

THEORY OF ORDERING IN SEMICONDUCTOR ALLOYS

INVITED PAPER

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ABSTRACT

Ordered phases have been recently predicted and observed in alloys of tetrahedrally bonded semiconductors. Using first-principles local-density total energy calculations, we study the structure and stability of both ordered and disordered phases of semiconductor alloys. Our calculations show that ordered alloys are stabilized by the reduction of microscopic strain and chemical interactions. If the alloys are grown on a substrate, an additional elastic energy term affects their relative stability.

Introduction

Alloys of tetrahedrally bonded semiconductors (e.g. $\text{Al}_x\text{Ga}_{1-x}\text{As}$, $\text{Si}_x\text{Ge}_{1-x}$, or $\text{GaAs}_x\text{P}_{1-x}$) are extensively used in electronic and opto-electronic devices using heterostructures and superlattices, like semiconductor lasers or infrared detectors, where the availability of a continuous range of band gaps (or of any other property) is extremely useful. These semiconductor alloys were believed to exist only in a *disordered* phase, until the recent surprising prediction¹ and observation² of the existence of *ordered* phases showed that their phase diagram is more complicated than at first suspected.

Previous theories^{3,4} of the stability of semiconductor alloys justified the lack of observation of ordered phases by assuming that isovalent atoms differed essentially only in their size. The strain due to the accommodation of atoms of different size gave a *positive* contribution to the enthalpy of mixing of the alloy $\Delta H^{strain} = N\Omega x(1-x) \geq 0$, where N is the number of atoms in the mixed (sub-)lattice, and Ω is the interaction parameter that scales with the square of the lattice mismatch between the end-point compounds. When we combine this form of the enthalpy with the entropy of mixing of a random distribution of atoms $\Delta S = -kN(x \ln x + (1-x) \ln(1-x))$, we obtain a regular solution thermodynamic model. According to the phase diagram calculated in the regular solution model with a positive definite enthalpy of mixing, the alloy disproportionates at sufficiently low temperatures, forms a solid solution at higher temperatures, and does not have any ordered phases.

The strain model should not be expected to hold if the chemical difference between the atoms in the alloy is significant, and as we will show later, it is not relevant for ordered alloys. A notable example of an ordered isovalent "alloy" is the well known compound SiC (isoelectronic with SiGe), which is observed in several ordered structures with different hexagonal stacking sequences, including the zincblende and wurtzite structures. However C is a first row atom that can be expected to have a chemical behaviour distinct from the isovalent atoms from the second and higher rows of the periodic table. Order-disorder transitions between the chalcopyrite and zincblende

structures are well known for ternary semiconductor compounds⁵ like CuInSe_2 , but in this case the ordering occurs between non-isovalent and therefore strongly different atoms. We notice that order-disorder transitions have also been observed⁶ for isovalent atoms in the *non-tetrahedrally* bonded CdZn_2P_2 semiconductor, but in this case even the disordered alloy has already three crystallographically distinct cation sites.

The observation of ordering in isovalent tetrahedrally bonded semiconductors is very recent (SiC excepted), but there are already several known ordered semiconductor alloys^{2,7-10} (Table I), including $\text{IV}^{\text{A}}\text{IV}^{\text{B}}$, $\text{III}^{\text{A}}\text{III}^{\text{B}}\text{V}$, and $\text{III V}^{\text{A}}\text{V}^{\text{B}}$ alloys, grown by different methods, and having both small and large lattice mismatches. This variety may indicate that ordering is a general feature of semiconductor alloys, although it is certainly difficult to obtain. The difficulty in the growth of an ordered semiconductor alloy is due to its small diffusion rate: at high temperatures the disordered solid solution, with its large entropy of mixing, is the equilibrium thermodynamic phase of the alloy, while at low temperatures, where the thermodynamically stable state is either the ordered phase or the segregated phase, the diffusion rate could be so slow that the alloy may be inhibited to reach its thermodynamic equilibrium within the laboratory time scale. The temperature range where ordering can be obtained by annealing could be extremely narrow, or even nonexistent. During growth however, the surface mobility could be sufficient for the ordered alloy to form, as long as it is possible to grow it at temperatures lower than the ordering temperature. Another possibility to significantly increase the diffusion rates is the use of impurities with the same effects¹¹ as the Zn and Si impurities in $\text{Al}_{1-x}\text{Ga}_x\text{As}$.

Table I

Experimentally observed ordered semiconductor alloys.

