Morphological stability of facet growth on nonplanar substrates

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We study the morphological stability of layer growth by chemical vapor deposition onto a nonplanar substrate patterned with a facetted groove. Our analytic treatment indicates that, except under conditions of very modest supersaturation, diffusion effects in the gas phase generally preclude the stable growth of crystallographic facets that form the sidewalls of the groove. Instead, heterogeneous nucleation and the kinetics of step flow combine to promote the evolution of an initially perfect facet into a stably propagating *vicinal* surface. Under more diffusion-limited conditions, even these "facets" do not survive and a characteristic rough morphology results.

Recent reports of the *in situ* fabrication of narrow quantum well and quantum wire structures on nonplanar substrates by organometallic vapor phase epitaxy (OMVPE)[1,2] crucially exploit the fact that different crystallographic facets grow at different rates. Implicit in the design of these structures is the assumption that the facets grow at a constant rate across their entire area. Here, we examine theoretically the range of conditions under which this assumption (which we call *stable* facet growth) is justified for the case of V-groove substrates.

We assume steady-state conditions so that the reactant concentration in the gas phase $c(\mathbf{r})$ is determined by Laplace's equation[3]

$$\nabla^2 c(\mathbf{r}) = 0. \tag{1}$$

The boundary conditions for this equation at the growth fronts are determined[4] by the requirement that the arrival rate of reactant molecules to the surface (by gas phase diffusion) equal the rate of mass incorporation into the crystal (by surface kinetic processes). Mathematically, this condition reads

$$\Omega D \frac{\partial c}{\partial n} = \Omega k [c(\mathbf{s}) - c_{\text{eq}}] \tag{2}$$

at every point $\mathbf{s}$ of the surface of each facet. Here, Ω is the volume of a growth unit, D is the gas phase diffusion constant, n denotes the normal to the surface, k is a first-order surface kinetic rate coefficient and c_{eq} is the concentration of reactant molecules in equilibrium with a facet. Equations (1) and (2) are sufficient to obtain $c(\mathbf{r})$ up to a constant which is taken here to be an adjustable parameter, σ_0, representing the value of the supersaturation $\sigma(\mathbf{s}) = [c(\mathbf{s}) - c_{\text{eq}}]/c_{\text{eq}}$ at the bottom of the groove.

Stable growth (as defined above) actually corresponds to a rather simpler boundary condition at every point along the surface of the ith facet:

$$\frac{\partial c}{\partial n_i} = q_i. \tag{3}$$

The q_i are *constants* which depend upon both material type and crystallographic orientation. We conclude that the true prerequisite for stable growth is that Eqs. (2) and (3)

be satisfied simultaneously. Notice that this implies that $c(\mathbf{s})$ itself must be constant across each facet.

We have solved Eqs. (1) and (3) in the region above a flat substrate (terrace growth rate q_1) patterned with a single triangular groove (sidewall growth rate q_2) for various values of σ_0, q_1, and q_2. The solution is obtained by a conformal mapping technique.[5] Quite generally, we find that $c(\mathbf{s})$ *decreases* in magnitude as one proceeds into the groove. This result is easy to understand; only very few molecules undergoing random walk (diffusive) motion make it to the bottom of the groove without hitting a sidewall first. Stable facet growth within a groove thus generally is inconsistent with surface incorporation kinetics [the right-hand side of Eq. (2)]. On the other hand, experiments[1,2] apparently show that such growth *does* occur.

The resolution of this paradox can be found in an old idea due to Chernov.[6] Briefly, Eq. (2) *always* can be satisfied if the kinetic coefficient k is presumed to *vary* across a facet in just such a way as to precisely compensate the variations in $c(\mathbf{s})$. This is not difficult to arrange because[7] the presence of steps on a nominally flat surface strongly affects its growth rate. Thus, a "facet" endowed with just the right variations in step density (now more properly termed a vicinal surface) can be expected to grow uniformly in a shape preserving manner.[8]

Our quantitative strategy[9] is to replace the right-hand side of Eq. (2) with an alternative expression for the growth rate which takes into account the fact that growth on facetted surfaces proceeds by the nucleation and spread of two-dimensional islands:[10]

$$R_n\{\sigma\} = A\sigma^{2/3} \log(1 + \sigma)^{1/6} \exp(-B/\sigma). \tag{4}$$

