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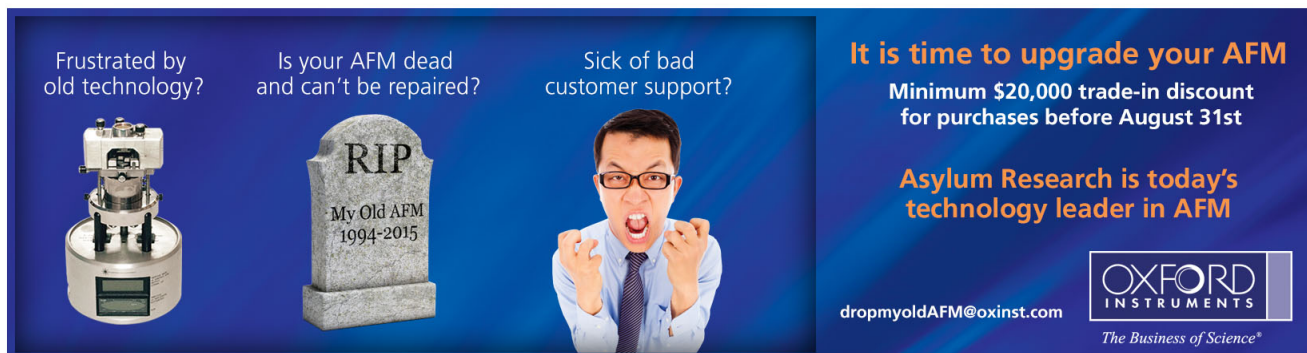
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Structural stability and selectivity of thin epitaxial semiconductors

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It is shown how the availability of structural degrees of freedom in various ternary $A_n B_{4-n} C_4$ adamantine semiconductors can lead to their energetic stabilization when grown epitaxially, and how the substrate strain can preferentially stabilize one structure over another even when the two are equally stable (or unstable) in bulk form.

Recent advances in *epitaxial* growth methods point to the possibility of formation of structural forms of semiconductors that do not appear in the equilibrium *bulk* phase diagrams of the same compounds. Such are, for example, rhombohedral¹ SiGe, Famatinite forms² of InGa_3As_4 and In_3GaAs_4 , chalcopyrite-like³ and CuAu-I-like³ (tetragonal) forms of Ga_2AsSb , CuAu-I-like⁴ GaAlAs_2 , and *cubic* phases of⁵ CdS and⁶ SiC (observed at temperatures where the bulk phase diagrams show only hexagonal phases). It has similarly been noted⁷ that epitaxial lattice matching to a substrate can significantly perturb the solid composition from that mandated by the bulk equilibrium phase diagram, lower the miscibility temperature,⁸ and even permit epitaxial growth of an alloy inside the bulk miscibility gap region (e.g.,⁹ $\text{GaAs}_{1-x}\text{Sb}_x$). In this letter we illustrate the general physical principles of epitaxial stability of adamantine semiconductor crystals using a simple valence force field method¹⁰ and the ternary $\text{Ga}_n\text{In}_{4-n}\text{P}_4$ system as a prototypical example.

The systems we will consider consist of two isovalent binary zinc blende semiconductors *AC* and *BC* (specifically, GaP and InP), and the stoichiometric ternary ordered compounds $A_n B_{4-n} C_4$ with face-centered-cubic sublattices which form by combining n units of *AC* with $4-n$ units of *BC*. There are eight such Landau-Lifshitz^{11,12} systems we wish to consider: for $n=0$ and 4, the binary endpoint compounds *AC* and *BC* (insert to Fig. 1); for $n=2$, the 50%-50% compound ABC_2 with either a CuAu-I-like structure⁴ [insert to Fig. 2(a)] or the chalcopyrite (CP) structure³ [insert to Fig. 2(b)], whereas for $n=1$ and 3 we have the 25%-75% and 75%-25% compounds AB_3C_4 and A_3BC_4 , respectively, each appearing either in the Luzonite (L) form [insert to Fig. 2(c)], or in the Famatinite² (F) form [insert to Fig. 2(d)]. A *disordered* $A_x B_{1-x} C$ alloy corresponds to a statistical mixture of all local atomic environments exhibited by these $\{A_n B_{4-n} C_4\}$ structures¹³; an *ordered* alloy^{2-4,13} corresponds to the preferential growth of one component. While binary phases have but a single structural degree of freedom in the zinc blende form (the cubic lattice parameter a), the ternary phases have, in addition to two *external* degrees of freedom (the lattice parameters a and c , where the tetragonal ratio is denoted here as $\eta = c/a$), *internal* degrees of freedom which control the position of the common atom *C* with respect to the fcc sites occupied by *A* and *B*.^{13,14} For example, in the CuAu-I structure^{12,13} the two nearest neighbor bond lengths can be expressed as $R_{AC} = [\eta u^2$

