STRUCTURAL PHENOMENA IN COHERENT EPITAXIAL SOLIDS

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We discuss theoretically a number of effects characteristic of coherent epitaxial (rather then bulk) solids, namely: (i) occurrence in epitaxial form of inter-semiconductor ordered phases with no counterpart in the bulk phase diagram, (ii) reversal of the order of stability of two structural modifications of the same ordered phase, (iii) epitaxy-enhanced solid solubilities, (iv) epitaxially-induced changes of order-disorder transition temperatures, (v) composition-pinning ("lattice latching") in epitaxial alloys, and (vi) changes in nearest-neighbor bond lengths in epitaxial versus bulk semiconductor alloys. First-principles total energy and cluster-variation calculations are used to illustrate these effects for a number of systems

1. Introduction

Recent perfection of epitaxial growth has revealed a number of effects peculiar to epitaxial (as opposed to bulk) systems:

(i) Epitaxial stabilization of bulk-unstable intersemiconductor ordered compounds [1-21], see table 1. These structures are absent in the bulk phase diagram but appear epitaxially either on latticematched [1-20] or mismatched [21] substrates even when grown *continuously* (i.e., not layer-by-layer). This effect has been predicted theoretically for bulk systems by Srivastava et al. [22] and for epitaxial systems by Martins and Zunger [23]. (ii) *Epitaxial selection between two competing structures for an ordered phase*. Here, the crystal structure that grows epitaxially is not the stable bulk structure, e.g., refs. [24-37] and table 2.

Table 1

Examples of observation of epitaxial stabilization of bulk-unstable inter-semiconductor ordered compounds

| Structure | Material | Substrate | Growth method | Reference |
|---------------|----------------------|-----------|------------------|-----------------------|
| Ternary CuAuI | GaInAs ₂ | InP | MBE | Kuan et al. [1] |
| · | GaAlAs, | GaAs | MOCVD, MBE | Kuan et al. [2] |
| | Ga ₂ AsSb | InP | MOCVD | Jen et al. [3–5] |
| Chalcopyrite | Ga ₂ AsSb | InP | MOCVD | Jen et al. [3-5] |
| Ternary CuPt | AlInAs ₂ | InP | OMVPE | Normal et al. [6] |
| | Ga ₂ AsSb | GaAs | MBE | Murgatroyd et al. [7] |
| | Ga_2AsSb | InP, GaAs | MBE | Ihm et al. [8] |
| | GaInP ₂ | GaAs | MOCVD | Gomyo et al. [9-11] |
| | GaInP ₂ | GaAs | MOCVD | McKernan et al. [12] |
| | GaInP ₂ | GaAs | MOCVD | Kondow et al. [13] |
| | GaInP ₂ | GaAs | MOCVD | Ueda et al. [15] |
| | GaInP ₂ | GaAs | MOCVD | Kurtz et al. [16] |
| | GaInP ₂ | GaAs | MOCVD | Nishino et al. [17] |
| | GaInAs ₂ | InP | MOCVD | Shahid et al. [18,19] |
| Famatinite | GaInAs ₂ | InP | LPE | Nakayama et al. [20] |
| CuPt | SiGe | Si | MBE | Ourmazd et al. [21] |

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Table 2 Examples of observation of epitaxial selectivity between competing structures for ordered phases

| Film material | Substrate | Bulk structure | Observed epitaxial structure | Ref. |
|------------------|----------------|-------------------|------------------------------------|------|
| Fe | Cu(111) | bcc | fcc | [24] |
| Fe | Cu(100) | bcc | fcc | [25] |
| Fe | Cu(110) | bcc | fcc | [26] |
| Ag | InSb(110) | fcc | bcc | [27] |
| Со | Ni(001) | hcp | fcc | [28] |
| Co | Cu(001) | hcp | fcc | [29] |
| Со | GaAs(110) | hcp | bcc | [30] |
| Cu | Fe(001) | fcc | bcc | [31] |
| Ni | Fe(001) | fcc | bcc | [32] |
| MnSe | ZnSe | NaCl | Zinc-blende | [33] |
| Sn | InSb(110) | β-Sn | α-Sn | [34] |
| Sn | CdTe(001) | β-Sn | α-Sn | [35] |
| InSb | Glass | Zinc-blende | NaCl | [36] |
| Cs halides | Alkali halides | CsCl | NaCl | [37] |

(iii) Epitaxy-enhanced solid solubility of alloys. Here, the minimum bulk miscibility temperature, which is very high for components such as GaP-GaSb [38], GaAs-GaSb [39], BaF_2-CaF_2 [40], or PbS-CdS [41] is enormously suppressed epitaxially even on a lattice-matched substrate.

(iv) Epitaxially-induced changes in order-disorder transition temperatures in alloys have been predicted for ultra-thin $Cu_3Au \leftrightarrow Cu_{0.75}Au_{0.25}$ [42].

(v) Composition pinning ("lattice latching") in epitaxial systems [43-47], whereby the measured composition of the epitaxial alloy tends to be pinned at a value where the alloy is lattice matched to the substrate, even though the composition of the corresponding bulk alloy under identical growth conditions varies widely. This has been observed in numerous systems in LPE growth [43-47]. The same effect appears in another guise in MBE growth [48].

(vi) Changes in A-C and B-C bond lengths in $A_x B_{1-x}C$ epitaxial alloys (relative to bulk alloys) have been predicted theoretically [49].

In this paper, we use a simple elastic continuum model (sections 2 and 3), discussed previously by others [49-58] and present a cluster-based statistical theory (section 4) to explain these six epitaxial effects. Our approach [22,23,42,59-64] is thermodynamic in nature, in that kinetic and two-dimensional growth effects, or the role of surface imperfections or impurities are not considered. As will be seen below, a thermodynamic approach can go a long way in explaining these phenomena; to the extent that it fails in certain instances (see below), such kinetic or extrinsic effects can be judged to be potentially important.

2. Qualitative discussion of epitaxial effects: continuum elasticity

We begin our discussion of the origin of epitaxial effects by considering a continuum elasticity description of bulk and epitaxially constrained cubic crystals to illustrate the general principles involved. A microscopic statistical description and quantitative results follow in sections 4 and 5. Our qualitative description in this section illustrates the main effects by considering *cubic* systems and retaining only *harmonic* terms in the energy. Quantitative total energy calculations using selfconsistent first-principles approaches (section 4) are, however, not restricted in this manner.

