Ordering in semiconductor alloys

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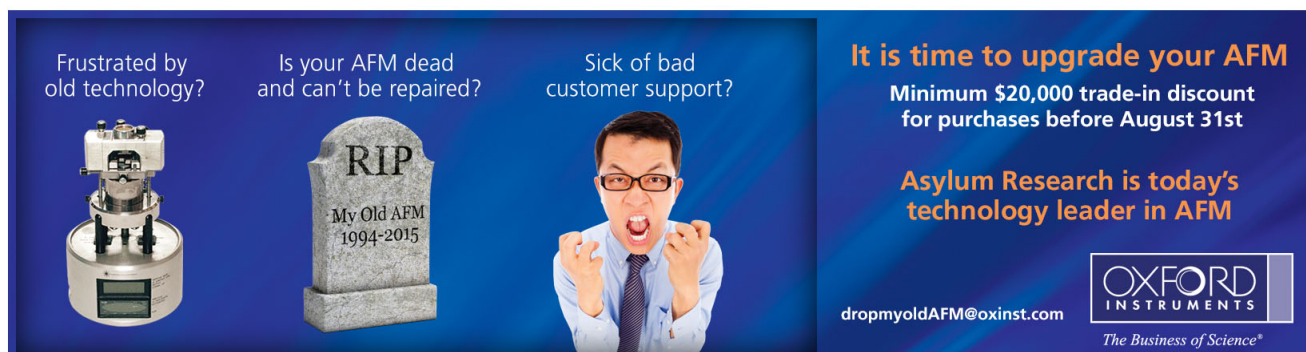Appl. Phys. Lett. **56**, 662 (1990); 10.1063/1.103307

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Ordering in semiconductor alloys

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A thermodynamic first-principles theory of stability, including charge transfer, elastic forces, and atomic relaxations reveals the physical origins of stable and metastable ordering in bulk and epitaxial semiconductor alloys and superlattices.

In this letter we address the following questions: (i) is a "bulk" (i.e., incoherent with a substrate) $(AC)_p (BC)_p$ superlattice (SL) thermodynamically stable or unstable with respect to either phase separation into its binary constituents $p(AC) + p(BC)$ or disordering into a random $A_{0.5}B_{0.5}C$ alloy; (ii) how does this stability depend on the SL repeat period p or orientation G; (iii) how does the condition of coherent epitaxial registry with a substrate or existence of a free surface during growth affect stability; and (iv) what overall classes of stability/metastability/instability are to be expected for II-VI and III-V SLs. We start by reviewing previous ideas on this subject. These are based on two facts: (i) classic thermodynamic models of alloys characterized their energy by a *single* constant interaction parameter[1] (e.g., the nearest-neighbor pair interaction); and (ii) all known disordered (D) semiconductor alloys have *positive* mixing enthalpies[2] $\Delta H^{(D)} \geqslant 0$. These two points led proponents of early models of pseudobinary $A_{1-x}B_xC$ semiconductor alloys[2] to assume that the interaction between the units forming these alloys is *repulsive*. The source of this repulsion was identified as the elastic energy[2] associated with packing a lattice with A and B atoms of dissimilar sizes. It followed then that $\Delta H^{(S)}$ must be positive also for many other atomic arrangements at the same composition, e.g., for ordered structures (S) such as superlattices. The purely repulsive nature of these interactions suggested that as the disordered alloy is cooled down the system first exhibits clustering (enhancement of the populations of pure AC-like and BC-like clusters relative to those in a random distribution), then a miscibility gap and phase separation. Ordering would then not exist except by virtue of artificial (e.g., shutter-controlled) growth of (super) structures. This behavior is opposite to that in "ordering" intermetallic alloys[1] (e.g., $Cu_{1-x}Au_x$) where attractive interactions lead to $\Delta H^{(S)} < 0$; cooling the disordered alloy leads there to anticlustering (reduction of the populations of the pure A-like and B-like clusters relative to those in a random distribution with the same composition), followed eventually by the formation of stable, long-range-ordered compounds at some stoichiometric compositions. In the classic models,[1,2] based on a single interaction parameter of a definite sign, phase separation [expected when $\Delta H^{(D)} > 0$] and ordering [expected when $\Delta H^{(S)} < 0$] are taken to be mutually exclusive phenomena.

