Epitaxial Effects on Coherent Phase Diagrams of Alloys

D. M. Wood and Alex Zunger
Solar Energy Research Institute, Golden, Colorado 80401

(Received 7 June 1988)

Using a cluster description of a coherent binary alloy, we predict and contrast bulk and epitaxial composition-temperature phase diagrams. For alloys with stable ordered compounds in bulk, epitaxial growth away from the lattice-matched composition distorts phase boundaries and changes ordering temperatures. For alloys insoluble in bulk below a miscibility-gap temperature $T_{\rm MG}$, the epitaxial alloy may remain stable to temperatures > 1200 K below $T_{\rm MG}$ even on lattice-matched substrates, with stoichiometric compounds possible at low temperature.

PACS numbers: 68.55.Rt, 64.60.My, 68.55.Nq

Gradual refinements now permit epitaxial growth of materials coherent with the substrate at temperatures low enough that phenomena peculiar to epitaxy occur. Even on substrates *lattice matched* to the overlayer material, (i) ordered isovalent ternary semiconductor compounds (e.g., $\rm GaInAs_2$) appear,[1,2] though the bulk alloys show no long-range ordering, and (ii) constituents insoluble in bulk (e.g., GaP-GaSb) below a miscibility-gap temperature $T_{\rm MG}$ become soluble epitaxially[3] even 1200 K below $T_{\rm MG}$.

While kinetic or surface-controlled mechanisms are possible, epitaxial effects on crystalline solids have been largely understood for semiconductors[4] and elemental metals.[5] Provided the substrate-overlayer lattice mismatch is accommodated elastically, the lowest-energy epitaxial phase is selected, subject to the *epitaxial constraint:* Cell dimensions $a_\parallel$ parallel to the interface are those of the substrate, of lattice parameter a_s. No microscopic calculations of composition-temperature (x,T) phase diagrams for epitaxial alloys have been reported; existing descriptions have mostly been phenomenological, using elasticity theory[6] or model calculations[7] to understand modes of epitaxial growth,[8] and classification of thermodynamic equilibrium between coherently stressed phases.[9] In this Letter we describe a microscopic formalism which can calculate and contrast bulk and epitaxial phase diagrams on exactly the same footing. This approach makes physically transparent the origins of the pronounced epitaxial effects noted above. It is illustrated with bulk and epitaxial phase diagrams for $\rm Cu_{1-x}Au_x$ and $\rm GaAs_xSb_{1-x}$, generically typical of compound-forming (ordering) and phase-separating systems, respectively.

Thermodynamic functions and phase diagrams of *bulk* fcc $A_{1-x}B_x$ alloys[10,11] have been successfully described (within 15% of experiment) by the expansion of the alloy energy as a linear combination of cluster energies,[10-12] e.g., the clusters $A_{4-n}B_n$ $(n=0\text{–}4)$ accounting for the principal interactions (up to four body[11]) in the bulk (bk) alloy,

$$E_{\rm bk}(x,T)=\sum_{n=0}^{4}P_n(x,T)E_{\rm bk}^{(n)}[a(x,T)]. \tag{1a}$$

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 $dE_{\rm bk}(x,T)/da=0$. To treat *epitaxial* (ep) alloys we apply the epitaxial constraint $a_\parallel=a_s$, to find

$$E_{\rm ep}(a_s,x,T)=\sum_{n=0}^{4}\tilde{P}_n(a_s,x,T)E_{\rm ep}^{(n)}[a_s,c(a_s,x,T)], \tag{1b}$$

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 $dE_{\rm ep}(a_s,x,T)/dc=0$. Since coherent growth is inhibited by nucleation of misfit dislocations beyond a critical thickness[13] h_c, we assume that the epitaxial film thickness h satisfies $(\text{monolayer})\ll h<h_c(x)$, so that surface energies are thermodynamically negligible and strain is accommodated elastically.

