Stable and Unstable Growth in Molecular Beam Epitaxy

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(Received 5 August 1993)

We consider the growth of films by molecular beam epitaxy in the presence of step-edge (Schwoebel) barriers using numerical simulation and experiments. We show that the growth of a singular surface is unstable, but that a miscut above a certain critical slope (which depends on growth conditions) leads to stable growth in a step-flow mode. For singular surfaces the instability gives rise to the formation of large mounded structures on the surface for which the slope is in the stable regime. We identify these in GaAs epitaxy using atomic force and scanning tunneling microscopy. We propose a continuum equation which exhibits these features.

PACS numbers: 68.35.Ja, 68.35.Bs, 68.45.Da, 68.55.Bd

The technique of molecular beam epitaxy (MBE) is among the most refined methods for the growth of thin solid films and is of great importance for applied studies. The purpose of this paper is to investigate one of the central problems in this area: We study the conditions for a film grown by MBE to be stable in the presence of inevitable thermal fluctuations and shot noise in the growth. We will show by experiment and by simulation that in the most common physical situation a singular surface (i.e., a low index crystal face) is unstable, but that a vicinal surface with a miscut above a certain value is stable except for very small statistical roughening, and that the two cases are distinguished by a critical slope which depends on the growth conditions. In the unstable case the surface develops large scale mounds which we identify experimentally: These are hills on the surface whose sides spontaneously develop and are steeper than the critical slope. Further, we suggest a continuum equation appropriate to this class of growth.

This subject has a long history which separates into two streams of theoretical development. The most basic model is the step-flow picture of growth of Burton, Cabrera, and Frank [1]. In this essentially deterministic picture, if we neglect nucleation, a train of steps proceeds uniformly across the surface when atoms from the incoming beam land on adjacent terraces and diffuse to be trapped at the step edges. The rate of advance of the steps is the rate of attachment to the step edge. Another, more recent, set of ideas arose from statistical studies [2] which consider the roughening due to fluctuations in the flux, and are, in the generic case, implicitly concerned with films which are either porous or allow partial sticking. In this picture the film inevitably eventually roughens and its roughness w (i.e., the rms width of the interface) grows as a power law in time, $w \sim t^{\beta}$, with $\beta < 1$. In fact, MBE films at high temperatures appear to show very little roughening [3-8] and very small β and, in the best characterized cases, grow by stable step flow.

In a seminal paper, Villain [9] pointed out why the generic case of statistical roughening cannot apply to the early stages of MBE. In MBE there is a conserved current on the surface; this is not true in the generic theory. Physically this results from nearly total sticking of the incoming flux, the near absence of desorption, and the lack of overhangs or vacancies. Unfortunately, the simplest theories with the conservation law built in [10-12], wherein surface diffusion is driven by the curvature of the surface, are not applicable to MBE growth either: They eventually give rise to grooved surfaces [13,14] with $\beta = 1$.

The way out of this quandary was also provided by Villain [9] by appealing to another physical effect. He pointed out that if the barrier to hopping of a particle at the edge of a step was different from that on a terrace, then the situation would change because this asymmetry could also drive surface diffusion. The usual assumption is that it is harder to step down from an upper terrace than to remain on the same level (even though a downward step results in being bound at a step edge): This is the case of a Schwoebel barrier [15]. In this case, Villain gave simple arguments indicating that step flow would be stable on a miscut, vicinal surface, in the sense that fluctuations in the spacing of a step train are damped, and unstable on a singular one, the difference being provided by the nucleation of new islands in the latter case. However, he did not explicitly treat the eventual fate of a singular surface. In this paper we will amplify and explicitly verify Villain's picture by simulation and experiment and we will provide the answer to both questions. In particular, for the unstable case, we introduce the idea of mounds which are related to the "sawtooth" structure of Villain. Villain's picture has also been recently theoretically justified by Zangwill *et al.* [16], who emphasize the importance of asymmetry at step edges in avoiding the pathologies of previous work. If the Schwoebel barrier happens to be very small, a transient regime corresponding to the theories of [10-12] might be observable.