It is now becoming clear that this picture is flawed.[3-5] Indeed ΔH reflects *a competition* between attractive and repulsive forces; however, the balance is different in ordered versus disordered phases of the same system, hence, $\Delta H^{(D)} > 0$ can be consistent both with ordering and anti-clustering. We first explain this point by a qualitative model, followed by a quantitative calculation. Consider the $A_{1-x}B_xC$ system in some (ordered S or disordered D) phase γ. When it is perfectly ordered in some structure S, it has a *single* local arrangement of A and B atoms around the common atom C; this cluster, denoted s, is repeated translationally throughout the lattice. When it is disordered, it exhibits *a few* local clusters $\{s\}$. In a particular phase γ at composition x there are $P_s^{(\gamma)}(x)$ clusters of type s. The excess enthalpy $\Delta H^{(\gamma)}$ of $A_{1-x}B_xC$ (measured with respect to equivalent amounts $1-x$ and x of pure AC and BC at their equilibrium volumes V_{AC} and V_{BC}) can now be thought of as having two distinct contributions, illustrated by a two-step process. First, deform pure AC and pure BC from their respective equilibrium volumes to the volume $V(x)$ of the final alloy. The required investment $G(x)$ of elastic energy depends only on the properties or pure AC and BC and on composition, but does not depend on the particular phase γ [since, to a good approximation,[4,5] $V(x)$ does not depend on γ]. Second, substitute at the fixed volume $V(x)$ the necessary number of A atoms by B in AC, and the necessary number of B atoms by A in BC to create $A_{1-x}B_xC$ in a particular phase γ. The energy involved in this step for cluster s will be called the "substitution energy" ϵ_s. In the pure clusters the C atoms are surrounded by the chemically identical and symmetry-equivalent atoms A_4 and B_4; we take the corresponding $\epsilon_{AC} = \epsilon_{BC} = 0$ to be our reference energies. In general, the mixed clusters can have $\epsilon_s \neq 0$ both due to $A \leftrightarrow B$ charge transfer, and most importantly, due to energy-lowering relaxation of C relative to its A and B neighbors. The excess enthalpy is the sum of the energies of these two steps, namely,

$$\Delta H^{(D)}(x) = G(x) + \sum_s P_s^{(D)}(x)\epsilon_s \qquad (1)$$

for the disordered alloy, and

$$\Delta H^{(S)}(x_s) = G(x_s) + \epsilon_s \qquad (2)$$

for the ordered structure S at its stoichiometric composition x_s. If the elastic energy $G(x)$ invested in deforming AC and BC is larger than the substitution energy ϵ_s, then $\Delta H^{(\gamma)} > 0$ and γ is unstable; if the opposite is true, γ could be stable. Experimentally, disordered semiconductor alloys have[2] $\Delta H^{(D)} \geqslant 0$; there, the elastic energy in Eq. (1) dominates the sum of the substitution energies. However, this does not necessarily imply the instability of ordered structures of Eq. (2), since their make-up in terms of clusters [i.e., the spectrum of $P_s(x)$] is different. What we have found is that certain clusters s, when arranged periodically in a specific man-

ner (e.g., in the chalcopyrite structure), have a particularly negative (stabilizing) ϵ_s, leading to low $\Delta H^{(S)}$ values. On the other hand, the existence in a disordered alloy of a distribution of clusters with an attendant range of ϵ_s's can lead to higher $\Delta H^{(D)}$. This can lead to $\Delta H^{(S)} < \Delta H^{(D)}$, hence the potential for (stable or metastable) ordering even when $\Delta H^{(D)} > 0$. The probability to find cluster s at (x, T) depends on $\exp(-\Delta H^{(s)}/kT)$. However, the probability relative to a random distribution depends only on $\exp(-\epsilon_s/kT)$, since at a fixed x, $G(x)$ is a common term. Hence, systems with $\epsilon_s < 0 (\epsilon_s > 0)$ will exhibit anticlustering (clustering) irrespective of whether they have $\Delta H > 0$ or $\Delta H < 0$.

We have calculated the formation enthalpy

$$\Delta H^{(\gamma)} = E^{(\gamma)}(V_\gamma) - (1-x)E^{(AC)}(V_{AC})$$
$$- xE^{(BC)}(V_{BC}), \qquad (3)$$

for a series of 50%-50% isovalent semiconductors in four phases γ: ordered chalcopyrite (CH), CuAu-I-like (CA), and CuPt-like (CP), and the disordered alloy. The three ordered arrangements can be described as $(AC)_p(BC)_p$ superlattices of repeat period p and orientation G: CH is $p = 2$, $G = [201]$, CA is $p = 1$, $G = [001]$, and CP is $p = 1$, $G = [111]$. We have used the local density formalism, as implemented in the linearized augmented plane wave (LAPW) method[6] and the nonlocal pseudopotential method.[7] For each structure we first calculate self-consistently its potential and band structure, then use the variational charge density and wave functions to compute the total energy, including all Coulomb and exchange-correlation interactions. Structural parameters are optimized to reach the minimum total energy. $\Delta H^{(D)}(x, T)$ for the disordered alloy is then obtained by solving the fcc Ising Hamiltonian using the cluster-variation method.[5] We include up to four-body and fourth fcc-neighbor interaction energies. These are extracted from the total energy calculations of the ordered compounds. The directly calculated $\Delta H^{(\gamma)}$ of Eq. (3) is then analyzed in terms of Eqs. (1) and (2) in order to isolate the physical factors controlling stability. Technical details of these theoretical methods and the establishment of our ≈ 5 meV precision in ΔH are described in Refs. 4, 5, and 8. The results are depicted in Figs. 1 and 2. We conclude the following:

(i) As correctly noted by the classic alloy theories,[2] the elastic contribution $G(x)$ to the enthalpy is positive and increases with the relative $A - B$ size difference and with covalency (Fig. 1, top). However, the substitution energy ϵ_s is negative for size-mismatched systems and becomes more negative as the relative size difference and covalency increase (Fig. 1, bottom). Hence, size difference is the cause of repulsion (through elastic volume deformation) and attraction (due to charge transfer and sublattice relaxation) *at the same time*.

(ii) Size-mismatched systems have $\epsilon_s < 0$ (Fig. 1, bottom); hence, they will exhibit anticlustering, whereas since size-matched alloys have $\epsilon_s > 0$ (inset to Fig. 1), they will show clustering.

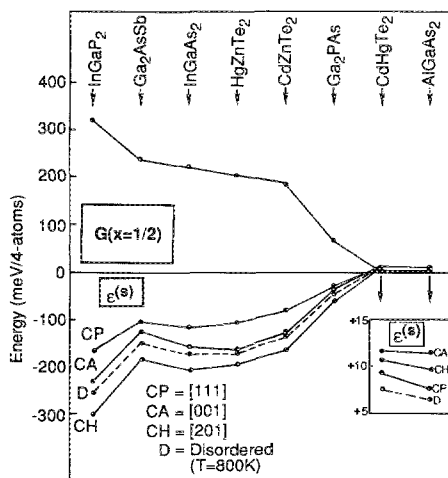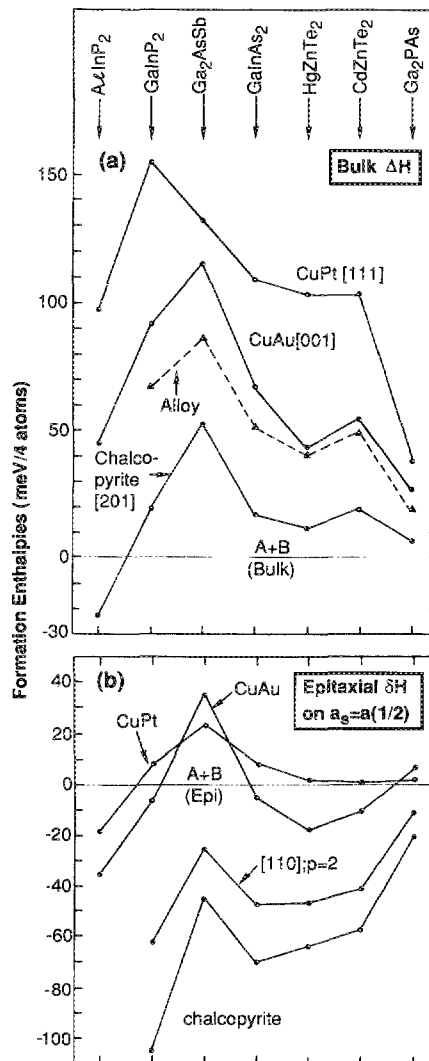FIG. 2. (a) Calculated bulk and (b) epitaxial formation enthalpies.

FIG. 1. Decomposition of calculated formation enthalpies at $x = 1/2$ into the elastic energy G and the substitution energy ϵ_s; see Eqs. (1) and (2). For the disordered alloy at $T = 800$ K we give the second term of Eq. (1). Systems are arranged in decreasing order of G, reflecting approximately size mismatch.

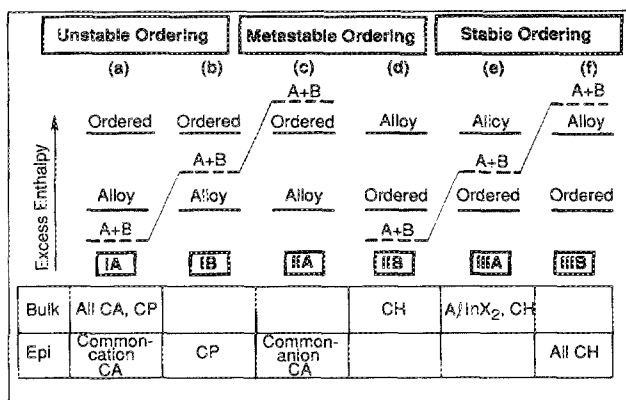|	Unstable Ordering		Metastable Ordering		Stable Ordering	
	(a)	(b)	(c)	(d)	(e)	(f)
Excess Enthalpy	Ordered	Ordered	A+B / Ordered	Alloy	Alloy	A+B / Alloy
	A+B				A+B	
	Alloy	Alloy	Alloy	Ordered	Ordered	Ordered
	A+B			A+B		
	IA	IB	IIA	IIB	IIIA	IIIB
Bulk	All CA, CP			CH	A/InX₂, CH	
Epi	Common-cation CA	CP	Common-anion CA			All CH

FIG. 3. Classification of types of ordering according to enthalpies.

