

Stress-Driven Alloy Decomposition during Step-Flow Growth

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(Received 24 May 1996)

A surface under stress is morphologically unstable. In normal step-flow growth, this is manifested as a step-bunching instability. Here it is shown that for alloy growth the resulting inhomogeneous strain drives decomposition of the alloy. At the same time, this decomposition “screens” the inhomogeneous strain, partially suppressing the instability. In contrast to a previous continuum model, stress-driven alloy decomposition during step flow is never destabilizing, nor does it ever fully stabilize the surface. A possible mechanism for spontaneous superlattice formation is suggested. [S0031-9007(96)01007-1]

PACS numbers: 68.55.-a, 61.66.Dk

Semiconductor technology relies increasingly on alloys to provide the optimum lattice constant and band gap for a particular application. However, this introduces the danger of alloy decomposition, with spatial variations in the local alloy composition [1–3]. Such variations can be disastrous for electronic devices, causing carrier scattering, charge trapping, etc. At the same time, decomposition sometimes takes fascinating and potentially useful forms, such as spontaneous formation of superlattices [2], or even of superlattices perpendicular to the surface [3]. Because of this broad technological importance, as well as the current intense interest in growth instabilities generally, it is essential to develop an understanding of alloy growth and uniformity.

One possible origin for alloy inhomogeneity is spinodal decomposition, i.e., the decomposition of an alloy in a regime of composition and temperature where it is thermodynamically unstable. However, recently Guyer and Voorhees [4] proposed another decomposition mechanism, which is active even for a nominally stable alloy during epitaxial growth of strained layers. Strained layers are morphologically unstable [5–7] (or metastable [8]), roughening as they grow. This results in inhomogeneous stress across the surface. Large atoms are then preferentially incorporated in regions of more tensile stress, and small atoms in regions of more compressive stress. The result is a lateral decomposition of the alloy coupled to, and in fact driven by, the morphological instability.

This mechanism is clearly quite general, and represents an important insight into alloy decomposition. However, the specific model of Ref. [4] is not directly applicable to ordinary semiconductor growth for two reasons. First, it treats the surface as continuous, as is appropriate above the thermal roughening temperature. But semiconductor layers are generally grown far below this temperature, so their growth is better described by a step-flow model [9]. Second, in that model some mass transport occurs by local equilibration of the surface with an ambient vapor. Typically no such local equilibration occurs in either molecular beam epitaxy (MBE) or low-pressure chemical vapor deposition growth [10].

Here I treat the initial stage of morphological and compositional evolution during step-flow growth. As expected, there is an instability in which the composition and morphology are jointly modulated. However, the continuum analysis [4] concluded that alloy decomposition is typically destabilizing for surfaces under compression, while under certain conditions surfaces under tension could be stabilized absolutely. In contrast, I show here that decomposition is *always stabilizing* in step-flow growth, regardless of the sign of the stress. The reason is simple: As large (or small) atoms incorporate preferentially in regions of tensile (or compressive) stress, they partially relieve the stress variations. Thus, the reduced instability reflects a “screening” of the stress by alloy decomposition. As suggested by the screening analogy, the instability is never completely suppressed—the surface always remains unstable. Moreover, the degree of screening depends on the wavelength of the modulation. In particular, the most unstable mode is not screened at all. Thus, in one sense, the earliest onset of the morphological instability is unaffected by the alloy decomposition.

Consider growth on a vicinal surface, i.e., one which is cut at a small angle to the atomic planes, so that the surface consists of a staircase of terraces and descending atomic-height steps. Step motion arises from attachment and detachment of adatoms, which diffuse over the terraces. (Bulk diffusion is negligible at typical growth temperatures, and is not included here.) For simplicity, I neglect any diffusion barriers at steps, as well as any dependence of the adatom energy or mobility on the local strain and composition. These effects are not always negligibly small, but when present, they can have either sign, hastening or suppressing the instability and decomposition. I prefer to focus here on those aspects which are *generic* to alloy strained-layer growth.

It is convenient to decompose the velocity v_m of step m into the contributions from attachment of the respective species ν , writing $v_m = \sum_{\nu} v_{\nu m}$. Then previous results for a one-component system [7] can be generalized [11]

as

$$v_{\nu m} = \frac{F_{\nu}}{2} (x_{m+1} - x_{m-1}) + D_{\nu} \left(\frac{\eta_{\nu, m+1} - \eta_{\nu m}}{x_{m+1} - x_m} - \frac{\eta_{\nu m} - \eta_{\nu, m-1}}{x_m - x_{m-1}} \right). \quad (1)$$

Here F_{ν} is the incident flux of component ν , in monolayers per unit time; D_{ν} is the adatom mobility; $\eta_{\nu m}$ is the adatom density (as a fraction of possible sites) in equilibrium with step m ; and x_m is the step position. Increasing m corresponds to increasing x_m and descending steps. The first term in (1), in effect, represents step motion due simply to adatoms arriving and diffusing to the nearest step. The second term gives the additional step motion due to the thermodynamic driving forces described below.