The constants A and B are material parameters. Now, since the supersaturation σ on any facet depends on the solution of the complete Laplace's equation, which in turn depends upon both q_1 and q_2 [from Eq. (3)], Eq. (2) rewritten using Eq. (4) (once for each facet) self-consistently determines the q_i as a function of σ_0:

$$\Omega D q_i = R_n[\sigma(q_1, q_2, \sigma_0)]. \tag{5}$$

Finally, we require an explicit expression for the kinetic coefficient. Following Ref. 9, we suppose that two-dimensional islands spread across a facet by the step-flow mechanism.[7] Then, if the slowly varying function $p(x)$
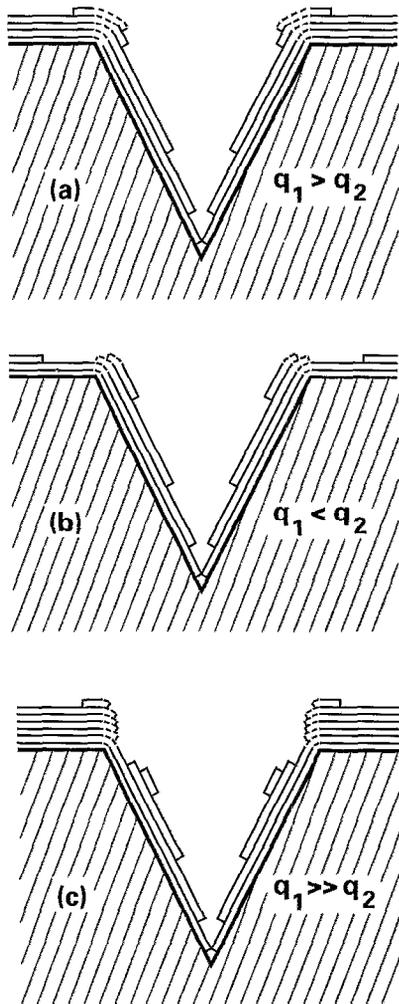
FIG. 1. Schematic view of shape-preserving (stable) vicinal surfaces which grow at a uniform rate across their entire length. The horizontal and inclined facets grow at rates q_1 and q_2, respectively. The height of a monoatomic step is greatly exaggerated in all cases. The dashed lines represent a best guess since the present theory cannot predict the step morphology in the immediate vicinity of a corner: (a) $q_1 > q_2$, (b) $q_1 < q_2$, (c) $q_1 \gg q_2$.
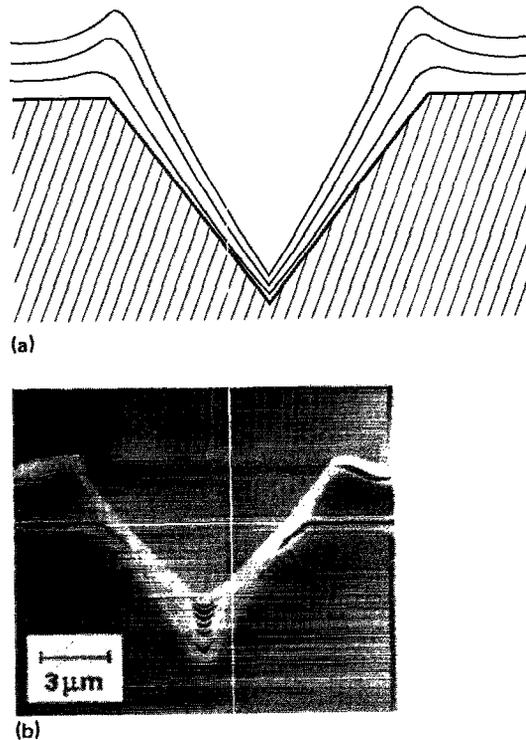

FIG. 2. Unstable growth morphology obtained from (a) this work for the case of $q_1 > q_2$ and (b) an OMVPE experiment (see Ref. 11). Note that the present theory neglects the possibility of enhanced nucleation at the very bottom of the groove.

characterizes the *local slope* of the surface (relative to the corresponding perfect facet orientation), the facet growth rate is obtained from the velocity of monoatomic steps as

$$R = p(x)V_{\text{step}} = \{Cp(x)\tanh[p_0/|p(x)|]\}\sigma(x)$$
$$= k(x)\sigma(x), \qquad (6)$$

where the constants C and p_0 are activated quantities which depend upon, e.g., terrace and step edge binding energies. As expected, the derived mass incorporation coefficient $k(x)$ depends strongly on the local surface step density. So, given σ_0 and the material parameters, we first solve Eqs. (1) and (3) parametrically as functions of the q_i for the supersaturation $\sigma(x)$ along each facet. Then, Eqs. (4) and (5) are used to compute the self-consistent growth rate for each facet. Finally, Eq. (6) determines the required compensating form of $k(x)$ and hence, $p(x)$.