In order to investigate these questions we have performed numerical simulations which allow us to study the effect of parameters such as miscut angle and Schwoebel barrier which would be difficult to vary experimentally. Our Monte Carlo activated hopping model is based on Refs. [17,18] which included interactions between nearest neighbors; we also include next-nearest neighbor interactions to provide a convenient means of incorporating the Schwoebel barrier [19]. In the model atoms are deposited randomly on the surface, and surface atoms are allowed to move by hopping over barriers of size E, with hopping rate $\sim e^{-E/kT}$ where T is the temperature and k is Boltzmann's constant. There are two parts to the barrier: One is determined by simply counting the number of nearest neighbor bonds n_n in the current position, the other depends on the number of next-nearest neighbors in both the starting and final locations for a given hop attempt. If there are more next-nearest neighbors in the final location then the additional barrier is 0, otherwise it is the difference in the number of next-nearest neighbors n_a multiplied by an energy parameter, E_a. The total barrier is given by $E = n_n E_n + n_a E_a$. The additional barrier changes S_c, a convenient measure of the Schwoebel effect. We have $S_c = 1 - r$ where r is the ratio of the probability to approach a step versus the probability to move away from a step, $r = e^{-n_a E_a/kT}$. For an adatom approaching a straight step, $n_a = 1$. The algorithm was tested for equilibrium behavior and found to obey detailed balance. Periodic boundary conditions were imposed and simulations were typically run with two dimensional substrate lattices having 40000 sites.

To explicitly investigate stability of the interface we examined the morphology of the simulated surface during growth. Simulations were performed on both vicinal and singular surfaces using realistic values of the model's parameters for GaAs growth. For singular surfaces we found that stable layer-by-layer growth did not occur. Rather we found the formation of large mounds for a wide range of conditions; see Fig. 1(a). After the mounds have formed, they increase in both height and lateral size keeping the cross-sectional angle, the angle sloping sides make with the terraces, approximately constant. Further growth causes the mounds to slowly coalesce until only one on the order of the size of the system remains at which point finite size effects cause the surface to saturate. In order to obtain mounds which are smaller than

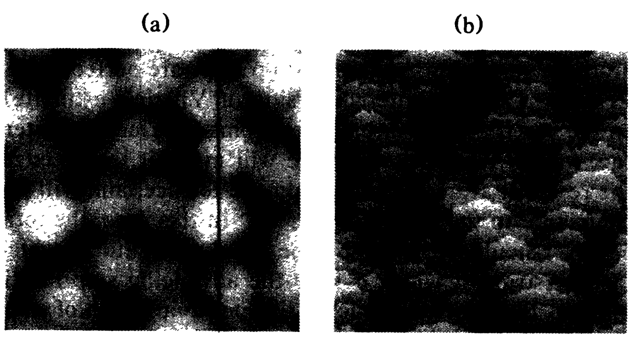

FIG. 1. Surfaces generated by a Monte Carlo activated hopping model with Schwoebel barriers after 50 layers of deposition. (a) Singular surface showing large mounds: $S_c = 0.40$ and $\sigma = 16$. (b) Vicinal surface with a slope of 0.1. Terraces were observed to fluctuate but remained stable: $S_c = 0.40$ and $\sigma = 8$.

the system size, the cross-sectional angle (typically 15°–25°) must be relatively large. However, this angle appears to be a function of S_c and we are able to reduce it though we have not been able to simulate a large enough system with a sufficient number of layers to obtain mounds with a cross-sectional angle of 1°, as is typical for GaAs MBE; see below. It should be noted that to compare the simulations with GaAs MBE, each lattice position in the simulation should be considered a (2×4) unit cell which would reduce angles measured in the simulation by a factor of ~ 3–5.

We should point out that these structures seem quite different from large instabilities seen in earlier theoretical work [14,20] where the slope of the structure quickly increases without bound. In our case, the slope is constant or possibly slowly increasing in time, and for our parameters remains rather small.

