Stability of Ordered Bulk and Epitaxial Semiconductor Alloys

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Using first-principles self-consistent total-energy calculations for unconstrained and epitaxially confined models of Si-C and Si-Ge alloys we study the general classes of stability of ordered phases of semiconductor alloys. The unusual ordering observed in SiGe grown on a Si substrate is explained.

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One of the most intriguing aspects of heteroepitaxial growth of thin semiconductor layers is the observation of apparently *stable* new atomic arrangements which either have no counterpart in the bulk phase diagram[1-3] or are known to be unstable in bulk form at the same composition and temperature ranges.[4-6] Such are, for example, the recent observation of hitherto unknown *ordered* phases of tetragonal[1] $AlGaAs_2$ and[2] $InGaAs_2$, rhombohedral[3] SiGe, the existence of *cubic* epitaxial phases of[4] CdS and[5] SiC at temperatures where the bulk phase diagrams show only the hexagonal phases to be stable, and the successful epitaxial growth[6] of disordered $GaAs_{1-x}Sb_x$ at compositions and temperatures well inside the miscibility gap.[7] The observation of ordered alloys is particularly interesting since disordered semiconductor alloys are *known* to be unstable at low temperatures: Unlike the situation encountered in metallurgy, where intermetallic alloys with either positive or negative enthalpy of formation ΔH can occur,[8] the analysis of liquidus and solidus data of disordered (D) bulk semiconductor alloys reveals universally[9] $\Delta H^{(D)} > 0$. While the recognition of this underlying instability led to the development of models[10,11] focusing on the destabilizing role of bond strain, Srivastava, Martins, and Zunger[12] predicted nevertheless ordered alloys to exist, by virtue of a strain-minimizing coherent arrangement of bonds and stabilizing chemical interactions. In this Letter we apply general topological arguments and a first-principles local-density total-energy minimization method[13] to study SiC and both bulk and epitaxial models for SiGe. We show that these systems suggest a general classification of three types of stabilities in semiconductor alloys and demonstrate that (i) two adamantine-ordered structures, zinc blende and rhombohedral (CuPt ordering, $R\bar{3}m$) have sufficient structural degrees of freedom to make all bond lengths and angles equal to the ideal tetrahedral values, so that both structures are *intrinsically strain free*; (ii) whereas in SiC chemical interactions favor heteropolar bonds, in SiGe the heteropolar bond is weaker than the average of the two homopolar bonds, and hence the rhombohedral structure (with 75% heterpolar bonds) is stabler than the zinc-blende structure (with 100% heterpolar bonds); and (iii) the existence of a finite lattice mismatch with a substrate—a situation which has traditionally been considered to be detrimental to successful epitaxial growth[14]—further stabilizes one species (rhombohedral SiGe) over the other (zinc-blende SiGe).

The enthalpy of formation of an ordered α phase of A_mB_n,

$$\Delta H^{(\alpha)}[A_mB_n] = H^{(\alpha)}[A_mB_n] - mH^{(o)}[A] - nH^{(o)}[B], \quad (1)$$

and the enthalpy of mixing of a disordered (D) alloy A_xB_{1-x},

$$\Delta H^{(D)}[A_xB_{1-x}] = H^{(D)}[A_xB_{1-x}] - xH^{(o)}[A] - (1-x)H^{(o)}[B], \quad (2)$$

are expressed, following Srivastava, Martins, and Zunger,[12] as a sum of a bulk microscopic strain (ms) and a chemical (chem) contribution,

