Composition pinning in epitaxial alloys

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Using a microscopic cluster representation for thermodynamic properties of an alloy, we demonstrate that recent observation of homogeneous coherent epitaxial alloys $>1000^\circ$C below the bulk miscibility temperature and the “pinning” of the composition near the lattice-matched value (“lattice latching” or “pulling”) above the bulk miscibility temperature, share a common origin. We trace these effects to the lattice mismatch between alloy constituents (not to alloy mismatch with the substrate) and predict they will exist for growth methods as different as liquid-phase and molecular-beam epitaxy.

Coherent epitaxial growth of disordered alloys shows two dramatic differences relative to bulk growth under otherwise identical conditions. First, even on lattice-matched substrates, homogeneous alloys may be grown epitaxially at temperatures for which the bulk constituents are not miscible, e.g., $^1\text{Ba}_x\text{Ca}_{1-x}\text{Fe}_2$, $\text{GaAs}_{1-x}\text{Sb}_x$, and $\text{GaP}_{x}\text{Sb}_{1-x}$. Second, the measured composition $x_{ep}$ of the epitaxial (ep) alloy tends to be “pinned” at a value near $x_{LM}$, where the alloy is lattice-matched (LM) to the substrate, even though the composition $x_{bk}$ of the corresponding (unsupported) bulk (bk) alloy varies widely. This pronounced deviation from behavior expected from the bulk phase diagram ("latching" or "pulling" effect) was first observed in an elegant experiment of Stringfellow, who found that large changes in the liquid composition in liquid-phase epitaxy (LPE) growth of $\text{Ga}_x\text{In}_{1-x}\text{As}$ on a GaAs substrate produced analogously large composition variations in bulklike platelets (as expected from the bulk phase diagram), while the composition of epitaxial layers was pinned to a narrow region near $x_{LM}$. For large $|x_{ep} - x_{LM}|$ misfit dislocations—which destroy coherence between the epitaxial alloy and the substrate—nucleate and remove the effect. This effect has since been seen in LPE for a variety of systems on diverse substrates of various orientations, but generally has not been recognized in other growth methods, e.g., molecular-beam epitaxy (MBE).

Epitaxy-enhanced solubility and composition pinning (CP) have been discussed theoretically by a number of authors. Quillec, Laroine, and Joncour argued that growth of disordered alloys inside the bulk miscibility gap is possible only because of CP, since $x_{ep} \approx x_{LM}$ yields minimal strain. However, this view cannot explain solubility at compositions $x_{bk}$ well away from $x_{LM}$. It has also been suggested that CP occurs because of fluctuations (present only) near the bulk miscibility-gap temperature; pinning has been clearly seen by $200^\circ$C above, however. The most detailed and rigorous treatment of epitaxial composition pinning has been given by Larché and Cahn, who focused on solid-liquid equilibrium to explain LPE results.

We consider isovalent semiconductor alloys $A_{1-x}B_xC$ such as $\text{Ga}_{1-x}\text{In}_{x}\text{As}$. Such a disordered alloy is stable for any $x$ at temperatures above the maximum miscibility-gap temperature. A homogeneous phase ceases to be stable for temperatures below the spinodal temperature $r(x)$, whose maximum coincides with the maximum miscibility-gap temperature. We show that for growth temperatures above the maximum bulk miscibility-gap temperature and the degree of composition pinning $Q(x_{LM}, T) \equiv d_{ep}/d_{bk}$ are related by $Q = (T - \theta_b)/(T - \theta_e - \Delta T)$. Using a thermodynamic description of a very different growth method—molecular-beam epitaxy—we show that (ii) composition pinning should be observable in incorporation rates of, e.g., $A$ atoms into $A_{1-x}B_xC$ alloys.

Thermodynamic functions and phase diagrams of bulk and epitaxial $A_{1-x}B_x$ alloys have been successfully described by expanding the alloy energy as a linear combination of the energies $E_n$ of constituent clusters, e.g., the nearest-neighbor $A_{4-n}B_n$ clusters accounting for the principal interactions in the alloy. Provided the substrate is thick in comparison to the epitaxial film, the alloy is subject to the epitaxial constraint: Cell dimensions $a_1$ parallel to the interface are those of the substrate of lattice parameter $a_s$. Since coherent growth is inhibited by nucleation of misfit dislocations beyond a critical film thickness (Ref. 16) $h_c$, we assume the film thickness $h$ satisfies $h < h_c(x)$, so that surface energies are thermodynamically negligible and the strain due to the mismatch between substrate and film is accommodated elastically. Referring enthalpies to equivalent amounts of bulk constituents, we find the excess alloy enthalpies

$$\Delta H^{ep}(a_s, x, T) = \sum_{n=0}^{4} \bar{P}_n(a_s, x, T) E_{n}^{ep}(a_s, c(a_s, x, T)), \quad (1a)$$

$$\Delta H^{bk}(x, T) = \sum_{n=0}^{4} P_n(x, T) E_{n}^{bk}(a(x, T)). \quad (1b)$$

