\tau_D = \exp[(E_D + E_B)/k_B T]/\nu\Omega_l C_{\text{eq}}$ is the characteristic time of lateral growth of islands, where E_D is the activation energy for diffusion in the liquid alloy, E_B is the activation energy for the attachment to the monoatomic step and ν is the frequency of thermal vibrations in the liquid [3]. From Eq. (15) it follows that the lateral growth rate of islands is proportional to ζ and that the nucleation function obeys an extremely steep exponential dependence on $\Delta\mu_l$. From Eqs. (1) and (15) the function $\alpha(\zeta)$ in the case of VNW growth is given by

$$\alpha(\zeta) = d^3 \left(\frac{1 + \zeta}{\zeta} \right) \sqrt{\frac{a}{\pi} \Delta\mu_l} \exp\left(-\frac{a}{\Delta\mu_l}\right), \quad (16)$$

$$\Delta\mu_l = \ln(1 + \zeta) - \frac{d_c}{d},$$

where $d = R/l_s$ and $d_c = R_c/l_s$ are the lateral size of the whisker and the characteristic size R_c in units of lattice spacing l_s .

In order to find the supersaturation ζ we use the equation of material balance in the drop

$$\frac{2}{3} \pi R^3 \frac{dC}{dt} = 2\pi R^2 \chi J - 2\pi R^2 \frac{l_a C}{\tau_A} - \pi R^2 \frac{h}{\Omega_s} dH/dt. \quad (17)$$

The first term on the right-hand side of Eq. (17) represents the number of atoms A coming from the vapor phase to the drop per unit time, the second term, the number of desorption acts from the drop surface, and the third term, the number of atoms transformed from liquid to solid phase. In Eq. (17) J is the material flux from the vapor phase, χ is the effective adsorption coefficient, $l_a \approx l_s$ is the interatomic distance in the liquid phase, h the height of a ML ($\Omega_s = h\sigma$), and $\tau_A = \nu^{-1} \exp(E_A/k_B T)$ is the lifetime of atoms A in the surface layer of drop, E_A being the corresponding activation energy

for desorption. In Eq. (17) we neglect the gradients of concentration C within the droplet volume. The steady-state Eq. (17) for ζ in view of Eqs. (10), (14), and (16) can be represented in the form

$$\Phi - \zeta = \frac{b}{d} \frac{\zeta}{y_*[\alpha(\zeta)]}. \quad (18)$$

Here the value of $y_*(\alpha)$ is still defined by Eq. (11), where α is given by Eq. (17), $\Phi = \chi\tau_A J / l_a C_{\text{eq}} - 1$ is the supersaturation of vapor phase determined by the balance of adsorption-desorption processes on the drop surface, and $b = (h/l_a \Omega_s C_{\text{eq}})(\tau_A/\tau_D)$ is the nondimensional parameter containing the ration between the characteristic lifetime of atoms on the drop surface and the characteristic time of island growth. In the chemical vapor deposition and molecular beam epitaxy techniques the quantity Φ is the technologically controlled parameter. From Eqs. (10) and (18), the growth rate of VNW is proportional to the difference between the supersaturations in vapor and liquid phases

$$dH/dt = \beta(\Phi - \zeta), \quad (19)$$

where $\beta = l_a \Omega_s C_{\text{eq}} / h \tau_A$. Equation (18) together with Eq. (16) allows us to find the stationary supersaturation of liquid alloy ζ and then to obtain the VNW growth rate from Eq. (19). The value of ζ is controlled by five parameters: the supersaturation of vapor phase Φ , the GC characteristic size d_c , the energetic parameter a , the kinetic parameter b , and the whisker diameter d .

IV. RESULTS AND DISCUSSION

The model of VNW growth leads to several general conclusions concerning the mechanisms of VNW formation. First, similarly to the GC theory, the minimum radius of growing VNW is given by $R_{\min} = R_c / \ln(1 + \Phi) \propto 1/T \ln(J/J_0)$, approximately decreasing the reverse proportional to the growth temperature and logarithmically with increasing the material flux onto the surface.

Second, it is well known [3,16] that the two potential candidates for the limiting process of the VLS growth are the processes at the gas-liquid (unlikely case) and liquid-surface (likely case) boundaries. Equation (19) shows that in the unlikely case of gas-liquid limitation of the VNW growth ($\Phi \gg \zeta$) the growth rate is determined simply by the balance of adsorption-desorption processes on the liquid surface: $dH/dt = (\chi\Omega_s J - l_a \Omega_s C_{\text{eq}}/\tau_A)/h$. A higher growth rate of whiskers in this case can be explained only by a better adsorption and slower desorption from the liquid surface or by a more efficient chemical reaction near the liquid surface.

