PHYSICAL REVIEW A VOLUME 44, NUMBER 4 15 AUGUST 1991

Generalized Burton-Cabrera-Frank theory for growth and equilibration on stepped surfaces

Andrea K. Myers-Beaghton and Dimitri D. Vvedensky
The Blackett Laboratory and Interdisciplinary Research Centre for Semiconductor Materials, Imperial College, London SW7 2BZ, United Kingdom

(Received 28 January 1991)

The theory of Burton, Cabrera, and Frank [Philos. Trans. R. Soc. London Ser. A **243**, 299 (1951)] for crystal growth on stepped surfaces is extended to include adatom interactions that are responsible for incipient island formation. By using a reaction-diffusion formulation of growth, a system of nonlinear diffusion equations is derived for the concentrations of surface clusters containing up to a prescribed number of atoms. By an appropriate choice of cells in the coarse graining of the lattice model, we show that the ostensibly one-dimensional equations obtained in the continuum limit in fact contain two-dimensional information averaged over the lateral length of the terrace. This allows the evolution equation for the averages of the various species to be decoupled from the higher-order correlation functions and simplifies the specification of the boundary conditions at the step edges. We have previously used this formalism to derive a nonlinear term for the formation of diatomic islands, from which we were able to predict quantitatively the transition to a step propagation mode for growth on stepped surfaces. Here, we extend the applicability of the original model away from growth by step advancement by allowing the surface atoms to form up to ten-atom islands. Furthermore, by including the breakup of atoms from the islands and adatom capture and detachment kinetics at the step edges, the model is capable of describing the relaxation of the surface toward equilibrium upon cessation of growth.

I. INTRODUCTION

Burton, Cabrera, and Frank (BCF) developed an analytical model for growth of crystals by step propagation in terms of the steady-state motion of an equidistant train of flat steps across a crystal surface [1]. The mechanism for step movement was the deposition of atoms onto the terraces and the subsequent capture and incorporation of the diffusing atoms at the step edge. A diffusion equation for the surface-adatom concentration was formulated subject to the following assumptions: (i) the effect of the moving boundary could be neglected, (ii) the concentration at the step edge was at equilibrium, and (iii) no interactions or reactions between the atoms were considered. This simplified model allowed an analytical solution for the step velocity and growth rate to be obtained and was applicable to systems near equilibrium.

There has been a renewal of interest in the BCF model for describing growth by molecular-beam epitaxy (MBE) and related epitaxial growth techniques, which are often carried out on stepped substrates. However, the far-from-equilibrium conditions of MBE due to the incoming mass and energy current of the particle beam mean that a number of modifications have been neccessary to apply BCF theory successfully. The effect of the moving boundary has been included [2,3] as well as deviations from equilibrium at the step edges [4]. Additionally, it was recognized that adatom nucleation on the terraces would be an important factor under typical MBE conditions [3].

There are several difficulties inherent in attempting to model the MBE process with continuum equations for general growth conditions, all of which stem from the interplay between surface diffusion and the formation and coalescence of clusters. In the early stages of growth during which the surface is smooth, the growth front is distributed over only a few layers. In this regime, a continuum approximation to the height distribution is not expected to be valid, so the coverage of the individual layers must be treated as separate dynamical quantities, within which there are growing clusters. This problem has been addressed using rate equations [5] where the rates of island formation are expressed in terms of gain and loss terms, which are nonlinear in the adatom and island concentrations. In solving these equations, no spatial dependence of the adatom or cluster concentration was included, which limits the applicability of the solutions to flat surfaces. This approach cannot be used for vicinal surfaces, since there is a diffusion-controlled adatom concentration gradient along the terrace due to the presence of the steps, which act as sources and sinks for adatoms. To treat the competing effects of diffusion and island formation requires considering the combined effects of the effective diffusivity mediated by the nonlinear interactions responsible for the capture and emission of adatoms by the surface clusters.

Growth on vicinal surfaces by step propagation presents a useful limiting case in which the competition between diffusion and cluster formation can be systematically addressed. The two important simplifications are that on any terrace, only a single layer is incomplete at any one time, so the growth of clusters upon clusters can be neglected, and that the effects of cluster formation are weak, in that the concentrations of islands are much smaller than the adatom concentration. Thus, although the formation of large islands can be explicitly incorporated, only small islands have an appreciable concentration, which is small compared to the adatom concentration. In this respect, the equations presented below generalize the BCF equation by allowing the full nonlinear interactions to be considered and to be checked for consistency as a function of the growth conditions. Clearly, if the island concentration shows an appreciable concentration in larger islands, alternative approaches should be considered which more faithfully reflect the growth front morphology.

In a recent paper [6], we have incorporated a quadratic interaction term to account for diatomic island formation in the BCF equations in addition to the above modifications. To simplify the complex problem of modeling nucleation on the terraces, we initially allowed only the formation of diatomic islands and assumed that adatoms could not detach back onto the terrace once incorporated into a step edge or island. A natural outcome of the nonlinear BCF model was the *quantitative* prediction of the temperature T_c at which nucleation may be neglected and epitaxial growth proceeds by step propagation. We also showed that the adatom interaction decreased the effective diffusivity of the adatoms by several orders of magnitude [6,7], a conclusion also reached by Stoyanov [8] following a different argument. The model was extended to the growth of semiconductor alloys on vicinal surfaces [9], where the transition to step propagation was studied as a function of the mobility parameters and of the alloy concentration. From the success of this model in predicting the transition to step-propagation mode, it is apparent that at least for determining the dependence of T_c on the growth conditions, detachment of atoms from islands balanced with detachment from the step and could be ignored to a first approximation. However, for a more detailed and realistic mode of MBE, it is necessary to explicitly include atom capture and detachment kinetics from the step and island edges as well as the formation of islands larger than pairs.

In this paper, we describe the generalization of the BCF theory to MBE on stepped surfaces to include complex adatom nucleation and detachment kinetics. Nonlinear adatom interaction terms are used to describe the nucleation and breakup of islands with up to ten atoms. The nucleation terms are similar to those used in kinetic rate equations on flat surfaces [5]; however, here we combine these terms with diffusion to model growth on stepped surfaces. We show how the formulation of the terms for nucleation via reaction sequences is quite general and can be used to describe the reactions of an arbitrary number of surface species. Deviations from equilibrium at the step edges are also included in the model through Arrhenius rate expressions for attachment and detachment from the step edges. The time-dependent nonlinear equations track the temporal evolution of the surface concentrations during the initial and steady-state stages of growth, as well as the equilibrium coverages once the molecular beam is turned off and the surface is allowed to relax.

The outline of this paper is as follows. In Sec. II, we review the master-equation formulation of MBE beginning with the representation of the growth process of our original model by chemical "reactions." The master equation is an evolution equation for the joint probability distribution function of the various "reactants" and is equally valid under the far-from-equilibrium conditions during growth, and the relaxation of the surface to equilibrium once the incident molecular beam is turned off [10]. The master equation also provides a basis from which to derive equations for various quantities such as average concentrations, and corrections thereto. In Sec. III, the master equation is used to derive the continuum equation used in our earlier work. By an appropriate choice of cells in the coarse graining of the lattice model, we show that the ostensibly one-dimensional equations used in our earlier work in fact contain two-dimensional information averaged over the lateral length of the terrace. The formulation of the generalized BCF equations is given in Sec. IV, with results for this model compiled in Sec. V. We show that although inclusion of pair formation is sufficient to model growth near step flow, for applicability of the model to a wider range of growth conditions for MBE on vicinal surfaces, higher-order island formation as well as atom detachment from the steps and islands must be considered. Also, breakup of atoms from islands is shown to be an essential mechanism for the modeling of recovery of the surface after the beam flux is switched off, which is to be expected from simulations of MBE. Our conclusions are summarized in Sec. VI.

