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Nonlinear equation for diffusion and adatom interactions during epitaxial growth on vicinal surfaces

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We present a continuum model for growth on vicinal surfaces that incorporates an approximation to adatom interactions in the form of diatomic island formation. The resulting nonlinear-diffusion equation is then integrated numerically to obtain the adatom- and diatomic-island-concentration profiles along the terrace. It is shown that due to the inclusion of adatom interactions, the model is applicable to molecular-beam epitaxy (MBE) on vicinal surfaces over a wide range of growth temperatures, beam fluxes, and terrace-misorientation angles. Furthermore, a natural outcome of the model is the identification of the transition temperature T_c, at which island formation may be neglected and epitaxial growth proceeds predominantly by step propagation. The excellent agreement between the value of T_c determined by the nonlinear model and those obtained from both Monte Carlo simulations and measurements on vicinal GaAs(001) surfaces for different Ga and As_2 fluxes shows that the inclusion of adatom interactions is an essential ingredient of a realistic model of MBE growth on misoriented surfaces.

I. INTRODUCTION

Vicinal (stepped) crystal surfaces, with a misorientation angle of a few degrees, are frequently used as substrates for growth of semiconductor heterostructures by molecular-beam epitaxy (MBE).[1,2] Furthermore, studies of growth on vicinal surfaces as a function of substrate temperature and beam fluxes have provided insights into the fundamental growth kinetics of MBE, as well as providing a framework within which to estimate the parameters characterizing the underlying microscopic kinetics.[3] Specifically, measurements of the temporal profiles of reflection high-energy electron-diffraction (RHEED) specular intensity oscillations during MBE of vicinal GaAs(001) have shown the growth mode to be strongly temperature dependent.[3] At low temperatures, an oscillating RHEED intensity suggests growth by the formation and coalescence of two-dimensional islands on terraces, while at higher temperatures, an approximately constant RHEED intensity indicates growth by step propagation, with arriving adatoms incorporated directly into the step edges.

These observations, and the importance of understanding the physics of epitaxial growth, have rekindled interest in the pioneering theory of Burton, Cabrera, and Frank[4] (BCF) for near-equilibrium crystal growth on stepped surfaces. In the BCF theory, linear-diffusion equations are used to determine the step velocity and distribution of adatoms on terraces. Extensions of the BCF theory to MBE have included the influence of the moving step boundary,[5,6] important in semiconductor growth, where step velocities are high, and deviations from local equilibrium at the step edges, including the case of differing attachment rates from above and below the step.[7] In none of these treatments, however, were lateral interactions of adatoms on the terraces included in the calculations, although it was recognized that corrections to BCF theory due to adatom interactions would be substantial for growth under typical conditions found for MBE.[6,8] Indeed, experiments[3] and simulations[9,10] have shown island formation of atoms on the terraces to be a very important process which competes with adatom capture at the step edges, eventually causing a breakdown of the step-flow mode at low temperatures.

A model for MBE must include both the migration of adatoms on the substrate and the interaction among these adatoms in the form of incipient cluster formation. Atoms collide to form islands, which then form capture sites that compete with the step edges as sinks for the migrating adatoms. Collisions among atoms produce nonlinear sink terms in the effective-diffusion equation for single adatoms, while the capture and subsequent emission of adatoms from cluster and step edges produce nonlinearities in the form of a concentration-dependent diffusion constant. Consequently, either interactions have been neglected entirely, as in the BCF-based theories discussed above, or the problem of island formation alone on a flat surface has been tackled with kinetic rate equations.[11] Within the rate-equation approach, rates of island formation are given by gain and loss terms which are nonlinear in the adatom and island concentrations. However, this approach is applicable only to flat surfaces, since no spatial dependence of the adatom or island concentration is considered (this greatly simplifies the solution of the growth equations). However, in the presence of steps, a diffusion-controlled adatom-concentration gradient is present along the terraces.[4] Thus a growth model which includes the full physics must explicitly combine adatom diffusion (and thus a spatial concentration dependence) with the nonlinear island-formation terms, a task which, as far as we know, has not been previously attempted.

In this work, we improve on existing step-growth theories by incorporating a first-order approximation to lateral adatom interactions in the form of diatomic island formation. One of the important results of this approach is that the effective diffusivity of the adatoms is decreased by *several orders of magnitude* as a result of island formation. In this regard, our work shares some similarity with recent studies of diffusion on dynamically disordered lattices.[12–14] However, an important difference is that in our approach the diffusing adatoms participate directly in the fluctuations of the disorder (through island formation), while in Refs. 12–14, the dynamical disorder arises independently of the diffusing species, whose total concentration is therefore a conserved quantity. A second, more practical result to emerge from our analysis is the determination—directly from the nonlinear-diffusion equation—of the temperature beyond which growth proceeds predominantly by step advancement. This result, together with the considerable reduction in effective diffusivity, highlights the role of the nonlinear interactions responsible for island formation as an essential ingredient in a realistic model of MBE on vicinal surfaces.

The outline of this paper is as follows. In Sec. II we derive the effective-diffusion equation in the presence of island formation using the formalism of reaction-diffusion equations. This formulation provides a prescription for deriving formally exact master and Fokker-Planck equations from a given "reaction" sequence, from which the effective-diffusion equation for the average concentration may be easily obtained. Additionally, the formalism provides the flexibility to study fluctuations and the evolution of the full probability-distribution function with full account taken of the far-from-equilibrium nature of MBE. The extent to which an analytical solution is possible is discussed in Sec. III, where the full equation is solved numerically for the adatom- and island-concentration profiles along the terrace. We show that under typical MBE conditions island formation cannot be neglected, and that the inclusion of island formation in the growth equation is of similar or greater importance than corrections to BCF theory due to the moving boundary. Furthermore, as described in Sec. IV, we are able to predict the regime of growth conditions in MBE where island formation is likely to be significant. Estimates of the transition temperature beyond which epitaxial growth proceeds predominatly by step advancement and island formation may be neglected, and are compared to Monte Carlo simulations in Sec. V and measurements on vicinal GaAs(001) surfaces for different Ga and As_2 fluxes in Sec. VI. Our conclusions are summarized in Sec. VII.

II. GROWTH MODEL

One of the most concise ways to formulate the interplay between diffusion and island formation due to lateral interactions is through reaction-diffusion equations. Each step of the deposition and growth process is represented by a "reaction" that describes the rate-determining conversions of different "species" among one another. The advantages of this approach are threefold. Once the basic reaction sequence is formulated, master and Fokker-Planck equations can be derived by well-established techniques, and effective-diffusion equations for the average concentrations can be obtained easily. Additionally, the original master and Fokker-Planck equations also contain valuable information concerning the spatial and temporal dependence of the nonequilibrium fluctuations. Finally, this formulation is ideally suited to the far-from-equilibrium conditions of MBE, since no assumptions regarding equilibrium are made.