$$\Delta H = \Delta E_{\text{chem}} + \Delta E_{\text{ms}}. \quad (3)$$

Here, $H[AB]$, $H^{(o)}[A]$, and $H^{(o)}[B]$ are the enthalpies of phases AB, A, and B, respectively, in their equilibrium bulk ("free floating") structures, ΔE_{ms} is the contribution to the enthalpy resulting from the deformation of bond lengths and angles occurring in the formation of the phase, and ΔE_{chem} is the contribution of all other (chemical) changes, i.e., charge transfer, polarization, or formation of new types of bonds.[15] Previous explanations[10,11] for $\Delta H^{(D)}[A_xB_{1-x}] > 0$ neglected ΔE_{chem} and focused on the destabilizing role of microscopic bond strain ΔE_{ms} [proportional[10,11,16] to the square of lattice mismatch $(a_A - a_B)^2$]. Since strain energies are positive definite, such models[10,11] predict $\Delta H^{(\alpha)}[A_mB_n] \geq 0$ for *ordered* phases as well. We first illustrate that this is not generally true by considering the bulk forms of SiC and SiGe. To select from the infinite number of possible ordered phases A_mB_n of adamantine compounds (i.e., tetrahedral structures with close-packed cubic sublattices) the few that are likely to be stablest, we utilize the Landau-Lifshitz (LL) theory of phase transformations,[17] adopted to fcc sublattices. These structures have the following remarkable properties: (i) They are the only ones where the order-disorder transformation *can* (but need not) be of second order,[17] (ii) all (and no others) are stable against antiphase boundaries,[18] and (iii) they can exist over a wide concentration range.[18] For *ternary* $A_mB_nC_{m+n}$ and binary A_mB_n adamantine semiconductors (with disorder on one and two fcc sublattices, respectively), there are eight and thirty-two LL structures, respectively.[12,19] Inspection of the number of independent structural degrees of freedom in each phase reveals that among all the LL adamantine phases only two structures—equimolar zinc blende (ZB) and rhombohedral (RH) (inset to Fig. 1)— have the remarkable property of possessing sufficient structural degrees of freedom *to make all bond angles exactly tetrahedral and all bond lengths equal to any arbitrary values* (in particular, "ideal" tetrahedral bond lengths). These two ordered bulk structures are hence *intrinsically strain free,* i.e., $\Delta E_{\text{ms}}^{(\alpha)}=0$. This topological argument alone shows that microscopic strain favors the ordered ZB and RH phases over both disordered and other ordered (microscopically strained) phases. This is so because disordered phases have a *distribution* of bond lengths and angles over numerous permissible configurations,[12,16] and hence $\Delta E_{\text{ms}}^{(D)} > 0$. Calculation of this quantity from optimization of a Keating-type[20] elastic valence force-field[16] model indeed shows larger positive values, e.g., $\Delta E_{\text{ms}}^{(D)}[\text{Si}_{0.5}\text{Ge}_{0.5}]=+9$ meV/atom (close to the observed[9,10] $\Delta H^{(D)}$ value of $+7$ meV/atom) and $\Delta E_{\text{ms}}^{(D)}[\text{Si}_{0.5}\text{C}_{0.5}]=+700$ meV/atom.

The question whether the two unconstrained phases are absolutely stable $[\Delta H^{(\alpha)}<0]$ or only metastable (i.e., unstable, but stabler than the disordered phase, or $\Delta H^{(D)} > \Delta H^{(\alpha)} > 0$) requires an explicit calculation of chemical interaction energies $\Delta E_{\text{chem}}^{(\alpha)}$. Figure 1 shows the self-consistently calculated[13] variation in cohesive energies with lattice constants for the diamond and zinc-blende structures of C, Si, Ge, SiC, and SiGe. For each set of systems AA, BB, and AB, we define the excess function $\Delta F_{AB}=F_{AB}-\frac{1}{2}(F_{AA}+F_{BB})$ measuring the deviation of the physical property F (bond energies, lattice constants a and bulk moduli B) in the heteropolar system from its average value in its homopolar constituents. [For $F=$ enthalpy, we obtain Eqs. (1) and (2).] Figure 1 shows the following: (i) Whereas the Si—C bond is stabler than the average of the Si—Si and C—C bonds ($\Delta H^{(\text{ZB})}[\text{SiC}]=\Delta E_{\text{chem}}^{(\text{ZB})}[\text{SiC}]=-0.33$ eV/atom, compared with the observed[21] value of -0.34 eV/atom) the opposite is true for the Si—Ge bond, for which we find small, but *consistently positive,* values $\Delta H^{(\text{ZB})}[\text{SiGe}]=+9$ meV/atom and[22] $\Delta H^{(\text{RH})}[\text{SiGe}]=+7$ meV/atom. (The approximate $\frac{3}{4}$ ratio between these latter two values reflects the relative number of Si—Ge bonds per formula unit in the RH and ZB structure.) We obtained similar positive values[22] for other LL SiGe structures, i.e., $+5$ meV/atom for chalcopyritelike SiGe_3 and $+23$ meV/atom for Cu_3Au-like Si_5Ge_3. (ii) The Si—Ge bond is stiffer than the average of Si—Si and Ge—Ge bonds [i.e., $\Delta B_{\text{SiGe}} > 0.5(\Delta B_{\text{Si}}+\Delta B_{\text{Ge}})$], and (iii) whereas SiGe obeys Végard's rule ($\Delta a_{\text{SiGe}}\simeq 0$ for $F=$ lattice constant), SiC shows a negative deviation ($\Delta a_{\text{SiC}}=-0.13$ Å, compared with the observed[21] Δa_{SiC} value of -0.14 Å). The reason for these fundamental differences between Si—C *vs* Si—Ge bonds is apparent from the calculated charge densities (Fig. 2): Whereas in SiC [Fig. 2(a)] the direction of charge transfer mandated by the atomic electronegativities (Si → C) coincides with increased cohesion (diamond having a larger cohesive energy than Si, see Fig. 1), in SiGe [Fig. 2(b)] there is little change in the charge density around the atoms (i.e., no charge transfer). Furthermore, the "healing" of the Ge-Ge and Si-Si charge discontinuity in the bond region of SiGe leads to a repulsive contribution[8] to ΔH.