II. MASTER-EQUATION FORMULATION

As in our earlier work, we describe each step in the growth process as a "reaction" among the various "species." The master equation corresponding to the reaction sequence can then be derived following a standard procedure, and then equations of motion for various quantities are obtained by taking the appropriate averages [10]. There are a number of advantages of this procedure, some of which have been discussed in Ref. [6]. One of the primary advantages for the present work is that by beginning from a lattice theory, the effect of the implicit averaging carried out by coarse graining is evident from the start. Thus, the level of spatial information that can be obtained from the theory is clearly displayed, which is important for identifying the pertinent quantities when making comparisons with the results of simultaneous (see, for example, Ref. [11]). We will first derive the master equation for the original model of MBE we proposed to illustrate the basic principles of our approach and then turn to the generalized BCF model discussed in the following sections.

The substrate is a vicinal surface with an underlying square lattice with nearest-neighbor spacing a [Fig. 1(a)]. The boundary conditions are, for the moment, left unspecified. We suppose that the system is coarse grained into N cells, the detailed nature of which will be discussed later. In our original model of MBE [6], three processes were considered: deposition of atoms from the molecular beam onto the substrate, the diffusion of atoms

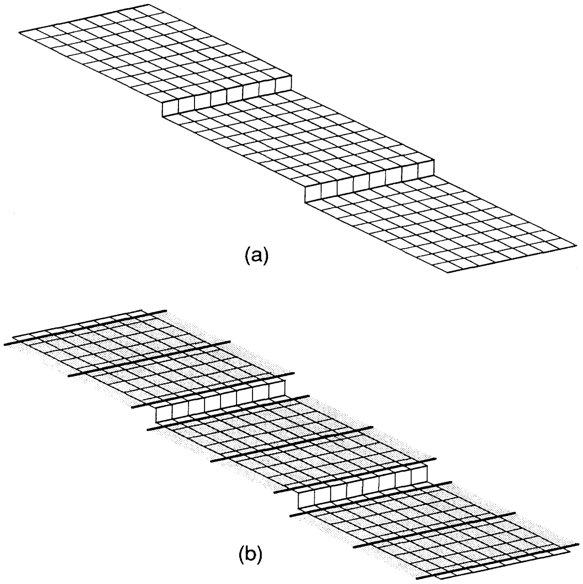

FIG. 1. (a) The representation of a vicinal surface with an underlying square lattice. (b) The coarse graining of the vicinal surface into cells that are extended along the step direction. The cell boundaries are marked in emboldened lines and the cell area is shaded.

on the substrate, and the formation of diatomic islands. Denoting incoming atoms from the molecular beam by A, substrate atoms by X, and diatomic islands by Y, the reactions for the deposition and growth process are given by

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

The first two reactions correspond to the deposition process, with the first reaction representing the deposition of single atoms onto the substrate and the second accounting for the direct collision of arriving atoms with single atoms on the substrate to form diatomic islands. The third reaction represents the formation of diatomic islands by the collision of mobile substrate atoms. Expression for the rate constants k_i are given in Ref. [6]. In addition to the reactions (1), we include the mobility of surface atoms in the form of the hopping rate from cell i to j, d_{ij}.

The joint probability of finding x_i atoms in the ith cell at time t will be denoted $P(x_1,x_2,\ldots,x_N;t)\equiv P(\mathbf{x};t)$. The master equation describing the evolution of P for the reaction-diffusion system (1) is given by

$$\begin{aligned}\frac{\partial}{\partial t}P(\mathbf{x};t)= &\sum_{i,j=1}^{N}[d_{ij}(x_i+1)P(x_i+1,x_j-1,\hat{\mathbf{x}},t)-d_{ij}x_iP(\mathbf{x},t)]\\ &+\sum_{i=1}^{N}[k_2(x_i+2)(x_i+1)P(x_i+2,\hat{\mathbf{x}};t)-k_2x_i(x_i-1)P(\mathbf{x};t)]\\ &+\sum_{i=1}^{N}\{k_0[A]P(x_i-1,\hat{\mathbf{x}},t)-k_0[A]P(\mathbf{x};t)\}\\ &+\sum_{i=1}^{N}\{k_1[A](x_i+1)P(x_i+1,\hat{\mathbf{x}},t)-k_1[A]x_iP(\mathbf{x};t)\}\ ,\end{aligned} \tag{2}$$

where the notation $\hat{\mathbf{x}}$ is an abbreviation for all of the x_i not explicitly written, and [ ] denotes the concentration of the enclosed quantity.

Equation (2) may be used to obtain coupled evolution equations for the correlation functions among the x_i. For example, the evolution equation for the average particle number in the kth cell,

$$\langle x_k(t)\rangle=\int\cdots\int\prod_{j=1}^{N}x_kdx_j\,P(\mathbf{x};t)=\int x_kdx_k\int\cdots\int\prod_{j\,(\neq k)}dx_jP(x_k,\hat{\mathbf{x}};t) \tag{3}$$

is obtained by multiplying both sides of (2) by x_k and integrating over all the x_j, $j=1,\ldots,N$. We obtain

$$\frac{d}{dt}\langle x_k(t)\rangle=\sum_{j=1}^{N}D_{jk}\langle x_j(t)\rangle+k_0[A]-k_1[A]\langle x_k(t)\rangle-2k_2\langle x_k(t)[x_k(t)-1]\rangle\ , \tag{4}$$

where the quantity D_{jk} is given by

$$D_{jk}=d_{jk}-\delta_{jk}\sum_{i=1}^{N}d_{ji}\ . \tag{5}$$

Because of the nonlinearity of the island-forming reaction in (1), the equation of motion for the average $\langle x_k(t)\rangle$ is coupled to the two-point function $\langle x_k(t)[x_k(t)-1]\rangle$. The evolution equation for this quantity is coupled to a three-point function, the evolution equation of which, in turn, is coupled to a four-point function, and so on. To make the solution of these equations tractable, this hierarchy of equations must be truncated.

III. THE CONTINUUM LIMIT

The coarse graining in Ref. [6] used square cells. As we will show below, an alternative construction of the cells is more useful not only for the decoupling $\langle x_k(t)\rangle$ from the higher-order correlation functions in the hierarchy of evolution equations, but also in specifying the boundary conditions at the step edges. Consider therefore the coarse graining shown in Fig. 1(b). Instead of using finite-volume cells, as is usually done in coarse graining, we divide the terrace into strips of width Λ that are extended parallel to the step edge and therefore have infinite volume.