Alloy	Structure	Growth method	Temperature of growth C	Remarks
$\text{AlGaAs}_2^{\text{a}}$	CuAu-I	VPE,MBE	~700	X-ray diffraction annealed
$\text{AlGaAs}_2^{\text{b}}$	CuAu-I	LPE		
SiGe^{c}	CuPt	MBE	~550	
$\text{Ga}_2\text{AsSb}^{\text{d}}$	CuAu-I	VPE	~600	
$\text{Ga}_2\text{AsSb}^{\text{d}}$	Chalcopyrite	VPE	~600	
$\text{In}_3\text{GaAs}_4^{\text{e}}$ (?)	Famatinite	LPE	~630	

^a Ref. 1; ^b Ref. 8; ^c Ref. 7; ^d Ref. 9; ^e Ref. 10

Theoretical framework

Our theory of ordering in semiconductor alloys^{1,12,13} is based on extensive total energy pseudopotential local density calculations with a plane wave basis set¹⁴.

For ordered alloys we minimize the total energy with respect to the structural parameters (e.g. lattice constant) obtaining both the structure parameters at equilibrium, and the binding energy. The enthalpy of formation of an $A_nB_mC_{n+m}$ ordered (O) phase (at 0 temperature and pressure) is then given by

$$\Delta H_{A_nB_mC_{n+m}}^O = E_{A_nB_mC_{n+m}}^{eq} - (nE_{AC}^{eq} + mE_{BC}^{eq}), \quad (1)$$

where E_{α}^{eq} is the binding energy at equilibrium (eq) of the phase α . To select from the infinite number of possible ordered phases of adamantine compounds (we will restrict ourselves to the tetrahedral structures with two fcc sublattices, that is, we will not consider compounds with different hexagonal stacking like wurtzite) the few that are more likely to be the most stable, we use the Landau-Lifshitz theory of structural phase transitions¹⁵. 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 order¹⁵, (ii) all (and no others) are stable with respect to antiphase boundaries¹⁶, and (iii) they can exist over a wide concentration range¹⁶. This last property is important if we want to observe ordering in a non-stoichiometric alloy. Figure 1 shows four (out of eight) of the Landau-Lifshitz structures for a pseudobinary alloy, as well as the zincblende disordered phase. It is remarkable that all the observed ordered alloys listed in table I are Landau-Lifshitz structures (see fig. 1).

For the disordered structures we use a model where the properties of the disordered alloys are obtained as an average over the same properties in the ordered structures^{1,17}. We consider that in a pseudobinary alloy $A_xB_{1-x}C$ the five possible distributions $A_{4-n}B_n$ of atoms A and B around an atom C (the A and B atoms are, of course, always surrounded by four C atoms) exist for each composition x with a random probability $P^n(x) = \binom{4}{n} x^n (1-x)^{4-n}$, and that the binding energy of the disordered (D) alloy at composition x is obtained by minimizing an average over the energies of ordered compounds¹,

$$E^D(x) = \min_a \frac{1}{4} \sum_{n=0}^4 P^n(x) E_{A_{4-n}B_nC_4}(a). \quad (2)$$

Here $E(a)$ is the energy of the reference ordered compounds (with a unique distribution of A and B atoms around every C atom), at a given lattice constant a , but minimized with respect to all other structural parameters. The minimization of equation (2) gives also the lattice constant of the disordered alloy, $a(x)$ and can be used to calculate the enthalpy of formation of the disordered alloy,

$$\Delta H^D(x) = E^D(x) - (xE_{AC}^{eq} + (1-x)E_{BC}^{eq}). \quad (3)$$

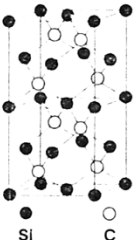
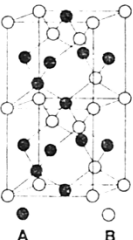
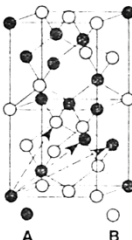
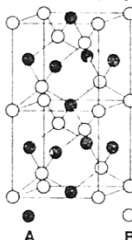
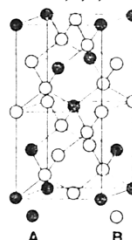
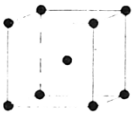
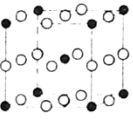
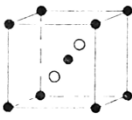
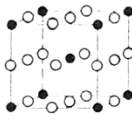
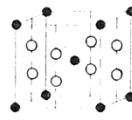
	Zincblende (Sphalerite) $n = 0,4; AB$	$n = 1,3; AB$	$n = 1,3; AB$	$n = 0,1,3,4; A_3B_5$	$n = 0,2,4; AB_3$
					