$+ 1/8]^{1/2} a$, $R_{BC} = [\eta(u - 1/2)^2 + 1/8]^{1/2} a$, where u is the cell-internal (*C*-atom) displacement parameter.^{12,13} The Luzonite structure has only two degrees of freedom (a and u), whereas the Famatinite structure has four: (a, η, v, w). When $\eta = \eta_0 = 1$ and $u = w = 1/4$ we have the "unrelaxed" structure with equal bond lengths $R_{AC} = R_{BC} = \sqrt{3} a/4$, generally different from the ideal bond lengths $R_{AC}^0 = \sqrt{3} a_{AC}/4$ and $R_{BC}^0 = \sqrt{3} a_{BC}/4$ in the strain-free zinc blende binary systems *AC* and *BC*.¹⁴ The significance of these structural degrees of freedom for relative phase stability stems from the fact that in these general adamantine *ternary* compounds $A_n B_{4-n} C_4$ it is structurally impossible for all bond angles to attain their ideal tetrahedral value (109.5°) with all bond lengths at their ideal values.¹⁵ These systems must lower the microscopic strain energy resulting from this failure to accommodate ideal bond configurations by adjusting the *internal* degrees of freedom, hence their crucial role in structural stability.

The enthalpy of formation^{7,8,13} (taken in this paper per eight atom cell) of *bulk* $A_n B_{4-n} C_4$ compounds in structure type λ is given by

$$\Delta H^{(\lambda, n)} = \{E^{(\lambda)} [A_n B_{4-n} C_4] - nE [AC] - (4-n)E [BC]\}. \quad (1)$$

When grown *epitaxially* in a dislocation-free coherent fash-

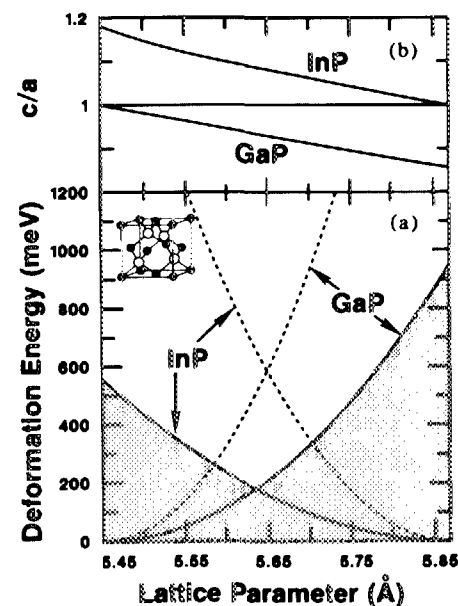


FIG. 1. (a) Deformation energy (per eight atoms) of GaP and InP and (b) the variation of the tetragonal ratio η with lattice parameter.