Because of the linear, invertible relationship between alloy and cluster energies,[11,12] it is most convenient to draw cluster properties from periodic structures, which also insures incorporation of effectively long-ranged interactions.[11] Thus the cluster energy functions $E_{\rm bk}^{(n)}$ and $E_{\rm ep}^{(n)}$ in Eqs. 1(a) and 1(b) could readily be calculated from first principles.[4,5,10-12] For small deformations these are accurately and conveniently described by harmonic elasticity theory.[4a] Per fcc site for bulk and epitaxial clusters,

$$E_{\rm bk}^{(n)}(a)=\Delta H_n+\tfrac{9}{8}a_nB_n(a-a_n)^2, \tag{2a}$$

$$E_{\rm ep}^{(n)}(a_s,c)=\Delta H_n+\tfrac{9}{8}a_n\tilde{B}_n(a_s-a_n)^2+\tfrac{1}{8}a_nC^{(n)}[c-c_n(a_s)]^2, \tag{2b}$$

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.[14] For [001]-oriented substrates, $\tilde{B}_n=\tfrac{2}{3}B_n[1-C_{12}^{(n)}/C_{11}^{(n)}]$, $C^{(n)}=C_{11}$, where C_{12} and C_{11} are conventional cubic elastic constants, and $c_n=a_n-2C_{12}^{(n)}/C_{11}^{(n)}(a_s-a_n)$ is the equilibrium tetragonal dimension.

Given $\{\Delta H_n,\ a_n,\ C_{11}^{(n)},\ C_{12}^{(n)}\}$ for ordered compounds $A_{4-n}B_n$ $(n=0\text{–}4)$, the cluster probabilities $P_n(x,T)$ and entropy S may be simultaneously determined under bulk or epitaxial conditions by minimization of the alloy free energy $F=E-TS$ with respect to the $\{P_n\}$ using the cluster variation method of Kikuchi[15] within the tetrahedron approximation (i.e., including effective nearest-neighbor interactions through four-body terms). One can hence evaluate F for each possible state of order (taken as ordered A_3B and AB_3 in the $L1_2$ structure,[12] ordered AB in the $L1_0$ structure,[12] or the disordered fcc alloy) and using parallel tangent constructions calculate the complete (x,T) phase diagram.

Equations (1) and (2) 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. (2b) into Eq. (1b), and using Eqs. (1a) and (2a), we find per fcc site

$$\Delta H_{\mathrm{ep}}(a_s,x,T)=\Delta H_{\mathrm{bk}}(x,T)+\tfrac{9}{8}a(x,T)\times\tilde{B}(x,T)[a_s-a(x,T)]^2, \quad (3)$$

where $\tilde{B}$ (which depends on substrate orientation) and a are ratios of sums over the $\tilde{P}_n$ of cluster elastic properties. Equation (3) is what one would predict[6] for an alloy described as a harmonic elastic continuum with an equilibrium lattice parameter $a(x,T)$ and an epitaxial elastic modulus $\tilde{B}(x,T)$; if $a_s=a(x,T)$, Eq. (1b) reverts to Eq. (1a). At $T=0$ for ordered compound m, $P_n=\delta_{n,m}$ and Eq. (1a) [(1b)] reverts to Eq. (2a) [(2b)], except that the last terms in Eqs. (2)—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 have higher strain energies than ordered compounds of the same composition (see Fig. 1).

