Temperature-Driven Change in the Unstable Growth Mode on Patterned GaAs(001)

T. Tadayyon-Eslami,[1,3] H.-C. Kan,[2,3] L. C. Calhoun,[3] and R. J. Phaneuf[1,3]
[1]*Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742, USA*
[2]*Department of Physics, University of Maryland, College Park, Maryland 20742, USA*
[3]*Laboratory for Physical Sciences, 8050 Greenmead Drive, College Park, Maryland 20740, USA*

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We observe a dramatic change in the unstable growth mode during GaAs molecular beam epitaxy on patterned GaAs(001) as the temperature is lowered through approximately 540 °C, roughly coincident with the preroughening temperature. Observations of the As_2 flux dependence, however, rule out thermodynamic preroughening as driving the growth mode change. Similar observations rule out the change in surface reconstruction as the cause. Instead, we find evidence that the change in the unstable growth mode can be explained by a competition between the decreased adatom collection rate on small terraces and a small anisotropic barrier to adatom diffusion downward across step bunches.

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Our ability to create a host of layered nanostructures which exploit confinement, interference, tunneling, and reduced dimensionality effects hinges on the production of flat interfaces during growth. Molecular beam epitaxy (MBE) is one of the standard techniques for the fabrication of such structures and might be expected to allow growth close to equilibrium due to the small incident atomic or molecular fluxes and relatively high growth temperatures, corresponding to fast diffusion. Nevertheless, MBE growth is often observed to result in departures from a generally desirable atomically flat surface topography, i.e., unstable growth [1–3]. This is usually attributed to kinetic barriers to equilibration, the assumption being that flat, atomically close-packed surfaces produce the lowest free energy, and so departures from flatness during growth should stem from kinetic barrier-based instabilities. While a number of different types of barriers have been proposed [4–7], there are relatively few cases in which observations of unstable growth can clearly be identified as due to the effect of a particular barrier. On the other hand, thermodynamics can also drive surfaces to roughen [8,9], and corrugated surfaces or interfaces might result from growth in a regime where roughness is favored. Assignment of the origin of unstable growth is, thus, often a complicated problem.

GaAs(001) is a technologically important substrate for growth of multilayer structures, for which MBE at standard conditions causes a transient instability [1,10]. Perturbing the flat surface by lithographic patterning followed by MBE growth at a relatively high temperature reveals an initial amplification of the perturbation. While this instability can be modeled phenomenologically [1], only recently has a physical mechanism been identified [10]. In this Letter, we show that the mode of this transient instability changes dramatically as we vary the growth temperature and that this change and its dependence on the incident arsenic flux allow us to distinguish between thermodynamic preroughening and kinetic barriers as responsible for this behavior.

We begin with a brief description of our experiments. To create well defined perturbations on our GaAs(001) substrates, we use photolithography followed by reactive ion etching, creating arrays of cylindrically shaped pits, ~50 nm in depth, on the surface, as described previously [1]. After removing the residual resist, we image the topography of the patterned substrates using atomic force microscopy (AFM) in the tapping mode. Next, they are introduced into the MBE growth chamber, whose base pressure is 2×10^{-11} mbar, heated to a temperature of 610 °C to thermally desorb the oxide, and then annealed at 550 °C for 1 h under an As_2 flux to reduce the roughness which results from oxide desorption. GaAs is next grown onto the surface at a rate of approximately 0.3 nm/s, typical for MBE homoepitaxy. We vary both the growth temperature and the As_2/Ga flux ratio as described below. Following growth, we cool the samples quickly (~3 °C/s initial cooling rate) by switching off the heating power. Although some rearrangement at the atom scale likely occurs during cooling, surface structures such as the islands of atomic layer height should mostly remain unchanged. Further, as we show below, in these investigations it is the changes that we see in growth mode as we change the temperature and As_2 flux which are of interest, rather than the absolute values of the growth parameters.