Consider a cubic crystal (e.g., zinc-blende) in a free-standing bulk (bk) form. Its total energy E (per fcc site), as a function of its cubic lattice parameter a, can be expanded about the equilibrium value a_{eq} as

$$E_{\rm bk}(a) = E_{\rm eq} + \frac{9}{8}Ba_{\rm eq}[a - a_{\rm eq}]^2 + \dots, \qquad (1)$$

where E_{eq} is the equilibrium total energy and $B = (C_{11} + 2C_{12})/3$ is the cubic bulk modulus. If the same crystal is grown epitaxially on a substrate with lattice parameter a_s , under coherent growth conditions (see below), the film's lattice parameters parallel (||) to the substrate are constrained to equal a_s , while in the other direction (c), it is free to relax. The total energy for this coherent epitaxial (ep) film is then

$$E_{\rm ep}(a_{\rm s}, c) = E_{\rm eq} + \frac{9}{8}qBa_{\rm eq}[a_{\rm s} - a_{\rm eq}]^2 + \frac{1}{8}Aa_{\rm eq}[c - c_{\rm eq}(a_{\rm s})]^2 + \dots$$
(2a)

Here, the elastic reduction factor q and the coefficient A depend on the substrate orientation. For

the principal orientations, these are q = (1 - B/A), or expressed in terms of the elastic constants C_{ii}

$$q[100] = \frac{2}{3} \left(1 - \frac{C_{12}}{C_{11}} \right), \tag{3a}$$

$$q[110] = \frac{1}{3} \frac{C_{11} - C_{12} + 6C_{44}}{C_{11} + C_{12} + 2C_{44}},$$
 (3b)

$$q[111] = \frac{4C_{44}}{C_{11} + 2C_{12} + 4C_{44}},$$
 (3c)

and

$$A[100] = C_{11}, (4a)$$

$$A[110] = C_{44} + (C_{11} + C_{12})/2,$$
(4b)

$$A[111] = (C_{11} + 2C_{12} + 4C_{44})/3.$$
 (4c)

 $c_{\rm eq}(a_{\rm s})$ is the equilibrium value of the tetragonal lattice parameter for a substrate lattice constant $a_{\rm s}$. It is given by $a_{\rm eq} - [3B/A - 1] (a_{\rm s} - a_{\rm eq})$, i.e.,

$$c_{\rm eq}(a_{\rm s}, [100]) = a_{\rm eq} - 2\frac{C_{12}}{C_{11}}[a_{\rm s} - a_{\rm eq}],$$
 (5a)

$$c_{eq}(a_{s}, [110]) = a_{eq} - \frac{C_{11} + 3C_{12} - 2C_{44}}{C_{11} + C_{12} + 2C_{44}} [a_{s} - a_{eq}], \quad (5b)$$

 $c_{eq}(a_s, [111])$

$$= a_{\rm eq} - \frac{2C_{11} + 4C_{12} - 4C_{44}}{C_{11} + 2C_{12} + 4C_{44}} [a_{\rm s} - a_{\rm eq}].$$
 (5c)

If the c dimension of the film is unconstrained, it attains its equilibrium value $c = c_{eq}(a_s)$ and the last term in eq. (2) vanishes. In this case, the ratio between the epitaxial and bulk energies, both referred to E_{eq} and taken at the same lattice constant a_s is $[E_{ep}(a_s) - E_{eq}]/[E_{bk}(a_s) - E_{eq}]$, i.e., q. This elastic reduction factor is considerably smaller than unity; using tabulated elastic constants [65] we have, for example, q[100], q[110], and q[111] values of 0.21, 0.35, and 0.39 for CdTe; 0.36, 0.48, and 0.51 for GaSb; and 0.37, 0.48, and 0.51 for GaAs, respectively. Since for most cubic metals and semiconductors [65] C_{44} is larger than the isotropic value $(C_{11} - C_{12})/2$, q[111] is the largest in this sequence. For alkali halides C_{44} is softer than the isotropic value [65], hence q[100] is the largest. Since q < 1, the energy of the coherent epitaxial film $E_{ep}(a_s)$ at $a_s \neq a_{eq}$ is lower than the energy of the bulk system $E_{\rm bk}(a)$ $(= a_s)$ at the same lattice parameter. This is illustrated in fig. 1a where the dashed line (E_{en}) is below the solid line (E_{bk}) for $a_s \neq a_{eq}$.



Fig. 1. Schematic plot of the total energy of bulk and thin epitaxial films as function of bulk lattice constant and substrate lattice constant, respectively (b). Part (a) shows the tetragonal c/a ratio for the epitaxial film, whereas part (c) shows how the epitaxial energy relaxes to the equilibrium bulk value, as a function of film thickness h.

For $a_s \neq a_{eq}$, the epitaxial film is strained, i.e., $E_{ep}(a_s \neq a_{eq}) > E_{eq}$. Its energy could, hence, be lowered towards E_{eq} by the nucleation of misfit dislocations [66]. This energy lowering is described within simple continuum elasticity by Matthews [66]. It modifies eq. (2a) for finite thickness (for $c = c_{eq}$) giving

$$E_{\rm ep}(a_{\rm s}, h) = E_{\rm eq} + \frac{9}{8}qBa_{\rm eq}[a_{\rm s} - a_{\rm eq}]^2 G(h),$$
(2b)

where

$$G(h) = 1, \quad h < h_{c},$$

$$G(h) = \chi(2 - \chi), \quad h \ge h_{c},$$

$$\chi(h) = \frac{h_{c}}{h} \frac{1 + \ln(h/b)}{1 + \ln(h_{c}/b)},$$

and where b is the Burgers vector of the relevant misfit dislocation. Fig. 1b illustrates how $E_{ep}(a_s \neq a_{eq})$ approaches E_{eq} as the film thickness h increases (eq. (2b)). The film is said to be coherently strained (i.e., in registry with the substrate) for h below the critical thickness [66] for nucleation of misfit dislocations (denoted h_c in fig. 1b). In practice, activation barriers against nucleation of such dislocations permit for semiconductors coherent growth considerably beyond the thermodynamic value of h_c [67]; such films are said to be metastably strained.

To illustrate the way in which the epitaxial constraint can be used to selectively stabilize certain structures, consider the symbolic solid state reaction between solids α and β to produce $\alpha_x \beta_{1-x}$

$$x \alpha + (1 - x) \beta \rightleftharpoons \alpha_x \beta_{1 - x}.$$
 (6)

If the reaction takes place incoherently in *bulk* form, all three species α , β , and $\alpha\beta$ can attain their own equilibrium lattice constants a_{α} , a_{β} , and $a_{\alpha\beta}$, respectively. The change in zero-pressure enthalpy per fcc site in this reaction is then

$$\Delta H_{\rm bk} = E_{\rm eq}[\alpha\beta] - xE_{\rm eq}[\alpha] - (1-x)E_{\rm eq}[\beta].$$
(7)

If, however, the reaction takes place epitaxially

and all species are coherent with the substrate, the change in internal energy (from eq. (2)) is

$$\Delta E_{\rm ep}(a_{\rm s}) = \Delta H_{\rm bk} + \Delta E_{\rm ss}(a_{\rm s}), \qquad (8)$$

where the excess substrate strain (ss) energy is

$$\Delta E_{\rm ss}(a_{\rm s}) = W_{\rm ss}(\alpha_x \beta_{1-x}) - x W_{\rm ss}(\alpha) -(1-x) W_{\rm ss}(\beta), \qquad (9)$$

and the substrate strain energies of the individual components are

$$W_{\rm ss}(\alpha\beta) = K_{\alpha\beta}(a_{\rm s} - a_{\alpha\beta})^2, \qquad (10a)$$

$$W_{\rm ss}(\alpha) = K_{\alpha}(a_{\rm s} - a_{\alpha})^2, \qquad (10b)$$

$$W_{\rm ss}(\beta) = K_{\beta}(a_{\rm s} - a_{\beta})^2, \qquad (10c)$$

where $K_{\alpha} = \frac{9}{8}q_{\alpha}B_{\alpha}a_{\alpha}$.

