Theory of impurity-induced step bunching

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We study in detail the impurity mechanism suggested by Frank for step bunching instabilities on crystal surfaces during crystal growth and evaporation. A two-dimensional model in which the impurities are treated microscopically is proposed. We perform a numerical simulation of the model and show that it leads to step bunching. In this paper we examine the large line tension limit, where the step train remains effectively one dimensional. Using a mean-field theory, we express the velocity of a step in terms of the widths of adjacent terraces and the parameters of the microscopic model. It is shown that the theory is valid over a wide range of physical parameters, and only outside this range does one have to use a more complicated exposure time formalism. We compare the velocity function predicted by the theory with results from Monte Carlo simulations of the two-dimensional model and find remarkable agreement. Our theory predicts a logarithmic growth of the average terrace width with time for noninteracting impurities, in agreement with Monte Carlo simulations. Lastly, we suggest new physical realizations of the impurity mechanism. We illustrate the robustness of the idea by considering generalized impurities, which are created by the kinetic process itself without involving an external impurity source. In some of these cases a power-law coarsening of the terrace widths may arise.

I. INTRODUCTION

Both equilibrium and nonequilibrium properties of vicinal crystal surfaces are strongly influenced by the presence of atomic steps produced by the miscut.[1-4] Modern observation techniques permit very accurate measurements of the behavior of these steps, sometimes with atomic-scale resolution and in real time. These experimental tools can be used to test existing theories and motivate the development of new theories that relate measurable macroscopic properties of the surface to the microscopic behavior of the steps.

This interplay between theory and experiment is especially important for understanding nonequilibrium processes. Of particular interest to us here are processes of crystal growth or evaporation where motion of the preexisting steps play the dominant role. Under appropriate experimental conditions, crystal growth and evaporation occur via step flow—the motion of more-or-less straight and equidistant steps. This is a favorable mode for growing high-quality crystals for devices. One reason is that in this growth mode the roughness of the surface does not increase with time (as can happen during layer-by-layer crystal growth where islands form on terraces). As a result, one can grow many layers of high-quality crystal. Another reason is that in the step-flow regime one can control the spatial variation of the electronic properties of the material. For example, this growth mode has been used to create a system of quantum wires.[3]

Many features of the step-flow regime can be understood using a simple one-dimensional model[5] of straight steps where the velocity of a step is some increasing function of the widths of the terraces in front (i.e., in the direction of step motion) and behind the step.[6] This simply reflects the increased area available for adatom exchange between the terraces and the vapor. This, in turn,

affects the motion of steps, which occurs mainly through exchange of atoms between the step edge and the adjacent terraces. The dependence of the step velocity on terrace width should saturate for terraces wider than some characteristic surface diffusion length, beyond which fluctuations in adatom concentration have little influence on step motion. Finally, to avoid overhanging steps, the step velocity should vanish when the terrace in front is of minimal width.

Examples of stable step-flow growth can be easily rationalized using this simple model. Suppose, for example, that adatom exchange at a step edge involves mainly the lower terrace rather than the upper one, as is often thought to be the case.[7] This model then predicts that the uniformly spaced step train is stable during crystal growth.

In other cases, however, the uniform step train becomes kinetically unstable. The steps then tend to aggregate together and from *step bunches*, sometimes of macroscopic size, separated by wide terraces. The physical origin of these phenomena is not clear in most cases, and several mechanisms have been proposed to explain them.

A widely cited mechanism, proposed by Schwoebel and Shipsey,[8] relates the instability of the uniform step train during growth or evaporation to an *asymmetry* in the attachment-detachment rates of atoms at step edges. In the typical asymmetry mentioned above, where exchange with the lower terrace dominates, these authors showed that while the uniform step train is stable during growth, it becomes unstable toward step bunching during evaporation. An asymmetry-driven instability during growth is also possible, but only if attachment from the upper terrace is more important.

A different and, we believe, more generally applicable bunching mechanism was proposed by Frank.[9] He related the instability to the existence of a flux of certain kinds

of impurities that impinge on the surface from the vapor. This impurity mechanism is the main focus of this paper. In the next section we give an intuitive explanation of the mechanism and the resulting step-bunching instability, while in the rest of the paper we analyze various one- and two-dimensional models of the effect and the relationship between them.

Before discussing the mechanism itself, let us explain the notation scheme we adopted to describe the system of steps. One of the attractive features of the impurity mechanism is its generality. For example, the mechanism is equally effective during growth and evaporation. Hence it is useful to introduce a general description of step flow, which is independent of whether the crystal is growing or evaporating. We thus label steps such that the step index n is increasing in the direction of step motion. The terrace in front of step n is the one that separates steps n and $n + 1$, whereas the terrace behind the nth step separates step n from step $n - 1$. This notation unifies the descriptions of growth and evaporation as is shown in Fig. 1. During growth the terrace in front of a step is lower than the terrace behind it [Fig. 1(b)]; during evaporation, on the other hand, the terrace in front is the higher one [Fig. 1(c)], but both cases are described by the step train of Fig. 1(a) with the same direction of step motion.

II. FRANK'S IMPURITY MECHANISM

The type of impurities envisioned by Frank[9] have two properties that together lead to step bunching.

(i) The presence of an impurity directly in front of a segment of a step impedes the motion of that step. As a
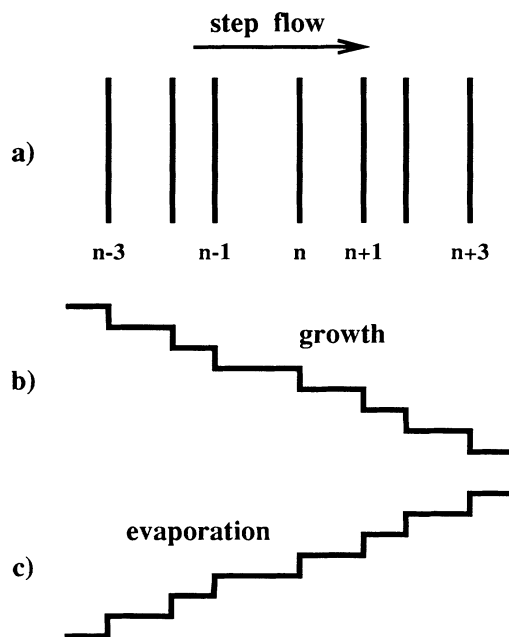

FIG. 1. (a) Unified notation for description of step flow during both growth and evaporation. The index n that labels the steps increases in the direction of step flow. (b) A side view of the step train of (a) during growth. (c) A side view of the step train of (a) during evaporation.

result, the velocity of a step is a decreasing function of the density of impurities immediately in front of it.

