PHYSICAL REVIEW B

VOLUME 38, NUMBER 17

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 °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 latticematched substrates, homogeneous alloys may be grown epitaxially at temperatures for which the bulk constituents are not miscible, e.g.,¹ Ba_xCa_{1-x}F₂, GaAs_xSb_{1-x},² and GaP_xSb_{1-x}.³ 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,⁴ who found that large changes of the liquid composition in liquid-phase epitaxy (LPE) growth of $Ga_x In_{1-x}P$ 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, 5-9 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.^{6,9-11} Quillec, Launois, and Joncour⁶ 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_{ep} well away from x_{LM} .¹⁻³ It has also been suggested⁶ that CP occurs because of fluctuations (present only) near the bulk miscibility-gap temperature; pinning has been clearly seen⁴ 200 °C above, however. The most detailed and rigorous treatment of epitaxial composition pinning has been given by Larché and Cahn,⁹ who focused on solid-liquid equilibrium to explain LPE results.

We consider isovalent semiconductor alloys $A_{1-x}B_xC$ such as $Ga_{1-x}In_xAs$. Such a disordered alloy is stable for any x at temperatures above the maximum miscibilitygap temperature. A homogeneous phase ceases to be stable for temperatures below the spinodal temperature $\tau(x)$, whose maximum coincides with the maximum miscibility-gap temperature. We show that for growth temperatures above the maximum bulk miscibility-gap temperature (i) the epitaxial suppression $\Delta \tau(x) = \tau_{ep} - \tau_{bk} < 0$ of the spinodal temperature $\tau(x)$ and the degree of composition pinning $Q(x_{LM}, T) \equiv dx_{ep}/dx_{bk}$ are related by $Q = (T - \tau_{bk})/(T - \tau_{bk} - \Delta \tau)$. 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^{12,13} and epitaxial¹⁴ $A_{1-x}B_x$ alloys have been successfully described by expanding the alloy energy as a linear combination of the energies E_n of constituent clusters¹⁵ n, e.g., the nearest-neighbor $A_{4-n}B_n$ (n=0-4)clusters accounting for the principal interactions in the allov.^{12,13} Provided the substrate is thick in comparison to the epitaxial film,⁹ the alloy is subject to the epitaxial constraint: Cell dimensions a_{\parallel} 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 (monolayer) $\ll h$ $< h_c(x)$, 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

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

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

Here \tilde{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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ergy and cluster energies, 12,13 it is most convenient to draw cluster properties from periodic structures. 15 Thus, the cluster-energy functions E_n^{ep} and E_n^{bk} in Eq. (1) can be calculated from first principles. 12,13 For small deformations they are accurately and conveniently described by harmonic elasticity theory; per fcc site

$$E_n^{\rm cp}(a_s,c) = \Delta H_n + \frac{9}{8} a_n \bar{B}_n (a_s - a_n)^2 + \frac{1}{8} a_n A_n [c - c_n(a_s)]^2, \qquad (2a)$$

$$E_n^{bk}(a) = \Delta H_n + \frac{9}{8} a_n B_n (a - a_n)^2,$$
 (2b)

where ΔH_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.¹²⁻¹⁴ For an [001]-oriented substrate the epitaxial elastic modulus¹⁷ is $\tilde{B}_n = \frac{2}{3} B_n [1 - C_{12}^{(n)}/C_{11}^{(n)}]$, where C_{12} and C_{11} are the cubic elastic constants, $A_n = C_{11}^{(n)}$, and $c_n = a_n - 2C_{12}^{(n)}/C_{11}^{(n)}(a_s - a_n)$ is the equilibrium tetragonal dimension for substrate a_s .