All epitaxial stabilization effects we discuss here have their origins in the excess substrate strain energy $\Delta E_{ss}(a_s)$. Its dependence on a_s , q, and Bcan be used to manipulate the relative stabilities of bulk and epitaxial systems. A simple illustration serves to make this point. Select, for example, a substrate lattice matched to a given reaction product, i.e., $a_s = a_{\alpha\beta}$. Since $W_{ss}(\alpha\beta) = 0$ in this case, $\Delta E_{ss}(a_s) \leq 0$ and $\Delta E_{en}(a_s) \leq \Delta H_{bk}$. If entropy effects do not strongly distinguish the bulk from the epitaxial film, the changes in free energies F also obey $\Delta F_{ep}(a_s) < \Delta F_{bk}$, so that the reaction proceeds epitaxially better than in bulk. In the particular case where $\Delta H_{bk} > 0$ (a situation encountered often when α and β are isovalent semiconductors) and $-\Delta E_{ss} > \Delta H_{bk}$, one may promote a reaction epitaxially even if it does not occur in bulk form. This situation is illustrated in fig. 2a: Its left-hand side shows the excess energies of bulk and thin epitaxial films; the right-hand side shows, as a function of film thickness, the energies with dislocations included. While because of the choice $a_s = a_{\alpha\beta}$ the energy of $\alpha\beta$ is constant for all film thicknesses, the strain energy of the constituents α and β can be lowered by nucleating misfit dislocations (eq. (2b)). Below the thickness H_c (shaded area in fig. 2a), the system $\alpha_x \beta_{1-x}$ has been epitaxially stabilized, i.e. $\Delta E_{ep} <$ 0 despite $\Delta H_{\rm bk} > 0$. In this case with substrate present the system is stable (not metastable)



Fig. 2. Schematic plot of bulk and epitaxial energies when $-\Delta E_{ss} > \Delta H_{bk}$. The left part shows energies for thin $(h \ll h_c)$ films while the right-hand side shows results as a function of thickness. Part (a) is for $a_{\alpha\beta} = a_s$, while part (b) is for $a_{\alpha\beta} \neq a_s$. Note the crossing of the energies of bulk and epitaxial systems.

against disproportionation into its (coherent) constituents. Only if the thickness exceeds H_c , or when the substrate is removed does it become unstable.

It is important to emphasize the qualitative difference between the critical thickness h_c for nucleation of misfit dislocations [65] and the new critical thickness H_c for epitaxial stability we introduce here. This is best illustrated by a simple example. Consider a crystal with two possible phases α and β , so that in bulk form α has a lower enthalpy $E_{\alpha}^{bk} < E_{\beta}^{bk}$. When grown epitaxially on a substrate lattice-matched to β $(a_s = a_{\beta})$, the energy of β is not perturbed, i.e., $E_{ep}^{\beta}(a_s = a_{\beta}) \equiv E_{bk}^{\beta}(a_{\beta})$. However, the energy of α is perturbed (when $a_{\alpha} \neq a_{\beta}$). If it is perturbed to the extent that $E_{ep}^{\alpha}(a_s = a_{\beta}) > E_{ep}^{\beta}(a_s = a_{\beta})$, phase β will be stabler than α until the thickness reaches H_c , where

$$E_{\rm ep}^{\beta}(a_{\rm s}=a_{\beta})=E_{\rm bk}^{\beta}(a_{\beta})$$
$$=E_{\rm ep}^{\alpha}(a_{\rm s}=a_{\beta},\ h=H_{\rm c}).$$

From eqs. (1) and (2b)

$$\frac{9}{8} \frac{q_{\alpha} B_{\alpha} a_{\alpha} \Delta a_{\alpha\beta}^2}{\Delta E_{\alpha\beta}} = \frac{1}{G(\bar{H}_{c})} \propto H_{c}$$

where $\Delta a_{\alpha\beta} = a_{\beta} - a_{\alpha}$ and $\Delta E_{\alpha\beta} = E_{eq}^{\beta} - E_{eq}^{\alpha}$. This shows that unlike the critical thickness for misfit dislocations h_c (which *decreases* as Δa increases), H_c *increases* with Δa ! Furthermore, H_c is larger the stiffer the film material is (B_{α}) and the smaller the bulk stability difference $(\Delta E_{\alpha\beta})$ is.

It is clear from the example of fig. 2a that the origin of the epitaxial stabilization is not the substrate-induced strain in the growing $(\alpha_x \beta_{1-x})$ film [since by assumption, $W_{ss}(\alpha\beta) = 0$ at $a_s = a_{\alpha\beta}$], but in the epitaxial destabilization of the constituents [since $W_{ss}(\alpha) + W_{ss}(\beta) > 0$]. This illustrates the fact that such effects are driven by the size mismatch between the constituents α and β ("microscopic strain"), not by the strain between the film $\alpha_x \beta_{1-x}$ and the substrate ("substrate strain"). This becomes obvious when one assumes, for simplicity, Vegard's rule

$$a_{\rm eq}[\alpha_x\beta_{1-x}] = xa_{\rm eq}[\alpha] + (1-x)a_{\rm eq}[\beta], \qquad (11)$$

giving, for $a_s = a(\alpha_x \beta_{1-x})$, an excess substrate strain energy

$$\Delta E_{ss}(a_s) = -(a_{\alpha} - a_{\beta})^2 [x(x-1)^2 K_{\alpha} + x^2 (1-x) K_{\beta}],$$
(12)

so only if the *constituents* are size-mismatched $(a_{\alpha} \neq a_{\beta})$ can epitaxy alter the excess energy ΔE_{ep} relative to ΔH_{bk} .

3. Illustration of generic epitaxial stabilization effects

In this section we illustrate the basic epitaxial effects observed experimentally or calculated theo-

retically (from full self-consistent anharmonic total energy models), using the results of the previous section to aid as a *classification scheme of basic phenomena*. We will discuss systems characterized by two phases, denoted " $\alpha + \beta$ " and " $\alpha\beta$ ". These generic phases could be, for example, (i) α , β are two solids and $\alpha\beta$ is a compound (ordered or disordered) between them, or (ii) " $\alpha + \beta$ " is a solid in a given crystal structure and " $\alpha\beta$ " is the same solid in another crystal structure. Such generic systems are characterized by their bulk excess enthalpy

$$\Delta H_{\rm bk} = E_{\rm eq}(\alpha\beta) - E_{\rm eq}(\alpha+\beta), \qquad (13)$$

and by the epitaxial excess energy

$$\Delta E_{\rm ep}(a_{\rm s}) = \Delta H_{\rm bk} + \Delta E_{\rm ss}(a_{\rm s}). \tag{14}$$

The classification of different cases is related to whether $-\Delta E_{ss}$ is larger or smaller than ΔH_{bk} . A (minor) sub-classification reflects whether $\alpha\beta$ is lattice matched to the substrate or not. Figs. 2 and 3 illustrates schematically the basic energetics of these classes.

Figs. 2a and 2b describe the situation where $\Delta H_{\rm bk} > 0$, but the negative substrate strain $-\Delta E_{\rm ss}(a_{\rm s})$ overwhelms it. Here $\alpha\beta$ is higher in energy than $\alpha + \beta$ in bulk form, but the situation is reversed epitaxially, hence $\alpha\beta$ has been rendered epitaxially stable (shaded regions in fig. 2) below a critical thickness $H_{\rm c}$ (not to be confused with the critical thickness $h_{\rm c}$ for misfit dislocations shown in fig. 1). This case can occur when $\alpha\beta$ is lattice matched to the substrate (fig. 2a), or when it is not (fig. 2b).