On vicinal surfaces the formation of instabilities depends on the growth conditions. The result of many simulations is that where there is sufficient nucleation of islands on terraces, mounds are present. Step flow growth occurs when the adatoms reach a step edge before nucleating, and thus cannot form mounds; see Fig. 1(b). The crucial parameter for the formation of mounds seems to be the ratio of the average separation of two dimensional islands during the first layer of growth, σ (measured on a singular surface) to the size of the terraces l; mounds form for $\sigma < l$, i.e., when the slope of the surface is small enough. We measure σ for each set of growth conditions. Its value depends upon growth rate, temperature, and to a lesser extent the size of the Schwoebel barrier S_c.

The conclusion that a generic singular MBE surface would be unstable led us to look for the instability experimentally. The experimental studies consisted of scanning tunneling microscopy (STM) and AFM investigations of MBE grown GaAs films on GaAs(001) substrates. A variety of substrate misorientations, overlayer thicknesses, and growth temperatures were used. The central experimental observation in this work is that we do find large mounds on the surface of films grown on flat surfaces whereas films grown on vicinal surfaces are relatively smooth. The STM studies were carried out *in situ* and the AFM studies were performed after removal of the sample and exposure to air. Investigation of the surface features by STM was problematic due to their large scale. Typically a 1 μm square STM scan region of the surface was atomically smooth, however, other regions which exhibited step bunching could also be observed [21]. Only when transferred to the AFM could large enough areas of the sample be imaged to discern the nature of the large scale morphology. Figure 2(a) shows an AFM image of a 500 bilayer thick film grown at 555 °C on a substrate with a miscut of approximately 0.1°. The elongated mounds are 8 nm high and 0.5 μm $\times$ 1.5 μm in planar dimension. The anisotropy is along the $(1\bar{1}0)$ direction. In contrast, Fig. 2(b) shows an AFM image of

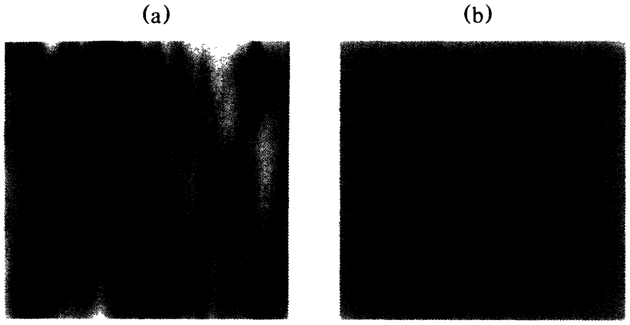

FIG. 2. (a) AFM image of nominally singular GaAs(001) surface after deposition of 500 bilayers on an oxygen desorbed substrate. (b) AFM image of 2.0° miscut GaAs(001) after deposition of 2000 bilayers on a 300 bilayer buffer layer. The gray scale contrast of (b) was adjusted to be comparable to that of (a).

a 500 bilayer film grown at 600 °C on a substrate with a miscut of approximately 2°. The vertical gray scale contrast in the two images is identical. It is clear that the vicinal sample is much smoother than the singular one. When a different region of the vicinal sample, one with a much lower temperature during growth, is scanned the mounds are again observed [22].

The observation of large scale structure on the surface of MBE films grown on nominally singular surfaces is quite striking and unexpected. It is difficult to study this structure using other more common surface analysis techniques, such as reflection high energy electron diffraction (RHEED) or scanning electron microscopy. Recent results obtained using light scattering during growth seem to show the same behavior [23]. We find that the mounds occur when samples are grown in a layer-by-layer mode and they are absent if the growth occurs by uniform step flow. As deposition proceeds the mounds grow both in height and width such that the slope which the inclined sides make with flat terraces remains approximately constant. The angle of inclination is typically between 1° and 2° for samples grown at a substrate temperature of 555 °C. As the growth temperature is increased and step flow begins to occur the angle of inclination decreases. This progression continues until for sufficiently high growth temperatures on vicinal surfaces the mounds vanish.

