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Post-growth relaxation on a vicinal surface

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We use a heuristic approach to find an approximate analytical solution to the reaction diffusion equation describing post-growth relaxation on a vicinal surface at near-step-flow conditions. The decay of the adatom and dimer densities is seen to be more like that resulting from a logistic equation rather than a sum of exponentials. An approximate solution for the steady-state growth equation that compares well with earlier numerical results is backed out from the solution for the relaxation process.

I. INTRODUCTION

Growth by molecular beam epitaxy (MBE) has been the focus of considerable interest during the past several decades.[1] For step-flow growth, an analytical description of both growth and relaxation can be obtained based on the earlier theory of Burton, Cabrera, and Frank[2] (BCF) developed for conditions of low supersaturation. The usual approximation that must be made is that the step motion can be neglected; otherwise analytical solutions can only be found during steady-state growth.[3] In the near-step-flow regime the BCF theory must be modified[3,4] to take into account the formation of dimers. This requires including a nonlinear reaction term in the adatom kinetic equation. If the dimers are unstable an additional term, accounting for their breakup, must also be included in the adatom equation. Both step-flow growth with the step motion taken into account and near-step-flow growth are nonlinear problems that are not amenable to current analytical techniques.[5] For this reason, computer simulations and numerical solutions have been the primary tools for studying these problems[1,3,4,6] along with simpler models that provide less detailed information.[6,7]

When the beam is turned off the system relaxes to a final equilibrium state. This process, referred to as post-growth recovery when the dimers formed are stable and post-growth relaxation when they are unstable, has not been extensively studied analytically, presumably because of the same difficulties that occur in studying growth. In describing recovery, the step boundary conditions must be treated more carefully than those during growth since at long times the adatom equilibrium density is no longer small compared to the adatom densities on the terraces and cannot be neglected. Experimental studies[8] using reflection high-energy electron diffraction (RHEED) have shown that the post-growth regime can be described by two distinct stages, and numerical studies[9] have suggested that this is a consequence of fast and slow relaxation modes associated with different island morphologies.

Our intent here is to provide an analytical description of post-growth relaxation that will add to the current understanding of this process. We simplify matters here by considering irreversible dimer formation[3] so that the final ‘‘equilibrium’’ state is an empty terrace; the adatoms are unable to detach from the steps. This idealization allows us to restrict our primary attention solely on the adatoms since the adatom kinetics are decoupled from the dimer kinetics; we will show later that the current into the steps contributed by the dimers can be neglected.[3] Our goal is to show that even when only dimers are formed, relaxation is initially fast (in some sense) and then slows, and is qualitatively better described by a logisticlike decay rather than a sum of exponentials decay. As an additional advantage, we show that our results can also be used to obtain an approximate solution for the steady-state growth densities for which no explicit exact analytical result is known.[3] Since the analytical technique we use, based loosely on the center manifold theory,[10] yields approximate solutions, we also consider the case of pure step flow, for which an exact solution can be found and the validity of the approximations made can be assessed.

In Sec. II we introduce the notation that will be used and go on to obtain a qualitative result for the decay of the adatom density during post-growth relaxation with irreversible dimer formation. More explicit results, allowing an assessment of the approximations made, are then obtained in Sec. III for the case of step-flow relaxation with the step motion taken into account. While the latter is an interesting mathematical problem, it is not likely to be relevant to experimental conditions, and is included here only to provide credibility for the results found in the preceding section. We conclude the paper with a brief discussion of how the results obtained can be applied to describe the dimer relaxation in the near-step-flow case and also, as an unexpected dividend, an approximate solution for the steady-state growth equations.