There are several beneficial consequences of this coarse graining. In the absence of long-range correlations, the variance of the distribution of single particles in any cell vanishes:

$$\langle [x_k(t)-\langle x_k(t)\rangle]^2\rangle=\langle x_k^2(t)\rangle-\langle x_k(t)\rangle^2=0\ , \qquad (6)$$

which, for large particle numbers, implies that the nonlinear term in (4) may be written as

$$\langle x_k(t)[x_k(t)-1]\rangle\approx\langle x_k^2(t)\rangle=\langle x_k(t)\rangle^2\ . \qquad (7)$$

This provides the justification of the truncation carried out in Ref. [6].

There are two further important consequences of this coarse graining. By construction, the intercell hopping is suppressed in the direction along the step. Furthermore, since the length of the cell along the step direction is infinite, all information about the step profile is lost and replaced simply by the *average position* of the step. In effect, all of the transverse fluctuations have been averaged out (Fig. 2). If, on the other hand, the cells are chosen to be of length Λ' along the step edge, then fluctuations of wavelength $\lambda\simeq\Lambda'^{-1}$ would have to be included. Additionally, for finite-volume cells, the variance in the particle-number distribution would be nonzero, which would mean that the evolution equations of higher-order correlations would also have to be considered explicitly.

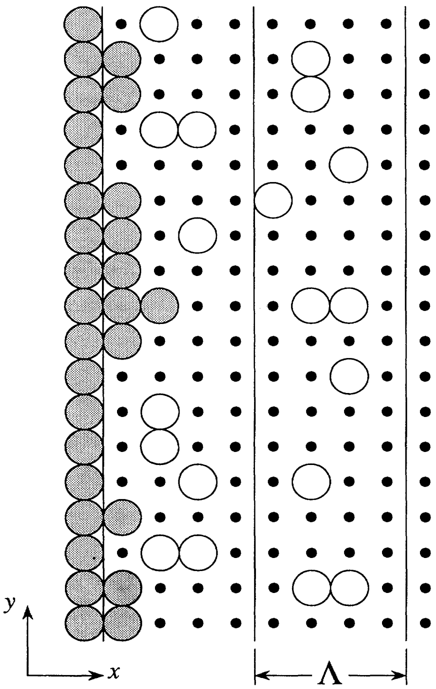

FIG. 2. Plan view of coarse-grained cells on a single terrace of a vicinal surface. The shaded atoms are part of the step edge and indicate the profile fluctuations that are averaged by the infinite extent of the cells along the y direction.

The continuum limit can now be taken as in Ref. [6], with the reinterpretation of $n_i(t)=x_i(t)/\Lambda$ as a concentration *per unit length* along the step. The effective nonlinear diffusion equation reads

$$\frac{\partial}{\partial t}n(x,t)=D\frac{\partial^2}{\partial x^2}n(x,t)+J-\frac{2m}{n_0}n(x,t)-2\sigma D[n(x,t)]^2\ , \qquad (8)$$

where D is the diffusion constant, J is the beam flux, $n_0\equiv a^{-2}$ is the site density, m is the number of sites around a single atom that when filled form a diatomic island, and σ is a capture efficiency for diatomic-island formation. Boundary conditions can then be applied at the bounding step edges of the terrace, which can be taken to be straight.

IV. GENERALIZED BURTON-CABRERA-FRANK EQUATIONS

We now describe the generalization of this approach to include the formation of islands with larger numbers of atoms, as well as the detachment of atoms from islands and steps. We consider first the interactions between adatoms and islands on the terraces. Each surface species with j atoms will now be denoted as Y_j. Thus, single adatoms, which were denoted X in the preceding section are now denoted Y_1. Atoms from the incoming beam are still denoted A. The reaction sequence describing the deposition, island formation, and growth processes, is constructed in analogy with (1). Allowing the formation of islands with larger numbers of atoms leads to the additional reactions that generalize the second and third reactions in (1) to include up to n-atom islands. The reactions that form the basis of the generalized BCF theory are thus given by

$$A\xrightarrow{k_0}Y_1,\quad A+Y_j\xrightarrow{k_j}Y_{j+1},\quad Y_1+Y_j\underset{q_j}{\overset{r_j}{\rightleftarrows}}Y_{j+1} \qquad (9)$$

for $j=1,2,\ldots,n$. Reactions involving A represent the deposition process, with the first reaction describing deposition of single adsorbed adatoms from the beam, and subsequent ones accounting for direct collision of arriving adatoms with substrate atoms and islands. Note that the reverse reactions in each, evaporation of atoms from the surface and islands, may be neglected for MBE as mentioned above. The forward reactions on the right-hand side correspond to the collision of a migrating atom with another atom or island. The reverse reaction corresponds to their breakup into a $j-1$ island and a free adatom. Since we do not include any reactions to account for the coalescence of islands, the following treatment is restricted to dilute concentrations of islands.

A. Master-equation formulation

The master equation for the reaction sequence (9) again involves first coarse graining the system into N cells as in Sec. II. The number of j-atom species in the ith cell is denoted $y_i^{(j)}$ and we employ the notation $\mathbf{y}^{(j)}=(y_1^{(j)},y_2^{(j)},\ldots,y_N^{(j)})$ for the collection of the $y_i^{(j)}$. We also introduce $\mathbf{Y}=(\mathbf{y}^{(1)},\mathbf{y}^{(2)},\ldots,\mathbf{y}^{(n)})$ as a collective abbreviation for all of the $y_i^{(j)}$ grouped according to the number of atoms in the island. The master equation for $P(\mathbf{Y};t)$ for the reactions (9) including the diffusion of adatoms is constructed in an analogous manner to (2). The steps involving the deposition of adatoms contribute the terms

$$\sum_{i=1}^{N}\{k_0[A]P(y_i^{(1)}-1;\hat{\mathbf{Y}};t)-k_0[A]P(\mathbf{Y};t)\}+\sum_{k=1}^{N}\sum_{j=1}^{n}\{k_j[A](y_i^{(j)}+1)P(y_i^{(j)}+1,y_i^{(j+1)}-1,\hat{\mathbf{Y}};t)-k_j[A]y_i^{(j)}P(\mathbf{Y};t)\}\ , \tag{10}$$

where the first term represents the deposition of single adatoms while the second term represents the creation of a $(j+1)$-atom island by deposition onto a j-atom island. We have defined $k_n=0$ to simplify the expressions.

Island formation and growth is divided into two types of terms. The first type involves the formation of a diatomic island by the collision of two single atoms, with the dissociation of the diatomic islands described by the reverse reaction. The contribution to the master equation is

$$\begin{aligned}&\sum_{i=1}^{N}[r_1(y_i^{(1)}+2)(y_i^{(1)}+1)P(y_i^{(1)}+2,\hat{\mathbf{Y}};t)-r_1y_i^{(1)}(y_i^{(1)}-1)P(\mathbf{Y};t]\\&\qquad+\sum_{i=1}^{N}[q_1(y_i^{(2)}+1)P(y_i^{(1)}-2,y_i^{(2)}+1,\hat{\mathbf{Y}};t)-q_1y_i^{(2)}P(\hat{\mathbf{Y}};t)]\ .\end{aligned} \tag{11}$$

The second type of term describes the growth of the islands by the capture of diffusing adatoms, and the decay of islands by the emission of single adatoms:

$$\begin{aligned}&\sum_{i=1}^{N}\sum_{j=1}^{N}[r_j(y_i^{(1)}+1)(y_i^{(j)}+1)P(y_i^{(1)}+1,y_i^{(j)}+1,y_i^{(j+1)}-1,\hat{\mathbf{Y}};t)-r_jy_i^{(1)}y_i^{(j)}P(\mathbf{Y};t)]\\&\qquad=\sum_{i=1}^{N}\sum_{j=1}^{n}[q_j(y_i^{(j+1)}+1)P(y_i^{(1)}-1,y_i^{(j)}-1,y_i^{(j+1)}+1,\hat{\mathbf{Y}};t)-q_jy_i^{(j+1)}P(\mathbf{Y};t)]\end{aligned} \tag{12}$$

In (11) and (12), we have introduced $r_j=0$ and $q_j=0$ to simplify the form of the expressions.