Fig. 3 describes the situation where $\Delta H_{\rm bk} > 0$ and the negative substrate strain energy $-\Delta E_{\rm ss}(a_{\rm s})$ does not overwhelm it. In this case, the critical thickness H_c does not occur since $\Delta E_{\rm ep}$ too is positive (but is reduced relative to $\Delta H_{\rm bk}$). Again, two subcategories can be distinguished: when $a_{\alpha\beta} = a_{\rm s}$ (fig. 3a) or when $a_{\alpha\beta} \neq a_{\rm s}$ (fig. 3b).

The quantities we need to calculate are $\Delta H_{\rm bk}$ and $\Delta E_{\rm ep}(a_{\rm s})$. Two basic methodologies are possible, and we will illustrate examples of both:

(i) Use harmonic elasticity theory to evaluate q (eq. (3)), A(eq. (4)), and $c_{eq}(a_s)$ (eq. (5)) from the (experimental or calculated) elastic constants C_{ij} .



Fig. 3. Schematic plot of bulk and epitaxial energies when $-\Delta E_{ss} < \Delta H_{bk}$. The left part shows energies for thin $(h \ll h_c)$ films while the right parts shows results as a function of film thickness *h*. Part (a) is for $a_{\alpha\beta} = a_s$ and part (b) for $a_{\alpha\beta} \neq a_s$. Note the absence of crossing between the energies of bulk and epitaxial systems.

The quantities $\{E_{eq}; a_{eq}\}$, however, are unspecified parameters within continuum elasticity and have to be obtained elsewhere (see below). Furthermore, while the elastic constants C_{ii} of isolated structures α and β are often known [65], those of the combined system $\alpha\beta$ are not. In this case, one must use approximate interpolations which often neglect explicit chemical effects (e.g., charge transfer between α and β in forming $\alpha\beta$). (ii) Calculate ΔH_{bk} and ΔE_{ep} directly (i.e., without the harmonic expansion of eqs. (1)-10) by performing self-consistent electronic structure calculations for bulk (i.e., as a function of a) and epitaxially (for $a_{\parallel} = a_{s}$ while c is varied), relaxing in all cases the cell-internal structural parameters. This method guarantees that chemical and elastic effects are treated on an equal footing. Using this classification, we now illustrate the basic epitaxial effects.

3.1. Epitaxial stabilization of a bulk-unstable intersemiconductor ordered compound

This situation is described generically by fig. 2. Some notable examples for this case are:

(i) First principles total energy calculations [64] (fig. 4) show that the chalcopyrite form of Ga₂AsSb has $\Delta H_{bk} = 52 \text{ meV}/4$ atoms, but epitaxially when constrained on a substrate lattice matched to it, $\Delta E_{ss} = -80 \text{ meV}/4$ atoms, so ΔE_{ep} = -28 meV/4 atoms and this ordered phase has been stabilized. Indeed, Jen et al. [3-5] have recently observed chalcopyrite Ga₂AsSb grown by MOCVD on a lattice matched InP substrate. No ordered compounds exist in bulk form between GaAs and GaSb.

(ii) First principles total energy calculations [23] show (fig. 5) that the 50%-50% ordered compound SiGe is unstable in bulk both in the zinc-blende (ZB) structure (where $\Delta H_{bk}^{ZB} = 9$ meV/atom, not



Fig. 4. First-principles calculated [64] energies of ordered (CP, CA, CH) and disordered (D) forms of $GaAs_{0.5}Sb_{0.5}$. The left-(right-) hand sides correspond to bulk (epitaxial, on a 50%-50% substrate) systems. CP, CA, and CH denote CuPt, CuAu, and chalcopyrite phases. The energy of the disordered phase is calculated at 300 K from nine clusters, using CVM. Note the level crossing between bulk and epitaxial energies for chalcopyrite.



Fig. 5. First-principles calculated [23] total energies of SiGe in the rhombohedral (RH) structure, shown for bulk (bk) and epitaxial (ep) forms (on a Si substrate). W_{ss} is the substrate strain. Note that since $\frac{1}{2}W_{ss}$ (Ge) (thin horizontal line) is larger than ΔH_{bk} (SiGe) + W_{ss} (SiGe) (shaded curve), the epitaxial form of RH SiGe has been stabilized.

shown) or in the rhombohedral (RH) structure (where $\Delta H_{bk}^{RH} = 7$ meV/atom). However, when constrained epitaxially to a Si substrate $W_{ss}(Si) =$ 0, $W_{ss}(Ge) = 26.6$, $W_{ss}(SiGe, ZB) = 4.4$, and $W_{\rm ss}({\rm SiGe}, {\rm RH}) = 4.0$, so that $\Delta E_{\rm ss} = -8.9$ meV/atom for ZB and -9.3 meV/atom for RH. This leads to a negative formation energy ΔE_{en} [RH] = 7.0-9.3 = -2.3 meV/atom for the epitaxial rhombohedral SiGe structure, whereas in bulk form it is positive (for ZB, $\Delta E_{ep} = 9-8.9 = 0.1$ meV). This is consistent with the observation [21] of RH SiGe grown on Si (no ZB SiGe is seen) and with the absence of any ordering in such bulk samples. This situation is akin to fig. 2b where " $\alpha + \beta$ " denotes Si + Ge and " $\alpha\beta$ " denotes RH SiGe.

(iii) Other theoretical examples of $\Delta H_{bk} > 0$ and $\Delta E_{ep} < 0$ include the valence force field (VFF) results of Mbaye et al. [49] showing (fig. 6 of ref. [49]) epitaxial stabilization of GaInP₂, GaIn₃P₄, and Ga₃InP₄ in various ordered structures, most notably the chalcopyrite and famatinite forms. A similar VFF calculation [42] (see fig. 7 below) shows Ga₄AsSb₃ to be epitaxially stable ($\Delta E_{ep} < 0$) on a substrate whose lattice constant matches that of GaAs_{0.5}Sb_{0.5}, whereas in bulk form $\Delta H_{bk} > 0$. (Such VFF calculations, however, under-

estimate ΔH_{bk} , so even though ΔE_{ss} is accurate, ΔE_{ep} may be underestimated too.)

A less extreme case of epitaxial stabilization of ordered compounds is illustrated in fig. 3. Here the initial instability of the compounds in bulk form is so large ($\Delta H_{\rm bk} \gg 0$) that epitaxial stabilization does not overcome it. This, for example, is the case for $\alpha = \text{GaAs}$, $\beta = \text{GaSb}$, with $\alpha\beta$ the CuPt-like or CuAuI-like ordered Ga₂AsSb (fig. 4). Here, first principles calculations predict for the CuPt form $\Delta H_{\rm bk} = 132$ meV/4 atoms and $\Delta E_{\rm ss} = -80 \text{ meV}/4 \text{ atoms on the } 50\%-50\% \text{ sub-}$ strate, so that $\Delta E_{ep} = 52 \text{ meV}/4 \text{ atoms} > 0$. The CuAuI form of Ga₂AsSb is a borderline case, where first-principles calculations predict $\Delta H_{\rm bk} =$ 115 meV, $\Delta E_{ss} = -80$ meV, and $\Delta E_{ep} = 35$ meV > 0, whereas VFF calculations [42] give $\Delta H_{\rm bk} =$ 75.5 meV, $\Delta E_{ss} = -80.7$ meV, hence $\Delta E_{ep} = -5.2$ meV < 0. Since the CuPt form of Ga_2AsSb , AlInAs₂, GaInP₂, and GaInAs₂ are observed epitaxially [6-19], whereas our calculations (for Ga₂AsSb) show $\Delta E_{ep} > 0$, we must conclude that effects neglected here (e.g., growth kinetics, surface steps) are at play, and further stabilize the epitaxial system.



