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Citation: Applied Physics Letters 49, 782 (1986); doi: 10.1063/1.97634
View online: http://dx.doi.org/10.1063/1.97634
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Structural stability and selectivity of thin epitaxial semiconductors

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(Received 14 July 1986; accepted for publication 29 July 1986)

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, rhombohedral \(^1\) SiGe, Famatinite forms \(^2\) of \( \text{InGa}_{x}\text{As}_{2-x} \) and \( \text{In}_x\text{GaAs}_4 \), chalcopyrite-like \(^3\) and CuAu-I-like \(^3\) (tetragonal) forms of \( \text{Ga}_x\text{As}_5\text{Sb}_3 \), CuAu-I-like \(^4\) \( \text{GaAlAs}_5 \), and cubic phases of \(^5\) CdS and \(^6\) SiC (observed at temperatures where the bulk phase diagrams show only hexagonal phases). It has similarly been noted \(^7\) 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, \(^8\) growth of an alloy inside the bulk miscibility gap region (e.g., \(^9\) \( \text{GaAs}_{0.8}\text{Sb}_{0.2} \)). In this letter we illustrate the general physical principles of epitaxial stability of adamantine semiconductor crystals using a simple valence force field method \(^10\) and the ternary \( \text{Ga}_x\text{In}_{4-x}\text{P}_4 \) 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 \( A_x B_{4-x} C_4 \) 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 \( A_2 B_2 C_4 \) with either a CuAu-I-like structure \(^4\) (insert to Fig. 2(a)) or the chalcopyrite (CP) structure \(^3\) (insert to Fig. 2(b)), whereas for \( n = 1 \) and \( 3 \) we have the 25%-75% and 75%-25% compounds \( A_3 B_1 C_4 \) and \( A_1 B_3 C_4 \), respectively, each appearing either in the Luzonite (L) form (insert to Fig. 2(c)), or in the Famatinite \(^2\) (F) form (insert to Fig. 2(d)). A disordered \( A_x B_{4-x} C_4 \) alloy corresponds to a statistical mixture of all local atomic environments exhibited by these \( A_x B_{4-x} C_4 \) structures; \(^13\) 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 \(^2\), \(^13\) the two nearest neighbor bond lengths can be expressed as \( R_{AC} = [\eta u^2 + 1/8]^{1/2} \), \( R_{BC} = [\eta (u - 1/2)^2 + 1/8]^{1/2} \), where \( u \) is the cell-internal (C-atom) displacement parameter. \(^12\), \(^13\) The Luzonite structure has only two degrees of freedom \( (a, \eta) \), whereas the Famatinite structure has four: \( (a, \eta, \varphi, \omega) \). When \( \eta = \eta_0 = 1 \) and \( u = w = 1/4 \) we have the "unrelaxed" structure with equal bond lengths \( R_{AC} = R_{BC} = \sqrt{3}/4 \), generally different from the ideal bond lengths \( R_{AC} = \sqrt{3}/4 \) \( a_{AC} \) and \( R_{BC} = \sqrt{3}/4 \) \( a_{BC} \) 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 \( A_x B_{4-x} C_4 \) 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 \(^7\), \(^8\), \(^11\) (taken in this paper per eight atom cell) of bulk \( A_x B_{4-x} C_4 \) compounds in structure type \( \lambda \) is given by

\[
\Delta H(\lambda) = \{E(\lambda)[A_x B_{4-x} C_4] - nE[AC] - (4-n)E[BC]\}. \tag{1}
\]

When grown epitaxially in a dislocation-free coherent fash-

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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 is
\[
\delta H^{(i,n)}(a_s) = \left\{ E^{(s)}[A_nB_{4-n}C_4]a_s = a_s \right\} - nE[AC,a_i = a_s] - (4-n)E[BC,a_i = a_s] \right\}.
\]
(2)

Parallel (||) to the substrate, the lattice parameters of the ternary compound and those of the effective enthalpy of formation is known. The constraints cost substrate strain energy, defined as
\[
W^{(s)}(a_s) = E^{(s)}[A_nB_{4-n}C_4]a_s = a_s - E^{(s)}[A_nB_{4-n}C_4]
\]
(3)

where all structural degrees of freedom not enumerated explicitly are taken to be their equilibrium values for the relevant \( a_i \). We see that the relative stability of epitaxial and bulk forms is given by the expression for the strain energy \( \delta E^{(s)}(a_s) = \delta H^{(s)}(a_s) - \delta H^{(s)}(a_s) \), which is simply the difference in \( W^{(s)}(a_s) \) for the ternary and binary systems taken at the same \( a_i \).