(ii) When a step segment finally moves past a given impurity, it weakens the effect of that impurity on other steps that may encounter it at a later time. Thus, impurities are essentially *covered* or *deactivated* by the moving steps.

Since new impurities continually arrive from the vapor, a time-dependent density profile of active (uncovered) impurities is established. This results in a gradient in the active impurity concentration on a terrace, with very low concentrations just behind a moving step.

An accurate description of the effects of such impurities may require more complicated models than those described in the Introduction. In the simplest case, impurities arrive and stick at random times and positions on the terraces. They directly affect only the motion of a *local* step segment when the impurity is directly in front. Other segments of that step that have not encountered impurities may move more rapidly. Thus, it is not clear that a one-dimensional model of straight steps is able to give an accurate description of step motion when impurities play a significant role. One of the main points of this paper is to introduce a more general two-dimensional model describing step motion with and without impurities and investigate when the one-dimensional limit is appropriate.

Even assuming for the moment that a one-dimensional model can be used, there is still another complication in the description of impurities that must be dealt with. In the discussion of the model describing motion in the absence of impurities, it was natural to assume that the velocity of a step was a function of the terrace width. However, given property (ii) above, the concentration of active impurities immediately in front of step n, at position x_n, is an increasing function of the *exposure time* τ_n that passed since step $n + 1$ was at x_n (τ_n is the time interval during which new impurities can impinge on this portion of the terrace). When impurities are important, the step velocity is thus a decreasing function of the exposure time of the terrace in front of it, rather than a simple function of the terrace width.

van der Eerden and Muller-Krumbhaar derived[10] a set of equations for one-dimensional steps that properly expressed the dependence of step motion on the exposure time as implied by Frank's physical picture.[9] Unfortunately, the resulting recursive delay-difference equations are exceptionally difficult to handle both analytically and numerically.

Much simpler equations result if we follow Frank and assume that the exposure time is an increasing function of the terrace width, thus associating wide terraces with long exposure times. One goal of this work is to determine the conditions under which this simplifying assumption is accurate. When it holds, we expect the velocity of a step to be a decreasing function of the width of the terrace in front of it for large terrace widths, when the effects of impurities dominate. For small terrace widths, the density of active impurities is small from property (ii), and the velocity should be an increasing function of terrace width, just as it is in the case without impurities. Fi-

nally, in order to avoid overhanging steps, the velocity of a step should vanish as the width of the terrace in front vanishes (as mentioned above).

When these simplifications can be made, we expect the step velocity $dx_n/dt \equiv \dot{x}_n$ to satisfy the following equation:

$$\dot{x}_n = f(W_n) , \qquad (1)$$

where $W_n \equiv x_{n+1} - x_n$ is the width of the terrace in front. The velocity function $f(W)$ is an increasing function of the terrace width W for small terrace widths, has a maximum value $V^m = f(W^m)$ at $W = W^m$, and decreases with increasing W for $W > W^m$.

In previous work[11] we analyzed in some detail step bunching described by Eq. (1) in the special (and somewhat artificial) *poisoning limit* where $f(W)$ vanished identically for terrace widths W greater than some finite poisoning distance W^p. Here we consider more general velocity functions f for which there can be a finite limiting velocity $V^{\infty} < V^m$ as $W \to \infty$. (Such functions arise naturally from the two-dimensional model and mean-field theory discussed later.)

Equation (1) can also describe step flow in the absence of impurities, using a *nondecreasing* function $f_0(W)$ that saturates beyond a characteristic diffusion distance to a value V_0^{∞}, as discussed earlier. Equation (1) predicts stable step flow for such an f_0. (The Schwoebel asymmetry is stabilizing in this case.) Thus it is the region of negative slope in the function f induced by impurities that leads to the instability.

Note that Eq. (1) does not conserve the average velocity of the surface. This is certainly consistent with a step-flow mode during evaporation, but one has to be more careful when considering crystal growth. In the latter case, the growth velocity of the surface (and hence the average step velocity) is fixed by the external flux unless there is significant desorption. We have therefore implicitly assumed that the experimental conditions are those of evaporation or of crystal growth with significant desorption. Equivalently, the average terrace width should be larger than the diffusion length, so that in the absence of impurities step velocities will depend very weakly on the terrace width. (Thus, the velocity function f_0 in the absence of impurities has saturated as explained above.)

It is easy to see from Eq. (1) why the uniform step train with step spacing $W > W^m$ is unstable towards step bunching. Assume that the width W_n of the terrace in front of step n is infinitesimally smaller than the widths W of other terraces. The velocity of step n is then larger than the velocity of other steps because f is a decreasing function of W in this region. As a result, W_n decreases further and the perturbation is amplified. One can also perform a linear stability analysis of Eq. (1) to show that the most unstable wave number is $k = \pi/W$, which means that the initial instability is towards *step pairing*.[5,11]

Note that the model of Eq. (1) is one sided; steps are affected only by the terrace in front. As in the Schwoebel effect, this asymmetry plays an important role in inducing the step-bunching instability. Here, however, the asymmetry arises naturally during both growth and evaporation because only impurities in front of a step can affect its motion, while impurities behind the step have no influence. One does not have to assume any asymmetry of the attachment-detachment kinetics of adsorbed atoms at step edges as is the case for the Schwoebel instability.

In the remainder of this paper we investigate the impurity-induced step-bunching instability in detail and make the heuristic ideas put forward by Frank more quantitative. In Sec. III we define a new "semimicroscopic" two-dimensional model of step flow, with an effective treatment of main component atoms, but a microscopic treatment of impurities. Fluctuations along a given step edge are controlled by a quadratic "line-tension" term. We carry out a Monte Carlo simulation of the model and show that it leads to step bunching. We also show that in the large line-tension or low-temperature limit the steps are relatively straight throughout the evolution of the system from the initially uniform step-train configuration to a bunched state. This provides justification for the one-dimensional models in this region of parameter space. Section IV gives a mean-field derivation of the velocity function f that appears in Eq. (1), in terms of parameters of the two-dimensional model. We also find a condition for the validity of the mean-field approximation and show that it holds if the impurity effect is not too strong (in a sense that will be explained in Sec. IV). We compare the velocity function predicted by the theory to the one that results from a simulation of the microscopic model.