The essential physics of epitaxy may be understood by contrasting actual calculated formation enthalpies ΔH for bulk and epitaxial conditions. Figure 1 shows $\Delta H^D(x)$ for the disordered (D) alloy and ΔH^O for ordered (O) compounds for a typical "ordering" alloy, $\mathrm{Cu}_{1-x}\mathrm{Au}_x$ [Fig. 1(a), with $\Delta H^D\leq 0$, $d^2\Delta H^D/dx^2>0$, and $\Delta H^O<0$], and for $\mathrm{GaAs}_x\mathrm{Sb}_{1-x}$, a typical "phase separating" alloy [Fig. 1(b), with $\Delta H^D\geq 0$, $d^2\Delta H^D/dx^2<0$, and $\Delta H^O>0$], under bulk conditions and epitaxially for a substrate lattice matched to the $x=0.5$ ordered compound. We note the following: (i) While at the lattice-matched composition the bulk (solid lines) and epitaxial (dashed lines) ΔH coincide since epitaxy poses no constraint [Eq. (3)], (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 $\mathrm{Ga_4AsSb_3}$ and $\mathrm{Ga_2AsSb}$ are *unstable* in bulk ($\Delta H^O>0$, solid circles), epitaxially they are lower in energy than equal amounts of the epitaxial constituents, (dotted lines in Fig. 1) and have hence been *epitaxially stabilized* with respect to decomposition into strained constituents. (iv) Epitaxy alters the *curvature* of ΔH^D with respect to composition (affecting alloy stability, discussed below). We next examine the consequences for phase diagrams.

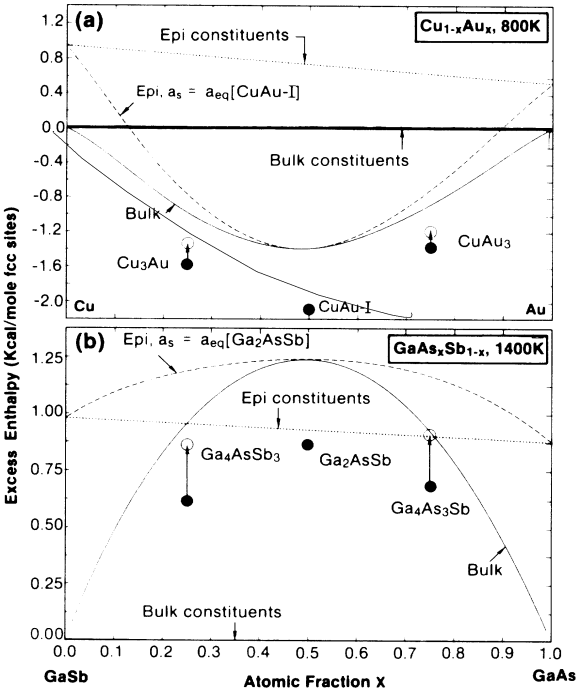

FIG. 1. Excess enthalpies of bulk and epitaxial alloys: (a) ordering alloy, $\mathrm{Cu}_{1-x}\mathrm{Au}_x$; (b) phase-separating alloy, $\mathrm{GaAs}_x\text{-}\mathrm{Sb}_{1-x}$. Filled (open) circles indicate bulk (epitaxial) formation enthalpies of ordered compounds at $T=0$. Solids (dashed) lines indicate mixing enthalpies of disordered bulk (epitaxial) alloy.

We turn first to the experimentally well-characterized $\mathrm{Cu}_{1-x}\mathrm{Au}_x$ phase diagram, typical of ordering systems. In Fig. 2(a) we show the *bulk* phase diagram, calculated as described above with use of $\{\Delta H_n, a_n, C_{11}^{(n)}, C_{12}^{(n)}\}$ extracted from experimental data on the ordered compounds[12]; critical temperatures agree well with experiment (see Ref. 12 and references therein). Figure 2(b) shows the corresponding *epitaxial* phase diagram for a substrate lattice matched to the ordered CuAu-I compound at $x=0.5$. Contrasting these figures, we note (i) an enhancement of the composition range over which ordered compounds are stable (shaded regions), reflecting better accommodation of the epitaxial constraint in ordered (rather than disordered) atomic arrangements; (ii) corresponding reductions of two-phase *coexistence,* e.g., at 400 K the Cu-rich disordered alloy is epitaxially stable to $x\simeq 0.13$, but to only about $x=0.02$ in bulk.