To illustrate the mechanisms of epitaxial stability and selectivity, we will use Keating's\textsuperscript{5} 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.\textsuperscript{10} This VFF is fitted to the phonon spectra\textsuperscript{10(a)} and correctly predicts impurity bond lengths\textsuperscript{10(b)} and enthalpies of mixing.\textsuperscript{10(b)} Fitting the numerically optimized deformation energies to the analytic anharmonic form \( E^{(s)}[A_nB_{4-n}C_4] = a_s \), 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 \( a_i = a_s \), 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 is observed experimentally, e.g., \( \text{In}_{17} \text{Ga}_{1-x} \text{As/InP} \). 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.\textsuperscript{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 \( E^{(s)}(a_s) \) 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 \( \{A_nB_{4-n}C_4\} \) structures,\textsuperscript{12} and

\begin{table}
\caption{Properties of unrelaxed and relaxed adamantine \( \text{Ga}_n\text{In}_{4-n}\text{P}_4 \) compounds. Energies are given per eight atom cells.}
\begin{tabular}{|c|c|c|c|}
\hline
System & \( a_{eq}^{(n)} \) (\( \AA \)) & \( \Delta E_{min} \) (meV) & \( B \) (GPa) & \( \Delta H \) (meV) & \( B^* \) (GPa) \\
\hline
\text{GaP} & 5.45 & 0.0 & 93 & 5.45 & 0.0 & 33 \\
\text{Ga}_x\text{In}_{4-n}\text{P}_4 \text{(L)} & 5.54 & 404.3 & 89 & 5.55 & 149.3 & 89 \\
\text{Ga}_x\text{In}_{4-n}\text{P}_4 \text{(F)} & 5.54 & 404.3 & 89 & 5.55 & 112.7 & 30 \\
\text{Ga}_x\text{In}_{4-n}\text{P}_4 \text{(Cu/Au)} & 5.64 & 572.4 & 85 & 5.61 & 162.0 & 27 \\
\text{Ga}_x\text{In}_{4-n}\text{P}_4 \text{(CP)} & 5.64 & 572.4 & 85 & 5.67 & 105.6 & 27 \\
\text{Ga}_x\text{In}_{4-n}\text{P}_4 \text{(L)} & 5.75 & 457.7 & 81 & 5.76 & 105.7 & 81 \\
\text{Ga}_x\text{In}_{4-n}\text{P}_4 \text{(F)} & 5.75 & 457.7 & 81 & 5.76 & 80.7 & 24 \\
\text{InP} & 5.87 & 0.0 & 77 & 5.87 & 0.0 & 21 \\
\hline
\end{tabular}
\end{table}
This effect is the origin of epitaxial stability and selectivity. This has been observed experimentally.\textsuperscript{7-9} \(B^*\) in the effective \(T_c\) of epitaxial relative to bulk systems. Strain energy shown as the shaded areas in Fig. 2) is reduced substantially strong relaxation-induced softening of the elastic modulus scales with the elastic formation enthalpy \(lJH(A.\mathbf{n})\) (which is proportional to \(a^{(\mathbf{n})}_{eq}\)), 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 \(\Delta E^{(\mathbf{n})}_{ss}\) can be negative (this effect was found to be negligible in GaAs-AlAs due to its small lattice mismatch\textsuperscript{51}). This effect can explain the observed stability of epitaxial adamantine compounds\textsuperscript{2-6} 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 (\(u,\nu,\eta\) 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 \(B^*a^{(\mathbf{n})}_{eq}\)) are favored. This explains why rhombohedral SiGe, with its smaller \(B^*\), grows epitaxially on Si in preference to the zinc blende phase,\textsuperscript{1,15} which is nearly as stable in bulk but has a larger \(B^*\). (iii) No obvious condition of “lattice matching” \(a^{(\mathbf{n})}_{eq}\approx a\) can be associated with the minimum of \(\delta H^{(\mathbf{n})}(a)\) in Fig. 3: the optimum \(a\) stabilizes \(A_nB_{4-n}C_4\) and at the same time destabilizes its binary constituents most. Hence, while the common approach of attempting to match \(a^{(\mathbf{n})}_{eq}\) to \(a\), permits growth of thicker, dislocation-free films, it also diminishes selectivity effects. (iv) Figure 3 shows that the selection of a substrate \(a\) can alter the relative stabilities of two phases, hence permitting one to grow in preference to the other (e.g., for \(a<5.53\) Å the chalcopyrite becomes less stable than the CuAu form).


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