In Sec. V we calculate the evolution of the average distance between step bunches as a function of time in the long time limit. The theory predicts a logarithmic growth of this distance with time, in accord with results from simulations of both the effective one-dimensional model of Eq. (1) and the two-dimensional microscopic model. Last, in Sec. VI, we consider several possible realizations of the impurity mechanism. We believe the impurity mechanism has a much wider range of applicability than might initially be supposed. For example, we argue that surface structures created during crystal growth or evaporation can sometimes serve as *effective impurities* with the crucial properties (i) and (ii) as envisioned by Frank. These can affect the growth rate and can cause step bunching, without the need for a flux of real impurities.

III. THE MICROSCOPIC TWO-DIMENSIONAL MODEL

We want to develop a simple model for step flow in the presence of impurities that incorporates the important physical ideas discussed above, but which is still reasonably easy to implement numerically. The most time-consuming physical process to describe microscopically is the diffusion of main component adatoms on the terraces. Fortunately, this process is not causing the instability in our case, and its effect is fairly well understood. We therefore treat main component diffusion effectively rather than microscopically, essentially describing the motion

of a step-segment in terms of a nondecreasing velocity function $f_0(W)$, as discussed in Sec. II and below. This approximation permits simulations of large systems for sufficiently long times that the late stages of the evolution can be investigated. Note that we are excluding here the possibility of any diffusional instability such as the one predicted by Bales and Zangwill.[12] This instability is not expected to play any role in the case discussed here, where the diffusion length is much smaller than the terrace width (see below).

Let us first describe our model for step flow in the *absence* of impurities, which is an effective treatment of adatom adsorption, diffusion and desorption. Consider N steps on a square lattice, where each step is composed of L coarse-grained segments that reside on the links of the lattice. We associate a line-tension energy favoring straight steps with each configuration of segments:

$$E = \gamma \sum_{m,j} [x_m(j+1) - x_m(j)]^2 , \qquad (2)$$

where $x_m(j)$ is the position of the jth segment of step m, and γ is the effective line tension.

We assume (as discussed in Sec. II) that initially the widths of all the terraces are larger than the diffusion length, so that the step velocity is essentially independent of terrace width. When steps bunch together, some terraces get wider while others become very narrow. When the width of narrow terraces is smaller than the diffusion length, the dependence of step velocities on terrace width becomes significant. However, it is reasonable to assume that the details of this dependence are not very important, since it is relevant only for the small-scale dynamics of steps within a bunch. The main role of these short-ranged processes is to suppress configurations with overhanging steps. In the absence of impurities, and for sufficiently closely spaced steps, asymmetric attachment kinetics could lead to Schwoebel-type step-bunching instabilities. In the case considered below, however, the larger-scale instability caused by the impurities manifests itself long before any asymmetry in the attachment-detachment kinetics of atoms at step edges can play a role. In fact, the impurity instability is so strong that even if we choose the most stabilizing Schwoebel asymmetry (i.e., such that the system without impurities is stable), impurities still can cause an instability in the uniform step train towards step bunching. In what follows we indeed choose the most stabilizing Schwoebel asymmetry and demonstrate this fact.

Thus, in the absence of impurities we choose the following rules for step motion.

(1) Select a step segment at random: say, segment j of step m.

(2) Attempt to move it backwards with probability

$$p_b = (1 - A_1)/2 , \qquad (3)$$

or forward with probability

$$p_f = p_b + A_1(1 - e^{-[x_{m+1}(j) - x_m(j)]/l_d}) , \qquad (4)$$

where l_d is the main component diffusion length and A_1 (the reason for the subscript 1 will become clear later) is a

monotonically increasing function of the flux of main component atoms, which vanishes when the flux is equal to the equilibrium flux.

(3) Always reject the attempted move if it leads to terraces of width smaller than 1. (This corresponds to overhanging steps.) If this no-overhang condition is not violated, reject the move with probability $1 - \exp(-\beta \Delta E)$ if it raises the energy by an amount ΔE, and accept it otherwise. Here, β is the inverse temperature and E is the line-tension energy defined in Eq. (2).

As explained above, the details of the short-scale dynamics in these rules are arbitrary and do not affect the physics of the instability induced by impurities. Their importance is only in maintaining the no-overhand condition. We could, for example, omit the exponential term in Eq. (4) without changing the qualitative results. We choose to include it only because it builds in the idea of a diffusion length for the main component atoms in a simple way. At equilibrium, when $A_1 = 0$, rules (1)–(3) produce the usual Monte Carlo kinetics of steps whose fluctuations are controlled by a line tension, and the no-overhand condition introduced here in a very simplistic way is enough to generate the equilibrium entropic repulsion of steps.[1] The dependence of p_f only on the terrace in front ensures that the system is stable towards Schwoebel-type step-bunching instabilities during both growth and evaporation as discussed above.

Now consider the effect of impurities. They arrive at random sites on the square lattice, such that each site can either be vacant or contain a single impurity. An impurity affects the motion of a step segment immediately behind it in the following way. If we attempt to move the step segment forward past the impurity, the acceptance probability of the move in Eq. (4) is reduced by a factor $0 < 1 - S < 1$ compared to the probability in the absence of an impurity [rule (3) above]. If the move is accepted the impurity is turned off. The microscopic parameter S is associated with the strength of impurities. If $S \approx 0$ the impurities are weak, whereas $S \approx 1$ is the strong impurity limit.

We simulate the model in the following way. Starting with uniformly spaced straight steps and a surface clean of impurities, we alternatingly perform sweeps of impurity deposition and step flow. We do not expect the long time behavior to be affected by these arbitrary choices. In an impurity-deposition sweep we pick at random $F_i N L W^0$ sites, where F_i is the flux of impurities and W^0 is the initial terrace width. Impurities are deposited in all the selected *vacant* sites. Each step-flow sweep consists of NL attempts to move step segments chosen at random. The attempts are done according to rules (1)–(3) above, taking into account the impurity effect on step motion as well.

Figure 2 presents snapshots of a portion of a system of $N = 30$ steps of length $L = 1000$ and initial terrace width $W^0 = 50$ after 1000 [2(a)] and 30 000 [2(b)] time steps. We use periodic boundary conditions in both directions. Each time step consists of an impurity deposition sweep followed by a step-flow sweep. We used the following values for the parameters of the model: the dimensionless parameter $K \equiv \beta \gamma$ relevant for the line-tension

strength parameter was $K = 3.5$, the impurity flux was $F_i = 0.0002$, the impurity strength parameter was $S = 0.65$, and the diffusion length was $l_d = 10$. We also used $A_1 = 0.9$. Steps flow from left to right. Figure 2(a) indicates that initially the steps remain quite uniformly spaced. At later stages, however, the uniform step train becomes kinetically unstable as expected and step bunching occurs, as is seen in Fig. 2(b). However, throughout the evolution the steps remain fairly straight, although there are some fluctuations. (Other choices of these parameters can lead to interesting two-dimensional bunching patterns and will be discussed elsewhere.)

