RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 56, NUMBER 8 15 AUGUST 1997-II

Spinodal decomposition during step-flow growth

J. Tersoff
IBM Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598

(Received 5 February 1997)

Relatively little is known about the epitaxial growth of alloys that are thermodynamically unstable. An analysis here suggests that spinodal decomposition can take place by formation of step bunches with alternating composition. This provides a possible mechanism for the spontaneous formation of superlattices during molecular beam epitaxy alloy growth. Kinetic effects reduce the degree of decomposition, relative to equilibrium. At sufficiently high growth rates, decomposition is completely suppressed. [S0163-1829(97)50132-9]

Most alloys are thermodynamically stable only in a limited range of composition and temperature. Outside this range, they tend to decompose into two alloy phases of stable composition. Such spinodal decomposition has been extensively studied, and is well understood for the case of decomposition by bulk diffusion.[1]

However, the situation becomes more complex for epitaxial alloy growth. When bulk diffusion is negligible, surface diffusion still provides a possible decomposition mechanism. Many semiconductor alloys may be thermodynamically unstable at typical growth temperatures, although the phase diagrams are not accurately known; and spinodal decomposition has been invoked to account for a variety of interesting observations. Yet such suggestions are invariably speculative —little is understood at present about spinodal decomposition by surface diffusion during epitaxial growth. There have been a few model numerical simulations;[2] but analytic treatments to date have focused on one-dimensional solids,[3] or on highly simplified continuum treatments of vapor-phase growth.[4] Spinodal decomposition during step-flow growth, the growth mode most relevant to semiconductor technology, has apparently never been treated except for dimensional arguments.[5]

Here I consider step-flow growth of a thermodynamically unstable alloy. A full treatment of the growth dynamics would be exceedingly difficult, for reasons outlined below. But I suggest that, even without such a treatment, one can expect spinodal decomposition to involve formation of step bunches with alternating composition. The bunch size is controlled by a competition between thermodynamics and kinetics. Growth by flow of such bunches suggests one possible (albeit speculative) explanation for the remarkable phenomenon of spontaneous superlattice formation,[6] as discussed below.

For step-bunch flow, one can calculate the degree of alloy decomposition. At low growth rate, the deposited material decomposes and attaches to the respective bunches at nearly the thermodynamically stable compositions. However, for a given bunch size, the degree of decomposition decreases with increasing growth rate, going to zero at a critical rate. Thus it should be possible to grow uniform alloys at temperatures where they are thermodynamically unstable.

Consider growth on a vicinal surface, i.e., one oriented at a small angle to the atomic planes. This misorientation creates a staircase of atomic-height steps. Step-flow growth occurs when all deposited material diffuses to a step and attaches there. I assume that these steps are straight, and that the system is uniform in the direction parallel to the steps. (Thus the possibility of alloy decomposition along a given step is excluded here.) Also, in alloys whose constituents have different atomic sizes, decomposition necessarily creates strain. Here I neglect this effect, treating the alloy decomposition as due simply to a preference for like neighbors.

With these assumptions, decomposition can only occur by having steps of different composition, which provide preferred sinks for the respective constituents. Some possible configurations are shown in Fig. 1. For an A-B alloy, the most obvious possibility is to have alternating A-rich and B-rich steps. This is shown in Fig. 1(a). However, such a situation is not realistic for most systems. It leads to inter-