In the likely case of liquid-solid limitation of the VNW growth the supersaturation of alloy is smaller but comparable to the supersaturation of vapor $\Phi \sim \zeta$ [16]. Due to steep exponential dependence of nucleation rate on $\Delta\mu_l$ Eq. (16) for $\alpha(\zeta)$ can be presented in the form [17]

$$\alpha(\zeta) = \alpha(\Phi) \exp[-\Gamma(\Phi - \zeta)]. \quad (20)$$

The large parameter of classical nucleation theory [1] $\Gamma = -(\partial F/\partial \zeta)|_{\zeta=\Phi} = i_c(\Phi)/(\Phi+1) \gg 1$ is of the order of critical

size of classical nucleation theory at $\zeta = \Phi$. Using Eq. (20) in Eqs. (18) and (19), the definition for the parameter Γ and introducing the new function $x \equiv \Gamma(\Phi - \zeta)$ we obtain the growth rate of VNW in the form

$$dH/dt = \frac{\chi\Omega_s J}{h} \frac{\Delta\mu_v^2}{a} x. \quad (21)$$

Similarly to Eq. (12) $\Delta\mu_v = \ln(1 + \Phi) - d_c/d$ is the difference of chemical potentials of atoms A in the vapor and solid phases. The function x is determined by the self-consistent equation

$$xy_*[\alpha(\Phi)e^{-x}] = \left(\frac{\Phi}{1 + \Phi}\right) \frac{b}{d} \frac{a}{\Delta\mu_v^2}. \quad (22)$$

Equations (21) and (22) are valid at $x \ll 1$ and $x \sim 1$. Equation (22) can be easily analyzed for the two limit cases of small and large facets. At $\alpha \ll 1$ and $\alpha \gg 1$ Eq. (22) is reduced to

$$xe^x = U \exp(-a/\Delta\mu_v), \quad \alpha \ll 1, \quad (23)$$

$$(x/3)e^{x/3} = V \exp(-a/3\Delta\mu_v), \quad \alpha \gg 1 \quad (24)$$

with $U = d^2(b/\sqrt{\pi})(a/\Delta\mu_v)^{3/2}$ and $V = (b/3^{4/3} \pi^{1/6}) \times (a^{7/6}/\Delta\mu_v^{11/6})[\Phi/(1 + \Phi)]^{2/3}$. Solution to the equation $xe^x = W$ beginning from $W \sim e$ becomes $x = \ln W$. Therefore, the growth rate of VNW at intermediate values of droplet size can be presented in the form

$$dH/dt = \frac{\chi\Omega_s J}{h} \left[\ln U \frac{(k_B T)^2}{\pi\sigma\varepsilon_{ls}^2} \Delta\mu_v^2 - \Delta\mu_v \right], \quad \alpha \ll 1, \quad (25)$$

$$dH/dt = \frac{\chi\Omega_s J}{h} \left[3 \ln V \frac{(k_B T)^2}{\pi\sigma\varepsilon_{ls}^2} \Delta\mu_v^2 - \Delta\mu_v \right], \quad \alpha \gg 1, \quad (26)$$

where we used the definition for the parameter a to explicitly present the major dependence of dH/dt on the interfacial energy ε_{ls} . Neglecting weak logarithmical dependencies on U and V , Eqs. (25) and (26) give approximately quadratic dependence of the whisker growth rate on $\Delta\mu_v$. This justifies the main assumption of the GC model [16] given by Eq. (12). The derived expressions contain the linear term in $\Delta\mu_v$, however, at larger vapor supersaturations the quadratic term dominates. The GC formula follows exactly from Eq. (21) at $x=1$.