The first thing we learn from this simulation is that in cases where the line tension is large or the temperature is low enough the steps remain fairly straight even when the instability occurs. We therefore conclude that in this regime it is consistent to describe the evolution of the system using an effective *one-dimensional* model where the steps are pointlike objects.

Next, we ask whether the model proposed in Sec. II [see Eq. (1)] reasonably describes the physics of the system or must we use the more complicated exposure-time
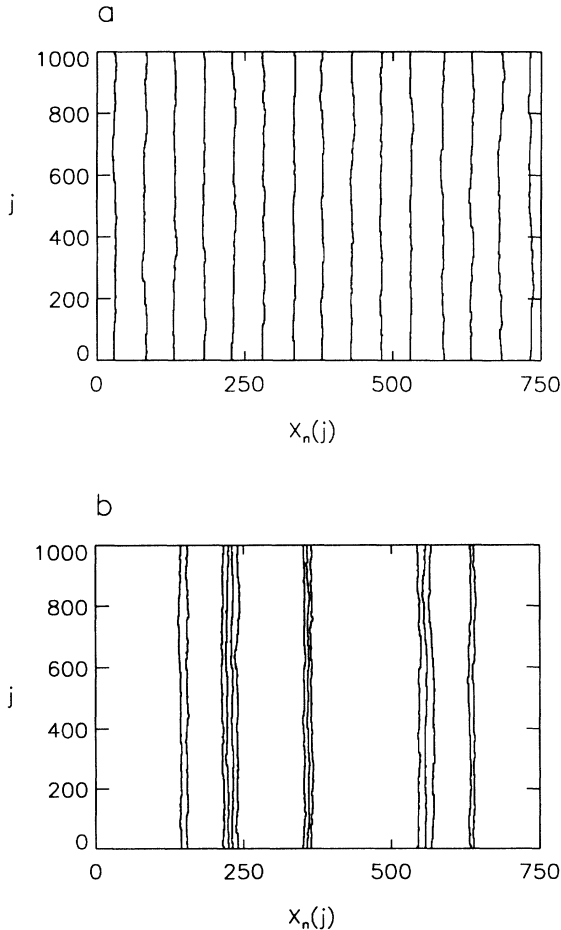

FIG. 2. Snapshots of a portion of the system after 1000 (a) and 30 000 (b) sweeps of the simulation. Each step is composed of 1000 segments. The parameters (see text for definitions) of the simulation are $K = 3.5$, $F_i = 0.0002$, $S = 0.65$, $l_d = 10$, and $W^0 = 50$.

formulation.[10] To answer this question we develop a self-consistent mean-field theory that predicts the form of the velocity function of Eq. (1).

IV. MEAN-FIELD THEORY

In this section we derive the effective velocity function $f(W)$ of Eq. (1) assuming knowledge of microscopic parameters and the velocity function, $f_0(W)$, in the absence of impurities. We also assume that the step train is effectively one dimensional, as is the case when the line tension is large enough (see Fig. 2). Our aim is to express $f(W)$ in terms of two microscopic parameters: the impurity flux F_i and the impurity strength parameter S. Recall that S is defined such that if the concentration of impurities in front of a step is $C_i = 1$, the velocity of that step is $f = (1 - S)f_0$.

With this definition of S the velocity f in the presence of impurities can be expressed as

$$f(W) = f_0(W)[1 - C_i(W) + (1 - S)C_i(W)] . \tag{5}$$

We have assumed here that C_i, the impurity concentration immediately in front of a step, depends only on the distance to the step ahead. In fact, as we pointed out in Sec. II, C_i is really a function of the terrace exposure time τ, and not of the width of the terrace, W. The crucial assumption of our theory is that the exposure time can be expressed in terms of the width of the terrace as

$$\tau(W) = \frac{W}{f(W)} , \tag{6}$$

and therefore the simpler formalism of Eq. (1) can be used. Note that we have omitted the terrace index n in Eq. (6), and in doing so we have made the mean-field assumption that the fluctuations from step to step of the step velocity can be neglected. We will return to this point later in this section and derive a self-consistency condition for the validity of these assumptions.

To complete the derivation of the velocity function we have to know how the impurity concentration behaves as a function of terrace width. To that end, consider the evolution of the impurity concentration at a given site of the lattice from the time $t = 0$ when step $n + 1$ passed that site until the time $t = \tau_n$ at which step n arrived (τ_n is the exposure time of the nth terrace as defined above). Since the impurities are deposited randomly, and since an impurity can be deposited only at a vacant site, the equation of motion for the impurity concentration is

$$\frac{dC_i}{dt} = (1 - C_i)F_i . \tag{7}$$

Therefore, when step n arrives at the chosen site the impurity concentration just in front of the step is

$$C_i = 1 - e^{-F_i \tau_n} = 1 - e^{-F_i \frac{W}{f(W)}} , \tag{8}$$

where we have used our approximation (6) for the exposure time.

Combining this equation with Eq. (5), we arrive at the main result of this section:

$$f(W)=f_0(W)[1-S+Se^{-F_i\frac{W}{f(W)}}] . \tag{9}$$

This is a self-consistent equation for the velocity function f in terms of the parameters S and F_i. It assumes knowledge of the velocity function f_0 in the absence of impurities, but makes no analytical assumptions about the functional form of f_0. f_0 can be obtained from experiments or from simulations without impurities, and then Eq. (9) can be solved numerically for the function $f(W)$.

We can analyze the form of the velocity function f of Eq. (9) for small and large values of the terrace width. We find the following results: For small terrace width $f(W)\approx f'(0)W$, where the derivative $f'(0)$ of the function f at $W=0$ satisfies the equation

$$f'(0)=f_0'(0)[1-S+Se^{-\frac{F_i}{f'(0)}}] , \tag{10}$$

while for large W the function f decays exponentially to $(1-S)f_0(\infty)$:

$$f(W)\approx f_0(\infty)[1-S+Se^{-\frac{F_i}{(1-S)f_0(\infty)}W}] . \tag{11}$$

To arrive at (11), we assumed that $f_0(W)$ approaches $f_0(\infty)$ exponentially in W with an exponent larger than $F_i/[(1-S)f_0(\infty)]$. This assumption holds for our choice of parameters. Since f is an increasing function of W for small terrace widths, but decreases with increasing W for large W, it must have a maximum as expected.

