Regimes of Precursor-Mediated Epitaxial Growth

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Abstract

A discussion of epitaxial growth is presented for those situations (OMVPE, CBE, ALE, MOMBE, GSMBE, etc.) when the kinetics of surface processes associated with molecular precursors may be rate limiting. Emphasis is placed on the identification of various *characteristic length scales* associated with the surface processes. Study of the relative magnitudes of these lengths permits one to identify regimes of qualitatively different growth kinetics as a function of temperature and deposition flux. The approach is illustrated with a simple model which takes account of deposition, diffusion, desorption, dissociation, and step incorporation of a single precursor species, as well as the usual processes of atomic diffusion and step incorporation. Experimental implications are discussed in some detail.

A well-founded conceptual and computational framework now exists for the theoretical description of molecular beam epitaxy (MBE). Surprisingly, it has proved sufficient to focus almost exclusively on the diffusion and incorporation kinetics of single adatoms both in atomistic Monte Carlo simulations[1,2] and in studies based on reaction-diffusion equations.[3−5] Within this context, not only is there an analytic theory of the transition between step flow and two-dimensional (2D) island nucleation and coalescence[4−6], as monitored, e.g., by the disappearance of reflection high-energy electron diffraction (RHEED) oscillations as a function of growth conditions but, for GaAs(001) under sufficiently As-rich conditions, *quantitative* agreement with RHEED oscillation data[2] can be achieved without any explicit reference to the As source (whether As_2 or As_4) in the theoretical model. Unfortunately, there is increasing evidence that these simple adatom models are *not* adequate to describe the growth kinetics for the general case when the atomic constituents of the growing film are delivered to the substrate in the form of heteroatomic molecules. For example, the very different kinetics observed for surface reactions[7,8] and growth[9,10] when trimethylgallium (TMG) or triethylgallium (TEG) is deposited onto GaAs makes clear that no single universal theoretical model is likely to be proposed for this case.

The purpose of the present Letter is to demonstrate the existence and nature of various qualitatively distinct kinetic regimes of epitaxial growth which can occur whenever *surface* chemical processes are important. We are motivated by detailed surface diffraction studies of GSMBE (using electrons)[11−13] and OMVPE (using x-rays)[14,15] which yield considerable information about the morphological evolution of the surface as growth proceeds. Since the existence and evolution of *characteristic length scales* emerge quite naturally from such studies we organize our discussion around the identification of these quantities. For this purpose, it is essential to take explicit account of surface diffusion, a feature missing from essentially all existing theoretical models of such growth. The latter[16,17] typically take the form of spatially uniform coupled rate equations and focus attention on the prediction of quantities such as the net growth rate and the average concentration of various surface species. Nonetheless, as will become clear below, these earlier studies readily can be generalized so that the rather different point of view we advocate here can be adopted.

To illustrate our method, we first describe a simple growth scenario and then work out the qualitative consequences which might be observed in a diffraction experiment of the sort noted earlier. We regard the model as a physically reasonable *minimal* generalization of the adatom models used to study MBE. It is not intended to describe any particular material system in detail.

Consider deposition onto a vicinal surface of a molecule that contains the atomic constituent of the growing substrate. We include (see Fig. 1) the processes of (i) desorption of the molecule back into the gas phase, (ii) surface diffusion of the molecule in a weakly bound precursor state, (iii) decomposition of the molecule on a terrace to release the atomic constituent, and (iv) decomposition of the molecule at a step edge and incorporation there of the atomic species. Included as well are (v) surface diffusion of the atomic species and (vi) incorporation of these atoms at a step edge. For simplicity only, we ignore all site-blocking effects and the presence (and fate) of all molecular decomposition fragments. Desorption of the atomic species is also neglected.

A quantitative theory results if we generalize the analysis of Burton, Cabrera and Frank[18] (BCF) to include the processes described above. The one-dimensional continuum model of BCF often is used to analyze MBE on vicinal surfaces.[3] In the present case, the evolution in time and space of the surface concentration of precursor molecules $n(x,t)$ and adatoms $c(x,t)$ is determined by the following coupled reaction-diffusion equations:

$$\frac{\partial n}{\partial t} = D_M \frac{\partial^2 n}{\partial x^2} - \frac{n}{\tau} - \kappa n + J \tag{1}$$

$$\frac{\partial c}{\partial t} = D_A \frac{\partial^2 c}{\partial x^2} + \kappa n \tag{2}$$