We find that the temperature has a striking effect on the nature of the growth instability, illustrated in Fig. 1, which shows AFM images after various stages of growth. The top panels are for growth at 600 °C and show an anisotropic evolution nearly identical to that which we reported for growth at 585 °C [1,10]. The initially cylindrical pits take on an elliptical shape, with the narrowing occurring most rapidly along the $[\underline{1}10]$ direction. In addition, elongated mounds [3] initially decorate the surface; these eventually disappear [1,11] as more GaAs is grown onto the surface, presumably via coalescence. The evolution of the surface depicted in the bottom panels, for growth at 500 °C, shows a noticeable and qualitative difference: the appearance of

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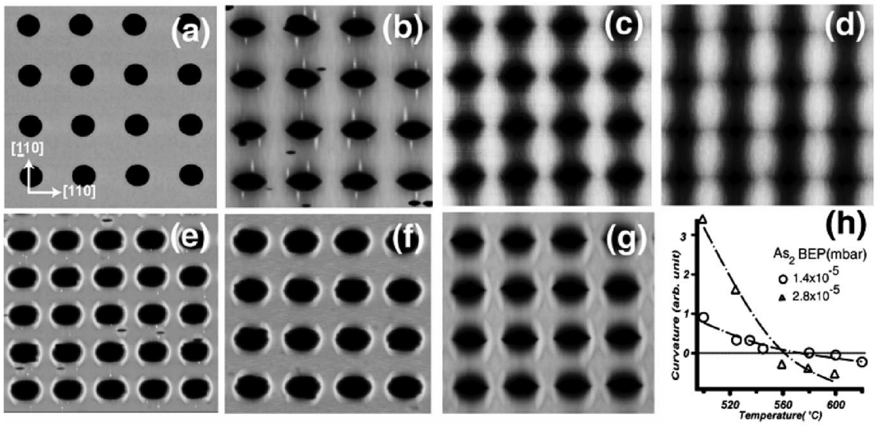

FIG. 1. AFM images of patterned GaAs(001) (a) before MBE growth, (b) after 100 nm growth at 600 °C, (c) after 200 nm growth at 600 °C, (d) after 500 nm growth at 600 °C, (e) after 100 nm growth at 500 °C, (f) after 200 nm growth at 500 °C, and (g) after 500 nm growth at 500 °C. For (b)–(g), the field of view is 7.5 μm, and As_2 flux for growth is 2.8×10^{-5} mbar (BEP). (h) Average curvature between pits along the [110] direction after growth of 100 nm vs temperature. (△): As_2 flux BEP $= 2.8 \times 10^{-5}$ mbar, zero crossing at $T_G = 552\,^\circ$C; (○): As_2 flux BEP $= 1.4 \times 10^{-5}$ mbar, zero crossing at $T_G = 570\,^\circ$C.

ring-shaped protrusions at the top edges of the pits along the more slowly evolving [110] direction. Below, we consider potential physically based mechanisms for the temperature dependence of the growth mode we observe. As we will show, an important consideration in ruling out certain possibilities comes from the variation in the growth mode transition temperature $T_{\mathbf{G}}$ with As_2 flux. To extract this dependence, we fit the surface curvature, measured between pits, along [110] as a function of temperature and flux. Figure 1(h) shows the results after growth of a 100 nm thick film in a region where 1.4 μm diameter pits are spaced at 2.8 μm. The presence of the rings causes a positive curvature, while in their absence the curvature is negative. We assign the temperature where the curvature changes sign as that of the growth mode transition. Figure 1(h) shows that this occurs near 552 °C for an As_2 flux with a beam equivalent pressure (BEP) of 2.8×10^{-5} mbar and near 570 °C for an As_2 flux with a BEP of 1.4×10^{-5} mbar. The growth mode transition temperature, thus, decreases with increasing As_2 flux.