For the simple microscopic model described in Sec. III we know f_0 for $L=1$ (i.e., each step is composed of one segment):

$$f_0^{(1)}(W)=A_1(1-e^{-W/l_d}) . \tag{12}$$

For longer but basically straight steps we expect the same dependence on terrace width, but a different length-dependent prefactor A_L. We therefore predict

$$f_0^{(L)}(W)=A_L(1-e^{-W/l_d}) , \tag{13}$$

where A_L is independent of terrace width, but does depend on the line tension γ and the temperature. We now verify that Eq. (13) is valid and determine the value of A_L for the case we simulated (see Fig. 2), where l_d in Eq. (4) equals 10.

To that end we repeat the simulation, but this time without impurities. In this case the uniform step train is stable, and one can easily measure the average step velocity as a function of terrace width by performing the simulation starting from several initial widths. The results are depicted in Fig. 3, where the numerically obtained velocities are drawn as full circles. The solid line is the function

$$f_0(W)=0.037(1-e^{-W/10}) . \tag{14}$$

Clearly, Eq. (13) is obeyed to a very good accuracy with the prefactor $A=0.037$.

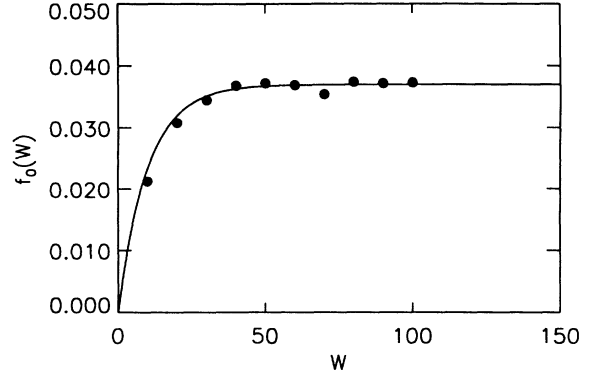Using this form for f_0 we can solve Eq. (9) for the velocity function $f(W)$ numerically. Before showing the

FIG. 3. Step velocity f_0 in the absence of impurities as a function of terrace width W. The numerical results are shown as full circles, while the theoretical fit is the solid line.

result of this calculation, let us explain how we measured $f(W)$ from simulations of the microscopic model and then compare the results of the two approaches. As we have seen above, the uniform step train is unstable towards step bunching when impurities are present. As a result, the terrace-width distribution evolves with time. In order to measure the velocity function we performed a single simulation of the microscopic model and followed the terrace width distribution. We recorded the average position of each step

$$\bar{x}_n=\frac{1}{L}\sum_j x_n(j) \tag{15}$$

as a function of time. From $\bar{x}_n(t)$ we obtained step velocities and terrace widths as a function of time, and from these we calculated the average velocity for each value of the terrace width.

This velocity function obtained from the simulations is shown as solid lines in Fig. 4 for $S=0.65$ [4(a)] and $S=0.5$ [4(b)]. The dashed lines are the numerical solutions of Eq. (9) for the same values of S. The agreement is clearly impressive. Note though that the agreement is better for $S=0.5$ than for $S=0.65$. Can we understand why the agreement deteriorates for stronger impurities (larger values of S)?

To answer this question we now derive a self-consistency condition for our mean-field assumption. Equation (6) holds only if the step velocity changes slowly, so that its fractional change $(1/f)df/dt$ during the time W/f it takes a step to move a distance of order W is relatively small. Mathematically, this corresponds to the following condition:

$$\frac{W}{f(W)}\frac{1}{f(W)}\left|\frac{df(W)}{dt}\right|$$

$$=\frac{W}{f(W)}\frac{1}{f(W)}\left|\frac{df(W)}{dW}\right|\left|\frac{dW}{dt}\right|\lesssim 1 . \tag{16}$$

From Eq. (1) we have

$$\frac{dW_n}{dt}=f(W_{n+1})-f(W_n) , \tag{17}$$

and therefore dW/dt is of the order of $f(W)$. As a result, condition (16) takes the form

$$\left| \frac{df}{dW} \right| \frac{W}{f} \lesssim 1 .$$ (18)

Our theory is self-consistent when condition (18) is satisfied. Otherwise, one has to use the exposure-time formalism.

$$-\frac{df}{dW}\frac{W}{f} = \frac{\dfrac{g-1}{g}\ln\left|\dfrac{S}{1-S}\dfrac{1}{g-1}\right| - \dfrac{df_0}{dW}\dfrac{W}{f_0}}{1-\dfrac{g-1}{g}\ln\left|\dfrac{S}{1-S}\dfrac{1}{g-1}\right|} ,$$

(19)

with $g(W) \equiv [1/(1-S)](f/f_0)$. Since $(df_0/dW)(W/f_0) > 0$, it is enough to require

$$\frac{g-1}{g}\ln\left|\frac{S}{1-S}\frac{1}{g-1}\right| < \tfrac{1}{2} ,$$ (20)

in order to satisfy condition (18), or equivalently,

$$\frac{S}{1-S} < (g-1)e^{g/[2(g-1)]} .$$ (21)

The minimal value of the expression on the right-hand side of condition (21) is $0.5\exp(\frac{3}{2})$. Inequality (21) is thus satisfied if $S/(1-S) < 0.5\exp(\frac{3}{2})$ or if

When is condition (18) satisfied? First, we note that at $W=0$ the equality in Eq. (18) holds. For $W>0$ the inequality is obviously satisfied as long as $df/dW > 0$, since f is a concave function in that region. To find out what happens when $df/dW < 0$ we take the derivative of both sides of Eq. (9) with respect to W, and obtain the following expression:

$$S < \frac{1}{1+2e^{-3/2}} \approx 0.69 .$$ (22)

Our mean-field assumption is thus self-consistent if the impurities are not too strong. As we have seen above (Fig. 4), the agreement between theory and simulations is better for $S=0.5$ than for $S=0.65$. We now understand that this deterioration occurs because $S=0.65$ is close to the limit of applicability of our theory. Still, it is somewhat surprising to us that when the equality in Eq. (18) is satisfied, the agreement between mean-field prediction and results from simulations is so good.

Note that the denominator of the right-hand side of Eq. (19) can vanish for sufficiently large S. In this case condition (18) can never be satisfied and the mean-field theory clearly breaks down. One can repeat the analysis above to find out when this catastrophe happens. The result is that if $S > 1/(1+e^{-2}) \approx 0.88$ there is a value of W for which $|df/dW|W/f$ diverges. Hence, condition (22) yields quite a good estimate of the value of S beyond which the mean-field theory breaks down.