	Si C	A B	A B	A B	A B
	Cubic SiC-type				
Bravais Lattice:	Face centered cubic	Trigonal	Trigonal	Simple cubic	Centered Tetragonal
Space Group:	$F\bar{4}3m, T_d^2, B3$	$R3m, C_3^2v$	$R\bar{3}m, D_{3d}^5$	$P43m, T_d^2$	$I\bar{4}2d; D_{2d}^{12}$
Positions:	A: 4 a $\bar{4}3m$ B: 4 c $\bar{4}3m$	A: 1 a 3m A: 3 b m B: 1 a 3m B: 3 b m	A: 2 c 3m B: 2 c 3m	A: 3 c $\bar{4}2m$ B: 1 a $\bar{4}3m$ B: 4 e 3m	A: 4 a $\bar{4}$ B: 4 b $\bar{4}$ B: 8 d 2
	FCC, FCC	Cu_3Au, Cu_3Au	$CuPt, CuPt$	Cu_3Au, FCC	"Chalcopyrite", FCC
Diffraction Pattern:					
	● Main ○ Superlattice				

Figure 1

Four possible ordered structures (out of eight) and the zincblende disordered structure of a semiconductor alloy $A_{1-x}b_xC$ or $AB_{1-x}C_x$ are shown in the top of the figure. Structural information (space group and atomic positions according to the International Tables for Crystallography) is given in detail, and the diffraction pattern is shown. We also indicate if an artificially grown superlattice has the same structure as these phases, e.g. if one alternates the growth of one AC layer, with one BC layer in the (0,0,1) orientation, i.e. a monolayer superlattice - (1,1), one obtains the CuAu-I ordered structure.

Microscopic strain

It is not possible, in general, to accommodate two different bond lengths in a compound (e.g. the Ga-As and the In-As bond lengths in $Ga_xIn_{1-x}As$), and at the same time keep all the bond angles at their tetrahedral values. A compromise must be obtained and the deviations from the ideal values of the bond lengths and bond angles have an energy cost that we call^{1,12,13} the microscopic strain (ms). Considering the composition dependence of the two bond lengths in an alloy $R_{AC}(x)$ and $R_{BC}(x)$, (to avoid complicated notations we will, for the moment, assume that we have

a pseudobinary $A_xB_{1-x}C$ alloy, the extension to other cases being trivial), two limiting possibilities were recognized quite early. First, Bragg's and Pauling's (P) notions that atomic radii are approximately conserved quantities¹⁸ (and are hence transferable) in different chemical environments suggested that the bond lengths are composition independent and equal to their ideal values, $R_{AC}^P = d_{AC}^0$ and $R_{BC}^P = d_{BC}^0$, of their end-point compounds. On the other hand, Vegard's discovery¹⁹ that the alloy lattice constant depends linearly on the composition $a(x) = xa_{AC} + (1-x)a_{BC}$, has led many workers in the field, in particular those using the Virtual Crystal Approximation (VCA), to assume that since the bond lengths in the pure zincblende crystal are proportional to the lattice constant, $d_{AC}^0 = \frac{\sqrt{3}}{4}a_{AC}$, the same would be true for the alloy, obtaining identical bond lengths, $R_{AC}^{VCA}(x) = R_{BC}^{VCA}(x) = \frac{\sqrt{3}}{4}a(x)$. We find it useful to express the true average bond length in the alloy in terms of a dimensionless relaxation parameter $\epsilon(x)$, which is equal to 1 in the Pauling limit and equal to 0 in the VCA limit, and is defined by²⁰

$$\bar{R}_{AC}(x) = \epsilon(x)R_{AC}^P(x) + (1 - \epsilon(x))R_{AC}^{VCA}(x). \quad (4)$$

The bond lengths calculated¹ for ordered $Ga_nIn_{4-n}P_4$ and for²¹ $Ga_nIn_{4-n}As_4$ are almost independent of the particular structure or stoichiometry (Fig. 2), as Bragg and Pauling would predict, $\epsilon \simeq 1$. To our knowledge, there is no experimental data for ordered alloys that could confirm our prediction. For the disordered alloy we calculate the average bond lengths by averaging over ordered structures using a method similar to Eq. 2. First for each reference ordered compound $A_nB_{4-n}C_4$ we calculate the bond lengths $R_{AC}^n(a)$ as a function of lattice constant and then we average using the known relationship between bond length and composition¹⁷,

$$\bar{R}_{AC}(x) = \sum_{n=0}^4 (4-n)P^n(x)R_{AC}^n(a(x)), \quad (5)$$

where the factor $(4-n)$ is just the number of AC bonds in unit n . The calculated results for $Ga_xIn_{1-x}P$ (Fig. 2) show a small but non negligible deviation from the Pauling values with $\epsilon(x) \simeq 0.8$. Similar values, $0.65 \lesssim \epsilon(x) \lesssim 0.85$ have been obtained for several *disordered* semiconductor alloys both by Extended X-ray Absorption Fine Structure^{17,22} (EXAFS), and by empirical theories^{17,20,23}.