The substrate consists of a square lattice with a nearest-neighbor spacing of a. The boundary conditions are for the moment left unspecified, though for growth on a vicinal substrate, some combination of reflecting, absorbing, and periodic boundary conditions could be applied. The lattice is coarse grained into N square cells of size Λ (Fig. 1). Denoting incoming atoms from the molecular beam by A, substrate atoms by X, and diatomic islands by Y, the "reactions" describing the deposition and growth processes are

$$A \xrightarrow{k_0} X, \quad A+X \xrightarrow{k_1} Y, \quad 2X \xrightarrow{k_2} Y . \tag{1}$$

The first two reactions in (1) describe the deposition process, with the first reaction representing the deposition of atoms from the molecular beam onto the substrate, and the second reaction accounting for the direct collision of arriving atoms with substrate atoms. The third reaction represents the formation of diatomic islands by the coalescence of mobile substrate atoms. The reverse reactions in each could be included and would correspond, respectively, to evaporation of single adatoms, evaporation of adatoms from diatomic clusters, and the dissolution of diatomic clusters into two free adatoms. We will show below that the neglect of evaporative processes does not significantly affect our results. Our reasons for neglecting the decay of diatomic clusters will be discussed below. The reaction-rate constants k_i are determined by the growth conditions in terms of the molecular-beam flux and substrate temperature, as well as microscopic hop-

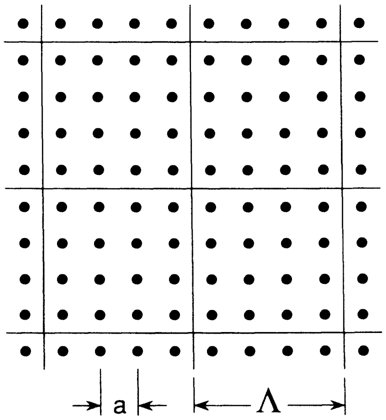

FIG. 1. Illustration of coarse graining on a length scale Λ of a square lattice with lattice constant a.

ping barriers, as will be discussed below.

The reaction sequence (1) may now be converted into a master equation,[15] from which an effective evolution equation can be derived for the average number $x_i(t)$ of atoms of X in the ith cell at time t:

$$\frac{dx_i}{dt}=\sum_{j=1}^{N} D_{ij}x_j+k_0 A-k_1 A x_i-2k_2 x_i^2 . \tag{2}$$

The first term on the right-hand side of (2) represents cell-to-cell diffusion, and the remaining terms account for the reactions (1).

The reaction rates k_i are required to complete the specification of (2). We consider first the deposition process. The deposition rate J is the arrival rate per unit area of atoms onto the substrate from the particle beam. Thus the rate at which atoms are deposited onto the ith cell is $J\Lambda^2$. According to the first two reactions in (1), there are two possible outcomes of the deposition process (Fig. 2): (i) the creation of a migrating atom, if the chosen site is unoccupied and if the nearest neighbors are unoccupied, or otherwise (ii) the creation of a diatomic island with an accompanying "annihilation" of a neighboring atom. Since there are Λ^2/a^2 sites in each cell, the probability of any site being occupied is $x_i/(\Lambda/a)^2$. The rate at which single atoms are deposited onto the substrate is thus the total deposition rate from which the effect of (ii) is subtracted:

$$k_0 A=J\Lambda^2\left[1-m\frac{x_i}{(\Lambda/a)^2}\right] , \tag{3}$$

where the second term accounts for the island-forming sites, with the factor m being the number of such sites around a single adsorbed adatom that form a diatomic island when filled. For example, for a (001) surface, $m=4$, since a single adatom has four nearest neighbors; if the site of the adatom itself is included, then $m=5$. The rate of diatomic island formation from the deposition process is calculated for (ii) as in (3):

$$k_1 A=J\Lambda^2\frac{mx_i}{(\Lambda/a)^2}=Ja^2mx_i . \tag{4}$$

The probability that two mobile atoms collide to form a diatomic island is derived by considering the probability that a migrating atom encounters a filled nearest-neighbor site. The average residence time of an atom on a particular site is denoted by τ_0. Thus, in a time $\delta\tau$, a migrating atom on average encounters $\delta\tau/\tau_0$ sites. The probability that the site is occupied is $x_i/(\Lambda/a)^2$. Thus the number of diatomic islands formed from the combination of migrating atoms during the time interval $\delta\tau$ is

$$k_2 x_i^2\,\delta\tau=\sigma\frac{\delta\tau}{\tau_0}\frac{x_i^2}{(\Lambda/a)^2} , \tag{5}$$

where σ is the capture efficiency, so that

$$k_2=\frac{\sigma}{\tau_0(\Lambda/a)^2} . \tag{6}$$

In our model, the entire process of island formation is represented by σ, which gives the *net* rate at which stable diatomic islands are formed. Clearly, σ has a temperature dependence; however, for a first approximation it is simplest to set σ equal to a constant, estimated to be of order 1.[11] Finally, substituting (3), (4), and (6) into (2), the evolution equation for x_i becomes

$$\frac{dx_i}{dt}=\sum_{j=1}^{N} D_{ij}x_j+J\Lambda^2-2Jma^2x_i-2\frac{\sigma}{\tau_0(\Lambda/a)^2}x_i^2 . \tag{7}$$

To obtain the continuum form of (7), we first divide both sides of (7) by Λ^2. The equation for the density $n_i(t)=x_i(t)/\Lambda^2$ is then

$$\frac{dn_i}{dt}=\sum_{j=1}^{N} D_{ij}n_j+J-2Jm\frac{n_i}{n_0}-2\frac{\sigma}{\tau_0/a^2}n_i^2 , \tag{8}$$

where $n_0\equiv a^{-2}$ is the site density. We now take the continuum limit $\Lambda\rightarrow 0$ at fixed particle density n_i and introduce the diffusion constant $D=\nu a^2\exp(-E/k_BT)$, where ν is an atomic vibration frequency ($\approx 10^{13}\ \mathrm{s}^{-1}$), E is the energy barrier to diffusion, and k_B is Boltzmann's constant. In the continuum limit, we have

$$n_i(t)\rightarrow n(\mathbf{x},t),\quad D_{ij}\rightarrow D\nabla^2,\quad \tau a^{-2}\rightarrow D , \tag{9}$$

so that the effective nonlinear-diffusion equation reads

$$\frac{\partial}{\partial t}n(\mathbf{x},t)=D\nabla^2(\mathbf{x},t)+J-\frac{2m}{n_0}Jn(\mathbf{x},t)-2\sigma Dn^2(\mathbf{x},t) . \tag{10}$$

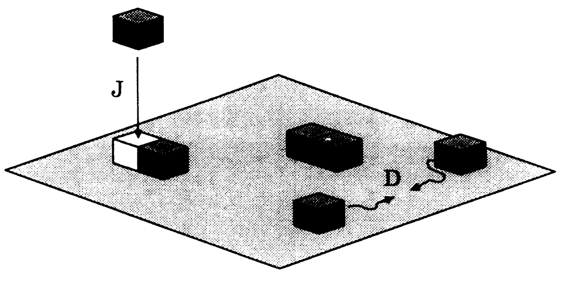

FIG. 2. Schematic illustration of processes contributing to diatomic island formation, including deposition onto sites with occupied nearest neighbors and collision during migration.