The adatom density at step m can be written

$$k_B T \ln \eta_{\nu m} = \mu_{\nu m} - E_{\nu}^{\text{ad}}. \quad (2)$$

Here T is temperature, and E_{ν}^{ad} is the energy of an adatom of component ν . The interesting physics all arises from the dependence of the local chemical potential μ upon the local composition and strain, where

$$\mu_{\nu m} = \frac{dE}{dN_{\nu}} \Big|_m. \quad (3)$$

Here E is the free energy, N_{ν} is the number of atoms of component ν , and the derivative refers to addition of an atom at step m .

The free energy may be written (up to a constant) as

$$E = N g_{\nu}(c_{\nu}) + E_{\text{el}} + \sum_{\nu} N_{\nu} U_{\nu}, \quad (4)$$

where U_{ν} is the energy per atom of component ν in its pure and unstrained bulk form, E_{el} is the elastic strain energy, $N = N_1 + N_2$, and $g_{\nu}(c_{\nu})$ is the free energy of mixing of the unstrained alloy [12] with fraction c_{ν} of component ν . Note that g_{ν} depends on ν only in that one must specify which component is taken as the argument. (I prefer to use notation which is symmetric in the two components, e.g., using c_1 and c_2 to denote the fractions of the respective components, even when this leads to extra indices.)

Assuming a linear dependence of volume and elastic constant on alloy composition, the elastic energy is

$$E_{\text{el}} = \frac{1}{2} \varepsilon^2 \sum_{\nu} N_{\nu} m_{\nu}, \quad (5)$$

where ε is the local strain, and $m_{\nu} = M_{\nu} V_{\nu}$, V_{ν} and M_{ν} being the atomic volume and elastic constant for the respective pure materials.

The strain at a given step can be written

$$\varepsilon = \varepsilon_e + \varepsilon_s, \quad (6)$$

where ε_e is the misfit strain of epitaxy, and ε_s is the strain from the elastic field of other steps [13]. The former

depends only on local composition, as

$$\varepsilon_e = 1 - \frac{\sum c_{\nu} a_{\nu}}{a_0}, \quad (7)$$

where a_{ν} and a_0 denote the lattice constants of component ν and of the substrate, respectively.

Substituting (4)–(7) into (3) gives

$$\mu_{\nu} = U_{\nu} + g_{\nu}(c_{\nu}) + c_{-\nu} g'_{\nu}(c_{\nu}) + \frac{1}{2} m_{\nu} \varepsilon^2 - \bar{m} \varepsilon c_{-\nu} \Delta_{\nu}, \quad (8)$$

where $\bar{m} = \sum_{\nu} c_{\nu} m_{\nu}$, g' denotes the derivative, $\Delta_{\nu} = (a_{\nu} - a_{-\nu})/a_0$, and the subscript $-\nu$ denotes the component other than ν (so $c_{-\nu} = 1 - c_{\nu}$).

Then substituting (8) into (2), and expanding in small deviations from the mean composition and strain, the adatom density at step m is

$$\eta_{\nu m} = \bar{\eta}_{\nu} + \frac{\bar{\eta}_{\nu}}{kT} [J_{\nu} \varepsilon_{sm} + K_{\nu} (c_{\nu m} - \bar{c}_{\nu})]. \quad (9)$$

Here $\bar{\eta}_{\nu}$ is the adatom density for the uniform reference system, and \bar{c}_{ν} is the average composition, equal to F_{ν}/F , $F = \sum_{\nu} F_{\nu}$ being the total flux. The linear-response coefficients are

$$J_{\nu} = m_{\nu} \bar{\varepsilon} - \bar{m} \bar{c}_{-\nu} \Delta_{\nu}, \quad (10)$$

$$K_{\nu} = \bar{c}_{-\nu} g''_{\nu} + \bar{m} \bar{c}_{-\nu} \Delta_{\nu}^2 - \Delta_{\nu} \bar{\varepsilon} (m_{\nu} - \bar{m}), \quad (11)$$

where $\bar{\varepsilon}$ is the average strain, i.e., the epitaxial strain for composition \bar{c}_{ν} .

The strain ε_{sm} at step m due to other steps is [7,14]

$$\varepsilon_{sm} = \beta h \sum_{n \neq m} \frac{\varepsilon_n}{x_m - x_n}. \quad (12)$$

Here h is the step height, and β is a ratio of elastic constants, of order unity. This neglects the short-range elastic strain field from the “force dipole” of the step, which is unimportant for the initial instability except at very high step densities [7].