In order to get a quantitative understanding of our results, we returned to the simulations, and monitored the surface mass current j per unit width of sample during the initial stages of deposition as a function of substrate slope; see Fig. 3(a). This measurement was suggested by Krug, Plischke, and Siegert [24] as a convenient way to measure the coefficient D_2 of the Laplacian term in the Langevin equation:

$$\partial h/\partial t = -\nabla \cdot \mathbf{j} + \eta(x,t) = D_2 \nabla^2 h + \eta(x,t) . \tag{1}$$

We have

$$D_2 = -\partial j/\partial m, \quad m = |\nabla h| . \tag{2}$$

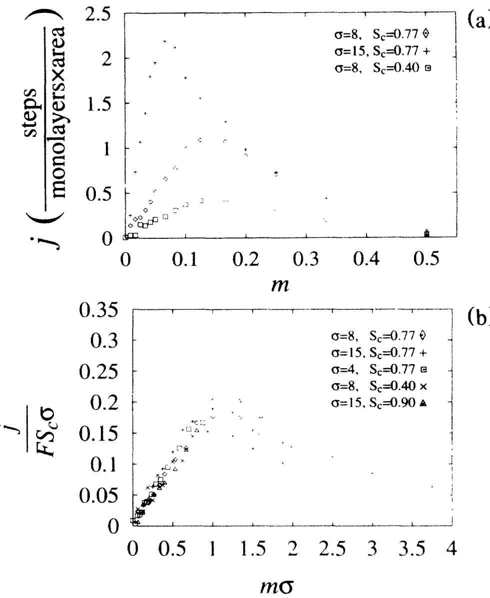

FIG. 3. (a) A plot of current j vs slope m for different values of the nucleation distance σ and Schwoebel barrier S_c. The current was measured on a substrate with a well defined slope for the first 0.1 monolayer of growth and was averaged over 10 realizations. Time is measured in monolayers so that the flux is constant (independent of growth rate). (b) Data collapse of five different data sets varying σ and S_c.

Here m is the slope. We observe that the surface will be unstable for $D_2 < 0$; see Fig. 3(a). As expected, the large m limit of the measured current has $\partial j/\partial m < 0$ and we have short terraces, little nucleation, and stable growth. The small slope limit has $\partial j/\partial m > 0$ where there is significant nucleation and the growth is unstable. Also we observed the peak of the curve occurs at $m = 1/\alpha\sigma$, where α is a constant of order unity as we suggested above. Our general picture, using Fig. 3 as a guide, is that if the local slope corresponds to $D_2 < 0$ then instability sets in, and the local slope increases until the peak of the curve is passed, and an operating point is found in the stable region.

To obtain a physical picture, consider the case where there is a Schwoebel barrier that does not allow any atoms to jump down a step and up steps are perfect sinks. (This is a slightly altered version of Villain's estimate). In the case of small m only the atoms that land on a terrace within σ of the step edge will make it to the edge; the rest will attach to islands on the terrace, and will not contribute to the net mass current. In this case, the total current should be given by the number of atoms which land in strips of width σ near the advancing step multiplied by the number of such strips per unit length of sample, $j = F\sigma^2 m$, where F is the incident flux/area. For larger m we postulate a scaling form for the current in terms of the dimensionless parameter $y = \sigma m$, namely,

$$j = F\sigma^2 m f(y) . \tag{3}$$

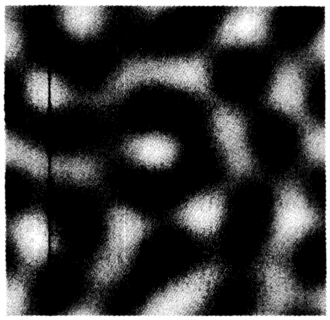

FIG. 4. Numerical solution of $\dot{h} = -\nabla\cdot \mathbf{j} + \eta$ in two dimensions where $\mathbf{j} = D_2\nabla h/[1+\lambda_4/D_2(\nabla h)^2] + D_4\nabla(\nabla^2 h)$. In this integration $D_2/\lambda_4 = 0.01$, $D_4 = 10$, and $\langle\eta\eta\rangle = 5\times 10^{-5}$. The large scale features are due to an instability for surfaces with a slope less than a critical value given by $m_c \sim \sqrt{D_2/\lambda_4}$.