Here $\bar{P}_n$ and $P_n$ are the probabilities of cluster $n$ in the epitaxial and bulk alloy at $(x, T)$, respectively, and $a(x, T)$ and $c(a_s, x, T)$ are, respectively, the bulk-alloy equilibrium lattice parameter (found from $d\Delta H^{bk}/da = 0$, corresponding to zero applied pressure) and epitaxial-alloy tetragonal dimension perpendicular to the substrate (from $d\Delta H^{ep}/dc = 0$).

Because of the linear relationship between the alloy en-
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energy and cluster energies,\textsuperscript{12,13} it is most convenient to
draw cluster properties from periodic structures.\textsuperscript{13} Thus,
the cluster-energy functions $E_n^{sp}$ and $E_n^{bk}$ in Eq. (1) can
be calculated from first principles.\textsuperscript{12,13} For small deformations
they are accurately and conveniently described by
harmonic elasticity theory; per fcc site

$$
E_n^{sp}(a_i,c) = \Delta H_n + \frac{\alpha}{2} a_n \bar{B}_n(a_i - a_n)^2 + \frac{\beta}{3} a_n A_n c_1 - c_n(a_i)^2, \quad (2a)
$$

$$
E_n^{bk}(a) = \Delta H_n + \frac{\alpha}{2} a_n B_n (a - a_n)^2, \quad (2b)
$$

where $\Delta H_n$, $a_n$, and $B_n$ are, respectively, the formation
enthalpy, equilibrium cubic lattice parameter, and bulk modulus
of the ordered compound from which cluster $n$ is drawn.\textsuperscript{12-14} For an [001]-oriented substrate the epitaxial
elastic modulus\textsuperscript{17} is $\bar{B}_n = \frac{3}{2} B_n [1 - C_{12}^\text{eff}/C_{11}^\text{eff}]$, where $C_{12}$ and
$C_{11}$ are the cubic elastic constants, $A_n = C_{44}^\text{eff}$, and
$c_n = a_n - 2C_{12}^\text{eff}/C_{11}^\text{eff}(a_i - a_n)$ is the equilibrium tetragonal
dimension for substrate $a_i$.

The alloy excess enthalpy $\Delta H$ and entropy $\Delta S$ depend
on the $[P_s(x,T)]$; these may be found under epitaxial or
bulk conditions by minimizing $\Delta F = \Delta H - T \Delta S$ with
respect to the $[P_s]$ using the cluster-variation method
(CVM) of Kikuchi\textsuperscript{18} within the tetrahedron
approximation, consistent with our choice of nearest-neighbor fcc
site clusters. For any $[P_s]$ we find per fcc site the following
relationship between excess enthalpies of the epitaxial and bulk alloy:

$$
\Delta H^{sp}(a_i,x,T) = \Delta H^{bk}(x,T) + \frac{\beta}{3} a(x,T) \bar{B}(x,T)[a_i - a(x,T)]^2, \quad (3)
$$

where $\bar{B}(x,T)$ (which depends on substrate orientation\textsuperscript{17})
and $a(x,T)$ are ratios of sums over the $P_s$ of cluster proper-
ties. The second term in Eq. (3) has the form predicted for a
harmonic elastic continuum with equilibrium lattice parameter $a(x,T)$ and epitaxial elastic modulus $\bar{B}(x,T)$. This
important result places the common phenomenologi-
cal elastic treatment of an alloy\textsuperscript{19} on a microscopic
footing.\textsuperscript{20,21} Our approach differs from another recent
cluster-based treatment,\textsuperscript{22} which incorrectly imposes
$dE^{sp}/dc = 0$ for each cluster (rather than $d\Delta H^{sp}/dc = 0$
for the alloy), so that the last term in Eq. (2a) does not appear.
As a result, $\Delta H^{sp} \neq \Delta H^{bk}$ when $a_i = a(x,T)$.