To apply (10) to epitaxial growth on a vicinal surface, we consider a substrate which consists initially of an infinite train of flat steps separated by terrace length $x=h$ in the x direction, pictured in Fig. 3. The crystal is infinite in the y direction and the steps are one atomic unit high. Step growth occurs both through the adsorption of single atoms onto the terraces and their subsequent diffusion into the step edges, as well as island formation through adatom collisions. Following the crystal-growth theory of BCF, we make the simplifying assumption of straight step edges. Meandering of the step edge in the y direction is neglected, and the step is treated as a continuous line sink with a constant adatom-capture potential in the y- direction. Consequently the dependence of the concentration on y may be neglected,

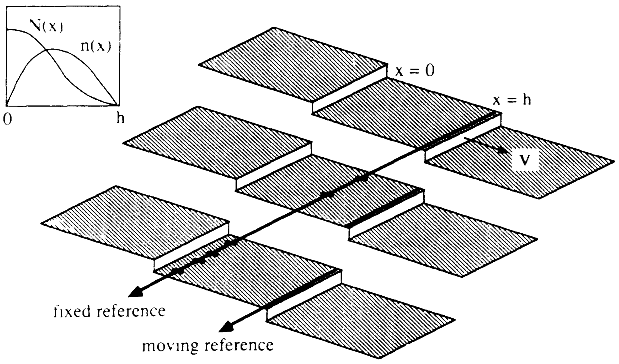

FIG. 3. Schematic representation of evolution of a stepped crystal and the concentration of adatoms, $n(x)$, and of diatomic islands, $N(x)$, along a terrace.

and (10) reduces to a one-dimensional problem of the form

$$\frac{\partial n(x,t)}{\partial t}=D\frac{\partial^2 n(x,t)}{\partial x^2}+J-R(n(x,t)) , \tag{11}$$

where the function R incorporates the two island-forming terms in (10). Assuming that the steps are moving at velocity v, it is convenient to switch to a moving reference frame by employing the coordinate transformation $x \to x-vt$. *In the steady state* and in the moving coordinate system, the continuity equation (11) becomes

$$D\frac{d^2n}{dx^2}+v\frac{dn}{dx}+J-R(n)=0 . \tag{12a}$$

In the BCF theory, the concentration of adatoms at the step edge is assumed to be in local equilibrium; thus the concentration at the step is a known value n_{eq}. However, this assumption is not likely to be valid at the far-from-equilibrium growth conditions of MBE. Therefore, we utilize absorbing boundary conditions at the step edges whereby all adatoms reaching the step from either above or below "disappear" due to incorporation by the step. Further, once an atom is attached to the step, subsequent detachment is forbidden. Thus the concentration of adatoms vanishes at the step edges:

$$n(x=0)=n(x=h)=0 . \tag{12b}$$

To be consistent we must also neglect the decay of diatomic clusters into single adatoms, since the effective-energy barriers should be comparable.

In order to solve (12) for a specified island-formation rate $R(n)$, we require an additional relation to give the unknown steady-state velocity v which appears in (12a). This is accomplished by invoking the law of mass conservation around a terrace. At steady state, the concentration of adatoms on the terraces must remain constant. Thus, all of the incoming flux per terrace (Jh) must be removed due to advancement of the steps at the two boundaries. For monatomic steps, the velocity is then given by

$$vn_0=Jh , \tag{13}$$

where n_0 is the concentration of lattice sites introduced in (8). Equation (12) is solved in the absence of island formation $[R(n)=0]$ in Appendix A, where solutions to other special cases are also given.

III. STEADY-STATE SOLUTION OF THE NONLINEAR-DIFFUSION EQUATION FOR A VICINAL SURFACE

It is convenient to introduce dimensionless variables into the steady-state nonlinear diffusion equation (12). The distance is scaled as $x \to x/h$, so that $0 \le x \le 1$. The natural concentration scale arising from the equations is $n_s=Jh^2/D$, which has units of surface concentration. Introducing the dimensionless concentration $y(x) \equiv n(x)/n_s=Dn(x)/(Jh^2)$, (12) takes the form

$$\frac{d^2y}{dx^2}+\alpha\frac{dy}{dx}+1-2\alpha\beta y^2-2\alpha m y=0 ,$$
$$y(0)=y(1)=0 \tag{14}$$

where the dimensionless parameter $\alpha=Jh^2/Dn_0$ represents the ratio of the diffusion time for an adatom to reach a terrace (h^2/D) to the interarrival time of atoms per site (n_0/J), and the dimensionless parameter $\beta=\sigma n_0 h^2$ is a measure of the misorientation angle (through the terrace length with monatomic steps) and of the lateral interaction (through the capture cross section). Note that the concentration scale $n_s=Jh^2/D=\alpha n_0$.

As in Appendix A, we introduce the variable p defined by

$$p=\frac{dy}{dx},\quad p\frac{dp}{dy}=\frac{d^2y}{dx^2} , \tag{15}$$

whereupon (14) becomes

$$p\frac{dp}{dy}=-\alpha p-1+2\alpha\beta y^2+2\alpha m y . \tag{16}$$

This expression is a first-order nonlinear equation: an Abel equation of the second kind.[16] Unfortunately, we cannot simply continue as in Appendix A since (16) is not separable in p and y. We notice that even if (16) were solvable for p, we would still be left with an integral of the kind in (A12); thus it is far simpler to solve (16) numerically. We use a fourth-order Runge-Kutta method with Kutta's coefficients[17] to integrate the set of two simultaneous first-order differential equations for y and p:

$$\begin{aligned}\frac{dy}{dx}&=p ,\\ \frac{dp}{dx}&=-\alpha p-1+2\alpha\beta y^2+2\alpha m y .\end{aligned} \tag{17}$$

Integration of these equations from $x=0$ to 1 requires a starting value at $x=0$ for $y(0)$ and $p(0)$. However, the boundary conditions in (14) yield only $y(0)=0$; $p(0)$ (the adatom flux into the step edge) is unknown. We proceed via shooting methods by assuming a value for $p(0)$ and iteratively performing the Runge-Kutta integration to $x=1$ until the assumed value for $p(0)$ is one which yields

$y(1)=0$. Successive improved guesses of $p(0)$ are found using the half-interval method;[17] the solution converges rapidly. Solutions of (14) for $n(x)$ are shown in Fig. 4(a) without adatom interactions, $R(n)=0$, and Fig. 4(b) with adatom interactions for $m=5$ and $\sigma=1$. The flattening of the profile due to island formation is pronounced at large α (low temperature).

Once the adatom concentration is known, the diatomic island concentration $N(x,t)$ may be computed from

$$2\frac{dN}{dt}=R(n)=2\sigma Dn^2+2Jm\frac{n}{n_0}\ . \qquad (18)$$

We assume that once an island is formed, it is immobile; thus islands do not move with the terrace. With reference to Fig. 3, we focus on a fixed frame of reference at the point where single adatoms are just forming a new sliver of step edge (at $x=h$) and observe the formation of adatoms *with time*. At this point ($t=0$), we assume that there are no islands on the freshly formed sliver of step; thus $N(0,0)=0$. As time increases, the step moves along with velocity v. At our fixed position (which is now position x according to the moving reference) the concentration of islands includes all of those islands which were formed during the time $t=(h-x)/v$ it took for the step to move distance $h-x$. Thus, using the dimensionless quantities defined above and introducing the dimensionless island concentration $Y(x)\equiv 2N(x)/(\alpha n_0)$, we obtain

$$Y(x)=2\beta\int_x^1 y^2(x)dx+2m\int_x^1 y(x)dx\ . \qquad (19)$$

When $t=h/v$ ($x=0$ in the moving reference frame), the next step has reached our fixed reference point, and all islands are instantaneously captured by the advancing step. The island-concentration profile along the terrace is pictured in Fig. 5 for various α; $Y(x)$ is seen to be greatest directly below the step edge at $x=0$.