The alloy excess enthalpy ΔH and entropy ΔS depend on the $\{P_n(x,T)\}$; these may be found under epitaxial or bulk conditions by minimizing $\Delta F = \Delta H - T\Delta S$ with respect to the $\{P_n\}$ using the cluster-variation method (CVM) of Kikuchi¹⁸ within the tetrahedron approximation, consistent with our choice of nearest-neighbor fcc site clusters. For any $\{\tilde{P}_n\}$ we find per fcc site the following relationship between excess enthalpies of the epitaxial and bulk alloy:

$$\Delta H^{\rm ep}(a_s, x, T) = \Delta H^{\rm bk}(x, T) + \frac{9}{8} a(x, T) \tilde{B}(x, T) [a_s - a(x, T)]^2, \quad (3)$$

where $\tilde{B}(x,T)$ (which depends on substrate orientation¹⁷) and a(x,T) are ratios of sums over the \tilde{P}_n of cluster properties. 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 $\tilde{B}(x,T)$. This important result places the common phenomenological elastic treatment of an alloy¹⁹ on a microscopic footing.^{20,21} Our approach differs from another recent cluster-based treatment,²² which incorrectly imposes $dE_n^{ep}/dc=0$ for each cluster (rather than $d\Delta H^{ep}/dc=0$ for the alloy), so that the last term in Eq. (2a) does not appear. As a result, $\Delta H^{ep} \neq \Delta H^{bk}$ when $a_s = a(x,T)$.

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

$$\delta x_{bk}(\mu) \equiv x_{bk}(\mu) - x_{LM}$$

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

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

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) μ is common to bulk and epitaxial alloys growing in equilibrium. We may thus conveniently measure the degree of composition pinning at the lattice-matched composition by the slope $Q(x_{LM}) \equiv \delta x_{ep} / \delta x_{bk}$ of the curve $x_{ep}(\mu)$ vs $x_{bk}(\mu)$ at x_{LM} , or

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

$$=\frac{T-\tau_{\rm bk}(x_{\rm LM})}{T-\tau_{\rm en}(x_{\rm LM})}.$$
(6)

The epitaxial spinodal temperature τ_{ep} is related to $\tau_{bk} = (d^2 \Delta H^{bk}/dx^2)/(d^2 \Delta S^{bk}/dx^2)$ via

$$\tau_{\rm ep}(x_{\rm LM}) = [\tau_{\rm bk}(x) - \frac{9}{4} B(x)a(x)(da/dx)^2/k_B]_{x_{\rm LM}}$$
$$\equiv \tau_{\rm bk}(x_{\rm LM}) + \Delta \tau(x_{\rm LM}) . \tag{7}$$

To derive Eq. (6) we note that $d^2\Delta F/dx^2 = 0$ defines the spinodal temperature $\tau(x)$ and assumed²³ $\Delta S^{ep}(x) = \Delta S^{bk}(x)$ 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 maximum 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 $Q \to 1$ as $T \to \infty$. [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 $d^{2}\Delta F^{bk}/dx^{\frac{1}{2}} < 0.$] 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 growth³ of $GaSb_{1-x}P_x$ 1200 K below the bulk miscibility-gap temperature. Larché and Cahn⁹ 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 $(da/dx)^2 \propto (\Delta a)^2$, where Δa is the lattice mismatch between the alloy constituents: nearly lattice-matched systems (e.g., $Ga_{1-x}Al_xAs$) will show no epitaxial effects. Both effects are larger for elastically stiff alloys via \tilde{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 phenomenological elastic descriptions or in first-principles cluster-based calculations. This dependence obviously may be traced to the size mismatch Δa between alloy constituents, reflecting different atomic sizes or distinct bond lengths and their imperfect accommodation in an alloy environment.

The remarks above hold for ordering $[\Delta H(x) \le 0, \text{ e.g.}, Cu_{1-x}Au_x]$ or phase-separating $[\Delta H(x) \ge 0, \text{ e.g.}, \text{ most}$ isovalent semiconductor] alloys; since formally the miscibility-gap temperature is negative for ordering alloys, we expect (and theoretical calculations²³ confirm)

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considerably less composition pinning for ordering alloys. Our calculations²³ also indicate an ordering (via \tilde{B}) of CP with substrate orientation $Q([111]) \leq Q([110]) < Q([100])$, in agreement with the predictions of elasticity theory.¹⁷