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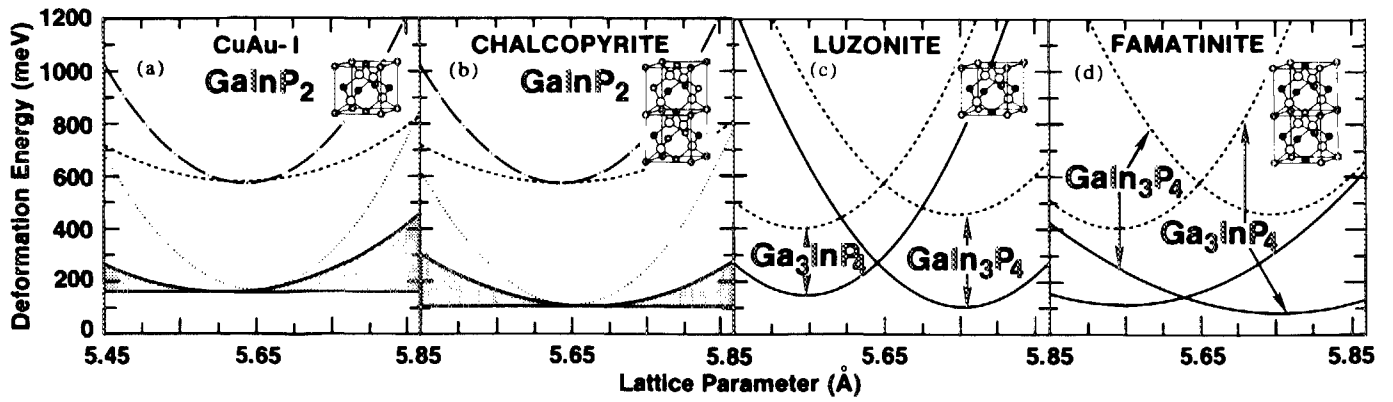


FIG. 2. Deformation energies (per eight atoms) of ternary $Ga_n In_{4-n} P_4$ structures. For (a) and (b) (dash-dot-dash line) u and η unrelaxed; (dashed line) η relaxed; (dotted line) u relaxed; (solid line) full (η and u) relaxation. For (c) and (d) (dashed line) unrelaxed; (solid line) full relaxation.

ion (i.e., the interface is registered) on a substrate s with lattice parameter a_s perpendicular to the growth direction, the effective enthalpy of formation is¹⁵

$$\begin{aligned} \delta H^{(\lambda,n)}(a_s) &= \{E^{(\lambda)}[A_n B_{4-n} C_4, a_{\parallel} = a_s] \\ &\quad - nE[AC, a_{\parallel} = a_s] - (4-n)E[BC, a_{\parallel} = a_s]\}. \end{aligned} \quad (2)$$

Parallel (\parallel) to the substrate, the lattice parameters of the ternary compound and those of AC and BC are constrained to equal a_s (assuming here a thick substrate and that the epilayer is thinner than the critical thickness for nucleating misfit dislocations¹⁶), and all other structural degrees of freedom are free to adjust to minimize the system's energy (in particular, phases AC and BC may tetragonally distort). This constraint costs substrate strain energy, defined as

$$\begin{aligned} W_{ss}^{(\lambda)}(a_s) &\equiv E^{(\lambda)}[A_n B_{4-n} C_4, a_{\parallel} = a_s] \\ &\quad - E^{(\lambda)}[A_n B_{4-n} C_4] \end{aligned} \quad (3)$$

(where all structural degrees of freedom not enumerated explicitly are taken to be their equilibrium values for the relevant a_{\parallel}). We see that the relative stability of epitaxial and bulk forms is given by the *excess* substrate strain energy $\Delta E_{ss}^{(\lambda,n)}(a_s) \equiv \delta H^{(\lambda,n)}(a_s) - \Delta H^{(\lambda,n)}$, which is simply the difference in $W_{ss}^{(\lambda)}(a_s)$ for the ternary and binary systems taken at the same a_s .

To illustrate the mechanisms of epitaxial *stability* and *selectivity*, we will use Keating's¹⁰ valence force field (VFF) approximation for the energies E appearing in Eqs. (1)–(3). In this model, the deformation energy due to both bond stretching and bond bending is expressed in terms of the elastic constants of AC and BC , taken from experiment.¹⁰ This VFF is fitted to the phonon spectra^{10(a)} and correctly predicts impurity bond lengths^{10(b)} and enthalpies of mixing.^{10(b)} Fitting the numerically optimized deformation energies to the analytic anharmonic form $E_0^{(\lambda,n)} + b_2 \delta^2 + b_3 \delta^3$ [where $\delta = (a - a_{eq}^{(n)})/a_{eq}^{(n)}$], we extract equilibrium properties summarized in Table I.