We note that for large slope m, σ must drop out of the problem, so that for large m, the scaling function f must obey $f \sim 1/y^2$, and $j \sim F/m$.

A data collapse is given in Fig. 3(b) using these ideas, generalized for finite Schwoebel barriers (by simply multiplying j by S_c). The measured current has the functional form we assume, to a first approximation.

Finally, we ask what sort of continuum dynamics can describe these surfaces. This question is particularly interesting since several recent studies have appeared [3,6,7] which have attempted to measure surface roughness, without a clear resolution of the problem. Since Schwoebel barriers are probably very common in the films grown, it is possible that what is being measured is the small-scale roughness superimposed on mounds. To study this question, we generalize the results of the last paragraphs, and take, as the simplest interpolation $\mathbf{j} \simeq FS_c\sigma^2\nabla h/[1+(a\sigma m)^2]$. Then we form a Langevin equation as above, $\partial h/\partial t = -\nabla\cdot \mathbf{j} + \eta(x,t)$ with this form for $\mathbf{j}$ as a function of the *local* slope.

A numerical solution of this equation has been found, and the results are shown in Fig. 4. There is general resemblance to the experimental and simulation results. We have not yet analyzed this equation in order to find the roughening exponents, but we think that it is reasonable to assume that if the surface stabilizes around a selected slope, the roughness will be small, $\beta = 0$. On a larger scale, it is far from clear to us that any scaling or well-defined exponents should be expected.

In summary, we believe that we have given a comprehensive picture of MBE growth in the case where there are substantial step-edge barriers. We think that the observation of mounds on the surface unifies the picture in a very satisfying way. Thus we believe that layer-by-layer growth leads to mound formation, and growth on a sufficiently miscut surface to stable step flow [22]. Our considerations apply in the long time regime after RHEED oscillations have died out. We should note that we seem to have observed that there may be a selected slope in the stable region of Fig. 4, but in simulation, experiment, and for our new continuum equation, we have not established what determines the selection.

L.M.S. and D.G. are supported by NSF Grant No. DMR-91-17249 and DOE Grant No. DEFG-0285FR5418. M.J., C.O., A.H., J.S., and B.O. are supported by Grants No. N00014-89-J-1519 and No. NSF/DMR-8857828. We would like to thank D. Kessler for very useful discussions.

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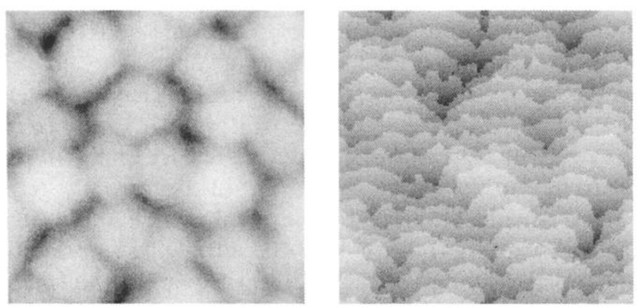
(a) (b)



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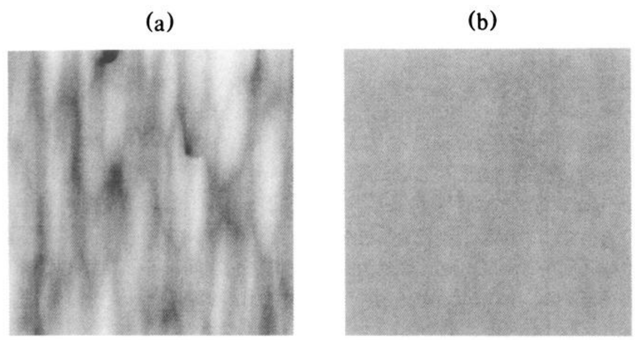

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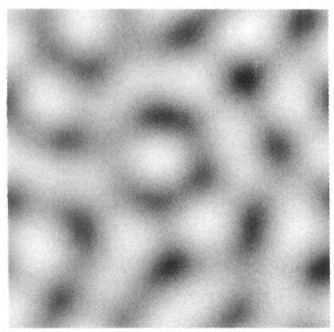

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