We now consider the possibility that the change in growth mode involves crossing through a "preroughening" transition [9] on GaAs(001) [12]. Above a temperature of ~527 °C, LaBella *et al.* observed a dramatic increase in the number density of islands on (001) terraces which exist at the surface. The approximate coincidence of this transition temperature with that of the change in growth mode suggests that it might somehow drive this change. We find, however, that the As_2 flux dependence of the transition temperature rules out this possibility. We annealed unpatterned GaAs(001) surfaces for extended periods at a series of temperatures in an As_2 flux (rather than in As_4 as was done by LaBella *et al.* [12]) to measure the preroughening onset temperature T_P. Our initial As_2 flux corresponds to what we used during the growth experiments of Fig. 1, and a BEP of 2.8×10^{-5} mbar. As the Ga flux is off, there is no growth. Following the procedure suggested by LaBella *et al.* [12], we preceded the annealing sequence by growing a 400 nm thick GaAs "buffer" layer at 580 °C; after annealing, we switch off the heating power. AFM images of the resulting surface topography are shown in Figs. 2(a)–2(d) and show a dramatic increase in the density of islands on the surface after annealing at temperatures of between 500 and 555 °C. In Fig. 2(e), we plot the root mean square (rms) roughness of the surface as a function of annealing temperature and assign the annealing temperature of the inflection point, 537 ± 13 °C, as the onset point of preroughening at this As_2 flux, T_P. Separate determinations reveal a monotonic *increase* in T_P with As_2 flux, as shown in Fig. 2(f), consistent with the observed

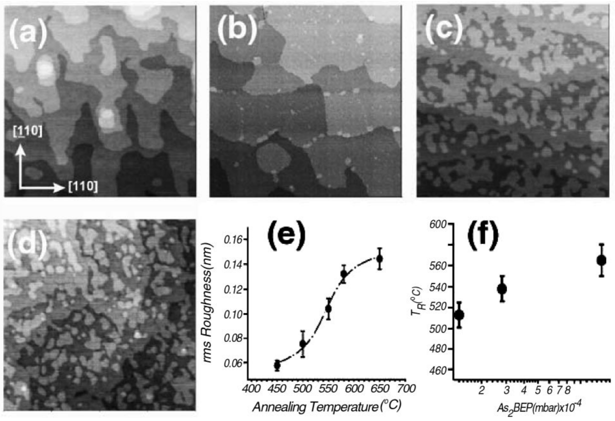

FIG. 2. (a)–(d) 1 μm × 1 μm AFM images of GaAs(001) surfaces subsequent to annealing in an As_2 flux BEP of 2.8×10^{-5} mbar. The crystalline orientations indicated in (a) also apply to (c)–(d). (a) Annealing temperature 450 °C, (b) annealing temperature 500 °C, (c) annealing temperature 580 °C, (d) annealing temperature 650 °C, (e) rms roughness measured from [001] terraces in the AFM images vs annealing temperature for As_2 flux BEP of 2.8×10^{-5} mbar, and (f) preroughening onset temperature vs As_2 flux BEP.

behavior during annealing in an As_4 flux [12]. This is in sharp contrast to the *decrease* of the growth mode transition temperature with flux. Based upon this contrasting behavior, we conclude that preroughening cannot drive the observed change in growth mode. This might seem surprising, as the extra density of step edges at islands would be expected to profoundly alter the growth mode. Our AFM observations of regions between steps reveal, however, that during growth the island density is larger at the lower temperatures we have explored. Layer-by-layer growth, i.e., island nucleation and coalescence, occurs between pits throughout the temperature range we explore, as indicated both by our AFM images and by observations of reflection high-energy electron diffraction oscillations [13]. We conclude that an effective "kinetic roughening" induced by growth dominates the effect of thermodynamic preroughening. In a similar manner, we rule out the $\beta_2(2 \times 4)$ to $c(4 \times 4)$ reconstructive transition, for which the transition temperature also shows an As_2 flux dependence opposite to that of the growth mode change [14] as causing this intriguing behavior. We, thus, turn to possible explanations based upon kinetic effects rather than thermodynamics.