Finally, there is a term describing the cell-to-cell diffusion of only the single adatoms:

$$\sum_{i,j=1}^{N}[d_{ij}(y_i^{(1)}+1)P(y_i^{(1)}+1,y_j^{(1)}-1,\hat{\mathbf{Y}};t)-d_{ij}y_i^{(1)}P(\mathbf{Y};t)]\ . \tag{13}$$

The time development of P from some prescribed initial condition is given by the sum of (10)–(13).

Equations of motion for the correlation functions among the $y_i^{(j)}$ can be obtained from the master equation for P as in Sec. II. The average number of j-particle clusters in the kth cell is given by

$$\langle y_k^{(j)}(t)\rangle=\int\cdots\int\prod_{i=1}^{N}\prod_{l=1}^{n}y_k^{(j)}dy_i^{(l)}P(\mathbf{Y};t)=\int y_k^{(j)}dy_k^{(j)}\int\cdots\int\prod_{i\,(\neq k)}\prod_{l\,(l\neq j)}dy_i^{(l)}P(\mathbf{Y};t)\ . \tag{14}$$

The coupled evolution equations for the $\langle y_k^{(j)}(t)\rangle$ are obtained in analogy with the procedure used in obtaining (4). We find

$$\begin{aligned}\frac{d}{dt}\langle y_k^{(1)}(t)\rangle&=\sum_{j=1}^{N}D_{jk}\langle y_j^{(1)}(t)\rangle+k_0[A]-k_1[A]\langle y_k^{(1)}(t)\rangle-2r_1\langle y_k^{(1)}(t)[y_k^{(1)}(t)-1]\rangle\\&\quad+2q_1\langle y_k^{(2)}(t)\rangle-\sum_{j=2}^{n}r_j\langle y_k^{(1)}(t)\rangle+\sum_{j=2}^{n}q_j\langle y_k^{(j+1)}(t)\rangle\ ,\\\frac{d}{dt}\langle y_k^{(j)}(t)\rangle&=k_{j-1}[A]\langle y_k^{(j-1)}(t)\rangle-k_j[A]\langle y_k^{(j)}(t)\rangle+r_{j-1}\langle y_k^{(1)}(t)y_k^{(j-1)}(t)\rangle\\&\quad-r_j\langle y_k^{(1)}(t)y_k^{(j)}(t)\rangle-q_j\langle y_k^{(j)}(t)\rangle+q_j\langle y_k^{(j+1)}(t)\rangle\ ,\end{aligned} \tag{15}$$

where D_{jk} is given by (5) and where in writing the second of equations (15) we have assumed $y_k^{(1)}-1 \approx y_k^{(1)}$. Note that the islands are assumed to be immobile. As in Sec. III, the absence of long-range correlations means that the variance of single adatoms in the cells vanishes. Thus, the averages of products can be written as the product of averages in (15), thereby decoupling the hierarchy of equations.

B. Rate constants, boundary conditions, and the continuum limit

We have previously derived the rate constants for the forward reactions in the continuum limit [6]. If J is the adatom beam flux to the surface, then $k_j = Jm_j/n_0$, where n_0 is the site density. The factor m_j is the number of sites around an adsorbed entity with j atoms that will form a $(j+1)$-atom island when filled. For a (001) surface, $m_1=4$ or 5 if the adatom site itself is included. For $j>2$, m_j will depend on the morphology of the island; here, we determine m_j assuming a shape for each island that is as close as possible to a square. Secondly, we showed that $r_j = \sigma_j D$ for the rate at which single mobile adatoms collide with other adsorbed entities. Here σ_j is the capture efficiency of a j-atom island, which we will take to be a constant σ of order 1 for all islands as a first approximation. D is the diffusivity of a single adatom, $D = \nu a^2 \exp(-E_D/k_B T)$, where ν is an adatom vibrational frequency on the order of 10^{13} s^{-1}, a is the nearest-neighbor hopping distance, E_D is the effective activation energy for diffusion of a lone adatom, k_B is Boltzmann's constant, and T is the substrate temperature. Thus the *net* rate at which an island with j atoms is formed is given in the continuum limit by

$$R_j(n_1,n_{j-1},n_j,n_{j+1}) = \sigma D n_1(n_{j-1}-n_j) + J\left[m_{j-1}\frac{n_{j-2}}{n_0} - m_j\frac{n_j}{n_0}\right] + q_{j+1}n_{j+1} - q_j n_j \tag{16}$$

for $j \geq 2$. The continuum form of the equations (15) is thus given by

$$\begin{aligned} \frac{\partial}{\partial t}n_1(x,t) &= D\frac{\partial^2}{\partial x^2}n_1(x,t) + J + R_1(n_1(x,t),n_2(x,t),\ldots)\,, \\ \frac{\partial}{\partial t}n_j(x,t) &= R_j(n_1(x,t),n_2(x,t)\ldots)\,, \end{aligned} \tag{17}$$

where $n_j(x,t)$ is the concentration per unit length of j-atom species.

The equally spaced steps move at a velocity $v(t)$. It is convenient to transform to a frame of reference that moves with the steps, in which case, Eqs. (17) become

$$\begin{aligned} \frac{\partial}{\partial t}n_1(x,t) &= D\frac{\partial^2}{\partial x^2}n_1(x,t) + J + v\frac{\partial}{\partial x}n_1(x,t) + R_1(n_1(x,t),n_2(x,t),\ldots)\,, \\ \frac{\partial}{\partial t}n_j(x,t) &= v\frac{\partial}{\partial x}n_j(x,t) + R_j(n_1(x,t),n_2(x,t),\ldots.)\,. \end{aligned} \tag{18}$$

It now remains to specify the boundary conditions at the step edges. Previously, we have utilized absorbing boundary conditions $[n(0,t)=n(h,t)=0]$. This assumption of "sticky" adatoms, which cannot detach themselves from the step once incorporated, was consistent with our neglect of breakup of atoms from islands. Now, assuming that islands have a finite probability of breaking up, we must also include the detachment of single adatoms from the step edge. In order to analyze the attachment and detachment processes of single adatoms from the step edge, we will again use a reaction representation.