For any phase there is a monotonic relationship between
the chemical potential $\mu = d\Delta F/dx$ and the composition $x$.
We may Taylor expand about $\mu_{LM}$ [where $a(x_{LM}) = a_f$,
and bulk and epitaxial alloys are indistinguishable accord-
ing to Eq. (3)] to find

$$
\delta x_{bk}(\mu) = x_{bk}(\mu) - x_{LM} = (\mu - \mu_{LM})/(d^2 \Delta F^{bk}/dx^2)|_{x_{LM}} + \cdots, \quad (4a)
$$

$$
\delta x_{sp}(\mu) = x_{sp}(\mu) - x_{LM} = (\mu - \mu_{LM})/(d^2 \Delta F^{sp}/dx^2)|_{x_{LM}} + \cdots, \quad (4b)
$$

where we have used the identity $dx/d\mu = (d\mu/dx)^{-1} = (d^2 \Delta F/dx^2)^{-1}$. Under identical growth conditions
(constant temperature and, for LPE growth, concentrations
of constituents in solution, and for MBE growth, constant applied
species pressures) $\mu$ is common to bulk and
epitaxial alloys growing in equilibrium. We may thus
considerably measure the degree of composition pinning
at the lattice-matched composition by the slope
$Q(x_{LM}) \equiv \delta x_{sp}/\delta x_{bk}$ of the curve $x_{sp}(\mu)$ vs $x_{bk}(\mu)$ at
$x_{LM}$, or

$$
Q = [d^2 \Delta F^{bk}(x_{LM})/dx^2]
\times [d^2 \Delta F^{sp}[x_{LM},a_i = a(x_{LM})]/dx^2]^{-1}, \quad (5)
$$

$$
= T - \tau_{bk}(x_{LM}) \quad \tau_{sp}(x_{LM}) \equiv \frac{T}{T - \tau_{sp}(x_{LM})}. \quad (6)
$$

The epitaxial spinodal temperature $\tau_{sp}$ is related to
$\tau_{bk} = (d^2 \Delta F^{bk}/dx^2)/(d^2 \Delta F^{sp}/dx^2)$ via

$$
\tau_{ep}(x_{LM}) = [\tau_{bk}(x) - \frac{\beta}{3} \bar{B}(x)a(x)(da/dx)^2/k_B]_{x_{LM}} \equiv \tau_{bk}(x_{LM}) + \Delta \tau(x_{LM}). \quad (7)
$$

To derive Eq. (6) we note that $d^2 \Delta F/dx^2 = 0$ defines
the spinodal temperature $T(\mu)$ and assumed\textsuperscript{23} $\Delta S^\text{eff}(x)
= \Delta S^\text{eff}(x_{LM})$ near $x_{LM}$; Eq. (3) was used to evaluate $\Delta \tau$.

Equations (5)–(7) make clear the intimate connection
between composition pinning and epitaxial stabilization
of alloys. Since $\Delta \tau$ is negative definite, for any finite $T$ above
the bulk miscibility-gap temperature $Q < 1$, i.e., composition pinning is a universal feature of coherent
epitaxial growth. Perfect CP ($Q = 0$) occurs at the bulk
spinodal temperature $T = \tau_{bk}(x)$, while $Q \rightarrow 1$ as $T \rightarrow \infty$.
While CP may persist below the bulk miscibility temperature,
in this case the analysis must be generalized to an
inhomogeneous ($AC$- and $BC$-rich) mixture since
$d^2 \Delta F^{bk}/dx^2 < 0$. Because $\Delta \tau \leq 0$, the miscibility
temperature for an epitaxial alloy even on a lattice-matched
substrate may be enormously lower than its bulk
counterpart. This effect explains recent epitaxial growth\textsuperscript{3} of
GaSb$_1-x$P$_x$ 1200 K below the bulk miscibility-gap temperature.
Larché and Cahn\textsuperscript{9} explained composition pinning
in LPE in precisely the same terms but failed to note
the quantitative connection with epitaxial stabilization
of alloys ($\Delta \tau < 0$). Equations (6) and (7) show that CP
and epitaxial stabilization both scale as $d\Delta F/dx^2 \propto (\Delta \tau)^2$, where $\Delta a$ is the lattice mismatch between the alloy
constituents; nearly lattice-matched systems (e.g.,
Ga$_{1-x}$Al$_x$As) will show no epitaxial effects. Both effects
are larger for elastically stiff alloys via $B$.