We have calculated¹⁴ { $\Delta H_n, a_n, C_{ij}^{(n)}$ } for the clusters $Ga_4As_nSb_{4-n}$ relevant to $GaAs_xSb_{1-x}$. Using Eqs. (1) and (2) and the CVM to find ΔH and ΔS , we show in Fig. 1 results for T = 1300 K for substrates lattice matched to the alloy at x = 0, x = 0.5, and x = 1. The epitaxy-induced increase in $d\mu/dx = d^2\Delta F/dx^2$ (i.e., Q < 1) in (a) is most pronounced at $x_{LM} = 0.5$; a given μ (fixed growth conditions) corresponds to different values of x_{ep} and x_{bk} . We note in (b) strong deviations from $x_{ep} = x_{bk}$ (i.e., Q = 1) even well away from x_{LM} and 50°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., $In_{1-x}Al_xAs$, at fixed T is determined by the applied partial pressures P_a^{ap} for a = In, Al, and As₄. A recent thermodynamic analysis of MBE growth of bulk pseudobinary semiconductor alloys²⁴ permits calculation of the equilibrium partial pressures P_a^{eq} of In, Al, As₂, and As₄ and the steady-state alloy composition x. These five quantities are determined by simultaneous solution of five equations, describing (i) incorporation



FIG. 1. CVM predictions for $GaAs_xSb_{1-x}$. (a) Dependence of alloy composition on chemical potential, (b) $x_{ep}(\mu)$ vs $x_{bk}(\mu)$, exhibiting composition pinning.

of vapor phase In (Al) and As₂ into solid-phase InAs (AlAs) in $In_{1-x}Al_xAs$ (two equations), (ii) $As_4 \leftrightarrow 2As_2$ interconversion, and the facts that the incorporation rates $r_a \propto P_a^{ap} - P_a^{eq}$ satisfy (iii) $r_{In} + r_{Al} = r_{As}$ and in the steady state (iv) $r_{In}/r_{Al} = (1-x)/x$. The two incorporation equations are characterized by (experimental) tabulated²⁴ equilibrium constants; the alloy excess Gibbs free energy $\Delta G = (N_{In} + N_{Al})(\Delta H - T\Delta S)$ (at zero pressure) enters via "activities" $a_\beta(x) = \exp(d\Delta G(x)/dN_\beta)$ where N_β is the number of moles of species β 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 $(x_{LM}=0.48)$ for



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.

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a temperature range common in MBE growth (over which the incorporation coefficient of Al is 1), for a variety of vapor phase compositions $x_{vap} = P_{AI}^{ap}/(P_{In}^{ap} + P_{AI}^{ap})$. The In incorporation coefficient $[=1 - P_{In}^{eq}/P_{In}^{ap}$, Fig. 2(a)] and alloy composition [Fig. 2(b)] show pronounced epitaxial effects (seen experimentally for this system and interpreted as epitaxial elastic effects^{22,25,26}). Agreement with available experiment for this system^{22,26} is good, except for a systematic shift in temperature, probably due to the large ($\geq 25\%$) uncertainty in the exponent of the InAs incorporation equilibrium constant. It is necessary to plot x_{ep} vs x_{bk} (for the same P_a^{ap} 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_{vap} . Composition pinning in a different guise during an In pressure scan for fixed sub-

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strate temperature has been recently reported.²⁵

In summary, we have demonstrated that for epitaxial alloys a pinning of the composition near the latticematched 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 measureable for alloys grown by molecular-beam epitaxy.

We are extremely grateful to Dr. A. E. Blakeslee for instigating our interest in composition pinning and providing early references, and to Dr. Jerry Olson for useful conversations.

- ¹⁷For [001], [110], and [111] orientations $\tilde{B} = B(1 B/A)$ and $c_{eq} = a_{eq} (a_s a_{eq})$ (3B/A-1), where $A([001]) = C_{11}$, $A([110]) = C_{44} + \frac{1}{2}(C_{11} + C_{12})$ and $A([111]) = B + 4C_{44}/3$.
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