Fig. 6. First-principles calculated [68] total energies of MgS in its stable B1 (rocksalt) form and in its B3 (zinc-blende) structure. Solid curves: bulk energies; dashed curves are epitaxial. Note that at a = 5.1 Å, the B1 form is the stablest whereas at $a_s \approx 5.6$ Å, the B3 form has been stabilized.



Fig. 7. Formation energies of ordered compounds (open circles: epitaxial; solid circles: bulk) and mixing enthalpies of disordered alloys (dashed lines: epitaxial; solid lines: bulk). The dotted lines show the energies of the epitaxial constituents. (a) Ordering alloy – $Cu_{1-x}Au_x$ and (b) phase-separating alloy – $GaAs_xSb_{1-x}$. Results for ordered compounds are for T = 0, results at finite T are obtained from CVM [42].

3.2. Epitaxial selection between two competing structures for an ordered phase

Identifying in fig. 2 " $\alpha + \beta$ " and " $\alpha\beta$ " as two structural modifications of the same compound (e.g., MgS in its bulk stable rocksalt B1 and zincblende B3 structures, respectively), this figure illustrates the possibility of reversing under epitaxial conditions the order of stability found in bulk form. For example, Froyen et al. [68] (see fig. 6) find in their first-principles total energy calculation that whereas in bulk form $E_{eq}(MgS, B1) < E_{eq}(MgS, B3)$, if grown epitaxially on a substrate with $a_s^* \approx a(MgS, B3)$ (a value they find to be 9% larger than a(MgS, B1)), then $E_{ep}(MgS, B3) < E_{ep}(MgS, B1)$. Hence, on such a substrate, growth of MgS below H_c is predicted to produce its zinc-blende modification even at ambient pressures! Similar calculations [68] predict growth of the β -Sn form of CdTe or the B3 form of NaCl (rather than their stable B3 and B1 forms, respectively) on suitable substrates. Similarly, valence force field calculations by Mbaye et al. (fig. 6 in ref. [49]) show that while in bulk form the chalcopyrite-type GaInP₂ is stabler than its CuAuI structure, epitaxially (on a_s close to the GaP value) the order of stability is reversed.

Apparent stabilization of unusual and even exotic structures through epitaxy is not new. Early observations (see table 2) include the growth of B1 cesium and thallium halides on mica or various alkali halide substrates [37], and B1 InSb obtained by sputtering on glass [36]. More recently, many metals that are normally fcc (bcc) have been grown in the bcc (fcc) structure (refs. [24-32], see table 2), and α -Sn has been grown outside its stable temperature range on InSb or CdTe substrates [34,35]. Some of the early examples may not have been stabilized through lattice coherence with the substrate, however, in many recent cases (the stabilization of bcc metals and α -Sn in particular) one observes a clear correlation between the substrate lattice constant and that of the pseudomorphic epitaxial phase.

3.3. Epitaxy-enhanced solid solubility of alloys

So far, we have discussed cases where α , β and $\alpha\beta$ are ordered phases. An interesting class of epitaxial stabilization problems is encountered when α and β are compound semiconductors and $\alpha\beta$ is a disordered alloy formed between them. Here, the calculation of $E(\alpha\beta)$ is more complicated, as the system possesses a large number of configurational degrees of freedom (2^N) , if there are two atomic types and N lattice points they can occupy). The way in which mixing energies of such disordered alloys can be calculated will be discussed in section 5. Here we discuss briefly this problem from the point of view of continuum elasticity. We use the same equations (1)-(10) as before, except that a and c are composition dependent and B, A, and q are suitable statistical averages (see section 5 below). With these qualifications, one notes (see below) that the reduction

of $\Delta E_{\rm ep}$ relative to $\Delta E_{\rm bk}$ (figs. 2 and 3) implies for a disordered alloy $\alpha\beta$ a reduction in its miscibility gap temperature. This becomes evident when one realizes that the miscibility gap, associated with (x,T) values for which $d^2F/dx^2 \leq 0$, represents a competition between $-Td^2S/dx^2 > 0$ and $d^2\Delta H_{\rm bk}/dx^2 < 0$, but that $d^2\Delta E_{\rm ss}/dx^2$ adds a *positive* contribution to it (even on a lattice matched substrate), hence suppressing the temperature below which the disordered alloy decomposes. As will be discussed in section 5, this effect is also related to composition pinning ("lattice latching"). Examples for this effect include:

(i) First-principles cluster variation calculations [64] for the disordered (D) GaAs_{0.5}Sb_{0.5} alloy show (fig. 4) at 300 K $\Delta H_{bk}^{(D)} = 103 \text{ meV}/4$ atoms, but $\Delta E_{ep}^{(D)} = 23 \text{ meV}/4$ atoms (on a 50%-50% substrate). Section 5 illustrates how these changes and the corresponding changes in the *x*-dependence of ΔE_{ep} relative to ΔE_{bk} lower the maximum miscibility temperature from ~ 1240 K in bulk to ~ 300 K epitaxially.

(ii) Strong enhancement of alloy solubility was observed for [38] GaP-GaSb (which is bulk immiscible) and for [40] BaF_2-CaF_2 .

We are unaware of cases (generic of fig. 2 with $\alpha\beta$ = disordered) where epitaxy renders the disordered phase absolutely stable ($\Delta E_{ep} < 0$).

3.4. Epitaxially-induced changes in order-disorder transition temperature

Identifying in fig. 3 " $\alpha + \beta$ " to be an ordered compound (e.g., Ga₄AsSb₂) and " $\alpha\beta$ " to be a substitutionally disordered alloy of the same composition (e.g., $GaAs_{0.25}Sb_{0.75}$), one sees that since the energy difference between these phases is different epitaxially than in bulk (fig. 7), the order-disorder transition temperatures will differ too. This is because the epitaxial constraint can destabilize one phase (in the example of fig. 7b, the ordered Ga₄AsSb₃ in fig. 7b) more than the other (disordered GaAs_{0.25}Sb_{0.75} in fig. 7b), modifying the order-disorder transition temperature (see fig. 8 below). A similar situation is encountered in Cu₃Au: identifying now " $\alpha + \beta$ " as ordered Cu₃Au and $\alpha\beta$ as its disordered Cu_{0.75}Au_{0.25} alloy, calculations show [42] that in



Fig. 8. CVM calculated [42] phase diagrams of (a) bulk, and (b) epitaxial $GaAs_xSb_{1-x}$ alloys. Note the large suppression of the miscibility gap and the appearance of a stable Ga_4AsSb_3 compound in (b) relative to (a).

bulk $T_c = 689.3$ K whereas epitaxially $T_c = 666.6$ K; the epitaxial constraint lowers the energy difference between the ordered and disordered structures relative to bulk, as shown in fig. 7a.

4. A cluster description of thermodynamic quantities: bulk and epitaxial

While the continuum elasticity approach used to describe the energies of bulk and epitaxially stressed solids serves well to make many qualitative points, it lacks configurational degrees of freedom necessary to describe transitions between ordered and disordered phases, or phase separation of disordered systems. This *can* be achieved with statistical cluster models [42,59–61].