Inspection of Fig. 2 tells us immediately that the microscopic strain contribution to the enthalpy of mixing is larger for the disordered phase than for the ordered phases, $\Delta H_{ms}^D(x) \geq \Delta H_{ms}^O(x)$. The actual numerical values calculated for $Ga_{0.5}In_{0.5}P$ are $\Delta H_{ms}^D(0.5) = 13\text{meV/atom}$ and $\Delta H_{ms}^{Chalc.} = 2\text{meV/atom}$, (here Chalc. denotes chalcopyrite ordering). If the two atoms, however, have very similar sizes as in $Ga_xAl_{1-x}As$, then the microscopic strain is negligible, $\Delta H_{ms} = 0$. In the binary systems SiC and SiGe there are two very special Landau-Lifshitz structures: the zincblende and one of the Cu-Pt orderings that have exactly zero strain. The other ordered structures and the disordered diamond structure are, of course, strained²⁴. Hence the existence of SiC despite the large lattice mismatch between Si and Diamond C (SiC has only one kind of bond which can take any desired length by adjusting the lattice constant of the crystal).

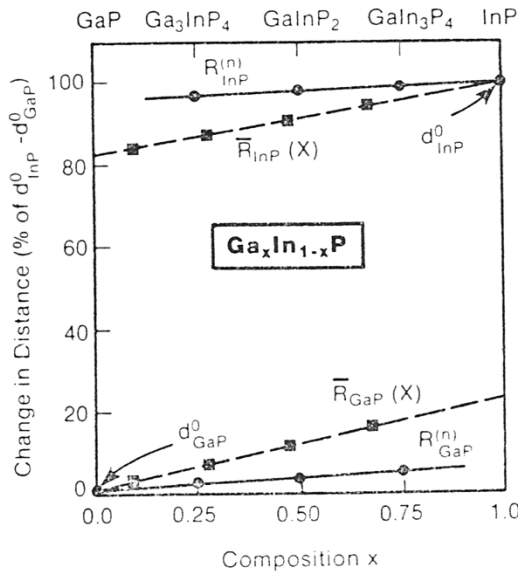


Figure 2

Percent change in the nearest-neighbour bond length in ordered phases (black dots) are compared with the change in random alloys (broken line).

Chemical interaction

The microscopic strain is not the whole contribution to the enthalpy of formation of semiconductor alloys. We define¹ the chemical interaction (Ch) contribution to the enthalpy of formation as the difference between the total enthalpy of formation and its strain contribution. For SiC which has zero strain, its large enthalpy of formation is exclusively of chemical origin¹², $\Delta H_{\text{SiC}} = \Delta H_{\text{SiC}}^{\text{Ch}} = -0.33$ eV/atom. This large value is due to the charge transfer¹² from Si to C when the Si-C bond is formed. For Zincblende SiGe, which also has zero strain, the charge rearrangement is different¹², giving a small positive enthalpy of formation¹² of $\Delta H_{\text{SiGe}}^{\text{Ch}} = 7$ meV/atom, whereas for GaInP₂, a strained compound, we find¹ a negative chemical contribution to the enthalpy of formation, $\Delta H_{\text{GaInP}_2}^{\text{Ch}} = -17$ meV/atom.

The energy dependence on the bond length (Eq. 2) is mainly a strain effect, and thus when the chemical energy of a disordered alloy is calculated a value similar to the the chemical energies of the ordered phases is found. It has been recently claimed, using a Madelung type of model²⁵, that the charge fluctuations in the disordered phases should give a large positive contribution to the enthalpy of mixing that is not included in equation 2. The model does not treat the screening self-consistently and it should be checked, if it can explain the experimental scaling of the enthalpies of mixing, deduced from the solidus-liquidus lines for the disordered phase, with the square of lattice mismatch. The microscopic strain energy, which scales with the square of the lattice mismatch, gives the biggest contribution to the enthalpy of mixing of *disordered*

semiconductor alloys, explaining why theories that consider only this contribution^{3,4} are successful in predicting the experimental values for the disordered phase.