(iii) In size-mismatched alloys, chalcopyrite has universally the most favorable substitution energy (Fig. 1). Since $\Delta H^{(CH)} < \Delta H^{(D)}$ [Fig. 2(a)], it could order metastably or even stably (we find $\Delta H^{(CH)} < 0$ for[8] AlInP$_2$). The $S =$ CA and CP structures have $\Delta H^{(S)} > \Delta H^{(D)} > 0$ [Fig. 2(a)] and are hence unstable with respect to disordering. The sequence is different for size-matched alloys (inset to Fig. 1) where bulk ordering is not expected for any S.

(iv) Adding the two contributions in Eqs. (1) and (2) (or Fig. 1) gives the total $\Delta H^{(\gamma)}$ depicted in Fig. 2(a). We distinguish here between (i) *unstable bulk ordering* [type I, where the ordered phase S is less stable than both the disordered alloy and phase separation; Figs. 3(a) and 3(b)] and (ii) *metastable bulk ordering* [type II, where the ordered phase is more stable than one of the two alternatives but less stable than the other; Figs. 3(c) and 3(d)], and (iii) *stable bulk ordering* [type III, where the ordered system is more stable than both alternatives; Figs. 3(e) and 3(f)]. In the absence of competition between attraction and repulsion, classic models using continuum elasticity depicted all semiconductor alloys to be essentially of type IA (or possibly IIB). Summarizing the results of Fig. 2 in Fig. 3, we find that other types of ordering exist as well, much like the case in intermetallic systems.

So far we have dealt with bulk systems where all three terms of Eq. (3) are free to adjust to their respective minimum energies. This is appropriate to "free-floating" (melt or solution) growth. In coherent epitaxial growth, on the other hand, the growing phase *and its constituents AC* and *BC* are constrained, for sufficiently thin films, to adopt the substrate's lattice constant a_s in the plane perpendicular to G. The appropriate epitaxial formation enthalpy[9] $\delta H^{(\gamma)}(a_s, G)$ is then taken with respect to the energies $E^{(AC)}(a_s,G)$ and $E^{(BC)}(a_s, G)$ of the constituents deformed to the substrate's dimension a_s and relaxed in the direction paralled to G. For a substrate lattice matched to the growing phase γ (but not to its constituents), this constraint can lower the epitaxial δH by raising the energy of the (epitaxial) constituents. Figure 2(b) shows our calculated epitaxial energies for $a_s = a(x = 1/2)$. It shows that

(v) Unstable bulk ordering (type IA, e.g., all CAs and CPs) can be transformed epitaxially into metastable ordering (type IIA, e.g., many of the common-anion CAs). Likewise, metastable bulk ordering (IIB) can be transformed into stable epitaxial ordering (IIIB, e.g., CHs). This is consistent with the observation of [201] ordering in liquid phase epitaxy (LPE) growth of GaInAs$_2$.[10]

(vi) The epitaxial destabilization of the constituents also reduces the enthalpy of the disordered alloy[9] (and reduces its compositional derivative). Hence, the epitaxial alloy can be stable with respect to phase separation to far lower temperatures than in bulk. Indeed, bulk-immiscible systems (GaP$_x$Sb$_{1-x}$) become epitaxially miscible.[11]

Our foregoing discussion of epitaxial stability dealt with constrained total energy minimization without the presence of a free surface, e.g., as appropriate to LPE growth. Metal-organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) growth, on the other hand, do involve a free surface; the energy-minimizing atomic configuration at the surface can then be different than in bulk. To the extent that this is so, and that subsequent coverage of the surface freezes its structure, a surface-stable configuration can grow to macroscopic dimensions. Indeed, our calculations for epitaxially constrained Ga$_{0.5}$In$_{0.5}$P on a lattice-matched GaAs substrate with a free [001] surface show that the order of stability of Fig. 2(b) is changed: one of the two possible CuPt-type ordering vectors is now more stable than CH due to a stabilizing surface reconstruction (dimerization). Recent observations of spontaneous CuPt ordering[12] are hence likely to reflect surface-induced thermodynamic ordering. Denoting by T_b the ordering temperature appropriate for 3-D epitaxial growth (e.g., LPE), this predicts that post-growth annealing at the growth temperature T_g will give, if sufficient atomic mobility exists, the epitaxial ordering of Fig. 2(b) (if $T_g < T_b$), or the disordered phase (if $T_g > T_b$).

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