Let Y_1^+ and Y_1^- represent single adatoms directly below and above a step edge, respectively. In reality, the step may have a complex two-dimensional profile; here we simplify it by denoting Y_s as singly bonded or kink-site atoms attached to the step (which may desorb onto the terrace), while S simply denotes the entire step edge. The reactions for the exchange of single adatoms between the step and the region on the terrace directly below and above the step are

$$\begin{aligned} &Y_1^+ \xrightarrow{s_a^+} S\,, \quad Y_s \xrightarrow{s_d^+} Y_1^+\,, \\ &Y_1^- \xrightarrow{s_a^-} S\,, \quad Y_s \xrightarrow{s_d^-} Y_1^-\,. \end{aligned} \tag{19}$$

The equations on the left-hand side represent the attachment of free atoms to the step edge, and the right-hand side equations indicate the detachment of weakly bonded atoms from the step back onto the terrace. These processes are depicted in Fig. 3. As has been done by others [4], we could assign different rates for attachment and detachment of atoms above and below a step, but here, for simplicity, we assume the kinetics are symmetric on either side of a step with $s_a^+ = s_a^- = s_a$ and $s_d^+ = s_d^- = s_d$. Below, $n_s(t)$ denotes the concentration of Y_s atoms on the step edge which can hop back onto the terrace. The concentrations of the different types of atom configurations (singly or multiply bonded) at the step edge will depend on the step morphology and may change during growth. However, modeling of the changes in n_s during growth would require an explicitly two-dimensional theory which would incorporate diffusion and interactions along the step edge. As a first approximation, assume that the step morphology remains the same throughout growth so that $n_s(t)=n_s$, a constant. Then, we recognize that the *net* flux of single adatoms incorporated into the step from either above or below equals the difference between the rates at which atoms attach and detach from the step edge:

$$D\left.\frac{dn}{dx}\right|_{x=0}=s_a n(0,t)-s_d n_s\ ,$$

$$D\left.\frac{dn}{dx}\right|_{x=h}=-s_a n(h,t)+s_d n_s\ . \tag{20}$$

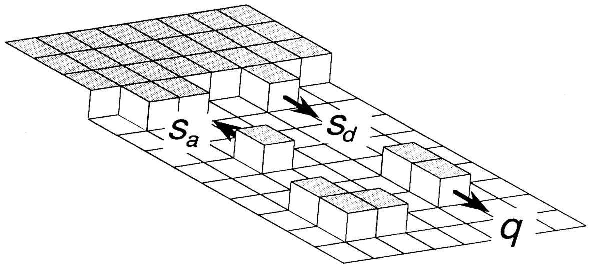

FIG. 3. Depiction of adatom attachment and detachment kinetics below the step edge and island breakup on the terraces.

It is convenient to introduce dimensionless variables by $y_j \equiv Dn_j/(Jh^2)$, $x \to x/h$, $t \to t/(n_0/J)$, and $v \to vn_0/(Jh)$. This results in the following set of nonlinear equations including islands with up to N atoms:

$$\alpha\frac{\partial y_1}{\partial t}=\frac{\partial^2 y_1}{\partial x^2}+1+v\alpha\frac{\partial y_1}{\partial x}-2\alpha y_1(\beta y_1+m_1)-\alpha\sum_{j=2}^{N-1} y_j(\beta y_1+m_j)+2\gamma_2 y_2+\sum_{j=3}^{N}\gamma_j y_j\ ,$$

$$\alpha\frac{\partial y_j}{\partial t}=v\alpha\frac{\partial y_j}{\partial x}+\alpha[\beta y_1(y_{j-1}-y_j)+(m_{j-1}y_{j-1}-m_j y_j)]+\gamma_{j+1}y_{j+1}-\gamma_j y_j\ ,\quad j\geq 2\ . \tag{21}$$

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), $\beta=\sigma n_0/h^2$ is a measure of the rate of island formation, and $\gamma_j=q_j h^2/D$ is the ratio of the diffusion time to the average lifetime of a j-atom island. The boundary conditions are

$$\left.\frac{dy_1}{dx}\right|_{x=0}=S_a n(0,t)-\frac{S_d n_s}{\alpha n_0},\quad \left.\frac{dy_1}{dx}\right|_{x=1}=-S_a n(h,t)+\frac{S_d n_s}{\alpha n_0};\quad y_j(1,t)=0,\quad j\geq 2\ . \tag{22}$$

Above, $S_a=s_a h/D$ and $S_d=s_d h/D$ in the radiation boundary conditions for the adatom concentration are a measure of the rates of attachment and detachment to the diffusion rate, respectively. The boundary conditions for the islands are determined by the requirement that there can be no islands atop a newly formed step at $x=1$, since the step edge has just been freshly formed.

Solution of these equations requires an expression for the velocity of the step train. This can be derived by considering the flux at the step edge due to diffusing adatoms from above and below the step, and the convective flux of immobile islands by the moving step:

$$v=\left.\frac{dy_1}{dx}\right|_{x=0}-\left.\frac{dy_1}{dx}\right|_{x=1}+v\alpha\sum_j jY_j(0,t)\ . \tag{23}$$

We now assign values to the several new parameters for island and step breakup that we have incorporated into the equations: q_j, s_a, s_d, and n_s. We will estimate the rates using Arrhenius expressions. Assuming that the average energy of attachment between two nearest-neighbor atoms is E_N yields $q_j=q=\nu\exp[-(E_D+E_N)/k_BT]$ for the rate of breakup of an atom from an island, assumed to be the same for all islands so that $\gamma_j=\gamma$. In Fig. 4, we show for up to four-atom clusters the atoms that are regarded to be kinetically "active," in the sense that detachment from the cluster occurs at the indicated sites. The detachment from other sites could be included in the model, but because of the longer lifetimes at sites with increasing numbers of nearest neighbors, these processes would not affect the growth in a significant way [12]. However, for a detailed study of

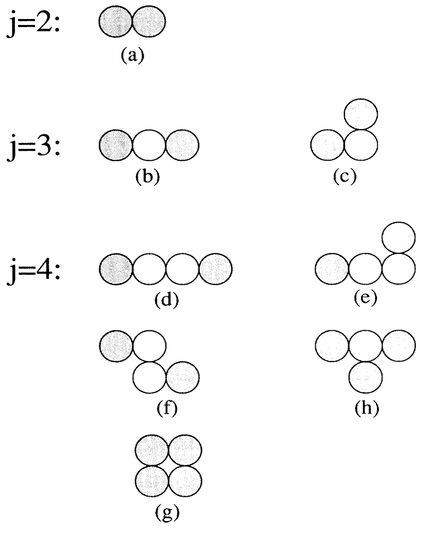

FIG. 4. Symmetrically distinct clusters including up to four atoms. The shaded atoms are those where detachment from the cluster occurs.

recovery pathways during the equilibration of the surface, these slower kinetic paths may have to be included.

Estimation of the step kinetic parameters s_a, s_b, and n_s is more difficult since the values of these parameters will depend on the two-dimensional morphology of the step edge, which is not included in our one-dimensional theory. Assuming a straight step edge, we obtain $s_d = \nu a \exp[-(E_D+E_N)/k_B T]/4$, where the factor of 4 occurs because only one hop in four directions [assuming a (001) surface] will result in detachment of the atom below (or above) the step. Furthermore, we assume that the rate of attachment of an atom to the step is proportional to its mobility; hence $s_a = \nu a \exp(-E_D/k_B T)/4$. As discussed previously, we take n_s to be an adjustable constant between zero and n_0.