The change in growth mode we observe is consistent with a small, anisotropic barrier to the crossing of steps from above by diffusing adatoms, i.e., an "Ehrlich-Schwoebel" (ES) barrier [4,5]. Such a barrier would need to be small, in that thermal promotion across it changes noticeably over the temperature range 500–600 °C. It would also need to be anisotropic, since we observe that the island stacks which form the rings occur only at edges bounding pits along the $[110]/[\bar{1}\bar{1}0]$ directions; furthermore, the shapes of the stacks are elongated along the orthogonal $[\bar{1}10]$ direction. The absence of growth mounds away from the edges is further evidence for the weakness of the ES barrier in this case and suggests a collective effect due to densely packed steps [6]. We, in fact, see evidence for such a barrier from AFM edges in the very early stages of growth. Figures 3(a) and 3(b) are images scanned after annealing for 1 h at a temperature of 580 °C, but before growth. The large islands result from preroughening, followed by coalescence. Figures 3(e) and 3(f) show the surface after growth of 1 nm of GaAs, at a temperature of 600 °C, in regions between pits along [110] and $[\bar{1}10]$, respectively. The surface now contains a moderate density of small islands, in addition to the larger island which resulted from annealing. The regions immediately adjacent to the pit edges, however, are nearly "denuded" of such small islands, as seen clearly in Figs. 4(c) and 4(d), where the density of these islands is plotted in the vicinity of [110] and $[\bar{1}10]$, respectively. Thus, at this temperature adatoms close to pit edges are relatively free to diffuse downward across and attach to the bunched steps which form the pit walls rather than coalescing to form islands; in this case, there is no qualitative evidence for the effect of an ES barrier. Similarly, in Fig. 3(d), the AFM image acquired after growth of 1 nm in the region between pits along $[\bar{1}10]$ shows a small denuded zone, visible in the island density plot in Fig. 4(b). Contrasting behavior is seen in Fig. 3(c) and in the island density plot of Fig. 4(a), where the islands extend up to [110] pit edges, consistent with the effect of an anisotropic multistep Ehrlich-Schwoebel barrier at this lower temperature.

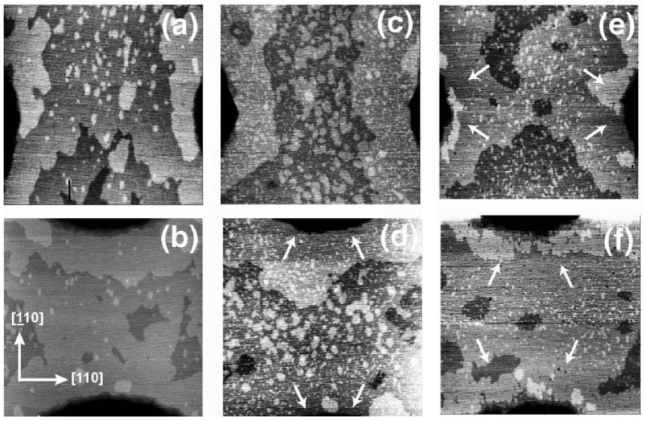

FIG. 3. AFM images of regions between pits (a),(b) after annealing for 1 h at 580 °C but before MBE growth, (c),(d) after growth of 1 nm at an As_2 flux BEP of 1.4×10^{-5} mbar and a temperature of 500 °C, and (e),(f) after growth of 1 nm at an As_2 flux BEP of 1.4×10^{-5} mbar and a temperature of 600 °C. For all images, the field of view is 1.4 μm. The arrows in (d)–(f) indicate zones denuded of small growth islands near the pit edges.

Finally, we consider the behavior shown above in light of our previous observations [1,10] that the detailed evolution of the surface morphology that we observe during