V. TERRACE COARSENING KINETICS

In this section we extract some dynamical information from the model of Eq. (1) and compare it to results of simulations. In particular, we study the behavior of the typical distance between bunches of steps as a function of time. To do that we make the ansatz that the system is always close enough to a steady state that its behavior can be well approximated by linearizing around a time-dependent steady state. At first glance this assumption may seem questionable, since all the steady states of model (1) except for the uniform step train with spacing $W < W^m$ are unstable. However, at the late stages of the evolution, the distance between the bunches is very large. Therefore, the system typically probes only very small widths (the distance between steps in a bunch) or very large ones (distances between bunches). In the first case, the derivative of f is positive, whereas in the latter it is negative but exponentially small. As we will see later in this section, such steady states are very weakly unstable, which makes our ansatz more legitimate. The final justification for the steady-state assumption will come from the comparison of its consequences to results of simulations.

In a steady state all the steps move at the same velocity. For each value of the velocity in the range
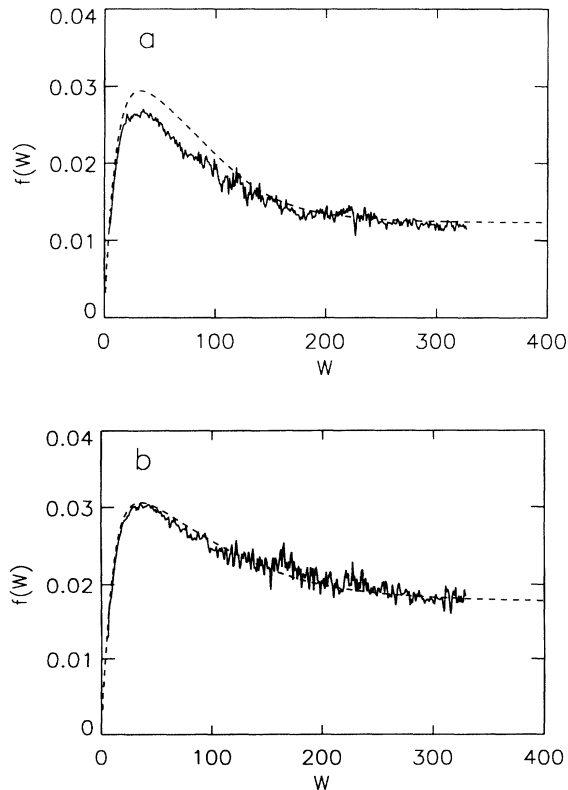
FIG. 4. Step velocity f in the presence of impurities as a function of terrace width W for impurity strengths $S=0.65$ (a) and $S=0.5$ (b). The solid lines are the numerical results and the dashed lines are the theoretical predictions.

$f(\infty) \leq V < f(W^m)$ there are two terrace widths $W^{(1)}(V) < W^m < W^{(2)}(V)$ such that $f(W^{(1)}) = f(W^{(2)}) = V$. Thus the sequence of terrace widths W_n that corresponds to a steady state with velocity V has the property that for any n the value of W_n is either $W^{(1)}(V)$ or $W^{(2)}(V)$. We can therefore decompose the system into bunches such that the distance between consecutive steps in the same bunch is $W^{(1)}$ while the distance between two consecutive bunches is $W^{(2)}$. Such a steady state is depicted in Fig. 5.

The steps within a bunch stick together during the evolution, and the probability of separation of a bunch into several bunches is negligible. It is therefore useful to think of the bunch as a single entity rather than a collection of distinct steps. Hence, we label the bunches by the index l, such that l increases in the direction of step motion (see Fig. 5). The stability of the bunch is due to the fact that it is essentially a uniform step train with $W \approx W^{(1)} < W^m$, and as we show below such a step train is stable. The instability of the steady state arises from the motion of the leading (rightmost) step in the bunch, since the terrace in front of it is wide $(W > W^m)$. Thus, the motion of a bunch is essentially determined by the evolution of its leading step. The other steps in the bunch follow it keeping the small distance between them more or less fixed. To a very good approximation we can therefore think of the bunch as a rigid array of steps whose motion is completely determined by the width of the terrace in front of it.

Mathematically this corresponds to keeping the distance Δ_l between the first and the last steps of the lth bunch (see Fig. 5) fixed. The position of the first step is then $\tilde{x}_l - \Delta_l$, where $\tilde{x}_l$ is the position of the last (rightmost) step in the bunch. In this notation the width Z_l of the terrace in front of bunch l is

$$Z_l = \tilde{x}_{l+1} - \tilde{x}_l - \Delta_{l+1} , \tag{23}$$

and the equation of motion (1) for $\tilde{x}_l$ becomes

$$\frac{d\tilde{x}_l}{dt} = f(Z_l) . \tag{24}$$

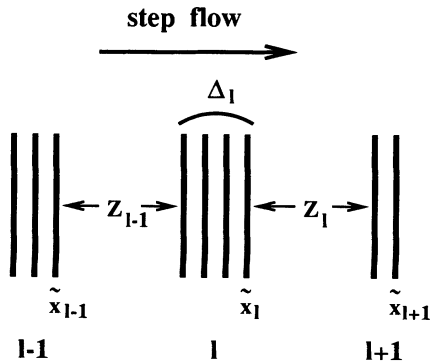The resulting evolution of Z_l is determined by the equation

step flow

FIG. 5. A steady state of the step train. The system is divided into bunches (labeled $l, l+1, \cdots$), with distances Z_l between bunches and bunch thicknesses Δ_l.

$$\frac{dZ_l}{dt} = f(Z_{l+1}) - f(Z_l) , \tag{25}$$

where we have used the assumption that the time dependence of Δ_l can be neglected.

Note that Eq. (25) becomes identical to Eq. (17) if we replace Z by W. This is not surprising, since within the rigid-bunch approximation we expect the behavior of a bunch of steps to be similar to the behavior of a single step. In a steady state, $Z_l = Z = W^{(2)}$ for any l, which is reminiscent of a uniform step train in the W variables. Let us now perform the linear stability analysis of Eq. (25) around this steady state.[11] The linearized form of the equation is

$$\frac{d\delta_l}{dt} = f'(Z)(\delta_{l+1} - \delta_l) , \tag{26}$$

with $\delta_l = Z_l - Z$. Assuming a solution of the form $\delta_l \sim \exp(ikZl + \omega t)(i = \sqrt{-1})$, we obtain the linear dispersion relation

$$\omega(k) = f'(Z)(e^{ikZ} - 1) . \tag{27}$$

We immediately see that if $f'(Z) > 0$ all the modes are stable $[\mathrm{Re}(\omega) < 0]$. This happens only if $Z < W^m$. If, on the other hand, $f'(Z) < 0$ (as is the case for $Z > W^m$), the system is unstable. The most unstable mode is the one with the maximal value of $\mathrm{Re}(\omega)$. From Eq. (27) it is easy to see that it corresponds to bunch pairing, i.e., $kZ = \pi$. For this mode we have

$$\omega(k = \pi/Z) \equiv \omega^{\max} = -2f'(Z) . \tag{28}$$

Since the most unstable mode corresponds to bunch pairing, we expect that after a time interval $\bar{t}(Z \rightarrow 2Z) = 1/\omega^{\max}(Z)$ the average distance between bunches, Z, will double. For large Z we can find an integer m such that $Z \approx 2^m W^0$ where W^0 is the initial terrace width. We can then estimate the time that it takes the system to reach an average distance of Z between bunches:

$$t = \bar{t}(W^0 \rightarrow Z) \sim - \sum_{j=0}^{m-1} \frac{1}{f'(2^j W^0)} . \tag{29}$$