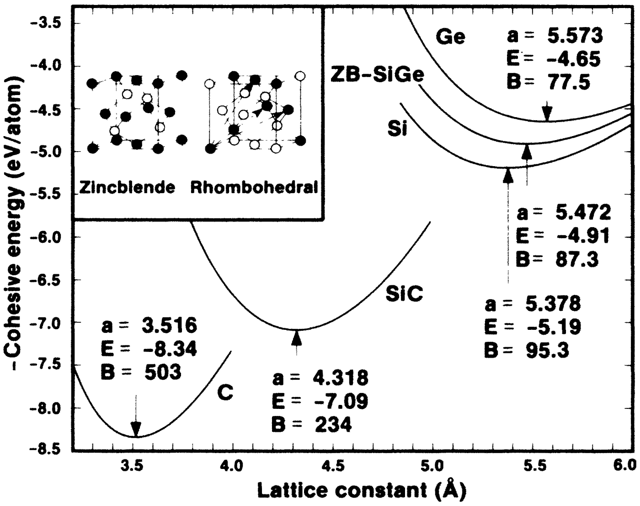

FIG. 1. Calculated ground-state properties of diamondlike C, Si, and Ge and zinc-blende SiC and SiGe, showing equilibrium lattice constants a (in angstroms), bulk moduli B (in gigapascals), and negative of the cohesive energy E (in electronvolts/atom). An energy cutoff for the plane-wave expansion of 50 Ry was used for C and SiC, and 24 Ry was used for Si, SiGe, and Ge.

The bulk forms of SiC and SiGe alloys exemplify two general classes of stabilities: (i) "type-I ordering" (e.g., in SiC), where $\Delta H^{(\alpha)}[A_mB_n]<0$ makes α a thermodynamically stable phase in some temperature and composition range as a result of a combination of a strain-reducing structure $[\Delta E_{\text{ms}}^{(\alpha)} < \Delta E_{\text{ms}}^{(D)}]$ and a stabilizing charge redistribution $[\Delta E_{\text{chem}}^{(\alpha)} < -\Delta E_{\text{ms}}^{(\alpha)}]$; (ii) "type-II ordering" (e.g., low-temperature bulk ZB or RH SiGe) where $\Delta H^{(\alpha)}[A_mB_n]>0$ renders the system unstable towards decomposition at sufficiently low temperatures, but for which the fact that $\Delta H^{(D)} > \Delta H^{(\alpha)}$ and that activation barriers exist for

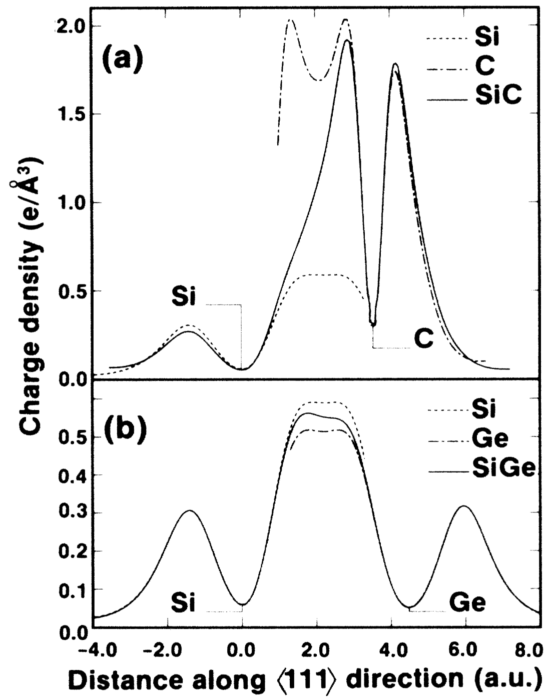

FIG. 2. The charge densities of C, SiC, Si, SiGe, and Ge are compared along the bond direction. For clarity of display, the densities of C, Si, and Ge are shown only in the side of the bond where the atomic positions coincide.