It is instructive to write the boundary condition relating advancement of the step in terms of the adatom and island fluxes:

$$vn_0=D\frac{dn}{dx}\bigg|_{x=0}-D\frac{dn}{dx}\bigg|_{x=h}+2\sigma D\int_0^h n^2(x)dx+2mJ\int_0^h (n/n_0)dx\ . \qquad (20)$$

The first and second terms on the right-hand side of (20) represent the flux of single adatoms at the step from below and above, and the last two terms represent flux due to islands. Note that the adatom flux is due to diffusion of the adatoms to the steps, while the island flux is due to the movement of the steps which sweep up the immobile islands. Because of mass conservation (13), $vn_0=Jh$, and all of the incoming flux per terrace must go toward advancing the step. Using (13) and switching to dimensionless quantities $x\to x/h$, $y\equiv n/(\alpha n_0)$, $\alpha=Jh^2/Dn_0$, and $\beta=\sigma n_0 h^2$, (20) becomes

$$1=\left[\frac{dy}{dx}\bigg|_{x=0}-\frac{dy}{dx}\bigg|_{x=1}\right]+\left[2\alpha\beta\int_0^1 y^2(x)dx+2m\alpha\int_0^1 y(x)dx\right]\ . \qquad (21)$$

The first term in large parentheses (21) represents the

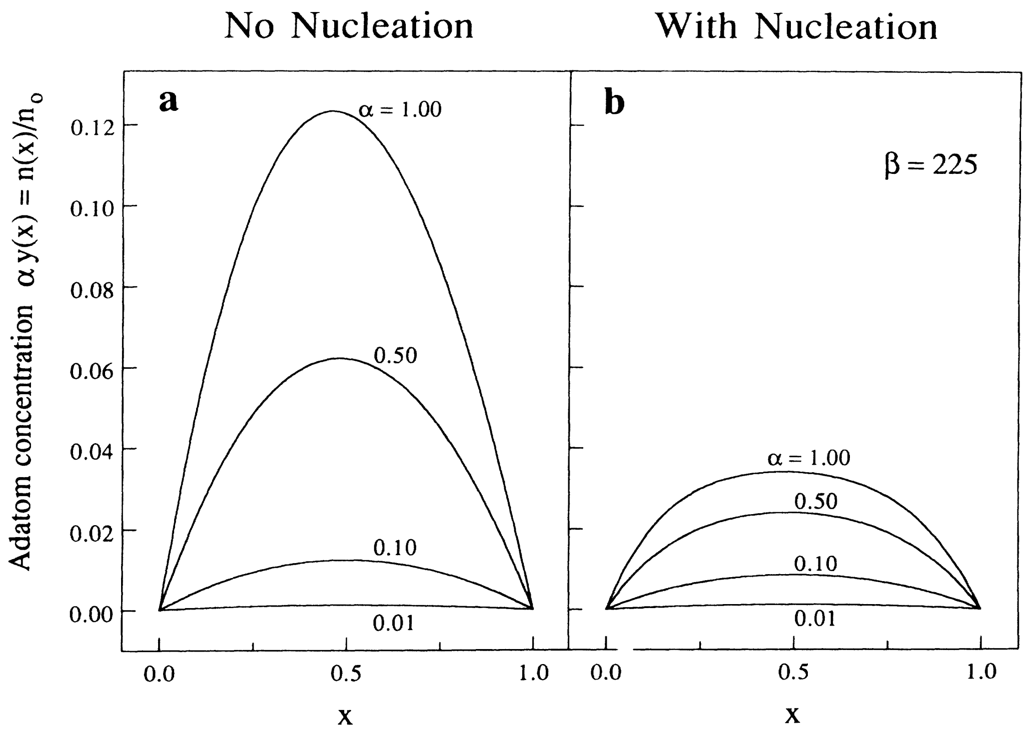

FIG. 4. Adatom concentration profiles along a terrace with length $h=15a$ for various α. The left panel (a) shows profiles with no island formation included [$\sigma=0$ and $m=0$ in (14)]. Note the flattening and lowering of the profile in the right panel (b), which includes island formation [$\sigma=1$ and $m=5$ in (14)].

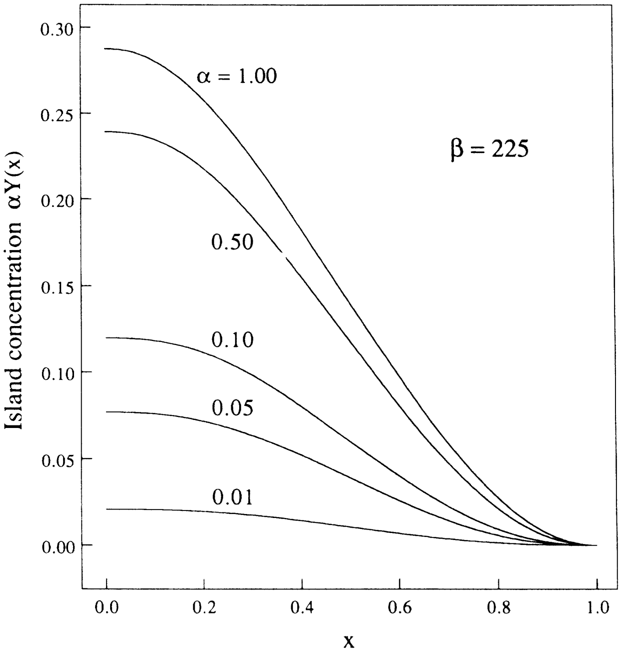

FIG. 5. Dimensionless diatomic island concentration along a terrace for $\beta=225$ and various α. Calculations use (14) and (22) with $m=5$.

fraction of material which adds to the step from above and below as single, free diffusing adatoms; the second term in large parentheses represents the fraction of material which is swept up by the step as immobile diatomic islands. In Appendix B, we show that the evaporation for free adatoms can be neglected under typical operating conditions of MBE.

IV. TRANSITION TO STEP-FLOW GROWTH

In the MBE experiments of Neave *et al.*[3] on GaAs, growth regimes were monitored with RHEED specular intensity oscillations. At low temperatures, oscillations are observed in the RHEED intensity which are indicative of the competition of island formation with incorporation of atoms at step edges. As the temperature is increased, the oscillations weaken until a critical temperature T_c is reached, at which oscillations are no longer visible. Above this temperature, growth is essentially step propagation since enhanced adatom mobility promotes direct incorporation at steps over island formation.