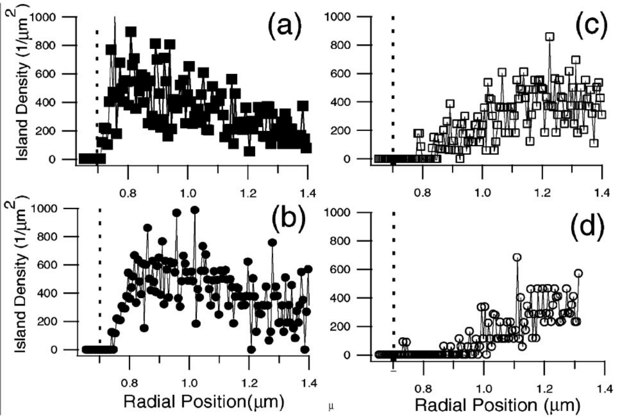

FIG. 4. Density of small growth islands vs radial position, with respect to pit center, after growth of 1 nm GaAs at an As_2 flux BEP of 1.4×10^{-5} mbar, determined from Fig. 3. (a) Growth temperature $T_G = 500\,^\circ\mathrm{C}$, island density determined over azimuthal range $[110] \pm 45^\circ$. (b) $T_G = 500\,^\circ\mathrm{C}$, azimuthal range $[\bar{1}10] \pm 45^\circ$. (c) $T_G = 600\,^\circ\mathrm{C}$, island density determined over azimuthal range $[110] \pm 45^\circ$. (d) $T_G = 600\,^\circ\mathrm{C}$, azimuthal range $[\bar{1}10] \pm 45^\circ$. The dashed lines show the position of the pit edges in all cases.

MBE growth on these patterned GaAs(001) surfaces at high temperatures is consistent with the modified, mass conserving form (CKPZ) of the Kardar, Parisi, and Zhang [15] equation proposed by Sun, Guo, and Grant [16]:

$$\frac{\partial h}{\partial t} = -\nabla^2\left[v_x \frac{\partial^2 h}{\partial x^2} + v_y \frac{\partial^2 h}{\partial y^2} + \lambda_x\left(\frac{\partial h}{\partial x}\right)^2 + \lambda_y\left(\frac{\partial h}{\partial y}\right)^2 \right] + \eta. \tag{1}$$

The major difficulty in applying this and related continuum models to the growth of GaAs is the lack of understanding of the physical significance of the coefficients in the corresponding equations. We now show that the change in the growth mode with temperature provides an important insight as to the physical processes corresponding to Eq. (1). In the CKPZ equation, the sign of λ_x and λ_y is taken to be positive. Reversing the sign of the nonlinear terms, as suggested by Lai and Das Sarma [17], results in nearly isotropic rings of material building up around the pit initially during growth [1]. While this latter prediction is quite different from our observations at temperatures above the growth mode transition T_G, it is qualitatively consistent with those below T_G, along the [110] direction. We have argued elsewhere that the nonlinear terms, which break the up-down symmetry of the equation, are consistent with the Zeno effect proposed by Elkinani and Villain [18] and based upon Villain's ansatz that the adatom density can be written as $\boldsymbol{\rho} = \boldsymbol{\rho}_0 + \boldsymbol{\rho}_1 \cdot (\boldsymbol{\nabla}\mathbf{h})^2$ [19]. Since the surface adatom flux, $\vec{j} \propto -\nabla\rho$, and $\frac{\partial h}{\partial t} = -\nabla \cdot \vec{j}$, a negative value of ρ_1, corresponding to a local depletion of adatoms near where the pit bottoms intersect the side walls leads to the CKPZ form. We note that a multistep Ehrlich-Schwoebel barrier also breaks the up-down symmetry of the problem but results in the opposite trend, i.e., an increase in the local adatom density near descending steps, leading to a positive contribution to ρ_1. At low enough temperatures, this effect becomes dominant, at least along [110], and the sign of the nonlinear term along this direction reverses, leading to the formation of the rings along the top edges of the pits. This model provides a physically based explanation for the excellent agreement, over a range of temperature, flux, and lateral length scales, that we observe between our results and the predictions of what, until now, has been a phenomenological model for growth.

In summary, MBE growth on patterned GaAs(001) shows complex transient behavior, with a dramatic change in the mode evolution on cooling through a temperature approximately coinciding with the thermodynamic preroughening transition. We find that this behavior is consistent with the predictions of the CKPZ model at high temperatures but that the sign of the nonlinear term in the height equation reverses along [110] beneath ~550 °C. Based on this, we propose a simple, physically based model involving a competition between decreased adatom collection rate during growth on small terraces [10,13,18] and a small anisotropic multistep Ehrlich-Schwoebel barrier. Undoubtedly, more complex models with additional effects, e.g., multiple types of diffusing species, and changes in diffusion length across transitions are possible. Further, it assumes that it makes sense to talk about steps in the presence of kinetic preroughening. Our results, along with the model we propose here, provide new physical insight to the significance of the nonlinear term in a commonly evoked growth equation [16,17,19] which describes our observations remarkably well but, until now, has been phenomenological.

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