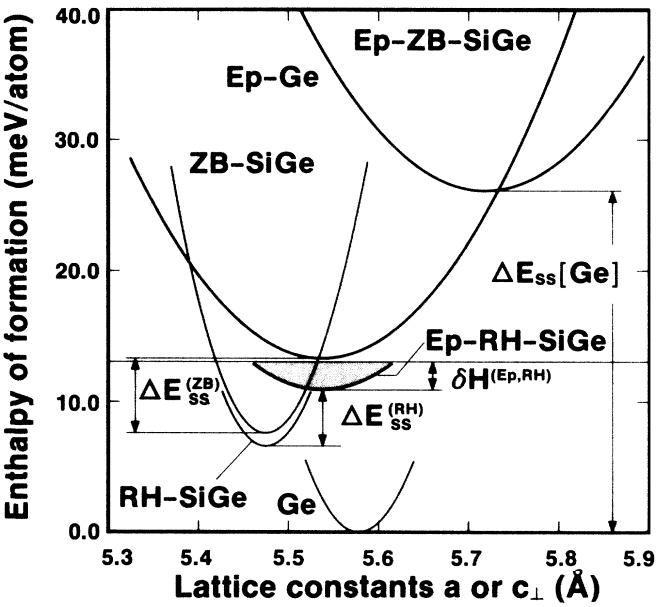

FIG. 3. Energy of bulk Ge, zinc-blende (ZB) SiGe, and rhombohedral (RH) SiGe as functions of the lattice constant a, and for epitaxially (Ep) confined (to $a_{\mathrm{Si}} = 5.387$ Å) ZB and RH SiGe as a function of $c_\perp$. For each curve the zero of the energy scale was adjusted such that the minimum of the curve gives the enthalpy of formation. ΔE_{ss} denotes the substrate strain; the shaded area denotes the *negative* enthalpy δh of Ep RH SiGe. Energy cutoff of 18 Ry was used.

decomposition (posed, for example, by the lattice mismatch between the alloy and its free components[23]) permit the metastable ordering to be observed on laboratory (if not geological) time scales. We now show that an additional, "type-III ordering" can occur in *epitaxial* systems, if the ranges of temperature and composition necessary for ordering can be affected by the presence of a substrate.

We model a thin pseudomorphic epitaxial semiconductor alloy grown on a substrate (s) with lattice constant a_s, by restricting the alloy lattice constant $a_\parallel$ parallel to the substrate to be equal to a_s and optimizing the self-consistently calculated total energy through variations of the remaining structural degrees of freedom (including the lattice constant $c_\perp$ in the direction perpendicular to the substrate). The enthalpy of formation $\Delta H^{(\mathrm{Ep},\alpha)}$ of an epitaxial (Ep) form of phase α is analogous to that of the bulk form [Eq. (1)] except that $H^{(\alpha)}[A_mB_n]$ of Eq. (1) is replaced by its epitaxially confined value $H^{(\alpha)}[A_mB_n, a_\parallel = a_s]$ (where all the structural parameters not specified in these expressions are taken at their relaxed values). $\Delta H^{(\mathrm{Ep},\alpha)}$ can differ from the enthalpy $\Delta H^{(\alpha)}$ of the bulk alloy by the substrate strain (ss) energy

$$\Delta E_{\mathrm{ss}}^{(\alpha)} = H^{(\mathrm{Ep},\alpha)}[A_mB_n, a_\parallel = a_s] - H^{(\alpha)}[A_mB_n]. \quad (4)$$

This energy can be thought of[23] as the elastic work performed in straining the alloy to match the substrate, and is hence proportional both to the square of the initial alloy-substrate lattice mismatch $\delta a_\parallel$ and to the effective planar elastic constant[23] $\sigma^{(\alpha)}$. Figure 3 shows our calculated enthalpies of the Ge and SiGe lattices matched to Si. First, note that the larger $\delta a_\parallel$ of Ge relative to Si results in a larger substrate strain for Ge on Si ($\Delta E_{\mathrm{ss}}[\mathrm{Ge}]$) than for SiGe on Si ($\Delta E_s^{(\mathrm{ZB})}[\mathrm{SiGe}]$) for Si on Si we have $\Delta E_{\mathrm{ss}}[\mathrm{Si}] = 0$). This suggests that the *effective* enthalpy of formation of an epitaxial film (relative to lattice-matched products)