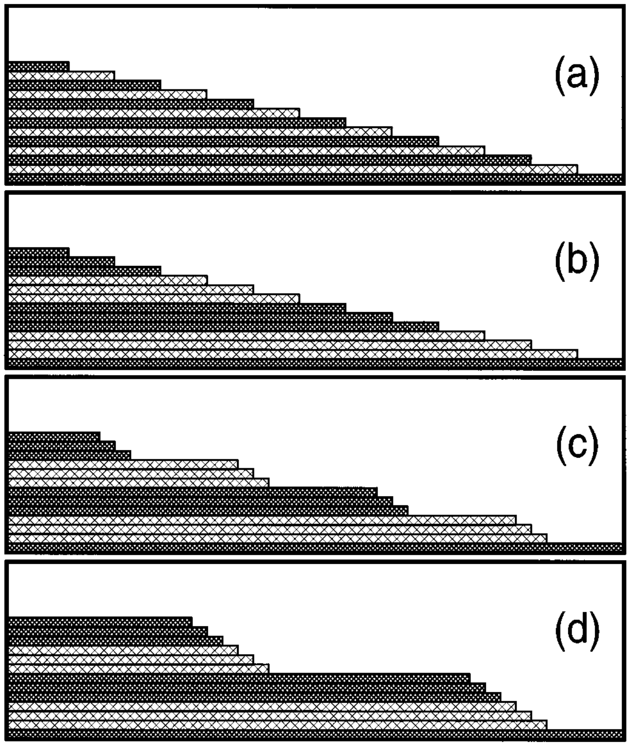

FIG. 1. Schematic illustration of possible growth configurations when decomposition occurs. A-rich and B-rich steps (and the corresponding material they leave behind as they flow) are indicated by light or heavy crosshatching.

leaving of the two phases in layers only one unit cell thick, so the interface energy becomes important. In fact, for typical cubic lattices there are at least as many A-B bonds in this structure as in a random alloy.

(Much interest centers on compound semiconductor alloys such as $\mathrm{In}_{1-x}\mathrm{Ga}_x\mathrm{As}$ and $\mathrm{ZnSe}_{1-x}\mathrm{Te}_x$, where only one fcc sublattice of the zinc-blende structure is alloyed. In such a case, references to an A-B alloy should be understood to refer only to the alloyed sublattice.)

A more favorable situation is shown in Fig. 1(b). In this case there are several A-rich steps, followed by several B-rich ones. If the number of steps per period is large, then the system decomposes into thick layers of alternating composition, with relatively little interface area per unit volume. Such a situation can lower the free energy of the system nearly to its equilibrium value.

However, to understand the growth, it is not enough to consider the thermodynamics. One must also address the kinetics, at least qualitatively. This is simpler if we restrict ourselves to the nearly immiscible limit for now. Then there are two kinds of steps, of almost pure A and B composition, respectively. We also assume that A atoms are in local equilibrium with A-rich steps (and B with B); and that A (B) steps pose no diffusion barrier to B (A) adatoms, but rather are effectively ''transparent'' to them.[7] Then either type ν of step obeys the equation of motion

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

Here ν denotes A or B; $x_{\nu,m}$ is the position of the mth step of type ν (i.e., there is a separate series $m=1,2,3\ldots$ for each ν); F_ν is the incident ν flux; D_ν is the adatom diffusion constant; and $\eta_{\nu m}$ is the ν adatom density in equilibrium with step νm. Eq. (1) is obtained by integrating the diffusion equation for $\eta(x)$, with boundary conditions $\eta_\nu(x_{\nu m})=\eta_{\nu m}$.[9,10]

The adatom densities at the steps have the form

$$\eta_{\nu m}=e^{(\mu_\nu-E_\nu)/kT}, \qquad (2)$$

where E_ν is the adatom formation energy, and μ is the chemical potential. Assuming a nearest-neighbor interaction, the chemical potential for A atoms at an A-rich step has its bulk value $\overline{\mu}_\nu$, unless the preceding step was B rich. In that case an A atom at this step has some B-atom neighbors in the layer below, raising the chemical potential by an amount $\delta\mu_\nu$, and increasing the equilibrium adatom density at the step by a factor $e^{\delta\mu_\nu/kT}$. The velocity (1) can then be written

$$v_m=\frac{F}{2}(x_{m+1}-x_{m-1})+\overline{\eta}D\left(\frac{\beta_{m+1}-\beta_m}{x_{m+1}-x_m}-\frac{\beta_m-\beta_{m-1}}{x_m-x_{m-1}}\right). \qquad (3)$$

Here $\overline{\eta}_\nu=e^{(\overline{\mu}_\nu-E_\nu)/kT}$ is the adatom density for the corresponding pure material; $\beta_{\nu m}=e^{\delta\mu_\nu/kT}-1$ for a step following an unlike step, and 0 otherwise; and the subscript ν has been suppressed for simplicity.

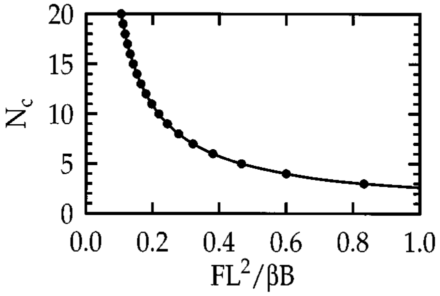

FIG. 2. Maximum stable bunch size N_c vs dimensionless growth rate $FL^2/\beta B$. Step pairs (bunches with $N=2$) are stable at any growth rate.