Figure 1 illustrates the three distinct vicinal morphologies predicted by this analysis. When the terrace facet growth rate exceeds the sidewall growth rate [Fig. 1(a)], the point of maximum supersaturation always occurs just at the corner where these two facets meet. Islands nucleate there and monatomic steps flow outward across the terrace and down the sidewall. The largest step density occurs deep in the groove where the supersaturation is minimum. The situation within the groove is largely unchanged when the sidewall growth rate exceeds that of the terrace facet [Fig. 1(b)]. For the latter, however, the corner is a point of *minimum* supersaturation, and steps flow toward that point from elsewhere on that facet (the precise point of maximum supersaturation depends on the lateral size of the total substrate). If, on the other hand, one has $q_1 \gg q_2$ [Fig. 1(c)], the value of σ_{max} on the sidewall facet occurs a finite distance down the groove and the final stable morphology reflects this fact. The case of $q_1 \ll q_2$ is not appreciably different from that of Fig. 1(a).

Stable growth eventually breaks down when the supersaturation difference across the total sidewall length, $\Delta\sigma$, becomes large. Very small values of $\sigma(x)$ near the bottom of the groove cannot be compensated by very large values of step density because $k(x)$ quickly saturates to the value Cp_0 [Eq. (6)]. When this occurs, the growth rate near the bottom of the groove rapidly lags behind the growth rate near the top of the groove. The facet is destroyed and morphological instability sets in [Fig. 2(a)]. The micrograph in Fig. 2(b) illustrates this phenomena for the case of alternating layers of *p*- and *n*-type InP grown by OMVPE.[11] Our calculations show that $\Delta\sigma$ increases as any
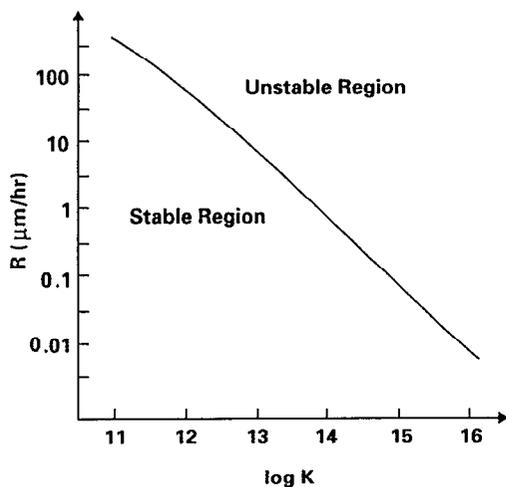
FIG. 3. Diagram illustrating the boundary between stable and unstable growth as a function of growth rate R and a material parameter K [see Eq. (7)] for a V-groove substrate.

one of the following increases: (i) the sidewall steepness, (ii) the sidewall length, or (iii) the growth rate, i.e., σ_0. We predict ultimate morphological instability if any of the foregoing becomes too large.

We have computed a growth stability "phase diagram" for the case of a 10-μm-deep groove with sidewalls inclined 72° from the horizontal (Fig. 3). The independent variables in this plot are the growth rate R and a parameter

$$K = \exp[+ (E_{\text{diff}} + 2E_{\text{des}} + 2E_k)/3kT] \tag{7}$$

which reflects the important material dependence in Eq. (4), i.e., the energies of surface diffusion, terrace desorption, and kink evaporation. For very low growth rates, $\sigma(x)$ is nearly constant across all the facets. No steps are required for compensation and a perfectly flat facet will propagate. As the mean supersaturation (and hence the growth rate) increases, steps appear on the stable growth front as sketched Fig. 1. At the most common experimental growth rates, the (nonuniform) step densities which

appear on these stable growth forms correspond to apparent *local* miscuts of no more than about 2° and thus still appear flat on a microscopic scale. We find that instability sets in when the apparent local miscut at the bottom of the groove approaches 4°.

In summary, morphological evolution during chemical vapor deposition onto nonplanar substrates has been studied with a phenomenological model. We find that facets which form the sidewalls of a triangular groove cannot be expected to grow outward at a uniform rate across their entire length unless the growth rate is quite low. At moderate growth rates, uniform shape-preserving growth occurs only for particular types of vicinal surfaces. At still higher growth rates, uniform growth is impossible and a morphological instability ensues.

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[3] We assume a reactor geometry which guarantees the existence of a "stagnant layer" within which reactant molecules diffuse to the substrate. See e.g., D. I. Fotiadis, A. M. Kremer, D. R. McKenna, and K. F. Jensen, J. Cryst. Growth **85**, 154 (1987).

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[8] See e.g., R.-F. Xiao, I. Alexander, and F. Rosenberger, J. Cryst. Growth **100**, 313 (1990) for a discussion of this point from a more microscopic point of view.

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[11] Courtesy of Dr. Rajaram Bhat, Bellcore. In this SEM image, the regions of dark and light contrast correspond to n- and p-type InP, respectively. The growth conditions are similar to those stated in R. Bhat, E. Kapon, J. Werner, D. M. Hwang, N. G. Stoffel, and M. A. Koza, Appl. Phys. Lett. **56**, 863 (1990).