We emphasize that the physical origin of both composition
pinning and epitaxial stabilization is not epitaxial
strain per se (since both occur even on lattice-matched
substrates), but rather the composition dependence of
the alloy parameter $a(x,T)$ present either in phenomenologi-
cal elastic descriptions or in first-principles cluster-based
calculations. This dependence obviously may be traced to
the size mismatch $\Delta a$ between alloy constituents,
reflecting different atomic sizes or distinct bond lengths
and their imperfect accommodation in an alloy environ-
ment.

The remarks above hold for ordering $[\Delta H(x) \leq 0$, e.g.,
Cu$_{1-x}$Au$_x$] or phase-separating $[\Delta H(x) \geq 0$, e.g.,
most isovalent semiconductor] alloys; since formally the
miscibility-gap temperature is negative for ordering
alloys, we expect (and theoretical calculations\textsuperscript{23} confirm)
considerably less composition pinning for ordering alloys. Our calculations also indicate an ordering (via B) of CP with substrate orientation $Q_{(110)}$ $Q_{(1101)} < Q_{(111)}$, in agreement with the predictions of elasticity theory. \(^{17}\)

We have calculated \(^{14}\) $\{\Delta H_n, \Delta S_n\}_{\{p\}}$ for the clusters Ga$_4$As$_{12}$Sb$_{4-n}$ relevant to GaAs$_2$Sb$_{1-n}$. Using Eqs. (1) and (2) and the CVM to find $\Delta H$ and $\Delta S$, we show in Fig. 1 results for $T$ $= 1300$ K for substrates lattice matched to the alloy at $x_{b_k}$ $= 0$, $x_{b_h}$ $= 0.5$, and $x_p$ $= 1$. The epitaxy-induced increase in $dH/dx = d^2\Delta F/dx^2$ (i.e., $Q < 1$) in (a) is most pronounced at $x_{b_k}$ $= 0.5$; a given $\mu$ (fixed growth conditions) corresponds to different values of $x_{b_k}$ and $x_{b_h}$. We note in (b) strong deviations from $x_{b_k}$ $= x_{b_h}$ (i.e., $Q $= 1) even well away from $x_{b_k}$ and $50^\circ C$ above the calculated maximum bulk miscibility-gap temperature ($= 1245$ K).

Equation (3) provides the link between bulk- and epitaxial-alloy thermodynamics. While it is commonly believed that composition pinning is peculiar to LPE, we demonstrate using Eq. (3) that it should also appear in MBE growth. Growth of, e.g., In$_{1-x}$Al$_x$As, at fixed $T$ is determined by the applied partial pressures $P_{\alpha}$ for $\alpha = \text{In}$, Al, and As$_4$. A recent thermodynamic analysis of MBE growth of bulk pseudobinary semiconductor alloys\(^{24}\) permits calculation of the equilibrium partial pressures $P_{\alpha}$ of In, Al, As$_2$, and As$_4$ and the steady-state alloy composition $x$. These five quantities are determined by simultaneous solution of five equations, describing (i) incorporation of vapor phase In (Al) and As$_2$ into solid-phase InAs (AlAs) in In$_{1-x}$Al$_x$As (two equations), (ii) As$_4$$\leftrightarrow$2As$_2$ interconversion, and the facts that the incorporation rates $r_{\alpha} = P_{\alpha} - P_{\alpha}^q$ satisfy (iii) $r_{\alpha} + r_{\alpha} - r_{\alpha}$, and in the steady state (iv) $r_{\alpha}/r_{\alpha} = (1-x)/x$. The two incorporation equations are characterized by (experimental) tabulated equilibrium constants; the alloy excess Gibbs free energy $\Delta G = (N_{\text{In}} + N_{\text{Al}})(\Delta H - T\Delta S)$ (at zero pressure) enters via “activities” $a_p(x)$ $= \exp(dAG(x)/dN_p)$ where $N_p$ is the number of moles of species $\beta$ in the alloy. Since we assume the alloy entropy is unmodified by epitaxy, \(^{23}\) Eq. (3) may be used directly to apply this analysis to coherent epitaxial MBE growth.\(^{24}\)

Figure 2 shows theoretical predictions for the epitaxial Al$_x$In$_{1-x}$As system on an InP substrate ($x_{b_k}$ $= 0.48$) for