In Fig. 3 we show results for $\mathrm{GaAs}_x\mathrm{Sb}_{1-x}$, a typical phase-separating system, with cluster parameters extracted from theoretical calculations[16] on ordered com-

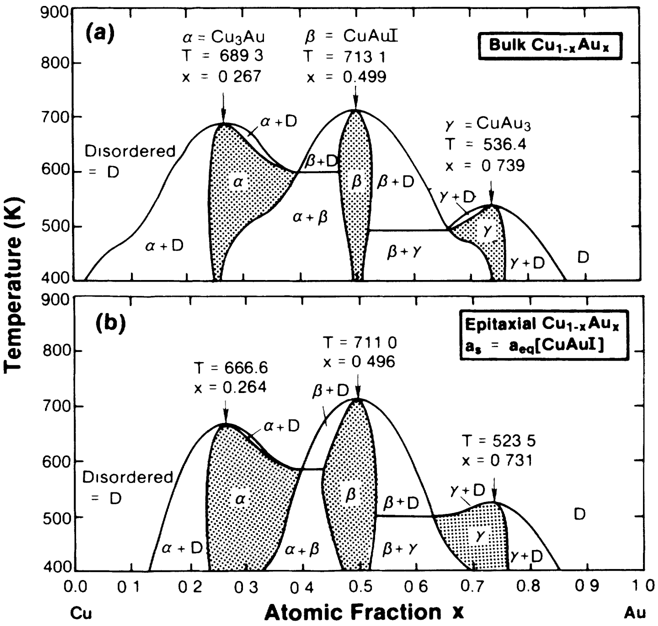

FIG. 2. Phase diagrams for $Cu_{1-x}Au_x$: (a) bulk; (b) epitaxially on substrate lattice matched to the ordered $x=0.5$ compound. Shaded areas indicate single-phase ordered compounds.

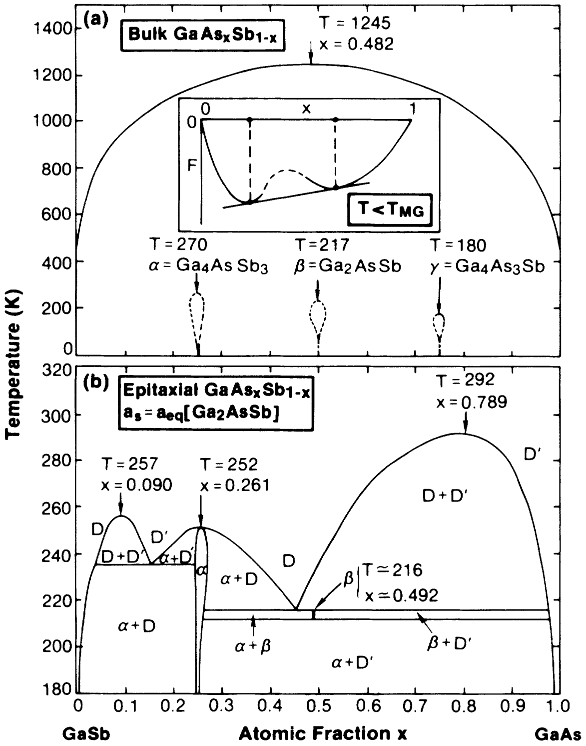

FIG. 3. Phase diagrams for $GaAs_xSb_{1-x}$: (a) bulk ($T=0$ values extrapolated); (b) epitaxially on substrate lattice matched to the ordered $x=0.5$ compound. In (a) dashed lines indicate spinodals of metastable ordered compounds. Inset: Schematic x dependence of free energy. In (b) $D+D'$ indicates coexistence between disordered alloys of distinct concentration. See inset to (a).