We can describe these observed growth regimes and predict the transition temperature T_c from our nonlinear theory simply by dimensional analysis of (14). In (14) the variables are scaled so that the diffusion and flux terms are both order 1, *independent* of the value of α. The prefactors of the other terms are all proportional to α, and these terms make varying size contributions to the equation as a function of α. By comparing the magnitudes of the individual terms, one may divide the parameter space into various regimes corresponding to the controlling growth mechanisms.

(a) *Island formation dominates,* $\alpha>1$, $y''+\alpha y'+1+2\alpha\beta y^2+2\alpha m y=0$. Since $\beta>100$, for $\alpha>1$, the adatom-interaction term is multiplied by a large factor $2\alpha\beta\gg 1$ and dominates the equation. The rate of island formation and the step velocity are high, and the full nonlinear equation must be used. Solution is only possible numerically. For very large α, the actual adatom-concentration profile is likely to be even lower than that given by (14), since in this region one would expect formation of tri- and higher-atomic islands and island coalescence to become increasingly important (see Appendix C).

(b) *Island formation competes with step flow,* $1>\alpha>1/\beta$, $y''+1+2\alpha\beta y^2+2\alpha m y=0$. For small α, the moving-boundary term $\alpha\, dy/dx$ is less than order 1 and can be neglected, but the prefactor of the adatom-interaction term $2\alpha\beta$ is still greater than 1, since β is a large number. It is significant that the interaction term is of similar or greater importance than corrections due to the moving boundary; this confirms previous predictions.[6] Adatoms interact to form islands on their diffusion path to the steps, although the step velocity is low enough that the effect of the moving boundary may be neglected. The solution is given by (A12) in terms of an elliptic integral.

(c) *Step-flow mode,* $\alpha<1/\beta$, $y''+1=0$. When α becomes much less than $1/\beta$, the adatom-interaction term is multiplied by a small number, $2\alpha\beta<1$, and can be neglected. The adatom concentration on the terrace is extremely low, island formation is negligible, and incident adatoms are directly incorporated into the step edge due to their high mobility. The exact solution is given by (A5).

Step-flow mode [regime (c)] is achieved below a threshold value of α: $\alpha_c<1/\beta\ll 1$, where the adatom-interaction terms are negligible compared to the diffusion and flux terms in (14). In Fig. 4, profiles of the adatom concentration with decreasing α show that there is no *sharp* transition to the step-flow growth mode, and so, although we have shown above that α_c is several orders of magnitude less than 1, α_c must be fixed using a further criterion. For example, a threshold α_c could be determined as that value which gives a maximum island concentration of less than 1%; this is discussed further below. The temperature T_c is then evaluated from α_c as

$$T_c=\frac{E_D}{k_B}\left[\ln\left[\frac{\nu\alpha_c}{Jh^2}\right]\right]^{-1}. \tag{22}$$

Previously, predictions of the transition temperature T_c have used the Einstein relation for surface diffusion $x^2=2D\tau$.[3] This linear model treats the migration of atoms as a random walk, taking no account of the effect of island formation on adatom mobility or the influence of the moving step boundary. Growth is therefore assumed to be step flow when the time for atoms to diffuse to a step is equal to or less than the adatom interarrival time at a specific site. At greater diffusion times, the buildup of adatom concentration in the center of the terrace is assumed to lead to cluster formation. With $x=h$, D given as in Sec. II, and $\tau=n_0/J$, the average time interval between deposition at a specific site, the Einstein relation yields the following expression for the transition temperature T_c:

$$T_c = \frac{E_D}{k_B}\left[\ln\left[\frac{2\nu}{Jh^2}\right]\right]^{-1} . \tag{23}$$

Comparing the above equation with (22), we note that α_c in (22) is replaced by the factor 2. However, the island-formation rate dominates the growth equation for $\alpha=2$, and so the assumption implicit in the use of the Einstein relation in calculating T_c that adatom interactions can be neglected is clearly invalid. It is necessary to utilize (14) which incorporates the full nonlinear behavior. Although a linear theory which neglects adatom interactions may be used accurately for calculating the *adatom concentration* at very low α, island formation must be explicitly included in the analysis to determine the α regime where step propagation dominates.

V. COMPARISON TO SIMULATIONS

We compare the results of our model to Monte Carlo simulations of MBE by Clarke, Vvedensky, and coworkers.[18-20] A full description of the details of the computer simulations is given in Ref. 20; thus a brief outline of the simulation model will suffice here. Atoms are randomly deposited on the stepped substrate and migrate by nearest-neighbor hopping, the probability of which is given by $k = k_0 \exp(-E/k_BT)$. Island formation is taken into account through the site dependence of the diffusion barrier E, which includes contributions from nearest-neighbor parallel bonding. Thus comparison of our model to the simulations is also a test of the validity of the continuum approach in representing the microscopic kinetic processes occurring on the surface.

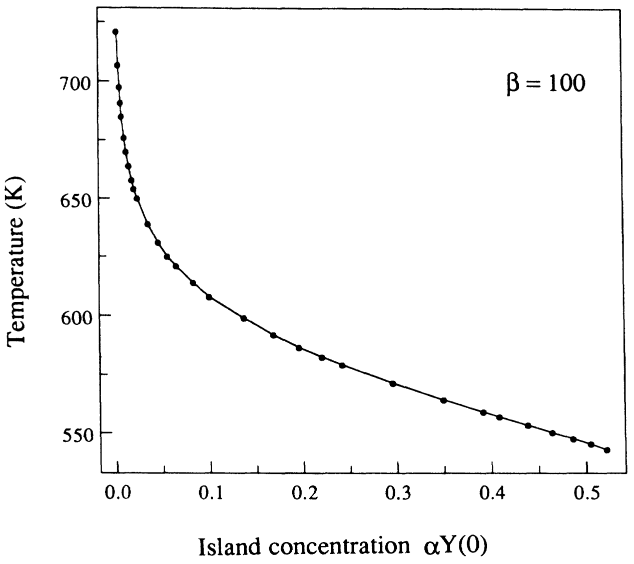

FIG. 6. Effect of temperature on the island concentration $\alpha Y(x) = 2N(x)/n_0$ at $x=0$. Note the sharp dependence of the temperature on $\alpha Y(x)$ for low concentrations. Calculations are done using (14), (19), and (22) for stepped GaAs(001) with $h=10a$, $n_0=1/a^2$, $a=3.98\times10^{-8}$ cm^{-2}, $E_D=1.3$ eV, $\nu=2.5\times10^{13}$ s^{-1}, $J=1\times10^{14}$ cm^{-2} s^{-1}, $\sigma=1$, and $m=5$.