C. Recovery and the equilibrium limit

It is also possible to model recovery of the surface morphology after cessation of growth since we have allowed for the possibility of breakup of atoms from steps and islands. The equations governing the recovery process are similar to (5), but with the adatom flux term J removed. Additionally, the island-formation terms corresponding to direct collision of atoms from the beam with adsorbed species are omitted by setting $m_j = 0$ for all j. The resulting equations are

$$\begin{aligned} \alpha\frac{\partial y_1}{\partial t} &= \frac{\partial^2 y_1}{\partial x^2} + v\alpha\frac{\partial y_1}{\partial x} - 2\alpha\beta(y_1)^2 \\ &\quad - \alpha\beta\sum_{j=2}^{N-1} y_j y_1 + \gamma\left[2y_2 + \sum_{j=2}^{N} y_j\right], \\ \alpha\frac{\partial y_j}{\partial t} &= v\alpha\frac{\partial y_j}{\partial x} + \alpha\beta y_1(y_{j-1}-y_j) \\ &\quad + \gamma(y_{j+1}-y_j), \quad j \ge 2 . \end{aligned} \tag{24}$$

The equilibrium concentrations correspond to the long-time solution of (24). In the original BCF theory, the equilibrium adatom concentration was determined by the balance between desorbing surface atoms and the equilibrium flux from the vapor as $n_1^{\mathrm{eq}} = \tau J^{\mathrm{eq}}$. Here, the equilibrium adatom concentration is determined by the atom attachment and detachment processes at the step edge:

$$y_1^{\mathrm{eq}} = \frac{S_d n_s}{S_a \alpha n_0} . \tag{25}$$

The equilibrium island concentrations are also constant across the terrace and are given by

$$\alpha\beta y_1^{\mathrm{eq}}(y_{j-1}^{\mathrm{eq}}) - (\alpha\beta y_1^{\mathrm{eq}} + \gamma)(y_j^{\mathrm{eq}}) + \gamma(y_{j+1}^{\mathrm{eq}}) = 0 , \quad j \ge 2 . \tag{26}$$

These equations for the island concentration form a tridiagonal matrix that can be easily solved by Gaussian elimination.

V. RESULTS AND DISCUSSION

Reflection high-energy electron-diffraction (RHEED) measurements, widely used as a probe during MBE on semiconductor surfaces [13,14], provide a means for testing our nonlinear theory. Full dynamical RHEED calculations from model surfaces for comparison with experiment have to date only been attempted with simple periodic configurations [15,16]. Another approach has been to compare the RHEED intensity with the surface step density, which appears to incorporate many of the qualitative features of the temporal RHEED measurements [12]. The continuum model, however, does not provide the information about surface-height correlations necessary to calculate the step density. Thus we utilize kinematic theory, which requires only the surface coverages, to compare the transient behavior of our nonlinear theory with RHEED measurements of MBE on stepped surfaces. Although an approximation for RHEED, single-scattering theory is directly applicable to He-atom or x-ray scattering measurements.

Since the step train is periodic in the terrace length down the staircase, an off-Bragg kinematic calculation at $S_x, S_z = 0$ will yield a zero intensity signal due to cancellation between alternate layers. Thus, it is more appropriate to calculate the kinematic intensity down the staircase at $S_z = \pi/a$ and $S_x = \pi/h$, where the terraces add constructively [17]:

$$I(S_x = \pi/h, S_z = \pi/a; t) = \left| \int_0^1 \left[1 - 2\sum_{j=1}^{N} j y_j(x,t) \right] e^{i\pi x} dx \right|^2 . \tag{27}$$

Figure 5 shows the kinematic intensity as a function of α for $\beta = 324$ calculated numerically from the nonlinear equations using a finite-difference method [18]. The intensity is shown for 5 monolayers of growth and a subsequent period of recovery. At the left is shown the intensity for the original theory with diatomic islands only and infinitely "sticky" adatoms ($E_N \to \infty$, $\gamma = 0$, $S_d = 0$, and $S_a \to \infty$). The transient behavior of the calculated intensity *during growth* exhibits a remarkable resemblance to temporal RHEED measurements of MBE on stepped surfaces [19]. Decaying intensity oscillations are observed at high α (low temperature) which disappear at low α (high temperature). In the RHEED measurements, a temperature T_c was defined as the temperature where the temporal oscillations are no longer detectable during growth; this was interpreted to correspond to the onset of step flow, i.e., growth dominated by incorporation of atoms at the step edge [19].

We have shown that T_c can be predicted from our original model [6] as the point at which pair formation may be neglected and epitaxial growth proceeds predominantly by step propagation: $T_c = (E_D/k_B)[\ln(\nu a^2/2Jh^4)]^{-1}$. We obtained excellent agreement between the values 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 [19]. Nucleation reduces the effective diffusivity of the adatoms by several orders of magnitude, and therefore a realistic model of MBE on vicinal surfaces must include the nonlinear interactions responsible for island formation.

Although the inclusion of diatomic-island formation as described above represents a considerable improvement

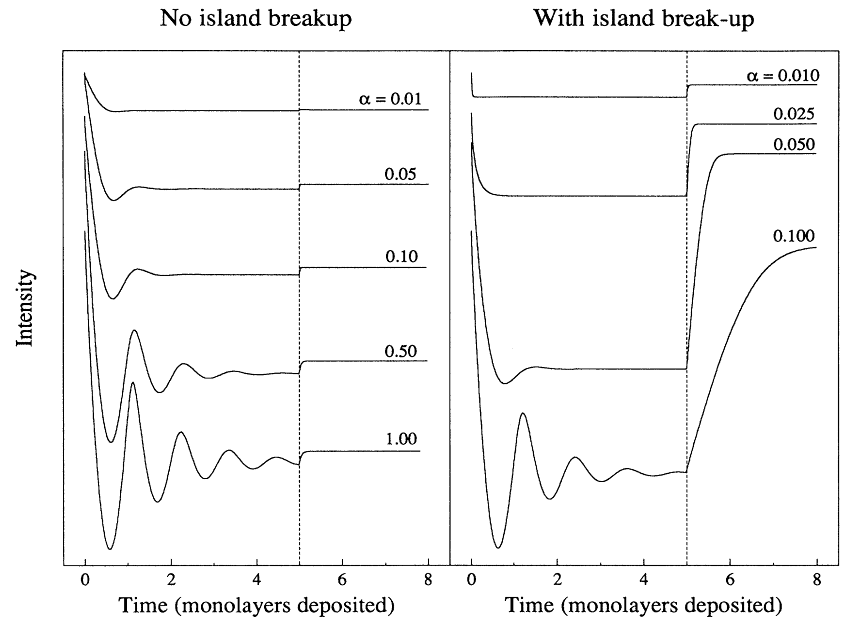

FIG. 5. Kinematic intensity at $S_x = \pi/h$ and $S_z = \pi/a$ for growth and recovery. The left panel shows the nonlinear theory including nucleation with diatomic islands only for $\beta = 324$, and the right panel includes islands with up to ten atoms as well as atom detachment from the islands and step edges.

over previous linear BCF theories, several important details of the nucleation kinetics have been omitted from the simplified equations; namely, inclusion of higher-order island-formation and atom-detachment kinetics. On the right-hand side of Fig. 5, we show the intensity of inclusion for islands with up to ten atoms in (21), with a finite probability of detachment $E_N/E_D = 0.2$ and with $n_s/n_0 = 0.25$, which was chosen to yield a total concentration of material under the step edge at T_c to be close to that for the original model, about 1%. The generalized theory shows not only a different recovery profile but also a quicker development of oscillations with increasing α. Below, we discuss these differences and the underlying growth kinetics which are responsible for them.