pounds in the zinc-blende GaSb and GaAs, "luzonite" Ga_4AsSb_3 and Ga_4As_3Sb, and "CuAu-I-like" Ga_2AsSb structures.[4a,10] (These results illustrate epitaxial effects but are only semiquantitative because the tetrahedron cluster variation method is only approximately valid for semiconductors.[17]) The principal feature of the bulk phase diagram [Fig. 3(a)] 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. 1(b)]. In Fig. 3(b) 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., $GaAs_xSb_{1-x}$ (Ref. 3a) and GaP_xSb_{1-x} (grown[3b] ~1200 K below the bulk miscibility gap). (ii) A metastable ordered Ga_4AsSb_3 compound deep within the bulk miscibility gap is now *stable* below 252 K with respect to the epitaxial disordered alloy, in qualitative accord with the discussion of epitaxial stabilization following Fig. 1 and with experimental observation of epitaxial ordering[1,2] absent in bulk. 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[2] on (001) substrates.

The very different response to epitaxy of ordering and separating alloys may be understood by noting that a miscibility gap, associated with regions where $d^2F/dx^2 \leq 0$ [inset of Fig. 3(a)], is possible for separating systems since $d^2E/dx^2<0$ [Fig. 1(b)] while $-Td^2S/dx^2>0$. However, Eq. (3) and Fig. 1 show that epitaxy even on a *lattice-matched* substrate adds a positive contribution to d^2F/dx^2 relative to bulk, profoundly suppressing the misciblity temperature.

As noted above, these pronounced epitaxial effects are relevant provided that the epitaxial film thickness does not exceed the critical thickness for nucleation of misfit dislocations, at which point the coherency condition $a_{\parallel}=a_s$ is partially lost. In practice, this restricts the validity of the analysis above to a "window" centered on the lattice-matched composition. Requiring, e.g., at least 500 Å of coherent growth for $a_s=a(x=0.5)$, this window is roughly $x=0.5\pm0.008$ for $Cu_{1-x}Au_x$; for $GaAs_xSb_{1-x}$ it is 0.5 ± 0.02. For semiconductors the experimentally observed h_c may exceed the theoretical value by a factor > 20, making this a very conservative estimate.

In conclusion, we have developed a microscopic cluster-based formalism which makes possible detailed comparison of bulk and epitaxial phase diagrams on a conceptually identical footing. We have demonstrated that under epitaxial conditions there can be pronounced modifications with respect to bulk of order-disorder transitions and regions of phase stability (for ordering systems), and enormous suppressions of miscibility-gap temperatures with epitaxial stabilization of ordered compounds (for typical phase-separating systems).

We thank L. G. Ferreira for many useful discussions. and S.-H. Wei and J. Bernard for providing first-principles data on the $GaSb_{4-n}As_n$ compounds.

---

[1] For, e.g., $GaInAs_2$, see T. S. Kuan, W. I. Wang, and E. L. Wilkie, Appl. Phys. Lett. **51**, 51 (1987); for Ga_2AsSb, see H. R. Jen, M. J. Cherng, and G. B. Stringfellow, Appl. Phys. Lett. **58**, 1603 (1986).

[2] For [111] ordering in $GaInAs_2$, see M. A. Shahid, S. Mahajan, and D. E. Laughlin, Phys. Rev. Lett. **58**, 2567 (1987); for $GaInP_2$, see P. Bellon, J. P. Chevalier, G. P. Martin, E. Dupont-Nivet, C. Thiebaut, and J. P. Andre, Appl. Phys. Lett. **52**, 567 (1988).

[3a] R. M. Cohen, M. J. Cherng, R. E. Benner, and G. B. Stringfellow, J. Appl. Phys. **57**, 4817 (1985).

[3b] M. J. Jou, Y. T. Cherng, H. R. Jen, and G. B. Stringfellow, Appl. Phys. Lett. **52**, 549 (1988).

[4a] A. A. Mbaye, D. M. Wood, and A. Zunger, Phys. Rev. B **37**, 3008 (1988).

[4b] J. L. Martins and A. Zunger, Phys. Rev. Lett. **56**, 1400 (1986).

[5] See, e.g., P. M. Marcus and V. L. Moruzzi, J. Appl. Phys. **63**, 4045 (1988).