Now consider a repeating sequence of N A-rich and N B-rich steps with equal spacing L, as in Fig. 1(b). We can view this as successive ''trains'' of A and B steps. Substituting the corresponding values for β and x into Eq. (3), a step inside a train will have velocity $v_m=FL$, but the leading and trailing steps will have velocities

$$v^{(\mathrm{first})}=\frac{F}{2}(2+N)L-\beta\overline{\eta}D\frac{(2+N)}{(1+N)L}, \qquad (4)$$

$$v^{(\mathrm{last})}=\frac{F}{2}(2+N)L+\beta\overline{\eta}D\frac{1}{(1+N)L}. \qquad (5)$$

(The second step is also slightly accelerated, but this does not affect the conclusions here.) Note that $v^{(\mathrm{last})}>FL$, i.e., the trailing step tends to move faster than interior steps. If $v^{(\mathrm{first})}<FL$ then the lead step moves more slowly than interior steps. Thus, as illustrated in Figs. 1(c) and 1(d), we will have bunching together of the A-rich steps, and separate bunching of B-rich steps, when

$$F<\beta\overline{\eta}D\frac{2(N+2)}{(N^2+N)L^2}. \qquad (6)$$

To fully understand when step bunches form, and how large they grow, one would need to address a difficult issue. I have assumed that a given step is either A rich or B rich at the outset, and remains so. However, in order for the statistical properties of the system to become independent of the precise initial conditions after sufficient time, it must be possible for an A-rich step to switch to B-rich, and vice versa. Such switching must play an important role if steps are ejected from one bunch and captured by the next. The detailed dynamics of the switching process is beyond the scope of this paper.

Nevertheless, for the restricted case of alternating A and B trains of N steps each, we now have an explicit criterion for stable bunching, Eq. (6). For a given temperature and flux, there is a critical bunch size N_c bounding the range $(N^2+N)/(N+2)<2\beta\overline{\eta}D/FL^2$. Bunches of size N_c or smaller are stable, while bunches larger than N_c are unstable.

The dependence of this bunch size N_c on growth rate and diffusion constant is shown in Fig. 2. Note that bunches of $N=2$ are stable for any flux F, since from Eqs. (5) and (4) $v^{(\mathrm{last})}>v^{(\mathrm{first})}$. Thus in this regime of nearly complete decomposition, increasing flux can never eliminate step pairing.

As discussed above, larger step bunches result in fewer A-B neighbors, and so lower free energy. Thus there is a competition between thermodynamics, which favors large bunches, and kinetics, which renders too-large bunches unstable. I speculate that during growth, the system reaches a steady state with bunches of size $\sim N_c$.

If this speculation is correct, it provides a mechanism for the spontaneous formation of superlattices. As illustrated in Fig. 1, as the step bunches flow the newly added material is segregated into A-rich and B-rich layers, whose thickness is fixed by the bunch size. Thus, continuous deposition of a uniform alloy results in growth of a superlattice. This may explain the remarkable observation of such spontaneous superlattice formation by Ahrenkiel *et al.*,[6] or provide an alternate mechanism for such formation. A related scenario has also been suggested by Barabási.[5] Related behavior has been previously,[8] but with a length scale which would seem to preclude the explanation suggested here.

This entire analysis assumes irreversible deposition of material onto the surface. If evaporation from the surface is also significant, then the effects described here occur only if the step density is sufficiently high (so that diffusion between steps dominates over evaporation). This might explain why spontaneous superlattice formation seems to disappear at low step density.

Up to this point I have considered only the case of nearly complete segregation, showing that spinodal decomposition naturally leads to bunching of same-component steps. The bunch size, and hence the period of the resulting composition modulation, is limited by the growth kinetics.

Let us now consider the actual degree of segregation, and the effect of growth kinetics on the decomposition process. To render this question tractable, I assume that the system consists of alternating N-step bunches of A-rich and B-rich steps, as suggested by the analysis above. Moreover, I assume that each bunch moves as a whole, so one can neglect the internal dynamics, and describe the bunch by a single chemical potential for each constituent. This is taken to be the bulk chemical potential for that composition, a good approximation when $N \gg 1$. Note that the A-rich (or B-rich) bunches are no longer assumed to be nearly pure A (or B); they each act as sinks for both A and B atoms.