To characterize the instability, one evaluates the response to a perturbations of step positions *and compositions*, and solves for the time evolution. Define a small periodic deviation ξ from ideal flow of equally spaced steps:

$$x_m = L(m + Ft) + \text{Re}(\xi e^{ikm}). \quad (13)$$

Here the complex coefficient ξ gives the amplitude and phase for a perturbation of wavelength λ , where $k = 2\pi L/\lambda$, L being the average step spacing. (The smallest possible period is two steps, $\lambda \geq 2L$, so $0 \leq k \leq \pi$.) As with v , ξ can be decomposed into the contributions ξ_{ν} from the respective species.

As long as there is any incident flux, all steps are initially advancing, so the composition at each step is

$$c_{\nu m} = \frac{v_{\nu m}}{v_m}. \quad (14)$$

Substituting (9) into (1), using (12), (13), and (14), gives

$$\begin{aligned} \dot{\xi}_\nu = & (Q_\nu + iF_\nu \sin k)(\xi_\nu + \xi_{-\nu}) \\ & + (S_\nu - iR_\nu) \frac{1}{FL} (c_\nu \dot{\xi}_{-\nu} - c_{-\nu} \dot{\xi}_\nu), \end{aligned} \quad (15)$$

where $\dot{\xi} = d\xi/dt$. Here

$$\begin{aligned} P_\nu &= D_\nu \frac{\bar{\eta}_\nu}{kT} \frac{2}{L} (1 - \cos k) \\ Q_\nu &= P_\nu J_\nu \beta h \bar{\epsilon} L^{-2} (\pi k - \frac{1}{2} k^2) \\ R_\nu &= Q_\nu \frac{\Delta_\nu}{\bar{\epsilon}} L \frac{2k - 2\pi}{k(2\pi - k)} \\ S_\nu &= P_\nu K_\nu. \end{aligned} \quad (16)$$

Equation (15) represents two simultaneous equations for the two components, or, equivalently, for the morphological and compositional degrees of freedom. One solution corresponds to a purely compositional perturbation ($\xi = 0$), which neither grows nor decays with time. The other solution corresponds to the instability of interest here. For that two-component eigenvector $\bar{\Xi}_\nu$ of Eq. (15), the perturbation grows exponentially with time, as

$$\xi_\nu = \bar{\Xi}_\nu e^{rt}. \quad (17)$$

The growth rate of the instability is

$$r = \frac{\sum_\nu (FL + S_{-\nu} - iR_{-\nu})(Q_\nu + iF_\nu \sin k)}{FL + \sum_\nu c_{-\nu}(S_\nu - iR_\nu)}. \quad (18)$$

If $K_\nu < 0$, the alloy is thermodynamically unstable against spinodal decomposition. The present analysis cannot properly describe that regime, though clearly decomposition would be exacerbated in that case. Conversely, for $K_\nu > 0$ the thermodynamic stability of the alloy reduces decomposition, but can never suppress it entirely.

Let us therefore focus on the case where K is negligible compared to strain effects, so $S \rightarrow 0$. In this case

$$\begin{aligned} \text{Re}(r) &\rightarrow \frac{1}{1 + \alpha^2} \sum_\nu Q_\nu, \\ \alpha &= \frac{2\pi - 2k}{\bar{\epsilon} F k (2\pi - k)} \sum_\nu c_{-\nu} \Delta_\nu Q_\nu. \end{aligned} \quad (19)$$

For comparison, without alloy decomposition $\text{Re}(r) \rightarrow \sum_\nu Q_\nu$. Thus, decomposition is *always stabilizing*—it always reduces the growth rate of the instability by a factor $1/(1 + \alpha^2)$. The reason is that larger atoms incorporate preferentially in more tensile regions, and smaller atoms in more compressive regions, so the alloy decomposition in effect “screens” the lateral variations in stress associated with the morphological instability.

To better see what factors control the instability, one can rewrite the terms in (19) as

$$\begin{aligned} Q_\nu &= L^{-3} (1 - \cos k) k (2\pi - k) \bar{\epsilon}^2 \\ &\times \beta h \frac{D_\nu \bar{\eta}_\nu}{kT} \left(m_\nu - \bar{m} \bar{c}_{-\nu} \frac{\Delta_\nu}{\bar{\epsilon}} \right), \\ \alpha &= F^{-1} L^{-3} (\pi - k) (1 - \cos k) 2\bar{\epsilon} \Delta_1 \\ &\times \beta h \sum_\nu c_{-\nu} (-1)^\nu \frac{D_\nu \bar{\eta}_\nu}{kT} \left(m_\nu - \bar{m} \bar{c}_{-\nu} \frac{\Delta_\nu}{\bar{\epsilon}} \right). \end{aligned} \quad (20)$$

Both the bare instability Q and the screening α decrease with decreasing step density as L^{-3} . Both effects increase with increasing strain $\bar{\epsilon}$. However, the bare instability is independent of the absolute atomic size difference Δ —only the ratio $\Delta/\bar{\epsilon}$ enters. In contrast, the screening term α is directly proportional to Δ as well as to $\bar{\epsilon}$. Also, the bare instability is independent of the growth flux F , while the screening depends sensitively on the flux, as F^{-1} . Thus, for very fast growth there is essentially no screening, while the screening becomes increasingly strong as the growth rate drops. (As discussed above, the model here is inapplicable for $F \rightarrow 0$, so there is no divergence in α in the range of conditions treated here.)