In the simulations, the transition temperatures to step flow are identified by the absence of oscillations of the step density. The nonlinear model is a steady-state model and will not exhibit oscillations, and so a different criterion must be chosen to pinpoint an exact value of α_c at which we can consider step flow to be achieved (we have shown above that $\alpha_c < 1/\beta \ll 1$). We will assume that step flow is achieved when the flux due to captured islands at the step edge [the second term on the right-hand side of (21)] is less than 1% of the total flux. This is equivalent to an island concentration below the step edge (at $x=0$) of $\alpha Y(0) = 2N(0)/n_0 = 0.01$. The temperature T_c is then found by determining the value of $\alpha = Jh^2/Dn_0$ for which $\alpha Y(0) = 0.01$ as follows: (a) Solve (14) for a given α and with fixed $\beta = \sigma n_0 h^2$, and (b) determine $\alpha Y(0)$ from (19). This process is repeated until a α_c is found which yields $\alpha Y(0) = 0.01$. We find that this cutoff [with corresponding $\alpha_c \approx 1/(2\beta)$] gives excellent agreement with the simulations over an order-of-magnitude variation in the flux J and for misorientation angles of 2°–4°, as shown in Table I. This is remarkable given the sharp dependence of the transition temperature on the value chosen for the island concentration (Fig. 6). Thus step flow is considered to dominate when the atomic flux due to islands into the step edge is approximately

TABLE I. Comparison of transition temperatures at which step flow occurs, calculated using Monte Carlo simulations (Ref. 19), nonlinear theory including adatom interactions (22), and the Einstein relation (23). Parameters used for a GaAs(001) surface with $a=3.98\times10^{-8}$ cm^{-2}, $n_0=1/a^2$, $E_D=1.3$ eV, $\sigma=1$, $m=5$, and $\nu=2k_BT/h$, where here h is Planck's constant.

			T_c (K)	
J (cm^{-2}s^{-1})	h/a	Simulation	Theory	Einstein relation
5.0×10^{13}	10	650	654	520
1.0×10^{14}	10	680	673	533
5.0×10^{14}	10	725	722	563
1.0×10^{15}	10	735	746	577
1.0×10^{14}	14	700	707	545
1.0×10^{14}	20	750	750	559
5.0×10^{14}	20	815	811	592
2.3×10^{14}	18	775	766	571

1%, a physically reasonable criterion. The results indicate that increasing the length of the terrace h and increasing the rate of deposition J will both lead to an increase in island formation, and thus a higher temperature T_c will be required to achieve a step-flow growth mode.

Also shown in Table I is the prediction of the Einstein relation (23). It consistently underestimates transition temperatures by 150°–200°; this can be directly traced to the neglect of interactions among the adatoms. It is assumed that mobile atoms are undeterred in their path to the steps and thus predicts that step flow will occur when their diffusion length is equal to the terrace length. In our model, diffusing adatoms are captured to form islands; thus much higher temperatures must be attained before island formation is negligible and adatoms move essentially freely. Our nonlinear theory shows that the diffusivity in the Einstein relation $x^2=2D\tau$ should be replaced by an effective diffusivity $D_{\rm eff}=D\alpha_c/2$ to account for the adatom interactions, where α_c is several orders of magnitude less than 1 for typical MBE conditions.

VI. COMPARISON WITH EXPERIMENT

We show in Fig. 7 values of T_c measured[3] during MBE for GaAs(001) for various Ga and As_2 beam fluxes. Unfortunately, comparison with the predictions of (22) is not as straightforward as with the simulations, since E_D for GaAs, which was fixed at 1.3 eV in the simulations, is not accurately known. Consequently, we allow E_D to be a variable parameter and find the best fit of (22) with α_c calculated at $\alpha Y(x)=0.01$ from our nonlinear theory in accordance with the results shown in Table I, and for comparison with $\alpha_c=2$ (the Einstein relation). The results are represented by dashed lines in Fig. 7. The solid line represents the best least-squares fit of (22) to the data with *both* E_D and α_c as adjustable parameters. The fitted parameters are presented in Table II. The correspondence between $\alpha_c=0.0017$ calculated from our nonlinear theory to the "best fit" of the data ($\alpha_c=0.000\,14$) confirms that due to island formation, step-flow-dominated growth is only reached in the parameter regime of $\alpha \ll 1$ when the diffusion time is several orders of magnitude less than the time for the step to move a terrace length. By contrast, attempting to fit the Einstein

TABLE II. Least-squares fit of (22) to experimental transition temperatures (Ref. 3) plotted in Fig. 7, with $\alpha_c=2$ for the Einstein relation and α_c as determined by (14) for the nonlinear theory with adatom interactions. A best fit with both E_D and α_c as variable parameters is also shown. The root-mean-square deviation $\sigma_{\rm rms}$ of the inverse transition temperatures $10^3/T_c$ from the data is also shown. Parameters used are for a GaAs(001) surface with $a=3.98\times10^{-8}$ cm^{-2}, $h=18a$, $\nu=3\times10^{13}$ s^{-1}, $\sigma=1$, and $m=5$.

	Best fit	Nonlinear theory	Einstein relation
E_D (eV)	1.3	1.4	2.0
α_c	1.4×10^{-4}	1.7×10^{-3}[a]	2[a]
$\sigma_{\rm rms}$	1.3×10^{-4}	6.9×10^{-3}	1.9×10^{-2}

[a] These parameters are fixed by theory, not fitted.

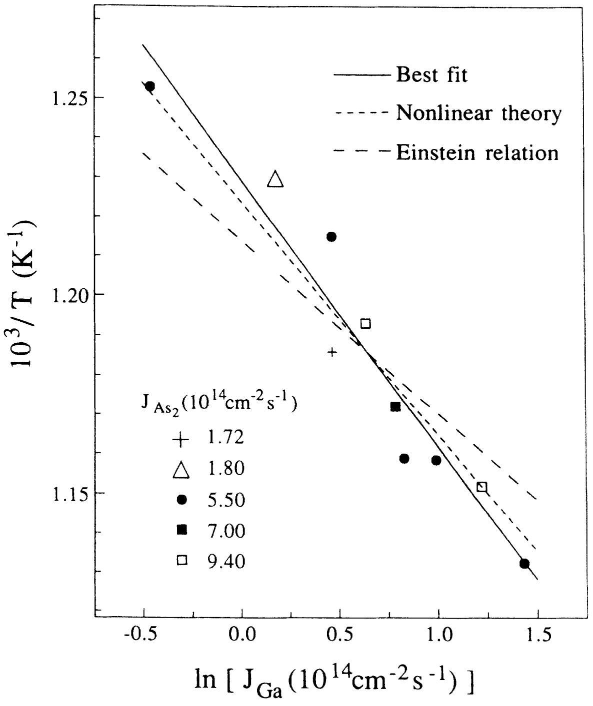

FIG. 7. Comparison between T_c measured during MBE on GaAs(001) for the indicated Ga and As_2 fluxes (from Ref. 3) with theoretical values calculated with (22) using $\alpha Y(0)=0.01$ and the indicated values of E_D.