Here, D_M and D_A respectively denote the surface diffusion constant of the precursor molecule and the atom, κ and τ^{-1} are the rate constants for decomposition and desorption of the precursor molecule on a terrace, and J is the molecular deposition flux. Equations (1) and (2) are supplemented by the boundary conditions

$$D_A c_x(0,t) = \beta_A[c(0,t) - c_0], \qquad -D_A c_x(\ell,t) = \beta_A[c(\ell,t) - c_0] \tag{3}$$

$$D_M n_x(0,t) = \beta_M n(0,t), \qquad -D_M n_x(\ell,t) = \beta_M n(\ell,t) \tag{4}$$

where ℓ is the terrace length and c_0 is the equilibrium concentration of atoms at the step edge. As discussed in detail elsewhere,[3] the choice (3) indicates that atoms incident on a step incorporate into the solid at a rate proportional to β_A. The choice (4) guarantees that every precursor molecule incident on a step decomposes (and its atomic constituent incorporated into the step) at a rate proportional to β_M. The steady-state (time-independent) solutions of these equations have simple analytic solutions[3] and one obtains an exact expression for the growth rate. We do not exhibit the explicit formula here since our aim in this paper is to identify the qualitative regimes of growth implied by (1)–(4). Instead, we proceed to the identification of the relevant length scales.

We begin with $x_s = \sqrt{D_M \tau}$ and $\ell_\kappa = \sqrt{D_M/\kappa}$. The quantity x_s is the average distance a molecule diffuses before desorbing while ℓ_κ is the average distance a molecule diffuses before decomposing to release an adatom. Thus, the first two regimes of importance are distinguished by whether $x_s/\ell_\kappa \gg 1$ or $x_s/\ell_\kappa \ll 1$, i.e., whether the diffusing species are predominantly adatoms or molecules. In the first case, we must consider the pertinent length scales associated with the kinetics of the adatoms. The quantity $J_{\text{eff}}(x) = \kappa n(x)$ is the effective "flux" of adatoms due to the decomposition of molecules. It then is natural to define the length $\ell_A = \sqrt[4]{D_A/J_{\text{eff}}}$, where J_{eff} is the constant value obtained by averaging $J_{\text{eff}}(x)$ over a terrace. Clearly, ℓ_A corresponds to the distance an adatom diffuses before another adatom is released by a molecular decomposition reaction.

There now are two new regimes to consider: $\ell_A/\ell \ll 1$ and $\ell_A/\ell \gg 1$. In the first case, the typical migration distance of a free adatom is much smaller than the terrace length, the encounter probability of adatoms is high, and growth proceeds by the nucleation, growth and coalescence of 2D islands on the terraces. In the second case, adatoms diffuse to the step edges before another atom is released, so growth proceeds by the advancement of steps, i.e., step flow. We note that the usefulness of the length scale ℓ_A has been demonstrated previously[5] for the case of MBE where J_{eff} is replaced by the vapor phase deposition flux of atoms.

Within the atomic step flow regime, there are two additional possibilities to consider. To see this, we define a length $d_A = D_A/\beta_A$ which is the *additional* distance an atom

diffuses (after its first arrival at a step) before incorporation into the solid occurs. If $d_A \ll \ell$, incorporation occurs very soon after the first encounter with a step. We refer to this as "fast atomic step flow." Clearly, $\ell_A \gg \ell \gg d_A$ in this regime. On the other hand, if $d_A \gg \ell$, step edge incorporation requires several attempts. If $d_A \ll \ell_A$, growth is reaction-limited at the step edges of the original surface and occurs by "slow atomic step flow". However, if $d_A \gg \ell_A$, attractive interactions between atoms on the terraces become important and growth occurs by a combination of slow step flow and 2D island formation. For growth under typical conditions of MBE, this latter mode appears to be appropriate.[19,20] In this regime we have $d_A \gg \ell_A \gg \ell$.

If $x_s/\ell_\kappa \ll 1$, the migrating species are predominantly the molecular precursors. To determine the growth regimes in this case, we first construct the molecular analogue to ℓ_A, i.e., $\ell_M = \sqrt[4]{D_M/J}$. The quantity ℓ_M is the average distance a molecule travels before encountering another molecule deposited by the incoming flux. We thus are lead to consider the regimes $\ell_M/\ell \ll 1$ and $\ell_M/\ell \gg 1$. In the first case the molecules diffuse to the step edge before encountering another molecule, while in the second case, the molecules collide on the terraces before arriving at the step edge. Both cases require further consideration.

If $\ell_M/\ell \ll 1$, the encounter probability of the molecules on the terraces is high and several scenarios can occur depending upon the precursor mean density. Possibilities include collisional decomposition with concomitant island nucleation, the formation of a molecular film, and the formation of a liquid-like state of adsorbed molecules. Since our model does not include interactions among the molecules we refer to this simply as the "molecular interaction" regime.