II. NEAR-STEP-FLOW CONDITIONS WITH STABLE DIMERS

A. Formulation

The generalized BCF equation describing the adatom density during post-growth relaxation is

$$n_t = n_{xx} + \alpha v n_x - 2\beta n^2, \tag{1}$$

where the notation is almost identical to that of Refs. 3 and 4. The density, length, and time are dimensionless according to $n \rightarrow FL^2/Dn \equiv \alpha n$, $x \rightarrow x/L$, $t \rightarrow Dt/L^2$, where F is the beam strength during growth, L the terrace width measured in lattice units, D the adatom surface diffusion coefficient, and $\beta \equiv \alpha L^2$. The coordinate system moves with the dimensionless step velocity $v \rightarrow v/FL$. For near step flow the current into the up step at $x=0$ is well approximated by the adatom current alone,[3] so that for stable islands with $n(0,t)=n(1,t)=0, v(t) \approx 2n_x(x,t)|_{x=0}$. Later we will show this is consistent with the level of approximation that we consider. It should be pointed out that Eq. (1) contains a simplifying approximation in that the relaxation term, $-2\beta n^2$, should contain a time-dependent prefactor, the capture number.[11] Here, as in previous studies,[3,4] we simplify by ignoring this complication and setting the capture number equal to 1 with the expectation that this will not alter the qualitative conclusions that follow.

When the step motion is neglected, Eq. (1) is an example of a ''simple'' reaction-diffusion equation. Such equations are known to be analytically intractable despite the considerable effort that has been expended to illuminate their behavior.[12] With the inclusion of the nonlinear step motion term in Eq. (1), this intractability becomes compounded. In view of the above, a heuristic approach to solving Eq. (1) seems to offer better prospects than more orthodox technical methods. Motivated in part by the procedure used to obtain normal solutions to the Boltzmann equation,[13] and in part by the more formal center manifold theory,[10] we adopt such a heuristic approach here to study Eq. (1). This does not lead to an explicit solution for n since the initial condition for Eq. (1) is not known, but in Sec. IV we show how an approximate initial condition can be found when growth is terminated after a steady state is reached. We are able to obtain explicit results for the nonlinear step-flow equation, i.e., Eq. (1) without the reaction term. These results, described in the next section, allow us to assess the validity of the approximations made since the initial condition is known in this case.

It is well known that methods of solution that rely on superposition, such as Fourier analysis, are not applicable to nonlinear equations. However, we will make use of the fact that n is small[3,4] to look for a Fourier series solution where the primary Fourier coefficient parameterises the other coefficients. Specifically, we consider

$$n=\sum_j n_j \sin(j\pi x), \tag{2}$$

where the n_j, $j>1$, are functionals of $n_1(t)$ and satisfy $n_j/n_1 \rightarrow 0$ as $n_1 \rightarrow 0$. Solutions of the above form are clearly approximations. In particular, the exact initial condition, which is unknown, can be written in a Fourier series $n(x,0)=\Sigma_j A_j \sin(j\pi x)$, where the A_j are numbers. If we expand $A_j = a_j A_1 + b_j A_1^2 + \cdots$, $j>1$, the coefficients can be chosen in an infinite number of ways, e.g., $a_j=(A_j/A_1)$, $b_j=0$, etc. However, the evolution equation for the Fourier coefficients derived from Eqs. (1) and (2) provide the constraint necessary to allow us to consistently formulate an algorithm to uniquely determine the n_j. We describe this next.

B. Determining the n_j

From Eq. (2) it follows that $v=\Sigma' n_j(2\pi j)$, where the prime indicates odd j only are included in the summation. The coupled set of equations for the n_j are found by substituting Eq. (2) into Eq. (1), multiplying the $\sin(\pi jx)$ and integrating over the terrace. The first and most important of these equations is

$$n_{1t}=-\pi^2 n_1-(16\beta/3\pi)n_1^2+O(n_1 n_2, n_1 n_3, \ldots). \tag{3}$$

There is no $O(n_1^2)$ contribution from the step motion. The equation for n_3 provides a basis for subsequent generalization,

$$n_{3t}=-9\pi^2 n_3+K_3 n_1^2+O(n_1 n_2, n_1 n_3, \ldots), \tag{4}$$

where K_3 is a constant. Our basic assumption, that the only explicit time dependence is through n_1, implies that the n_j for $j>1$ can be expanded in a power series in n_1 so that if $n_3=A_3 n_1+B_3 n_1^2+\cdots, n_{3t}$ in Eq. (4) becomes replaced by $(dn_3/dn_1)n_{1t}$ so that