Thermodynamic functions and phase diagrams of *bulk* fcc $A_{1-x}B_x$ alloys [59–61] have been successfully described by expanding the alloy en-

ergy as a linear combination of cluster energies, e.g., the clusters $A_{4-n}B_n$ (n = 0-4) accounting for the principal interactions (up to 4-body) in the bulk alloy

$$E_{bk}(x, T) = \sum_{n=0}^{4} P_n(x, T) E_{bk}^{(n)}[a(x, T)].$$
(15a)

Here P_n is the probability of cluster *n* in the bulk alloy at (x, T) and a(x, T) is the bulk equilibrium lattice parameter, determined by the requirement $dE_{bk}(x, T)/da = 0$. To treat *epitaxial* alloys [23,49] we apply the epitaxial constraint $a_{\parallel} = a_s$, to find

$$E_{\rm ep}(a_{\rm s}, x, T) = \sum_{n=0}^{4} \tilde{P}_{n}(a_{\rm s}, x, T) E_{\rm ep}^{(n)}[a_{\rm s}, c(a_{\rm s}, x, T)],$$
(15b)

where \tilde{P}_n is evaluated for the epitaxial alloy and $c(a_s, x, T)$ is the tetragonal dimension perpendicular to the substrate, determined via the condition $dE_{ep}(a_s, x, T)/dc = 0$. We assume the epitaxial film thickness h satisfies (monolayer) $\ll h < h_c(x)$, so that surface energies are thermodynamically negligible and strain is accommodated elastically.

Because of the linear, invertible relationship between alloy and cluster energies [59–61], it is most convenient to draw cluster properties from periodic structures. Thus the cluster energy functions $E_{bk}^{(n)}$ and $E_{ep}^{(n)}$ in eqs. (15a)–(15b) could readily be calculated from first principles [59–61]. For small deformations these are accurately and conveniently described by applying harmonic elasticity theory on a cluster-by-cluster basis. Applying eqs. (1) and (2) to describe *each* cluster, we find, the excess energies per fcc site for bulk and epitaxial clusters,

$$\Delta E_{\rm bk}^{(n)}(a) = \Delta H_n + \frac{9}{8}a_n B_n [a - a_n]^2, \qquad (16a)$$

$$\Delta E_{\rm ep}^{(n)}(a_s, c) = \Delta H_n + \frac{9}{8}a_n q_n B_n (a_s - a_n)^2 + \frac{1}{8}a_n A_n [c - c_n (a_s)]^2, \qquad (16b)$$

where ΔH_n , B_n , and a_n are the formation enthalpy, bulk modulus, and equilibrium lattice parameter of the ordered compound from which cluster n is drawn and q_n , A_n , and c_n are given by eqs. (3), (4), and (5), respectively, for cluster n.

The equilibrium lattice parameter a(x,T) of a bulk disordered alloy is found from $dE_{bk}(x,T)/da = 0$ using eqs. (15a) and (16a). The A-C and B-C bond lengths in the bulk alloy could then be modelled for this a(x,T) by assuming

$$R_{AC}(x, T) = \frac{\sum_{n} W_{BC}^{(n)} P_n(x, T) R_{AC}^{(n)} [a_{eq}(x, T)]}{\sum_{n} W_{AC}^{(n)} P_n(x, T)}, \quad (17a)$$

 $R_{\rm BC}(x, T) = \frac{\sum_{n} W_{\rm AC}^{(n)} P_n(x, T) R_{\rm BC}^{(n)} [a_{\rm eq}(x, T)]}{\sum_{n} W_{\rm BC}^{(n)} P_n(x, T)}, \quad (17b)$

where $R_{AC}^{(n)}[a]$ and $R_{BC}^{(n)}[a]$ are the equilibrium A-C and B-C bond lengths of the ordered structure *n* (which depend on the different cell-internal structural degrees of freedom in each structure) held at a = a(x, T), and $W_{ij}^{(n)}$ are the number of *ij* bonds in structure *n*.

For an epitaxial alloy at fixed a_s , the equilibrium lattice parameter $c(a_s, x)$ is found from $dE_{ep}(a_s, x, T)/dc = 0$ using eqs. (15b) and (16b). This gives for a (001) substrate

$$c(a_{s}, x, T) = \frac{\sum_{n} \tilde{P}_{n}(x, T) C_{11}^{(n)} a_{n} c_{n}(a_{s})}{\sum_{n} \tilde{P}_{n}(x, T) C_{11}^{(n)} a_{n}}, \quad (18)$$

where $c_n(a_s)$ is given by eq. (5) applied to cluster *n*. Eq. (18) shows that $c(a_s, x_n, T) \neq c_n(a_s)$. To find the A-C and B-C bond lengths under *epitaxial* conditions, we use eq. (17) but calculate the cluster bond lengths $R_{AC}^{(n)}$ and $R_{BC}^{(n)}$ as the equilibrium values for the ordered compound $A_n B_{4-n} C$ held at the lattice constants a_s (parallel to the substrate) and $c(a_s, x, T)$ (perpendicular to the substrate).

Given $\{\Delta H_n, a_n, C_{11}^{(n)}, C_{12}^{(n)}, C_{44}^{(n)}\}\$ for ordered compounds $A_{4-n}B_n$ (n=0-4), the cluster probabilities $P_n(x, T)$ and entropy S may be simulta-

neously determined under bulk or epitaxial conditions by minimizing the alloy free energy F = E-TS with respect to the $\{P_n\}$ using the cluster variation method (CVM) of Kikuchi [69] within the tetrahedron approximation (i.e., including effective nearest-neighbor interactions through 4body terms). Once can hence evaluate F for each possible state of order (taken as: ordered A₃B and AB₃ in the L1₂ structure [22-23], ordered AB in the L1₀ structure, or the disordered fcc alloy) and using parallel tangent constructions calculate the complete (x, T) phase diagram.

Eqs. (15) and (16) provide a complete, consistent microscopic description of bulk and epitaxial phase diagrams. For an epitaxial alloy, referring alloy energies to equivalent amounts of bulk equilibrium constituents, i.e., $\Delta H(x) = E(x, T) - (1 - x)E(0) - xE(1)$, substituting eq. (16b) into eq. (15b) and using eqs. (15a) and (16a), we find per fcc site

$$\Delta H_{\rm ep}(a_{\rm s}, x, T)$$

$$= \Delta H_{\rm bk}(x, T) + \frac{9}{8}a(x, T) \tilde{B}(x, T)$$

$$\times [a_{\rm s} - a(x, T)]^2, \qquad (19)$$

where $\tilde{B}(x, T)$ (which depends on substrate orientation) and a(x, T) are ratios of sums over the \tilde{P}_n of cluster elastic properties. Eq. (19) is what one would predict for an alloy described as a harmonic elastic continuum (section 2) with an equilibrium lattice parameter a(x, T) and an epitaxial elastic modulus $\tilde{B}(x, T) = q^{B}$; if $a_s = a(x, T)$, eq. (15b) reverts to eq. (15a). At T = 0 for ordered compound m, $P_n = \delta_{n,m}$ and eqs. (15a) and (15b) revert to eqs. (16a) and (16b), respectively, except that the last terms in eq. (16b) - due to alloy-induced cluster distortions - vanish for ordered compounds. Disordered alloys (for which these are important since $P_n \neq \delta_{n,m}$ will thus usually have higher strain energies than ordered compounds of the same composition (see fig. 7).