![FIG. 1. CVM predictions for Ga$_4$As$_{12}$Sb$_{1-x}$. (a) Dependence of alloy composition on chemical potential, (b) $x_{b_k}(\mu)$ vs $x_{b_h}(\mu)$, exhibiting composition pinning.](image)

![FIG. 2. Predictions of elastic thermodynamic model for MBE growth of Al$_x$In$_{1-x}$As on InP substrate. (a) In incorporation coefficient, (b) steady-state alloy composition, and (c) composition pinning for various values of vapor composition $x_{vap}$. Filled circles indicate lattice-matched composition.](image)
a temperature range common in MBE growth (over which the incorporation coefficient of Al is 1), for a variety of vapor phase compositions $x_{\text{vap}} = P_{\text{Al}}^M/(P_{\text{Ga}}^M + P_{\text{Al}}^M)$. The In incorporation coefficient $1 - P_{\text{Al}}^M/(P_{\text{Ga}}^M + P_{\text{Al}}^M)$, and alloy composition [Fig. 2(b)] show pronounced epitaxial effects (see experimentally for this system and interpreted as epitaxial elastic effects). Agreement with available experiment for this system is good, except for a systematic shift in temperature, probably due to the large ($\gtrsim 25\%$) uncertainty in the exponent of the InAs incorporation equilibrium constant. It is necessary to plot $x_{\text{vap}}$ vs $x_{\text{Ga}}$ (for the same $P_{\text{Ga}}^M$ and $T$) to reveal the presence of composition pinning [Fig. 2(c)]; the qualitative resemblance to LPE-like results [Fig. 1(b)] is evident, although the degree of CP depends on $x_{\text{vap}}$. Composition pinning in a different guise during an In pressure scan for fixed substrate temperature has been recently reported.

In summary, we have demonstrated that for epitaxial alloys a pinning of the composition near the lattice-matched value and a stabilization of the alloy to lower temperatures are both universal features of epitaxial growth. We have traced this behavior to the imperfect accommodation of different atomic sizes or bond lengths in the alloy environment and, using a simple thermodynamic description, predicted that these effects should be measurable for alloys grown by molecular-beam epitaxy.

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17. For [001], [110], and [111] orientations $\frac{\partial H}{\partial T} = B(1 - B/A) + A(110) = C_{\text{Al}} + \frac{1}{2}(C_{\text{Al}} + C_{\text{Ga}})$ and $\Delta H^{\text{th}} = B + 3C_{\text{Al}}/5$.
20. Unlike the cluster representation, a continuum theory cannot give the $\Delta H_{\text{th}}$ (hence order-disorder transitions) or $\Delta H^{\text{th}}(x, T)$, which must be found from another source, e.g., experiment or an empirical model, e.g., $\delta$ lattice parameter (DLP) model of Ref. 21. However, the continuum description should work well for temperatures well above ordering temperatures of ordered $\text{A}_{x-2}\text{B}_{x}\text{C}_{x}$ compounds.
22. A. Mbaye, F. Turco, and J. Massies, Phys. Rev. B 37, 10419 (1988). This approach should be contrasted with A. A. Mbaye, D. M. Wood, and A. Zunger, Phys. Rev. B 37, 3008 (1988), where it is demonstrated that $\delta H_{\text{th}}(x, T)$ must be found from another source, e.g., experiment or an empirical model, e.g., $\delta$ lattice parameter (DLP) model of Ref. 21. However, the continuum description should work well for temperatures well above ordering temperatures of ordered $\text{A}_{x-2}\text{B}_{x}\text{C}_{x}$ compounds.
23. D. M. Wood and A. Zunger (unpublished). We find, for example, $\delta H_{\text{th}}(x, T)$, at 1400 K, that $\delta S_{\text{th}}$ and $\delta S_{\text{th}}^{\text{th}}$ differ by less than 1% over the entire composition range.
24. H. Seki and A. Koukitu, J. Cryst. Growth 78, 342 (1986). Like these authors, we use the MBE model of Ref. 21 for $\Delta H^{\text{th}}(x, T)$, a random mixing entropy, and find $a(x)$ and $C_{\text{f}}(x)$ from $x$-weighted averages of values for $x = 0, 1$.
25. M. Allonon, J. Primot, Y. Gao, and M. Quillec, (private communication) and in 1988 Electronic Materials Conference, Boulder CO (unpublished), abstract J3, find $\ldots$ In incorporation adjustments itself to compensate a small excess or shortage in the incident In flux, in order to ensure perfect lattice matching with the substrate. . . .