$$\begin{aligned} n_{3t}&=(A_3+2B_3 n_1+\cdots)n_{1t}=-9\pi^2(A_3 n_1+B_3 n_1^2+\cdots) \\ &\quad +K_3 n_1^2+\text{higher-order terms}, \end{aligned} \tag{5}$$

where we have anticipated that all the n_j for $j>1$ are $O(n_1^2)$ and no longer explicitly identify the higher-order terms. Substituting from Eq. (3) for n_{1t} and equating like powers of n_1, we then find

$$n_3(K_3/7\pi^2)n_1^2+\text{higher-order terms}. \tag{6}$$

Thus, to $O(n_1^2)$ we have, from Eq. (3),

$$\begin{aligned} n_1(t)&=n_1(0)\exp(-\pi^2 t)\{1+[16\beta n_1(0)/3\pi^3] \\ &\quad \times[1-\exp(-\pi^2 t)]\}^{-1}. \end{aligned} \tag{7}$$

Since the n_j for $j>1$ are $O(n_1^2)$, the long-time decay is given by Eq. (7) and is exponential, while the initial decay is much faster, due to the exponential term in the denominator, and more like a logistic decay.[11]

III. STEP FLOW

Relaxation following step-flow growth provides a nonlinear model for which the initial condition is explicitly known, allowing us to assess the approximations of the heuristic solution. This is, for the most part, a mathematical exercise in the context of MBE since the conditions for which step motion will be significant are those where reaction effects cannot be ignored.[3] Furthermore, as shown in the preceding section, the reaction term provides the dominant nonlinear effect. Nevertheless, step-flow growth with step motion taken into account has been the subject of several, mostly numerical, studies.[6]

Our starting point here is Eq. (1) with the reaction term omitted, i.e., β set to zero. As an aside, we note that for small values of α a perturbation solution provides little in the way of useful information with successive terms containing multiple infinite summations that, unlike the heuristic solution, do not provide insights into the relaxation process. The initial condition is[3]

$$n(x,0)=[1-e^{-x}][1-e^{-1}]^{-1}-x, \tag{8}$$

where for convenience we take $\alpha=1$. Knowing the initial condition allows us to make an assessment of the accuracy of the heuristic solution.

Since our interest is in assessing the accuracy of the heuristic solution we restrict our discussion to those details necessary for this purpose. Proceeding as before we find that for all j the n_j satisfy

$$n_{jt}=-j^2\pi^2 n_j+4\pi n_1^2\int_0^1 dx\ \pi\cos\pi x\sin j\pi x$$
$$+\text{higher-order terms} \tag{9}$$

and that the equation for n_1 contains no $O(n_1^2)$ term. Determining the n_j as before, we find

$$n_j[1+(-1)^j]4jn_1^2/[\pi(j^2-2)(j^2-1)]$$
$$+\text{higher-order terms},\quad j>1. \tag{10}$$

The maximum error for the heuristic solution should occur at $t=0$. This is similar to the initial slip error found in normal solutions to the Boltzmann equation.[14] As the solution decays, n_1 slower than the remaining n_j, the error due to the higher order terms is reduced. Therefore, a stringent error assessment can be based on a comparison of the n_j at $t=0$ found using Eq. (10) with the ''true'' Fourier coefficients determined from Eq. (8).

The initial value of the primary Fourier coefficient, n_1, is given by the ''true'' value, $n_1(0)=0.127$, and from Eq. (8) we find

$$n_j=[(1+e^{-1})/(1-e^{-1})]^{\delta}[1+(j\pi)^2]^1(2/j\pi), \tag{11}$$

where $\delta=0$, j even, and $\delta=1$, j odd. For all j we easily find that the numerical difference between the approximate n_j determined from Eq. (10) and the true n_j given by Eq. (11) is of $O(n_1^3)=10^{-3}$. In fact, the only n_j, approximate or true, that is itself larger than $O(10^{-3})$ is the approximate value of n_2, 0.014, compared to the true value of 0.008, resulting in an error of $0.006=O(10^{-3})=O(n_1^3)$. These results, while by no means conclusive, provide a degree of creditability for the heuristic method of solution used in this paper.