If $\ell_M/\ell \gg 1$, it is useful to determine whether one or several encounters with a step are required before the molecule decomposes. This issue is addressed by introducing the length $d_M = D_M/\beta_M$ which may be regarded as the distance a precursor diffuses before a successful step- catalyzed decomposition and incorporation reaction occurs. Again, two regimes are distinguished: $d_M/x_s \ll 1$ or $d_M/x_s \gg 1$. If $d_M/x_s \ll 1$, most of the molecules immediately decompose upon arrival at a step edge. We call this the regime of "fast molecular step flow". Note that $\ell_\kappa \gg x_s \gg d_M$ in this case.

When $d_M/x_s \gg 1$, we must specify the relative magnitudes of d_M and ℓ_κ since both are much greater than the mean desorption length x_s. If ℓ_κ is the shorter of the two, the molecule decomposes on the terrace and the growth mode is determined by atomic kinetics as discussed earlier. But if d_M is the shorter length, the molecules decompose predominantly at the step edge, albeit with some difficulty. We refer to this latter regime as "slow molecular step flow" to indicate that even though molecular diffusion to the step edge is fast, the subsequent attachment of the atom is slow.

The preceding discussion can be summarized conveniently in graphical form. To do so, note that the model parameters D_A, D_M, κ, τ, β_A and β_M typically exhibit an Arrhenius form. Thus, the molecular deposition flux J, the mean terrace width ℓ and the substrate temperature T are the true control parameters of the problem. We choose to display the various regimes discussed above as a "kinetic phase diagram" in the T-J plane (Figure 2). This diagram was generated by making several physically reasonable choices for the energy barriers and pre-exponential factors in the foregoing rate constants and computing the relative magnitudes of the various characteristic lengths. Only the gross topology of the phase fields should be noted since the precise placement of the phase boundaries depends on the details of the system in question.

What are the experimental implications of such a diagram? For definiteness, consider a diffraction experiment where the time evolution of the intensities of both Bragg reflections and diffuse scattering are recorded. By tuning the control parameters so that oscillations in the former disappear, one straddles one of the curved phase boundaries in Figure 2 (where either $\ell = \ell_M$ or $\ell = \ell_A$) and the surface diffusion constant of the primary migrating species can be extracted. By comparison with corresponding MBE results, one likely can determine if one is to the left or right of the long vertical line in Figure 2. At elevated deposition rates, the diffuse scattering from such an experiment reveals the time evolution of the mean size of 2D islands and their average separation. An abrupt change in these quantities with increasing temperature could be interpreted consistently (from Figure 2) as a kinetic transition from a regime of molecular interaction to a regime of 2D atomic island formation. Recent extensive surface x-ray scattering measurements of OMVPE growth of

GaAs(001) onto a slightly misoriented substrate[14,15] provide an attractive data base for an analysis of the sort we propose.

As a more concrete example, consider a recent systematic study of the disappearance of RHEED oscillations as a function of temperature for GaAs(001) grown by MOMBE using TMG as the source of gallium.[10] A transition to step flow is observed to occur for both vicinal A-type surfaces (Ga-terminated step edges) and vicinal B-type surfaces (As-terminated step edges). But, when compared to the result found in MBE, the transition temperature T_C is *increased* on the A surface and *decreased* on the B surface, both by approximately $30\,°C$. We speculate that this behavior reflects the presence of slow molecular step flow where As-terminated step sites are required to catalyze precursor[21] decomposition. In that way, the B surface would be in slow step flow automatically. A reduced T_C is expected due to the presence of Ga-terminated kink sites exposed by thermal fluctuations of the step edge. Conversely, more temperature is needed to effect step flow on the A surface since a significant density of As- terminated kink sites (again exposed due to thermal fluctuations) is required in that case.

Evidently, the simple model described in this paper must be generalized if additional important kinetic steps are demonstrated to exist for any particular growth problem. This would complicate both the length scale analysis and the construction of the kinetic phase diagram. Nonetheless, such an exercise fosters a mode of thinking which, we believe, ultimately will help create a conceptual framework for the chemically-based epitaxial growth techniques comparable to that already achieved for MBE.

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21. Presumably, the mobile precursor in this case is not TMG, but dimethylgallium or monomethylgallium. See, e.g., Refs. 7 and 8.

Figure Captions

Figure 1. Schematic illustration of the dominant kinetic processes included in the model defined by equations (1)–(4).

Figure 2. Kinetic phase diagram of the different growth regimes exhibited by the model defined by equations (1)–(4) as a function of molecular deposition flux (J) and substrate temperature (T). Each phase boundary is the locus of points where the relevant ratio of length scales is unity.