$$\delta H^{(\mathrm{Ep},\alpha)} = H^{(\mathrm{Ep},\alpha)}[A_mB_n, a_\parallel = a_s] - mH[A, a_\parallel = a_s] - nH[B, a_\parallel = a_s] \quad (5)$$

can be negative (shaded areas in Fig. 3) *even if the bulk alloy is metastable.* Second, Fig. 3 shows that despite similar $\delta a_\parallel$'s for the ZB and RH phases of SiGe, $\Delta E_{\mathrm{ss}}^{(\mathrm{RH})} < \Delta E_{\mathrm{ss}}^{(\mathrm{ZB})}$, i.e., *the stability of the RH phase is increased under epitaxial strain* (type-III ordering). This is consistent with the observation[3] that the lowering of substrate strain induced by Ge out-diffusion from SiGe during prolonged annealing leads to a reduced ordering (we note, however, that the same observation can be also explained by the fact that composition changes after the Ge diffusion). We have also optimized $\Delta H^{(\mathrm{Ep},\alpha)}[\mathrm{SiGe}, a_{\parallel} = a_{\mathrm{Si}}]$ for $\alpha = \mathrm{ZB}$ and RH using a Keating valence force field,[20] obtaining practically the same $\delta a_{\parallel}$ for both phases. We find that if the *ab initio* calculated SiGe force constants are used in this optimization, the resulting difference in elastic strain energy $\Delta E_{\mathrm{ss}}^{(\mathrm{RH})} - \Delta E_{\mathrm{ss}}^{(\mathrm{ZB})}$ is essentially identical to those shown in Fig. 3, favoring RH over ZB, whereas if we replace these force constants by the averages over Si and Ge, the two epitaxial phases have the same enthalpies. Hence, the larger proportion of Si—Ge bonds in the RH phase and the excess stiffness of this bond relative to its homopolar average (Fig. 1) lead to the preferred epitaxial stability of the RH phase. This illustrates how a substrate imposes a natural selection of species, preferring the "fittest" [better $\delta a_{\parallel}$ and $\sigma^{(\alpha)}$] over the others. A similar calculation for $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloys gives $\Delta E_{\mathrm{ss}} < 0.1$ meV/atom, showing that the substrate strain has a negligible effect on ordering for this case.

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[19] To construct the 32 LL structures for adamantine A_mB_n we start from the fcc lattice, and its eight ordered LL superstructures. We then form ordered adamantine superstructures by combining (i) two fcc sublattices (giving zinc blende), (ii) one fcc sublattice with one of the eight LL structures (giving twelve structures), and (iii) identical ordered LL structures in both sublattices (giving nineteen structures). Notice that the sublattices can differ in composition, and relative position (but not orientation).

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[22] The rhombohedral geometry has four independent structural parameters and a full determination of the Born-Oppenheimer surface is hence time consuming. A partial optimization yielded readily the structure identical to what a geometric construction of a strain-free model gives. Because of its extremal character, we obtain a good value for the minimum of the total energy.

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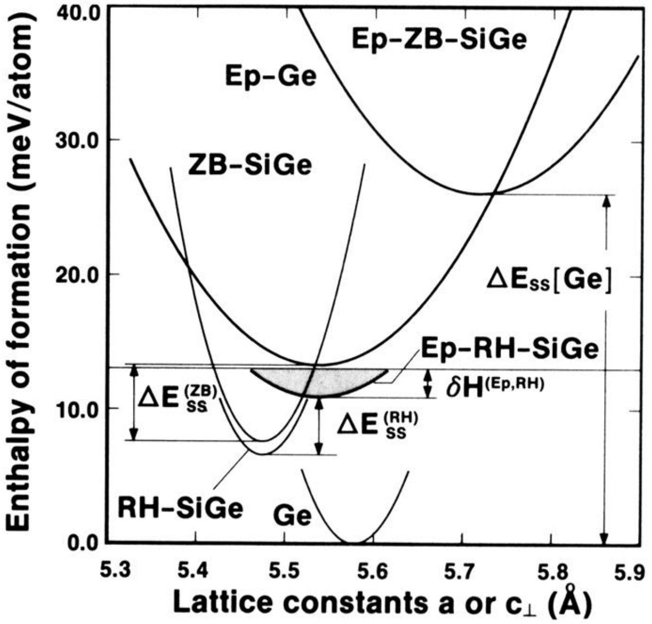

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