Considering first the pure binary compounds AC and BC in bulk form, Fig. 1 shows that when constrained epitaxially to $a_{\parallel} = a_s$, the lattice parameter c in the perpendicular

direction changes [i.e., $\eta_{eq} \neq 1$ in Fig. 1(b)] from its bulk value, thereby changing the unrelaxed energy (dashed curves) to the relaxed energy (solid curves). Such tetragonal deformation has been observed experimentally, e.g., in¹⁷ $In_x Ga_{1-x} As/InP$. Note that since the epitaxial $E(\delta)$ curves differ from the bulk curve, we would predict a different stability ordering for various phases (wurtzite, zinc blende, rock salt), a tendency noted experimentally.^{5,6}

Turning to the *ternary* compounds, Fig. 2 shows unrelaxed (broken lines) and relaxed (solid lines) deformation energies. We note the following: (i) Calculated equilibrium lattice parameters $a_{eq}^{(n)}$ (Table I) are very close to their concentration weighted average $(n/4)a_{AC} + [(4-n)/4]a_{BC}$ (Vegard's rule). (ii) The lowering of deformation energy upon relaxation measures the flexibility of each structure in approaching ideal bond lengths and angles. Hence, the Luzonite structure, with its only parameter u , exhibits the smallest relaxation energy, whereas the chalcopyrite structure [which, by altering u can adjust the bonds in the xy direction] has the largest (Table I). (iii) The important result of Fig. 2 is that *relaxed* energy curves $E^{(\lambda,n)}(a_s)$ for systems with several degrees of freedom (all but the Luzonite structure) are considerably flatter than the *unrelaxed* curves (compare B and B^* in Table I). This has two important implications: *first*, since disordered alloys correspond to a statistical mixture of all $\{A_n B_{4-n} C_4\}$ structures,¹³ and

TABLE I. Properties of unrelaxed and relaxed adamantine $Ga_n In_{4-n} P_4$ compounds. Energies are given per eight atom cells.

System	Unrelaxed			Relaxed		
	a_{min} (Å)	ΔE_{min} (meV)	B (GPa)	$a_{eq}^{(n)}$ (Å)	ΔH (meV)	B^* (GPa)
GaP	5.45	0.0	93	5.45	0.0	33
$Ga_3 InP_4$ (L)	5.54	404.3	89	5.55	149.3	89
$Ga_3 InP_4$ (F)	5.54	404.3	89	5.55	112.7	30
$GaInP_2$ (CuAu)	5.64	572.4	85	5.61	162.0	27
$GaInP_2$ (CP)	5.64	572.4	85	5.67	105.6	27
$GaIn_3 P_4$ (L)	5.75	457.7	81	5.76	105.7	81
$GaIn_3 P_4$ (F)	5.75	457.7	81	5.76	80.7	24
InP	5.87	0.0	77	5.87	0.0	21