The essential physics of epitaxy of disordered alloys may be understood by contrasting actual calculated mixing enthalpies ΔH for bulk and epitaxial conditions. Fig. 7 shows $\Delta H^{\rm D}(x)$ for the disordered (D) alloy and $\Delta H^{\rm O}$ for ordered (O) compounds for a typical "ordering" alloy,

 $Cu_{1-x}Au_x$ (fig. 7a, with $\Delta H^D \leq 0$, $d^2\Delta H^D/dx^2$ > 0, and $\Delta H^{\circ} < 0$), and for GaAs_xSb_{1-x}, a typical "phase separating" alloy (fig. 7b, with $\Delta H^{\rm D} \ge$ 0, $d^2 \Delta H^D / dx^2 < 0$, and $\Delta H^O > 0$), under bulk conditions and epitaxially for a substrate latticematched to the x = 0.5 ordered compound. We note that (i) while at the lattice-matched composition the bulk (solid lines) and epitaxial (dashed lines) ΔH coincide since epitaxy poses no constraint (eq. (19)), (ii) away from x = 0.5 the constraint $a_{\parallel} = a_s$ raises the energy of epitaxial ordered compounds (open circles) and the disordered epitaxial alloy by different amounts; thus order-disorder transition temperatures change under epitaxial conditions; (iii) while ordered Ga_4AsSb_3 and Ga_2AsSb are unstable in bulk $(\Delta H^{O} > 0, \text{ solid circles})$, epitaxially they are lower in energy than equal amounts of the epitaxial constituents (dotted lines in fig. 7) and have hence been epitaxially stabilized with respect to decomposition into strained constituents; (iv) epitaxy alters the *curvature* of $\Delta H^{\rm D}$ with respect to composition (affecting alloy stability, discussed below). We next examine the consequences for phase diagrams.

In fig. 8, we show the calculated phase diagram for $GaAs_xSb_{1-x}$, a typical "phase separating" system, with cluster parameters extracted from theoretical calculations [42] on ordered compounds in the zinc-blende GaSb and GaAs, "luzonite" Ga₄AsSb₃ and Ga₄As₃Sb, and "CuAu-I-like" Ga2AsSb structures. Here, the formation enthalpies ΔH_n are taken from valence force field calculations. The principal feature of the bulk phase diagram (fig. 8a) is a miscibility gap separating the disordered phase above $T_{MG} =$ 1245 K (experimental extrapolated value: ~ 1100 K) from a GaSb- and GaAs-rich two-phase mixture below. Note the presence (indicated by dashed spinodals $d^2F/dx^2 = 0$ defining the limits of stability) of ordered compounds $Ga_4As_mSb_{4-m}$ metastable with respect to decomposition into the bulk constituents, but stable (because of lower strain energy) with respect to disordering (fig. 7b). In fig. 8b we show the *epitaxial* phase diagram for $a_s = a(x = 0.5)$. We note dramatic changes in the epitaxial case:

(i) The disordered alloy is now present down to

292 K. Indeed, bulk insoluble alloys have recently been grown epitaxially over a large composition range, e.g., $GaAs_xSb_{1-x}$ [39] and GaP_xSb_{1-x} (grown [38] ~ 1200 K below the bulk miscibility gap).

(ii) A metastable ordered Ga₄AsSb₃ compound deep within the bulk miscibility gap is now *stable* below 252 K with respect to the epitaxial disordered alloy. The situation here is analogous to what has been depicted in fig. 2a. If, instead of using ΔH_n values from VFF (yielding fig. 8) we use *larger* values (as obtained by first principles LAPW calculations), the stable ordered phases become metastable, analogous to fig. 3a. In contrast to the three-dimensional [001] ordering considered here, growth kinetics and the existence of [111] surface steps may control the (~ 500 K higher) ordering temperatures in [111]-type ordered samples on (001) substrates [10].

5. Composition pinning ("lattice latching") in epitaxial alloys

It has been observed [43-47] that the measured composition x_{ep} of the epitaxial 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 $x_{\rm pk}$ of the corresponding (unsupported) bulk 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 [43], 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 bulk-like 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 [44-47], but has not generally been recognized in other growth methods, i.e.g, molecular beam epitaxy (MBE).

Epitaxy-enhanced solubility and composition pinning have been discussed theoretically by a number of authors [45,46,54,70,71]. 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 [42] about μ_{LM} (where $a(x_{1M}) = a_s$ and bulk and epitaxial alloys are indistinguishable according to eq. (19)), to find

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

= $(\mu - \mu_{LM}) / \{ d^2 \Delta F^{bk} / dx^2 \} |_{x_{LM}} + ...,$
(20a)

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

= $(\mu - \mu_{LM}) / \{ d^2 \Delta F^{ep} / dx^2 \} |_{x_{LM}} + ...,$
(20b)

where we have used the identity $dx/d\mu = (d\mu/d\mu)$ $(dx)^{-1} = (d^2 \Delta F / dx^2)^{-1}$. Under identical growth conditions (constant temperature and, for LPE growth: concentrations of constituents in solution; for MBE growth: constant applied species pressures) μ is common to bulk and epitaxial allows 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 $x_{ep}(\mu)$ versus $x_{bk}(\mu)$ at $x_{\rm LM}$, or

$$Q = \frac{d^2 \Delta F^{bk}(x_{LM})/dx^2}{d^2 \Delta F^{ep}[x_{LM}a_s = a(x_{LM})]/dx^2}.$$
 (21)

Using eq. (19) we find

$$Q = \frac{T - \tau_{\rm bk}(x_{\rm LM})}{T - \tau_{\rm ep}(x_{\rm LM})}.$$
(22)

The epitaxial spinodal temperature τ_{ep} is related to

$$\tau_{\rm bk} = \frac{\mathrm{d}^2 \Delta H^{\rm bk} / \mathrm{d} x^2}{\mathrm{d}^2 \Delta S^{\rm bk} / \mathrm{d} x^2}$$

١

via

$$\tau_{ep}(x_{LM}) = \left\{ \tau_{bk}(x) - \frac{9}{4}\tilde{B}(x) a(x) \left(\frac{da}{dx} \right)^2 / k_B \right\}_{x_{LM}} \equiv \tau_{bk}(x_{LM}) + \Delta \tau(x_{LM}).$$
(23)

To derive eq. (23) we note that $d^2\Delta F/dx^2 = 0$ defines the spinodal temperature $\tau(x)$ and assume $\Delta S^{ep}(x) = \Delta S^{bk}(x)$ near $x_{1,M}$; eq. (19) was used to evaluate $\Delta \tau$.

Eqs. (21)-(23) make clear the intimate connection between composition pinning (Q < 1) and epitaxial stabilization of disordered alloys ($\Delta \tau <$ 0). 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 composition pinning (Q = 0) occurs at the bulk spinodal temperature $T = \tau_{bk}(x)$, while $Q \to 1$ as $T \rightarrow \infty$. (while composition pinning may persist below the bulk miscibility temperature, in this case the analysis must be generalized to an inhomogeneous (AC- and BC-rich) mixture since $d^2 \Delta F^{bk}/dx^2 < 0.$) Larché and Cahn [54] explained composition pinning in LPE in precisely the same terms, but failed to note the quantitative connection with epitaxial stabilization of alloys $(\Delta \tau < 0)$. Eqs. (21)–(23) show that composition pinning 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, x)T), present either in phenomenological elastical descriptions or in first principles cluster-based calculations. This dependence obviously may be traced to the size mismatch Δa between allow constituents, reflecting different atomic sizes or distinct bond lengths and their imperfect accomodation in an alloy environment.