According to the mean-field theory of Sec. IV, $f'(Z)$ decays exponentially to zero for large Z [see Eq. (11)]:

$$f'(Z) \sim -e^{-\eta Z} \tag{30}$$

with

$$\eta = \eta_{\mathrm{mf}} \equiv \frac{F_i}{(1-S)f_0(\infty)} . \tag{31}$$

η_{mf} is the mean-field prediction for the value of η. Using this result in Eq. (29) we get

$$t \sim \sum_{j=0}^{m-1} e^{\eta 2^m W^0} . \tag{32}$$

This sum is clearly dominated by the last term and, hence,

$$t \sim e^{\eta 2^{m-1} W^0} = e^{(\eta/2)Z} . \tag{33}$$

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Inverting Eq. (33) we obtain an expression for the long-time behavior of the average distance between bunches:

$$Z(t) \approx \frac{2}{\eta}\ln t + \text{const} .$$ (34)

The logarithmic dependence on time is in agreement with the result obtained by van der Eerden and Muller-Krumbhaar[10] using the exposure-time formalism in a mean-field approximation. Note that (34) and (31) make a definite prediction about the prefactor $2/\eta$ as well as the logarithm.

We now check this result on two levels. First, how accurate is our ansatz that the system is always close to a steady state? This can be checked by comparing the prediction (34) to numerical results from simulations of the one-dimensional equations (1) with computer-generated noise, using a velocity function f that satisfies Eq. (30) at large Z. Second, how well does model (1) describe the coarsening effect of the microscopic two-dimensional system? The two relevant comparisons are shown in Fig. 6.

Figure 6(a) is a comparison with simulations of a one-dimensional model with $\eta = \frac{1}{95}$. The numerical results are shown as full circles, whereas the solid straight line is the theoretical prediction. The slope of the line in this logarithmic plot corresponds to $2/\eta = 190$, which agrees extremely well with the numerical results. In Fig. 6(b) we show results from simulations of the full two-dimensional model (full circles) with $F_i = 0.0002$, $S = 0.65$, and

$f_0(\infty) \approx 0.035$. The slope of the straight line is $2/\eta = (1-S)f_0(\infty)/2F_i \approx 123$, and it agrees with the data from the simulations after a transient of about 2×10^4 time steps. We clearly need to perform a longer simulation of a much larger system and to average over several such simulations in order to achieve a reliable comparison such as the one of Fig. 6(a). However, the agreement with this small-scale simulation is very promising and reassures us that the model of Eq. (1) describes impurity-induced step bunching very accurately.

VI. PHYSICAL REALIZATIONS AND GENERALIZED IMPURITIES

We now argue that the impurity mechanism for step bunching is extremely robust and may occur in a variety of physical situations. We support this statement by giving several examples. First, we discuss conventional "external" impurities associated with the foreign atoms in the flux from the vapor under both growth and evaporation conditions.

The remaining examples are concerned with effective or *generalized impurities* that are generated on the surface during the process of step flow itself. As discussed below, examples of these generalized impurities are domains in the uppermost *complete* layer of the crystal, on which step motion is slower than its motion in the background (the rest of the uppermost complete layer).

A. External impurities

Imagine a crystal growing from a vapor of main component atoms in the presence of a small concentration of impurity atoms. These impurities usually impinge and stick on the surface independently of each other, and we therefore call them "free" impurities. In this case their concentration C_i at a fixed position on the surface far from a step increases exponentially in time [See Eq. (8)]:

$$C_i = 1 - e^{-F_i t} .$$ (35)

Let us assume that these impurities have the following features.

(1) They attach to the surface more strongly than do main component atoms. They therefore diffuse on the surface more slowly, and we will assume that their diffusion can be neglected.

(2) Once they attach to a step edge, their bonds are saturated (perhaps because they have fewer free bonds than main component atoms do). As a result, a main component atom is less likely to attach to the step edge at a site where there is an impurity than at a clean site.

(3) After a new layer has grown on top of the impurity, it no longer affects the attachment probability of atoms on the surface.

Feature (2) implies that these impurities indeed impede the motion of steps in their vicinity. Feature (3) ensures that the impurities will be turned off after being passed by two steps. The first feature maintains the dependence of impurity concentration of terrace width and the necessary impurity concentration gradient in front of steps. Thus all the conditions for step bunching are met.
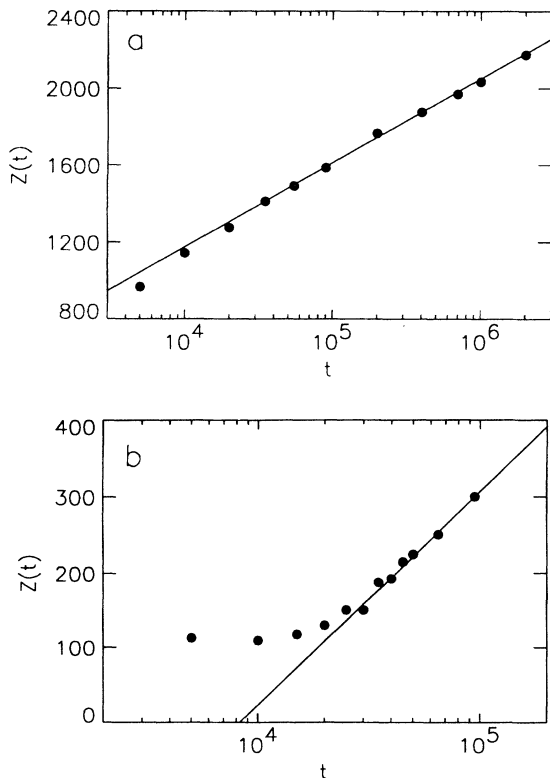

FIG. 6. Log plot of the average distance between bunches, Z, as a function of time t from simulations of one- (a) and two- (b) dimensional models. The solid lines are the theoretical predictions for the long-time asymptotic behavior.