[6] B. de Cremoux, J. Phys. (Paris) Colloq. **43**, C5-19 (1982); see also G. B. Stringfellow, J. Electron. Mater. **11**, 903 (1982), for the closely related question of coherency strain in bulk alloys.

[7] C. P. Flynn, Phys. Rev. Lett. **57**, 599 (1986); P. B. Littlewood, Phys. Rev. B **34**, 1363 (1986).

[8] R. Bruinsma and A. Zangwill, Europhys. Lett. **4**, 729 (1987), and J. Phys. (Paris) **47**, 2055 (1986).

[9] W. C. Johnson and P. W. Voorhees, Metall. Trans. A **18A**, 1213, 1093 (1987); F. E. Larché and J. W. Cahn, Acta Metall. **33**, 331 (1985).

[10] A. A. Mbaye, L. G. Ferreira, and A. Zunger, Phys. Rev. Lett. **58**, 49 (1987); G. P. Srivastava, J.-L. Martins, and A. Zunger, Phys. Rev. B **31**, 2561 (1985).

[11] S.-H. Wei, A. A. Mbaye, L. G. Ferreira, and A. Zunger, Phys. Rev. B **36**,4163 (1987); L. G. Ferreira, A. A. Mbaye, and A. Zunger, Phys. Rev. B **37**, 10547 (1988).

[12] J. W. D. Connolly and A. R. Williams, Phys. Rev. B **27**, 5169 (1983).

[13] J. W. Matthews, in *Dislocations in Solids,* edited by F. R. N. Nabarro (North-Holland, Amsterdam, 1979), Vol. 2, Chap. 7, p. 461.

[14] For the $A_{4-n}B_nC_4$ clusters in semiconductor alloys, structural parameters describing the common C sublattice must be relaxed (Refs. 4a and 10).

[15] See, e.g., R. Kikuchi, J. Chem. Phys. **60**, 1071 (1974).

[16] Bond bending and stretching force constants extracted from first-principles total energies for GaAs and GaSb were used in valence force field calculations (e.g., Ref. 4a) for ordered compounds to find ΔH_n ($n=1-3$).

[17] In the nearest-neighbor tetrahedron approximation it is impossible to distinguish, e.g., at $x=0.5$, CuAu-I-like from chalcopyrite ordering, or luzonite from CuPt (Ref. 2).

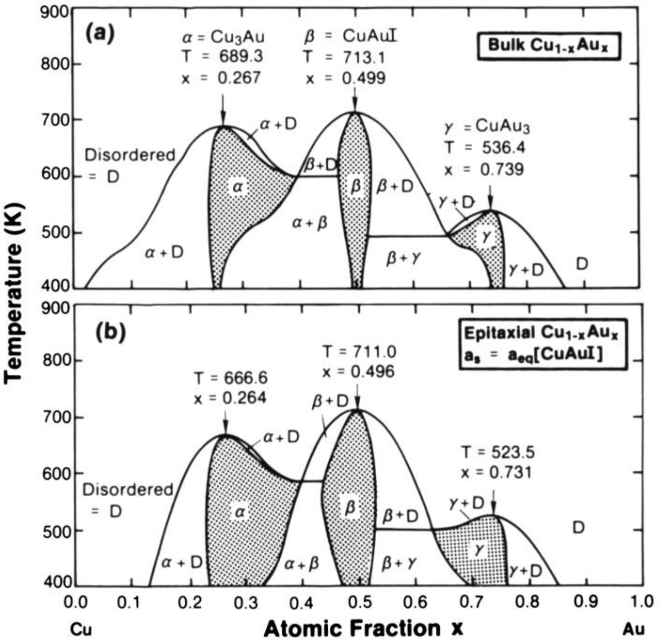

FIG. 2. Phase diagrams for $Cu_{1-x}Au_x$: (a) bulk; (b) epitaxially on substrate lattice matched to the ordered $x = 0.5$ compound. Shaded areas indicate single-phase ordered compounds.