The distribution of material on the terrace during growth is shown in Fig. 6 for the generalized theory with

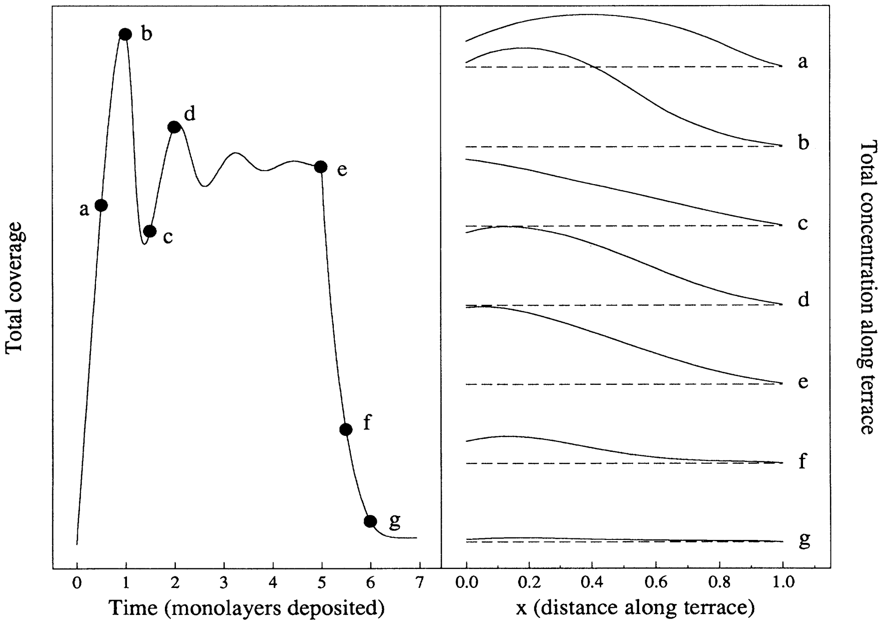

FIG. 6. Total concentration of adatoms and islands for the generalized theory (4) for $\alpha = 0.1$, $\beta = 324$, $E_N/E_D = 0.2$ eV, $J = 1$ monolayer/s, and $n_s/n_0 = 0.25$. The left panel shows temporal evolution of total coverage, and the right panel depicts the concentration distribution along the terrace for selected times.

the above parameters at $\alpha=0.1$, well removed from step propagation mode. The left panel shows the total coverage, $\Theta=\int_0^1(\sum_{j=1}^{N} jn_i/n_0)dx$ as a function of time, while the right panel shows the distribution of the total material over the terrace at selected times. Growth of 5 monolayers is shown as well as a brief recovery period. At the beginning of growth (*a*), the velocity is still small and the atoms and islands build up almost symmetrically around the center of the terrace. After the deposition of about 1 monolayer (*b*), a large amount of material has nucleated on the terrace, slightly skewed due to the increasing velocity (note that steps are assumed to move to the right in the figure). As the step pushes through the area of high island concentration, its velocity increases sharply due to incorporation of these islands and the step shoots across the surface; at 1.5 monolayers of growth (*c*) the total amount of material on the terrace has decreased significantly and the distribution is almost linear. The nucleation and island buildup process repeats itself, but to a lesser extent, as seen in point *d*, until a steady-state concentration profile is achieved (*e*). After the cessation of growth at 5 monolayers, the total concentration on the terrace drops swiftly as shown in *f* and *g*. At lower α, due to the small amount of nucleation and high mobility of the adatoms, the coverage does not oscillate as shown in Fig. 6 but instead increases monotonically to its steady-state distribution.

In marked contrast to the generalized theory, the intensity for the original model in Fig. 5 does not recovery after the cessation of growth, aside from a very small initial increase due to attachment of adatoms at the steps, since the diatomic islands are not allowed to decay. The recovery profile for the generalized theory, on the other hand, compares qualitatively well to measurements [19]. Recovery is swifter at lower α (higher temperature) and proceeds from an initial decrease of single-adatom concentration due to incorporation at steps and nucleation, and a slower decay of the islands themselves through the release of adatoms which are adsorbed into the step edge. Since the recovery of the intensity is calculated using kinematic theory, it represents the decrease of coverage of the terraces due to atom capture at steps. Thus their detailed shape may differ from those of RHEED recovery curves, which may incorporate information about changes in the intralayer morphology due to smoothing of rough step and island edges. The kinematic analysis should, however, be directly applicable to other types of measurements where multiple scattering does not play such a strong role, such as He-atom and x-ray scattering.

Unlike the model without island and step-edge breakup, the generalized theory exhibits equilibrium concentrations of atoms and islands which are constant across the terrace. The equilibrium coverage of the terrace with adatoms is determined solely by the balance of attachment and detachment processes at the step edge: $n_1^{\text{eq}}/n_0=(S_d/S_a)(n_s/n_0)$. A larger rate of absorption of adatoms by the step edge compared to the emission rate yields a smaller equilibrium concentration. The equilibrium island concentrations are determined by the interplay between the collision rate of adatoms with other species, which is proportional to $\alpha\beta$, and the breakup rate of islands γ.

Additionally, if no detachment is allowed from the step edges, the steps can only move forward or remain stationary. However, if a finite detachment rate is included, there is a very short period at the beginning of growth for the generalized theory where the step velocity is negative. Since at the start of growth the rate at which atoms detach from the step edge outweighs the small initial flux to the step edge from adsorbed atoms on the terrace, the step moves backwards. As growth proceeds, however, buildup of concentration on the terraces leads to a net positive flux of material to the terraces and the steps move forward. This effect may be suppressed by allowing the step to equilibrate prior to growth by releasing atoms to the terrace.