Adapting Eq. (1), we can write an equation of motion for the bunches:

$$\begin{aligned} v_{\nu m} &= F_\nu L + D_\nu \left(\frac{\eta_{\nu,m+1} - \eta_{\nu m}}{(1+\alpha)NL} - \frac{\eta_{\nu m} - \eta_{\nu,m-1}}{(1-\alpha)NL} \right) \\ &= F_\nu L + \frac{2D_\nu}{NL(1-\alpha^2)} (\eta_{\nu,m+1} - \eta_{\nu m}). \end{aligned} \tag{7}$$

Here L is the average step spacing, so NL is the average bunch spacing; and I have assumed a two-bunch period, so bunches $m+1$ and $m-1$ are equivalent. The two inequivalent terraces between bunches have sizes $(1 \pm \alpha)NL$. [The possible range of α is illustrated in Fig. 1(c) and 1(d).] Note the change in notation—each bunch now has a unique index m, whereas before there were separate indexes m for each ν.

At this point we need an explicit model for the alloy thermodynamics. The simplest applicable model is ''regular solution theory,'' with free energy

$$f = 4Hc_\nu c_{-\nu} + kT(c_\nu \ln c_\nu + c_{-\nu} \ln c_{-\nu}), \tag{8}$$

where c_ν is the fraction of species ν in the alloy, and H is a measure of the energy cost of unlike neighbors. Here $-\nu$ denotes the constituent other than ν, so $c_{-\nu} = 1 - c_\nu$. This model free energy would be exact for a random alloy whose energy of mixing is given simply by the number of A-B neighbors, and including only the configurational contribution to the entropy.

Taking pure bulk A and B as our references, the chemical potentials are then

$$\mu_\nu = 4Hc_{-\nu}^2 + kT \ln c_\nu \tag{9}$$

and the adatom densities at the bunches are

$$\begin{aligned} \eta_{\nu m} &= \exp[(\mu_{\nu m} - E_\nu)/kT] \\ &= c_{\nu m} \overline{\eta_\nu} \exp[4Hc_{-\nu m}^2/kT]. \end{aligned} \tag{10}$$

Here E_ν is the adatom formation energy, and $\overline{\eta_\nu} =$ $\exp(-E_\nu/kT)$ is the equilibrium adatom density for the corresponding pure material. Note that c is the composition of the crystal, and not of the adatoms. Substituting Eq. (10) into Eq. (7),

$$v_{\nu m} = F_\nu L + \frac{2\overline{\eta_\nu} D_\nu}{NL(1-\alpha^2)} (c_{\nu,m+1} e^{4hc_{-\nu,m+1}^2} - c_{\nu m} e^{4hc_{-\nu,m}^2}), \tag{11}$$

where $h = H/kT$.

From Eq. (8), the alloy is thermodynamically stable against spinodal decomposition above a critical temperature $T_c = 2H/k$. Thus in all equations here h may be referred to measurable properties via $h = T_c/2T$.

The composition at each step is $c_{\nu m} = v_{\nu m}/v_m$. If we further restrict ourselves to a 50:50 alloy with the two bunches moving at equal velocity (as for $D_\nu = D_{-\nu}$ etc.), then $v_m = FL$ and $c_{\nu,m} + c_{-\nu,m} = c_{\nu,m} + c_{\nu,m+1} = 1$. Then Eq. (11) becomes

$$\delta = \Phi^{-1}[(1-\delta)e^{h(1+\delta)^2} - (1+\delta)e^{h(1-\delta)^2}], \tag{12}$$

where $\delta = 2c_{\nu m} - 1$ is the degree of decomposition of the 50:50 alloy, up to 1 for complete decomposition; and $\Phi = FNL^2(1-\alpha^2)/2\overline{\eta}D$ is the dimensionless growth rate, a measure of the degree to which kinetic factors are important.

Figure 3 shows the decomposition δ as a function of Φ for several values of $T/T_c = 1/2h$. In the limit $\Phi \to 0$, the growth is so slow relative to the diffusion that the system is in equilibrium. Then Eq. (12) reduces to the bulk equilibrium condition

$$h = \frac{1}{4\delta} \ln \frac{(1+\delta)}{(1-\delta)}, \tag{13}$$

with $\delta = 0$ for $h \leqslant 1/2$.