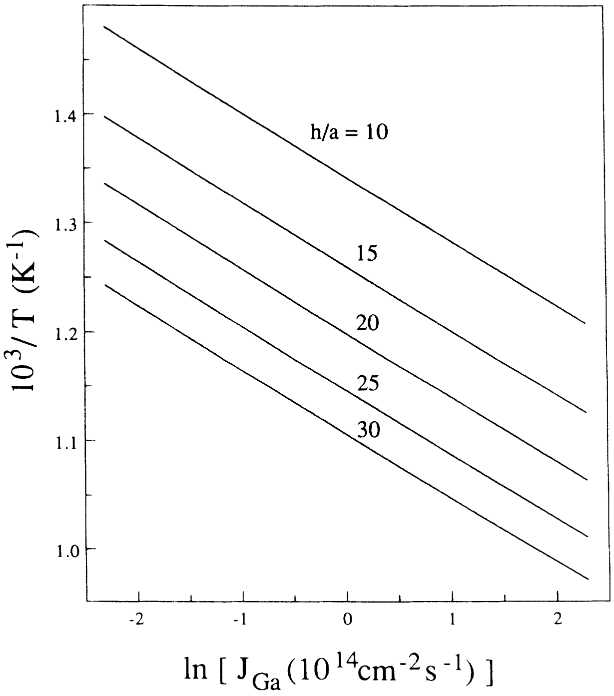

FIG. 8. Calculated values of T_c for the indicated Ga fluxes and terrace widths using (22) with the parameters determined for the nonlinear theory in Fig. 7.

relation with $\alpha_c = 2$ to the measurements requires $E_D = 2.0$ eV, and extremely high value; if a lower, more realistic energy were used (e.g., 1.3–1.4 eV as predicted by the "best fit"[3] and the nonlinear theory), the Einstein relation would predicted T_c several hundred degrees below the measurements. (It is also interesting to note that if Monte Carlo simulations are fitted to the measurements of Neave *et al.*,[3] $E_D = 1.45$ eV is required to quantitatively reproduce the experimental transition temperatures.[19])

Using the value of α_c determined above, we can extend the range of external parameters over which the model can be applied to predict T_c. In Fig. 8 we show plots of T_c as a function of the Ga flux for the indicated terrace widths. Based upon the comparison in Fig. 7, this diagram should provide reliable estimates for T_c for a wide range of vicinal angles and growth conditions.

Finally, it is also worth pointing out that measurements with widely varying values of As_2 beam fluxes, from 1.72 to 9.4 $cm^{-2} s^{-1}$, all fall within a quite narrow range around the curve predicted by our model. This confirms that for typical conditions of MBE it is reasonable to treat the two-component GaAs system as a one-component system by neglecting the presence of the As_2 flux.

VII. CONCLUSIONS

In this paper we improve on continuum models of growth on vicinal surfaces by including the effect of adatom interactions to a first approximation via diatomic island formation. The resulting nonlinear-diffusion equation is then integrated numerically to obtain the adatom- and diatomic-island-concentration profiles along the terrace. Comparison of the results with and without island formation show that adatom interactions are a significant component of growth under typical MBE conditions. Regimes of growth conditions where island formation competes with capture at the step, and where it can be neglected, are estimated theoretically. It is found that a dimensionless parameter α, which represents the ratio of the time for diffusion of a single atom to a step to the time for a step to move one terrace length, must be several orders of magnitude less than 1 in order for the concentration to be represented by a linear equation. Below this critical value of the parameter α_c (alternatively above a critical temperature T_c), growth occurs almost exclusively due to direct incorporation of atoms at steps with negligible island formation; this regime is the step-flow mode. We compare T_c calculated from our nonlinear model with Monte Carlo simulations of MBE growth over a wide range of beam fluxes and misorientation angles, and find that step propagation can be considered to be achieved when the atomic flux due to captured islands into the step edge is 1% of the total flux. Using this criterion, we find that the nonlinear model gives an excellent fit of measurements of T_c on GaAs(001) for a variety of Ga and As_2 beam fluxes. We conclude that adatom interactions are an integral part of the fundamental physics of growth on stepped crystals, and that they must be explicitly included in the diffusion equations for a model which is generally applicable over a wide range of growth conditions.

ACKNOWLEDGMENTS

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APPENDIX A: SPECIAL SOLUTIONS

In order to evaluate the effect of adatom interactions on step growth, we will first completely neglect any island formation. In this case, (12) is written with $R(n)=0$ as

$$D\frac{d^2n}{dx^2} + v\frac{dn}{dx} + J = 0, \quad n(0)=n(h)=0 . \tag{A1}$$

Combining (13) with (A1) and introducing the dimensionless concentration $y \equiv n/(\alpha n_0)$ and distance $x \to x/h$, so that $0 \le y \le 1$ and $0 \le x \le 1$, yields

$$\frac{d^2y}{dx^2} + \alpha\frac{dy}{dx} + 1 = 0, \quad y(0)=y(1)=0 . \tag{A2}$$

The dimensionless parameter $\alpha = Jh^2/Dn_0$ represents the ratio of the diffusion time for an adatom to reach a terrace (h^2/D) to the interarrival time of atoms per site (n_0/J). Using (13), α may also be written as a Peclet number,[21] $\alpha = vh/D$, and can therefore, alternatively, be thought of as the ratio of the adatom-diffusion time to a terrace to the time for a step to move one terrace length (h/v). The solution is

$$y(x) = \frac{1}{\alpha}\left[\frac{1-e^{-\alpha x}}{1-e^{-\alpha}}\right] - \frac{x}{\alpha} . \tag{A3}$$

The concentration is plotted in Fig. 4(a) as a function of α. Note that as α increases (corresponding to decreasing temperature through the diffusion constant D or increasing flux J), adatom concentration builds up in the center of the terrace. The asymmetry in the concentration profile noticeable at large α is due to the effect of the moving coordinate system. For small α, the effect of the moving boundary may be neglected and the governing equation becomes

$$\frac{d^2y}{dx^2} + 1 = 0, \quad y(0)=y(1)=0 , \tag{A4}$$

with the simple solution

$$y(x) = \tfrac{1}{2}x(1-x) , \tag{A5}$$

which is simply the limit of (A3) as $\alpha \to 0$.

The nonlinearity in (12) introduced by the interaction term $2\alpha\beta y^2$ greatly complicates its analytical solution. We first attempt to solve (14), retaining only the difficult nonlinear term and the diffusion term:

$$\frac{d^2y}{dx^2} - 2\alpha\beta y^2 = 0 . \tag{A6}$$

The general solution of the above equation is[16]

$$y(x)=\frac{6}{\alpha\beta}\wp(C_2+x;0,C_1)\ , \tag{A7}$$

where $\wp(x;a,b)$ is the Weierstrass elliptic function. C_1 and C_2 are integration constants determined by the boundary conditions at $x=0$ and 1. For the boundary conditions (12b), it is clear that the only solution to (A6) is the trivial one $y(x)=0$, since there is no flux term to replace the adatom concentration lost due to island formation.

We now proceed one step further in complexity and include the flux term and the term due to the flux collision contribution to island formation ($2\alpha my$). However, we will still neglect the effect of the moving boundary ($\alpha\, dy/dx$) as in BCF theory; this is likely to be valid only at low step velocities. The resulting dimensionless continuity equation is

$$\frac{d^2y}{dx^2}+1-2\alpha\beta y^2-2\alpha my=0\ . \tag{A8}$$

First, we define the variable p where

$$p=\frac{dy}{dx},\ p\frac{dp}{dy}=\frac{d^2y}{dx^2}\ . \tag{A9}$$

After rearrangement, (A8) becomes

$$p\,dp=(-1+2\alpha\beta y^2+2\alpha my)dy\ . \tag{A10}$$

Integration of the above equation yields

$$p^2=2(-y+\tfrac{2}{3}\alpha\beta y^3+\alpha my^2)+C_1\ . \tag{A11}$$

Since $p=dy/dx$, we obtain

$$\int\frac{dy}{[4\alpha\beta/3)y^3+2\alpha my^2-2y+C_1]^{1/2}}=x+C_2\ . \tag{A12}$$

The integral on the left-hand side of (A12) is not expressible in terms of any classical elementary functions; however, it may be expressed in terms of elliptic functions. The integration constants C_1, embedded in the integral, and C_2 will be determined by application of the boundary conditions.