IV. CONCLUSIONS

We have shown that even in the simple case where only stable dimers are formed the initial fast relaxation of the adatoms slows as the final equilibrium state is reached in which the terraces are empty. If the dimers are unstable, so that a true equilibrium is established with adatoms and dimers present on the terraces, the problem becomes more complex. A complication here is that the usual boundary condition for immobile dimers[3,4,8] is that no dimers are present at the down step, $N(1,t)=0$, where N is the dimer density. This implies that there is no true equilibrium with space-independent dimer and adatom densities. If the dimers are able to diffuse,[1] even slowly relative to the adatoms, this difficulty is avoided, and a true space uniform equilibrium is established. In this paper we only consider the case where dimers are stable and Eq. (1) does not need to be modified to include a gain term accounting for dimer breakup. In this case the dimer density satisfies

$$N_t=\alpha v N_x+\beta n^2. \tag{12}$$

Unlike the adatoms, which continually leave the terraces by diffusion, reaction, and by being collected by the advancing step, the dimer density continues to be increased by the diminishing reaction process and simultaneously decreased due to collection by the slowing step. Therefore, it seems reasonable to set $N_t\approx 0$ in Eq. (12) so that we find

$$N(x,t)\approx(\beta n_1^2/\alpha v)\int_x^1 dx(\sin\pi x)^2+\text{higher-order terms}. \tag{13}$$

Then $N_1\sim O(n_1)$ and each of its Fourier modes decays as n_1. It follows that the dimers do not contribute to n_j through $O(n_1^2)$ and that the contribution of the dimers to the step velocity can also be neglected through this order of approximation. Note that the above approximation for N preserves the correct initial condition since the same relationship holds when n and N are given by their steady-state solutions, the $t=0$ condition here.

The initial condition for near step flow can be approximated by making use of the known value of $v(0)=1$, so that

$$1=2n_x(x,0)|_0+2\alpha N(0,0). \tag{14}$$

The n_j are easily determined as shown in Sec. II C, and we find

$$n_j=16\beta n_1^2/(j^2-2)(j^2-1)\pi^3,\quad j=3,5,\ldots \tag{15}$$

where the step motion can be neglected (Sec. III) so that only odd j is required.
Substituting from Eq. (13) for $x=0$, and Eq. (15) into Eq. (14), we find

$$1=2\pi n_1(0)+2\pi\sum_{j=3}{}' \ 16\beta n_1^2(0)/\pi^2(j^2-2)(j^2-1)$$
$$+\beta n_1^2(0)+\text{higher-order terms}. \tag{16}$$

As an example we take $\alpha=10^{-1}$, $\beta=22.5$, which allows us to compare with the numerical results shown in Ref. 3. The latter are $\alpha n=0.01$ and $\alpha N=0.12$, while we find $\alpha n_1=0.01$ and $\alpha N=0.11$, where both n and N are evaluated at their maxima. The coincidence is certainly fortuitous and also somewhat misleading as some additional small effects are considered in Ref. 3. Also, the higher Fourier modes will have a very small numerical effect on our results. Still, the close order of magnitude match indicates that the approach taken here should provide an adequate qualitative description of the post-growth recovery. Serendipitously, we have also provided an approximate method of solution for the steady-state growth equation. This was unexpected, since the heuristic method is not directly applicable to the adatom growth equation due to the presence of the beam term.

In summary, we have shown that post-growth relaxation occurs in two distinct stages, fast and then slow, and that there is no need to invoke morphological-based arguments[9] to reach this conclusion, which follows directly from Eq. (1). While this qualitative behavior has been our major focus, we have also found a quantitative solution for the steady-state growth equation that compares favorably with earlier numerical results.

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