Finally, we note that oscillations appear more quickly with increasing α (decreasing temperature) when a greater degree of nucleation is included. This is in closer agreement with RHEED measurements [19], which exhibit several noticeable oscillations already at 40° below T_c. Figure 7 shows the total number of atoms in each type of surface species at steady state for two different α corresponding to a step-flow regime and to an island-formation-dominated regime. At $\alpha=0.1$ it is clear that at least 10-atom islands must be included; for lower tem-

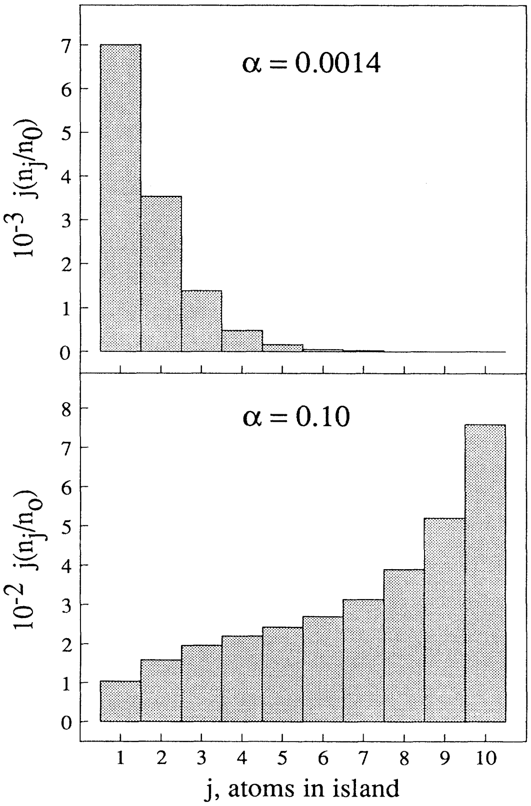

FIG. 7. Number of atoms in each species on the terraces, $j(n_j/n_0)$, as a function of α for $\beta=324$, $E_N/E_D=0.2$ eV, $J=1$ monolayer/s, and $n_s/n_0=0.25$ in the generalized theory. Note the difference in scale.

perature it will be necessary to include terms for coalescence of islands, and other models for deposition on flat surfaces are probably more appropriate. However, at step flow $\alpha = 0.0014$, the total concentration of material on the terrace is very small, and formation of triatomic islands or higher only counts for a small percentage of the total material on the terrace. This confirms the assumption of our original theory, that *near-step-flow* inclusion of only diatomic islands is sufficient.

Although the nonlinear theory only explicitly considers one spatial dimension, it does contain some of the features of the full two-dimensional system in an indirect way. Instead of representing growth confined to a stepped one-dimensional chain of lattice sites, the theory instead treats a mean-field concentration in the y direction. For instance, the two-dimensional shape of the islands in incorporated through m_j, which are calculated assuming square islands and would be different for a strictly one-dimensional system. Since scanning-tunneling-microscope images have shown that flucutations in the step profile can be quite large [20], we also incorporate some of the effects of the two-dimensional step morphology in an average way. Determination of the detailed two-dimensional step profile would require inclusion of the y dependence of the concentrations and y diffusion directly in the equations; unfortunately the equations then become intractable. So, our approach is to try to include those aspects of growth which depend on the step morphology in our one-dimensional model in an indirect way by decoupling growth along the step edge with growth along the step train. We include the effect of step roughness implicitly by varying the step kinetic parameters s_a, s_b, and n_s to model different capture and emission rates for different surface morphologies. A very rough, meandering step, for example, might have a larger capture rate s_d than a smooth step. Due to this inclusion of an approximation to the two-dimensional step kinetics, the generalized theory is qualitatively superior to the original model and is applicable to a much larger variety of systems and growth conditions, although the increase in the number of parameters in the generalized theory does mean an inevitable loss of predictive power. We plan to incorporate the y dimension into our growth equations in the future so that the effects of step-edge fluctuations may be treated more exactly.

VI. CONCLUSIONS

The inclusion of interactions between the surface species in BCF theory is shown to provide a realistic model of MBE on stepped surfaces over a wide range of growth conditions. Due to the inclusion of adatom interactions in the form of nucleation, the nonlinear theory reproduces the full time-dependent behavior of RHEED measurements of MBE during growth on stepped surfaces, including intensity oscillations, decay, and dependence on the growth conditions. Here, we have shown that recovery of the stepped surface as well as growth can be modeled by including breakup of atoms from the islands and the step edge. Additionally, we have shown that the original model (with diatomic nucleation only) is valid near step propagation mode, but that it is necessary to include islands with an increasong number of atoms (up to ten in this work) as well as their breakup to model growth regimes where nucleation competes with incorporation at steps.

In addition to including nucleation of a single species on a stepped surface, the equations could also treat an arbitrary number of different diffusing species. Thus the model may be easily extended to more complicated systems. Recently, we have used the theory to model the growth of semiconductor alloys [9] and quantum wires with various degrees of interaction among the two diffusing species. The formalism of the reaction-diffusion equations could also be used to incorporate decomposition and reaction of molecular adsorbates, such as SiH_4 in Si MBE, or $Ga(CH_3)_3$ and similar organo-metallic compounds in metal-organic molecular-beam epitaxy. In conclusion, the nonlinear diffusion equations provide a detailed and flexible model of epitaxial growth on vicinal surfaces, within the intrinsic limitations of the assumption of one dimensionality of the step train.

ACKNOWLEDGMENTS

This work was supported by Imperial College and the Research Development Corporation of Japan under the auspices of the "Atomic Arrangement: Design and Control for New Materials" Joint Research Program. A.K.M.-B. also acknowledges support from NATO.

[1] W. K. Burton, N. Cabrera, and F. C. Frank, Philos Trans. R. Soc. London, Ser. A **243**, 299 (1951).
[2] K. Voigtlaender and H. Risken, Appl. Phys. **39**, 31 (1986).
[3] V. Fuenzalida and I. Eisele, J. Cryst. Growth **74**, 597 (1986).
[4] R. Ghez and S. S. Iyer, IBM J. Res. Dev. **32**, 804 (1988).
[5] J. A. Venables, G. D. T. Spiller, and M. Hanbücken, Rep. Prog. Phys. **47**, 399 (1984).
[6] A. K. Myers-Beaghton and D. D. Vvedensky, Phys. Rev. B **42**, 5544 (1990).
[7] A. K. Myers-Beaghton and D. D. Vvedensky, J. Phys. A **23**, L995 (1990).
[8] S. Stoyanov, Appl. Phys. A **50**, 439 (1990).
[9] A. K. Myers-Beaghton and D. D. Vvedensky, Surf. Sci. **240**, L599 (1990).
[10] C. W. Gardiner, *Handbook of Stochastic Methods* (Springer, Berlin, 1983).
[11] A. K. Myers-Beaghton and M. R. Wilby, J. Phys. A **24**, L35 (1991).
[12] D. D. Vvedensky and S. Clarke, Surf. Sci. **225**, 373 (1990).
[13] J. H. Neave, B. A. Joyce, P. J. Dobson, and N. Norton, Appl. Phys. A **31**, 1 (1983).
[14] J. M. Van Hove, C. S. Lent, P. R. Pukite, and P. I. Cohen, J. Vac. Sci. Technol. B **1**, 741 (1983).
[15] T. Kawamura and P. A. Maksym, Surf. Sci. **161**, 12 (1985).
[16] T. Kawamura, T. Natori, T. Sakamoto, and P. A. Mak-

sym, Surf. Sci. **181**, L171 (1987).

[17] G. S. Petrich, P. R. Pukite, A. M. Wowchak, G. J. Whaley, P. I. Cohen, and A. S. Arrott, J. Cryst. Growth **95**, 23 (1989).

[18] B. Carnahan, H. A. Luther, and J. Wilkes, *Applied Numerical Methods* (Wiley, New York, 1969).

[19] J. H. Neave, P. J. Dobson, B. A. Joyce, and J. Zhang, Appl. Phys. Lett. **47**, 100 (1985).

[20] A. J. Hoeven, D. Dijkkamp, E. J. van Loenen, J. M. Lenssinck, and J. Dieleman, J. Vac. Sci. Technol. A **8**, 207 (1990).