The instability also depends sensitively upon wavelength. This dependence plays an important role in determining how the surface morphology evolves with time. The dependence calculated from Eq. (20) is shown in Fig. 1. The surface is most unstable at short wavelengths—the bare instability Q is a monotonically decreasing function of wavelength. The degree of screening, however, has a more complex behavior. Like the instability itself, the screening becomes weak at long wavelengths. But the screening also goes to zero at short wavelengths. Thus the rate of step pairing (the earliest manifestation of the instability) is entirely unaffected by alloy decomposition.

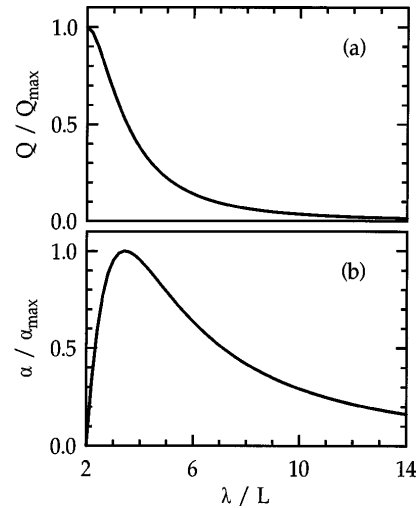


FIG. 1. Dependence of (a) bare instability Q and (b) screening factor α on wavelength $\lambda = 2\pi L/k$, from Eq. (20).

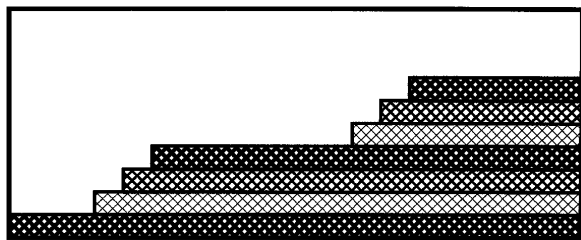


FIG. 2. Schematic illustration of a possible late-stage growth mode. The varying heaviness of cross-hatching represents varying composition in successive layers, as discussed in text. The resulting superlattice is clearest at right of the figure.

Finally, it is interesting to speculate about the later stages of alloy step-flow growth. As for the single-component case [7], one expects the surface to form step bunches, as shown schematically in Fig. 2. Consider for concreteness the case of SiGe on Si. From Eq. (12), the overall compressive stress is reduced at the top of the bunch, giving enhanced Ge incorporation there. However, the compression is increased at the base of the step bunch, favoring Si incorporation there. Under growth conditions where the step bunch flows as a whole [15], the layers terminating at the top and bottom of a bunch will incorporate disproportionate concentrations of Ge and Si, respectively. As illustrated in Fig. 2, this corresponds to spontaneous formation of a superlattice, when a uniform alloy is continuously deposited.

Spontaneous superlattice formation has in fact been observed experimentally, and is clearly related to steps [2]. However, it would be premature to suggest that the mechanism proposed here is responsible for the observed phenomenon. Spinodal decomposition has also been cited as a possible cause. A more complete analysis of the later stages of growth will be necessary in order to clarify the role of stress-induced alloy decomposition in such fascinating phenomena.

Discussions with Peter Voorhees and Andrew Zangwill are gratefully acknowledged.

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- [10] The situation is a bit complex for compound semiconductor alloys. For example, for InAs-GaAs alloy MBE, there may be substantial equilibration with the As vapor. However, the components relevant to decomposition, In and Ga, are certainly not both in equilibrium with the vapor.
- [11] This assumes that $\eta \ll 1$, as is always the case in normal MBE growth.
- [12] It is no doubt simplistic to use the bulk g in this surface context, but I will focus on the case where this term is unimportant.
- [13] In general, there are also stresses arising from composition gradients left behind by the moving steps. However, when growth is sufficiently rapid, the *lateral* gradients are negligible. A sufficient condition for this is $F \gg (\lambda/L) \text{Re}(r)$. (These terms are defined in the text.)
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- [15] The present model does not lead to a strict steady state of step bunches flowing intact, but under appropriate conditions robust step bunch flow can be obtained as a long-lived transient regime of growth, which suffices for practical purposes. These conditions will be discussed elsewhere.