As Φ increases, as for higher growth rate or lower step density, the decomposition is increasingly suppressed by the growth kinetics, as shown in Fig. 3. For a given thermody-

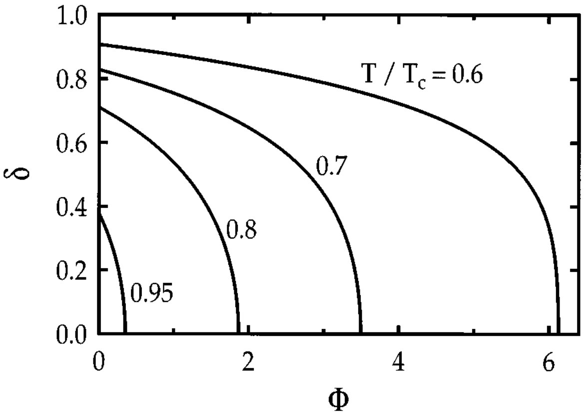

FIG. 3. Degree of decomposition δ vs dimensionless growth rate Φ, for indicated values of the dimensionless temperature $T/T_c = kT/2H$, in the large-N limit. (For $T \leqslant T_c$ there is no decomposition even in equilibrium.)

namic driving force h, there is a critical value of Φ at which $\delta \rightarrow 0$ and there is no decomposition. This value Φ_c is given by

$$\Phi_c = (4h-2)e^h. \tag{14}$$

This analysis assumed that $N \gg 1$. For finite N, interface effects further reduce the decomposition. The chemical potential at the leading step (9) becomes

$$\mu_\nu = 4Hc_{-\nu}^2 + 2Hf(1-4c_{-\nu}^2) + kT \ln c_\nu,$$

where f is the fraction of out-of-plane bonds in the bulk, and using $c_{\nu,m+1} = c_{-\nu,m}$. For the bunch, μ_ν may be approximated by the average over its steps, since short-range step interactions will shift μ_ν for individual steps without changing the average. Then Eq. (14) becomes

$$\Phi_c = [4h(1-2fN^{-1})-2]e^h. \tag{15}$$

The analysis here raises as many questions as it answers, because of the lack of a full dynamical treatment. Do the bunches move intact, or are steps exchanged between bunches, perhaps changing their composition as they cross the terraces? And what factors determine the relative spacing α of the two bunches?

Nevertheless, the present work provides some much-needed insight into how spinodal decomposition may manifest itself during step-flow growth. In particular, there is clearly a competition between thermodynamics and kinetics. Even when the alloy is thermodynamically unstable, the growth kinetics can completely suppress decomposition. When decomposition does occur, it involves step bunches of alternating composition; and the bunch size, like the degree of decomposition, is controlled by the thermodynamics-kinetics competition.

Discussions with Andrew Zangwill are gratefully acknowledged.

---

[1] J. W. Cahn, Acta. Metall. **9**, 795 (1961); Trans. Metall. Soc. AIME **242**, 166 (1967).

[2] R. Kaspi and S. A. Barnett, J. Vac. Sci. Technol. A **7**, 1366 (1989); F. Leonard, M. Laradji, and R. C. Desai, Phys. Rev. B **55**, 1887 (1997).

[3] D. E. Temkin, J. Cryst. Growth **130**, 101 (1993).

[4] I. P. Ipatova, V. G. Malyshkin, and V. A. Shchukin, J. Appl. Phys. **74**, 7198 (1993).

[5] A. Barabási, Appl. Phys. Lett. **70**, 764 (1996).

[6] S. P. Ahrenkiel *et al.*, Phys. Rev. Lett. **75**, 1586 (1995).

[7] It may seem inconsistent to sometimes treat the adatoms as in equilibrium with the step, while at other times treating them as not interacting. However, this is determined by the thermodynamics. Adatom-step equilibrium normally arises because adatoms can diffuse to a kink in a step and incorporate into the crystal there. If it is sufficiently unfavorable for A atoms to incorporate at B-rich steps (precisely the limit under discussion here), this process will not occur. The adatom remains always an adatom, and the step affects it only as a possible obstacle to diffusion. If we assume that any extra diffusion barrier at the step is negligible, then it is appropriate to treat B-rich steps as in equilibrium with B atoms but transparent to A atoms, and vice versa.

[8] I. T. Ferguson *et al.*, Appl. Phys. Lett. **59**, 3324 (1991); A. G. Norman *et al.*, Semicond. Sci. Technol. **8**, S9 (1993).

[9] J. Tersoff, Phys. Rev. Lett. **77**, 2017 (1996).

[10] J. Tersoff, Y. H. Phang, Z. Zhang, and M. G. Lagally, Phys. Rev. Lett. **75**, 2730 (1995).