APPENDIX B: EFFECT OF EVAPORATION

The full diffusion equation for growth on stepped surfaces at steady state and with respect to a moving reference frame is

$$D\frac{d^2n}{dx^2}+v\frac{dn}{dx}+J-\frac{n}{\tau}-R(n)=0\ ,$$

$$n(0)=n(h)=0\ , \tag{B1}$$

with

$$R(n)=2\sigma Dn^2+2mJ(n/n_0)\ . \tag{B2}$$

We assume that the rate of evaporation of adatoms is given by

$$1/\tau=\nu\exp[-E_{\text{des}}/(k_BT)]\ ,$$

where $\nu\approx10^{13}\ \text{s}^{-1}$ and E_{des} is the adatom desorption energy. Under typical MBE conditions, $\tau\gg1$, and the evaporation term may be neglected; however, we will include it in the following analysis.

The velocity is given by the sum of the flux due to single adatoms and the flux due to upswept islands:

$$vn_0=D\frac{dn}{dx}\bigg|_{x=0}-D\frac{dn}{dx}\bigg|_{x=h}+2\sigma D\int_0^h n^2(x)dx+2mJ\int_0^h(n/n^2)dx\ . \tag{B3}$$

If evaporation is neglected, the velocity v in (B1) can be determined simply from a mass balance as $vn_0=Jh$. However, if atoms are also leaving the system through evaporation, the velocity is given from (B1) and (B3) as

$$vn_0=Jh-\frac{1}{\tau}\int_0^h n(x)dx\ . \tag{B4}$$

Thus (B1) and (B4) must be solved simultaneously. We introduce the dimensionless variables $x\rightarrow x/h$, $y(x)=Dn(x)/(Jh^2)$, $\alpha=Jh^2/(Dn_0)$, and $\beta=\sigma n_0h^2$ to obtain

$$\frac{d^2y}{dx^2}+V\frac{dy}{dx}+1-\gamma y-2\alpha\beta y^2-2m\alpha y=0\ ,$$

$$y(0)=y(1)=0\ , \tag{B5a}$$

$$V=\alpha\left[1-\gamma\int_0^1 y(x)dx\right]\ , \tag{B5b}$$

where $\gamma=h^2/(D\tau)$ is the ratio of the diffusion time to a step edge to the residence time of an atom on the surface and can also be written as

$$\gamma=(h/a)^2\exp[-(E_{\text{des}}-E_D)/(k_BT)]\ .$$

$V=vh/D$ is the dimensionless velocity. The set of equations is solved iteratively as follows: A starting value of $V_0=\alpha$ is used in (B5a), which is solved using a fourth-order Runge-Kutta method. A new V is then determined using the calculated $y(x)$ in (B5b). This improved value is then used in (B5a) to recalculate $y(x)$, and this process is repeated until the assumed V satisfies both (B5a) and (B5b).

As temperature increases, α decreases, and for very small $\alpha<1/\beta$, the nucleation terms in (B5a) may be neglected with respect to the diffusion and flux terms. However, the magnitude of γ *increases* with increasing temperature. The temperature at which the evaporation term becomes important compared with the other terms depends on the difference between the adatom desorption energy and the diffusion barrier, $\Delta E=E_{\text{des}}-E_D$. As a rough guide, $\gamma=10$ for $h/a=20$ at 970 K if $\Delta E=0.3$ eV, but 3180 K must be reached to give $\gamma=10$ for $\Delta E=1$ eV.

APPENDIX C: EFFECT OF TRIATOMIC ISLAND FORMATION

We consider the effect of allowing the formation of triatomic islands in addition to diatomic island formation. The concentration of diatomic islands will be denoted as N_2 and that of triatomic islands as N_3. We assume that triatomic islands can be formed in two ways: the collision of a mobile adatom with an existing diatomic island and direct collision of incident atoms with a diatomic island. Assuming that the capture efficiency σ is the same for the collision of an adatom and a diatomic island as it is for an adatom-adatom collision, and letting l represent the number of sites around a diatomic island that will form a triatomic island when filled, we obtain the following rates of island formation:

$$R_2(n,N_2)=\frac{dN_2}{dt}=\sigma Dn^2+Jm\frac{n}{n_0}-\sigma DnN_2-Jl\frac{N_2}{n_0}\ , \tag{C1}$$

$$R_3(n,N_2)=\frac{dN_3}{dt}=\sigma DnN_2+Jl\frac{N_2}{n_0}\ . \tag{C2}$$

The net rate of disappearance of single adatoms is then $R=2R_2+3R_3$. Using the dimensionless quantities defined in the text and $Y_2=N_2/(\alpha n_0)$, we obtain the continuity equations

$$\begin{gathered}\frac{d^2y}{dx^2}+\alpha\frac{dy}{dx}+1-2\alpha\beta y^2-2\alpha m y-\alpha\beta y Y_2-\alpha l Y_2=0\ ,\\ \frac{dY_2}{dx}+\beta y^2+my-\beta y Y_2-lY_2=0\ .\end{gathered} \tag{C3}$$

The second-order equation in $y(x)$ and the first-order equation in $Y_2(x)$ must be solved simultaneously with the boundary conditions $y(0)=y(1)=0$ and $Y_2(1)=0$. Note that (C3) may be extended to include island formation of an arbitrary size; then j differential equations must be solved simultaneously, where $j+1$ is the number of atoms in the largest island included. Equation (C3) may be solved numerically using the Runge-Kutta method. The dimensionless triatomic island concentration $Y_3=N_3/(\alpha n_0)$ is then calculated from

$$Y_3(x)=\beta\int_x^1 y(x)Y_2(x)dx+l\int_x^1 Y_2(x)dx\ . \tag{C4}$$

Concentration profiles including triatomic island formation were computed for a typical misorientation, $\beta=225$, using $l=8$ for a (001) surface, and compared to those with diatomic island formation alone [Fig. 4(b)]. Differences in the adatom profiles are unnoticeable for $\alpha\ll 1$, but for $\alpha\approx 1$ the profile is lowered by about 25% due to triatomic island formation. We also find the transition temperatures T_c to step flow in Table I are only increased by a few percent by inclusion to triatomic island formation.

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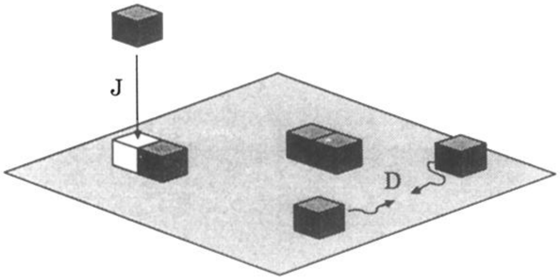

FIG. 2. Schematic illustration of processes contributing to diatomic island formation, including deposition onto sites with occupied nearest neighbors and collision during migration.