External impurities can cause step bunching during evaporation as well. Assume now that the crystal evaporates in the presence of a small concentration of impurities. If these impurities have feature (1) above, they tend to stick to the surface, and a step that approaches such an impurity may have to wait until the impurity either evaporates or diffuses away before it can continue moving. Thus the conditions for step bunching are again satisfied in an even more natural way than during growth [we do not have to assume a saturation effect such as feature (2) above]. Almost any atom with a stronger attachment to the surface could act as an effective Frank impurity during evaporation and induce step bunching.

B. Generalized impurities

The examples we give below are related to surface reconstruction, and are meant to be physically suggestive of the kinds of processes we have in mind. However, we emphasize that any ordering process on the surface may cause step bunching provided that properties (i) and (ii) outlined in Sec. II are satisfied.

If the crystal is grown at a temperature where the equilibrium surface is reconstructed, one might expect that immediately behind the moving step the newly formed surface will mostly have the order of the bulk crystal, or at least a different ordering than the equilibrium reconstructed surface. Surface reconstruction allows for an additional surface ordering, which, e.g., tends to satisfy more atomic bonds within the layer. The energy gained from this ordering serves as a driving force for formation of the reconstructed surface, and small reconstructed regions may nucleate in the newly formed terrace behind the growing step.

Consider now the growth of a second step on such a terrace. We assume that step motion is fast enough that the new terrace has not completely reconstructed and that the reconstructed regions remain widely separated from each other, perhaps because the nucleation and growth of the reconstructed regions is relatively slow. It is reasonable to assume that it is easier to grow on top of the unreconstructed parts of the surface than on the reconstructed regions, since the reconstruction may have to be destroyed during the growth process. We therefore conclude that the reconstructed regions slow the step down, just as the impurities of Sec. VI A do. Moreover, as a function of time, the reconstructed area (and hence the "impurity" concentration) near a given position on the surface grows, until another step passes and creates an initially unreconstructed layer on top of it. The terrace width dependence and the gradient of the impurity concentration come out naturally in this case. If nucleation and growth processes are slow enough, different reconstructed regions do not affect each other, and these generalized impurities are noninteracting.

In other cases, nucleation and growth of many different reconstructed regions of the terrace may occur much more rapidly than the time scale for step motion over a distance equal to the average terrace width. Then the above instability based on the distinction between isolated reconstructed and unreconstructed parts of the terrace will probably not be seen. However, in such cases, a different mechanism could lead to step bunching.

The nucleation of reconstructed regions behind a step could start at many different positions. If nucleation and growth are fast enough, many domains will grow until they touch each other. Since the different domains may not be in registry, domain boundaries may be created.

Using the same idea as before, we assume that it is easier to grow near domain boundaries than on top of a reconstructed region. Moreover, because of the fast nucleation, steps create regions with a large initial concentration of domain boundaries behind them as they move. We thus see that once again all the conditions for step bunching are fulfilled, and the reconstructed regions can serve as generalized impurities.

The system will coarsen as a function of time, and the domain boundaries will be slowly eliminated in favor of a homogeneous reconstructed phase. The domain size R will grow with time as

$$R \sim t^\alpha , \tag{36}$$

with a value of α that depends on the symmetries of the particular system considered. Typically $\alpha = \frac{1}{2}$ for coarsening without conservation laws, and $\alpha = \frac{1}{3}$ for kinetics that conserve the order parameter,[13] but other values are also possible. Therefore, the concentration of the reconstructed regions immediately in front of a step increases algebraically in time as follows:

$$C_i = 1 - \frac{a}{t^\alpha} . \tag{37}$$

It is clear that when the coarsening kinetics obey Eq. (37) the generalized impurities strongly affect each other, and we therefore refer to them as "interacting" impurities. Such a behavior will lead to a velocity function with a power-law decay for large terrace widths. As a result, the typical length scale will grow as a power of time, which is much faster than the logarithmic coarsening that occurs when the impurities are noninteracting.

Let us conclude this section by noting that the first bunching mechanism discussed in this subsection during growth works equally well during evaporation. We again need only assume that a step advances faster when the evaporating surface in front of it is unreconstructed than when it is reconstructed, and that the surface exposed immediately behind the step is initially unreconstructed. It may be rather difficult to achieve a rapid enough evaporation rate at temperatures where there is surface reconstruction. However, if this can be done, and the time scale associated with nucleation of surface reconstruction is long enough, we expect this mechanism to cause observable step bunching.

VII. SUMMARY AND DISCUSSION

In this work we have reached a fairly detailed understanding of Frank's impurity mechanism[9] for step bunching. We started from a two-dimensional model that treats the impurities microscopically and showed numerically that it leads to step bunching. We investigated the large line-tension limit and showed that in this case the

steps are fairly straight throughout the step-bunching process, which can therefore be described by a one-dimensional model. We then developed a mean-field theory for such a model under the assumption that the velocities of steps are determined by the widths of adjacent terraces. The theory predicts the step velocity as a function of terrace width, and its prediction agrees surprisingly well with results from simulations. The theory also gives an accurate prediction of the evolution of typical length scales (i.e., the distance between step bunches) with time. We argued that the mean-field approach should work well when the impurities are not too strong ($S \lesssim 0.69$), while for very strong impurities an exposure-time formalism[10] should be used.

We believe that the impurity mechanism for step bunching is very robust and general. It is effective during both crystal growth and evaporation and, moreover, the impurities need not originate from an external source. We argued that generalized impurities such as reconstructed regions on the surface can cause step bunching as well.

Another reason for the generality of this mechanism is the fact that the behavior of the system does not depend strongly on the small-scale kinetics of steps that are very close together. For example, the attachment-detachment kinetics of adatoms at step edges affects the small-scale dynamics significantly, but is irrelevant in our case. One consequence is that the behavior of a bunch of steps is very similar to the behavior of a single step. This is not the case for the instability of Schwoebel and Shipsey,[8] where small-scale kinetics and the details of energy barriers for diffusion of adatoms are very important.[14]

Throughout this work we assumed that desorption of adatoms from the surface to the surroundings is significant. This assumption is also important for the robustness of the model. Some materials (e.g., Si and GaAs) are grown under conditions where desorption is negligible. In these cases a more complicated model with a conservation law has to be considered. It is not clear yet how robust and general such a model would be, and we intend to study this problem in detail.

ACKNOWLEDGMENTS

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