The presented kinetic model also gives the value of the kinetic coefficient of crystallization from the liquid alloy. Equations (25) and (26) show that it is approximately reverse proportional to the squared interfacial energy of the liquid-solid boundary. This dependence holds in both limit cases of very small and very large drop size. Assuming that the supersaturation of adatoms on the nonactivated parts of the substrate surface is close to Φ , for the intermediate drop sizes d [$\ln(U/V) \sim 1$] the ratio of whisker height H_w (grown by the VLS mechanism) and the height of nonactivated surface H_s (grown by the conventional vapor-solid mechanism) is given by

$$H_W/H_S \approx \frac{1}{3} \frac{\chi_{vl}}{\chi_{vs}} \left(\frac{\varepsilon_{vs}}{\varepsilon_{ls}} \right)^2, \quad \alpha \ll 1, \quad (27)$$

$$H_W/H_S \approx \frac{\chi_{vl}}{\chi_{vs}} \left(\frac{\varepsilon_{vs}}{\varepsilon_{ls}} \right)^2, \quad \alpha \gg 1. \quad (28)$$

In these equations we take into consideration that the nucleation on the nonactivated surface is always polycenter. The ratio H_W/H_S contains an obvious ratio of adsorption coefficients on liquid (χ_{vl}) and solid (χ_{vs}) surface and a less obvious squared ratio of interfacial energies of vapor-solid (ε_{vs}) and vapor-liquid (ε_{ls}) boundaries. The height of small whiskers grown in the monocenter mode is at least three times smaller than that of larger ones. The whiskers grow faster than the nonactivated surface because of the lower energy of the liquid-solid boundary so that at given vapor supersaturation it is easier to form the nuclei from the liquid alloy, the explanation previously discussed by Givargizov [16]. Our results provide the formula for the growth rate of whiskers and show that its dependence on the interfacial energy within the range of parameters is approximately reverse squared. Taking for an estimate the typical values $\varepsilon_{vs}/\varepsilon_{ls}=5-6$, even at the same adsorption coefficients the ratio of whisker/surface growth rates will be ~ 10 for the small and ~ 30 for the large drop size.

Figure 5 compares the numerical solution of Eqs. (11), (16), (18), and (19) for the whisker growth rate with the KJMA result for the infinite facet area at the same growth conditions. It is seen that the finite size of growing whisker considerably decreases the growth rate and changes the shape of the curve. Both curves, however, provide the same value for the minimum diameter of drop at which the growth rate goes to zero. They also go to the same asymptotic value at $D \rightarrow \infty$ when the growth is controlled by the transport of atoms through the vapor-liquid interface. Figure 5 demonstrates a reasonable fit to the experimental results for the GaAs VNW and shows the significance of size-dependent effects in the whisker growth process.

In conclusion, the model described here is the first (to the best of our knowledge) that can systematically handle the growth kinetics of crystal facets of arbitrary size and the size dominated effects beyond the limits of the KJMA model. The model was applied to the study of the growth of VNW's in

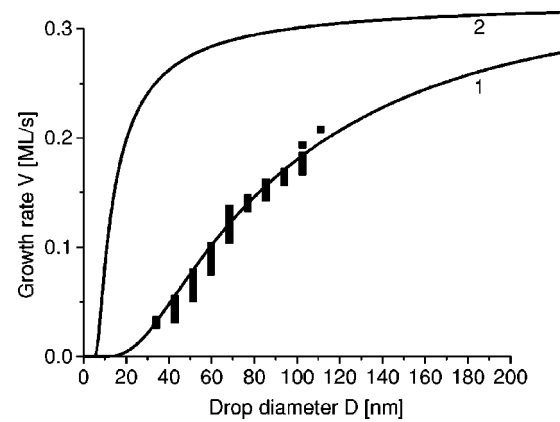


FIG. 5. Dependences of the growth rate of VNW on the drop diameter. Line 1 is calculated by means of Eqs. (11) and (16)–(19) at $b=33, \Phi=3, \beta=0.35$ ML/s, $a=15$, and $R_c=2.5$ nm. Line 2 corresponds to the pure polycenter regime of nucleation at the same conditions. The black rectangles represent the experimental data obtained from the analysis of scanning electron microscopy images of GaAs VNW. The VNW's were grown on the GaAs(111)B surface activated by the 2.5 nm Au layer annealed at 610 °C, the amount of deposited GaAs was 200 nm, the growth temperature 550 °C, and the growth rate of GaAs 0.4 ML/s [19].

the VLS mechanism. The self-consistent kinetic model accounts for the material balance in the drop of the liquid alloy. As a result, the formula for the whisker growth rate was obtained which shows why the growth rate within the range of parameters approximately obeys quadratic dependence on the vapor metastability, why the whiskers grow much faster than the nonactivated surface and how the growth rate depends on the size of drop and the growth conditions.

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