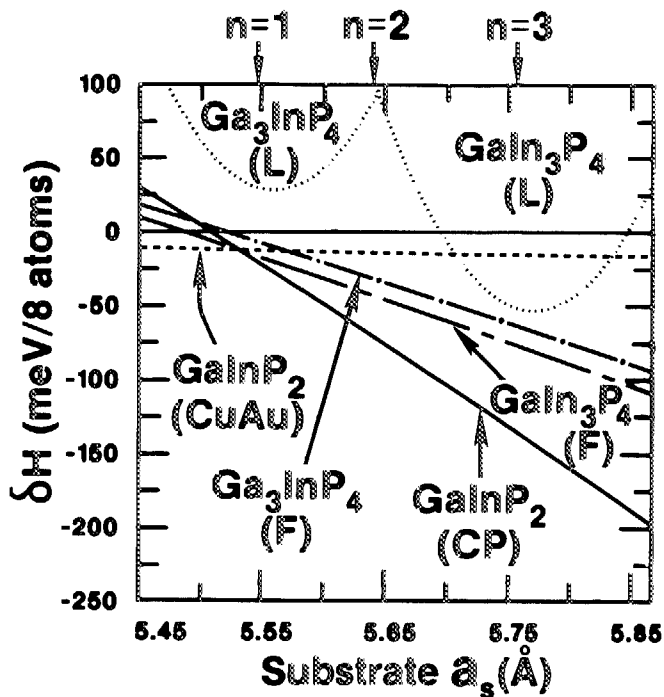


FIG. 3. Effective epitaxial enthalpy $\delta H^{(\lambda,n)}(a_s)$. The arrows at the top point to the average equilibrium lattice constants in the bulk forms.

since the critical immiscibility temperature T_c of such alloys scales with the elastic energy^{8,13} our calculated softening of B^* relative to B suggests a considerable reduction (by $\sim B^*/B$) in the effective T_c of epitaxial relative to bulk systems. This has been observed experimentally.⁷⁻⁹ Second, the strong relaxation-induced softening of the elastic modulus B^* in epitaxial ternary systems means that the substrate strain energy $W_{ss}^{(\lambda)}(a_s)$ (which is proportional to B^* and shown as the shaded areas in Fig. 2) is reduced substantially relative to the binary constituents (shaded areas in Fig. 1). This effect is the origin of epitaxial stability and selectivity. Figure 3, depicting the epitaxial $\delta H^{(\lambda,n)}(a_s)$, shows the following. (i) The epitaxial formation enthalpy $\delta H^{(\lambda,n)}(a_s)$ can be considerably lower than the bulk formation enthalpy $\Delta H^{(\lambda,n)}$, hence epitaxial stabilization. This is so because the availability of internal degrees of freedom for the ternary (but not the binary) systems lowers their substrate strain, hence the excess strain energy $\Delta E_{ss}^{(\lambda,n)}$ can be negative (this effect was found to be negligible in GaAs-AlAs due to its small lattice mismatch¹⁵). This effect can explain the observed stability of epitaxial adamantine compounds²⁻⁶ which have no counterparts in the bulk form. (ii) Substrate strain performs a "natural selection" between different ternary species, preferring the "fittest": whereas the Luzonite and Famatinite forms (or the CuAu-I and chalcopyrite

forms) have the same deformation energies in the unrelaxed bulk forms (Table I), under epitaxial conditions the substrate strain removes this degeneracy, strongly preferring the Famatinite (u, v, η degrees of freedom) over the Luzonite (just the u degree of freedom), or the chalcopyrite over the CuAu-I form. In general, phases with the smallest substrate strain (proportional to $B^* a_{eq}^3 \delta^2$) are favored. This explains why rhombohedral SiGe, with its smaller B^* , grows epitaxially on Si in preference to the zinc blende phase,^{1,15} which is nearly as stable in bulk but has a larger B^* . (iii) No obvious condition of "lattice matching" [$a_{eq}^{(n)} \simeq a_s$] can be associated with the minimum of $\delta H^{(\lambda,n)}(a_s)$ in Fig. 3: the optimum a_s stabilizes $A_n B_{4-n} C_4$ and at the same time destabilizes its binary constituents most. Hence, while the common approach of attempting to match $a_{eq}^{(n)}$ to a_s permits growth of thicker, dislocation-free films, it also diminishes selectivity effects. (iv) Figure 3 shows that the selection of a substrate a_s can alter the relative stabilities of two phases, hence permitting one to grow in preference to the other (e.g., for $a_s < 5.53$ Å the chalcopyrite becomes less stable than the CuAu form).

Our analysis opens the way to material engineering in epitaxial systems by utilization of the selectivity and stability rules formulated here.

Note added in proof: P. B. Littlewood [Phys. Rev. B **34**, 1363 (1986)] and C. P. Flynn [Phys. Rev. Lett. **57**, 599 (1986)] also address the question of epitaxial stabilization.

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