Using the same VFF $\{\Delta H_n, a_n, C_{ij}^{(n)}\}$ values for the clusters $Ga_4As_nSb_{4-n}$ used in figs. 7 and 8 and the CVM to find ΔH and ΔS , we show in fig. 9 results for substrates lattice-matched to the alloy at x = 0, $x \simeq 0.5$, and x = 1. The epitaxy-induced increase in $d\mu/dx = d^2\Delta F/dx^2$ (i.e., Q < 1) in fig. 9a is most pronounced at $x_{LM} = 0.5$; a given μ (fixed growth conditions) corresponds to different



Fig. 9. CVM predictions for T = 1300 K for $GaAs_xSb_{1-x}$: (a) dependence of alloy composition on chemical potential; (b) $x_{cp}(\mu)$ versus $x_{bk}(\mu)$, exhibiting composition pinning.

values of x_{ep} and x_{bk} . We note in fig. 9b strong deviations from $x_{ep} = x_{bk}$ (i.e., q = 1) even well away from x_{LM} and 150 °C above the calculated maximum bulk miscibility gap temperature (\approx 1245 K).

Eq. (19) provides the link between bulk and epitaxial alloy thermodynamics. While it is commonly believed that composition pinning is peculiar to LPE, we demonstrate [42] using eq. (19) that it should also appear in MBE growth. Growth of, e.g., $\ln_{1-x}Al_xAs$, at fixed T is determined by the applied partial pressures P_{α}^{ap} for $\alpha = \ln$, Al, and As₄. A recent thermodynamic analysis of MBE growth of bulk pseudobinary semiconductor alloys [72] permits calculation of the equilibrium partial pressures P_{α}^{eq} of In, Al, As₂, and As₄ and the steady-state alloy composition x. These 5 quantities are determined by simultaneous solution of 5 equations, describing (i) incorporation 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 $r_{\alpha} \propto P_{\alpha}^{ap} - P_{\alpha}^{eq}$ satisfy (iii) $r_{1n} + r = r_{As}$ and in the steady state (iv) $r_{1n}/r_{Al} = (1-x)/x$. The two incorporation equations are characterized by (experimental) tabulated [72] equilibrium constants; the alloy excess Gibbs free energy $\Delta G = (N_{1n} + N_{Al}) (\Delta H - T\Delta S)$ (at zero pressure) enters via "activities" $a_{\beta}(x) =$



Fig. 10. 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} . Heavy dots indicate lattice-matched composition.

 $\exp(d(\Delta G(x)/k_B T)/dN_\beta)$ where N_β is the number of moles of species β in the alloy. Since we assume the alloy entropy is unmodified by epitaxy, eq. (19) may be used directly to apply this analysis to coherent epitaxial MBE growth [42].

Fig. 10 shows theoretical predictions for the epitaxial $Al_x In_{1-x} As$ system on an InP substrate $(x_{\rm LM} = 0.48)$ for a temperature range common in MBE growth (over which the incorporation coefficient of Al is 1), for a variety of vapor-phase compositions $x_{\text{vap}} = P_{\text{AI}}^{\text{ap}} / (P_{\text{In}}^{\text{ap}} + P_{\text{AI}}^{\text{ap}})$. The In incorporation coefficient (= $1 - P_{ln}^{eq}/P_{ln}^{ap}$, fig. 10a) and alloy composition (fig. 10b) show pronounced epitaxial effects (seen experimentally for this system and interpreted as epitaxial elastic effects [48,73,74]). Agreement with available experiment for this system [73,74] 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} versus x_{bk} (for the same P_{α}^{ap} and T) to reveal the presence of composition pinning (fig. 10c); the qualitative resemblance to LPE results (fig. 9b) is evident, although the degree of composition pinning depends on x_{van} . Composition pinning in a different guise during an In pressure scan for fixed substrate temperature has been recently reported [48].

6. Epitaxial alloy bond lengths

Mikkelson and Boyce [75] have shown that in an $A_x B_{1-x}C$ bulk alloy, the A-C and B-C bond lengths do not follow Vegard's rule but remain instead close to the values R_{AC}^0 and R_{BC}^0 of the pure, end-point AC and BC compounds, respectively. Martins and Zunger [76] have calculated R_{AC} and R_{BC} for 64 different bulk alloys, using the valence force field method. They noted that for high-temperature grown alloys, the dependence of R_{AC} and R_{BC} on the composition x (eq. (17)) is nearly linear, hence it suffices to calculate R_{AC} for a BC compound with an impurity A and R_{BC} for an AC compound with an impurity B; the alloy results for $R_{AC}(x)$ are then given by a linear interpolation between $R_{AC}[BC:A]$ and R_{AC}^0 , with



Fig. 11. VFF calculations [49] for the Ga-P and In-P bond lengths for the epitaxial alloy $Ga_x In_{1-x}P$ (continuous lines) on three substrates. Symbols give bond lengths for *ordered* $Ga_n In_{4-n}P_4$ compounds grown epitaxially on GaP (squares), on $Ga_{0.5}In_{0.5}P$ (stars) and on InP (solids circles). The dashed horizontal lines give the bond lengths of pure GaP and InP.

a similar expression for $R_{BC}(x)$. Direct calculations of $R_{AC}(x)$ and $R_{BC}(x)$ for the full composition range (using eq. (17)), performed either with the valence force field method [49] or from firstprinciples [22] confirmed this result. Using for $P_n(x, T)$ the random probability or the more accurate CVM probabilities produced but small differences for temperatures near bulk growth values. This approach has been repeated since then by Sasaki and co-workers for a series of bulk alloys [77].

Here we report an extension of our earlier calculations [49,76] for *epitaxial* alloys, using eqs. (17)–(18) and the text surrounding them. The results for $Ga_x In_{1-x}P$, obtained by VFF and assuming random probabilities are shown in fig. 11. This figure shows the Ga–P and In–P bond lengths for the disordered epitaxial alloy (solid lines) and the ordered compounds $Ga_n In_{4-n}P$ (symbols), comparing these to the ideal bond lengths d_{Ga-P}^0 and d_{In-P}^0 in the zinc-blende compounds.

As in the bulk case, the epitaxial disordered alloy shows a bimodal bond length distribution. Ga-P and In-P bond lengths for bulk ordered compounds are monotonic across the sequence n = 0-4; under epitaxial conditions (at fixed a_s , [1] but at $c_{eq}^{(n)}(a_s)$); they are also monotonic across this series (squares in fig. 11 for fixed substrate), except for R(Ga-P) for $a_s = a_{GaP}$ and for R(In-P) [1] for $a_s = a_{InP}$. This is yet another manifestation of the extreme selectivity between ordered structures associated with epitaxial growth and a reflection of the differing numbers of structural parameters with the target (2.0.1) structure (for fixed a

available to each (2,0,1) structure (for fixed a_s , one for the binaries, three for famatinite, two for chalcopyrite). These fluctuations are not apparent in the bond lengths for the alloy. The ideal bond Ga-P and In-P bond lengths are shown as horizontal dashed lines. It is apparent, as in the bulk case, that Ga-P and In-P bond lengths in the disordered alloy lie farther from the ideal values than the corresponding bond lengths in epitaxial ordered Ga_nIn_{4-n}P₄ compounds, except for Ga-P bond lengths for $a_s = a_{GaP}$ and for In-P bond lengths for $as = a_{InP}$.

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