The chemical contribution to the the enthalpy of mixing can have either a positive or a negative sign in contrast to the strain energy that is always positive. The full enthalpy of mixing is the sum of the strain and chemical parts

$$\Delta H = \Delta H_{ms} + \Delta H_{Ch}. \quad (6)$$

When the enthalpy of mixing of an ordered alloy is negative like in SiC or GaInP₂, then the ordered phase is stable below an ordering temperature $T^O \sim (\Delta H^D - \Delta H^O) / \Delta S^D$, where for an estimation of the mixing entropy of the disordered phase, ΔS^D , we can use the value for the random alloy. More accurate ordering temperatures can be obtained by using a better thermodynamic model for the entropy of mixing^{26,27}, in particular combining total energy calculations with the cluster variational method²⁷. When the enthalpy of formation of the ordered phase is positive like in the case of SiGe then the segregated phase is the stable phase below the segregation temperature $T^S \sim \Delta H^D / \Delta S^D$.

Epitaxial strain

In a pseudomorphic epitaxial (Ep) growth of a sufficiently thin layer the lattice constant in the two directions parallel to the interface is the same in the layer and in the substrate. This constraint modifies the stability of the layer, adding a substrate strain energy (ss), and as pointed out by Ourmazd and Bean⁷ in their experiments with SiGe epitaxial layers, the epitaxial strain can drive and stabilize the ordering in a semiconductor alloy. We will illustrate this point with our calculations for SiGe. There are only two adamantine Landau-Lifshitz ordered structures that have zero strain: the zincblende (ZB), observed in SiC, and the Rhombohedral (RH) CuPt ordering observed in SiGe. All other structures²⁴ are discriminated against by the microscopic strain energy. The difference between the two structures is that zincblende has only one kind of bond between different atoms whereas the rhombohedral phase has several kinds of bonds, including 25 % between like atoms. Therefore, when the formation of bonds between different atoms is favored, like in SiC, the ordered zincblende phase is the most stable of the two, whereas when the formation of bonds between different atoms is unfavorable like in SiGe, the rhombohedral structure is the less unstable, the stable phase being the dissociated form (fig. 3). When we consider SiGe epitaxial on Si we should consider two references for the enthalpy of formation: (i) the bulk Si and Ge are used (the reference we used up to now), in this case the epitaxial is even more unstable by the epitaxial strain energy ΔE_{ss} (fig. 3); (ii) the epitaxial Si and Ge, in this case Ge has a larger epitaxial strain energy than the alloy and the new the reference line for the measure of epitaxial enthalpies moves up (fig. 3) sufficiently to make the ordered rhombohedral alloy stable by δH . The ordered SiGe alloy is thus metastable: it is stable with respect to epitaxial products of disproportionation but it is unstable with respect to diffusion into the substrate. We stress again that our calculations show that the stability of the rhombohedral phase with respect to the zincblende phase is due to the different number of bonds between identical atoms.

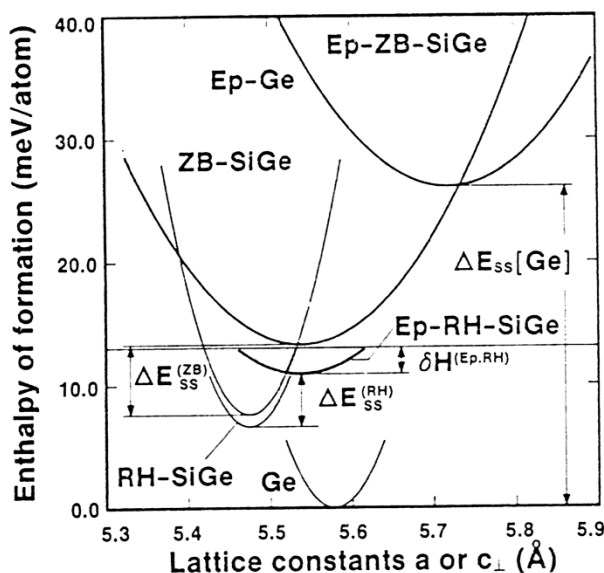


Figure 3

Energy of bulk Ge, zincblende (ZB) SiGe, and rhombohedral (RH) SiGe as function of the lattice constant a , and for epitaxially (Ep) confined (to $a_{\text{Si}} = 5.387\text{\AA}$) Ge, ZB SiGe and RH SiGe as a function of normal lattice constant 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. The shaded area accentuates the *negative* enthalpy δH for Ep RH SiGe.

Conclusions

We studied the ordering in semiconductor alloys with first principles total energy calculations. The ordering is driven by the reduction of the microscopic strain and by other chemical interactions (e.g. charge transfer) for the bulk alloys. For epitaxially grown alloys the influence of the epitaxial strain should be taken into account. The calculations are sufficiently sensitive to discriminate between the different possible orderings available to the alloy.

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