RAPID COMMUNICATIONS

The purpose of this Rapid Communications section is to provide accelerated publication of important new results in the fields regularly covered by Journal of Materials Research. Rapid Communications cannot exceed four printed pages in length, including space allowed for title, figures, tables, references, and an abstract limited to about 100 words.

Ordering and decomposition in semiconductor alloys

José Luís Martins[a] and Alex Zunger
Solar Energy Research Institute, Golden, Colorado 80401

(Received 31 December 1985; accepted 16 May 1986)

The stability of ordered semiconductor alloys has been studied, using total energy pseudopotential calculations. The ordered alloys are found to be stabilized with respect to disordered alloys via reduction of the internal strain and by chemical interactions. The Si–C and Si–Ge systems are used as illustrations, finding that ordered Si_xGe_{1-x} should be a metastable alloy, in agreement with experimental observations.

Alloys of tetrahedrally bonded semiconductors, e.g., $A_{1-x}B_xC$, have generally been grown in a disordered (D) phase.[1] Their enthalpy of mixing,

$$\Delta H^{(D)}(A_{1-x}B_xC) = H(A_{1-x}B_xC) - (1-x)H(AC) - xH(BC)$$

as calculated from the liquidus and solidus lines, was found to be positive in all cases.[1] Such alloys are nevertheless stable at high temperatures due to the large entropy of mixing. Recently[2] we have shown, based on a quantum mechanical calculation of ordered $Ga_nIn_mP_{n+m}$ alloys, that these semiconductor phases may be stable at low temperatures against disproportionation. Ordered phases of the $Al_xGa_{1-x}As$ alloy[3] and of the Si_xGe_{1-x} alloy[4] have been observed.

Concomitant with the empirical observation that all conventionally grown bulk semiconductor alloys are disordered, contemporary theories of structure and stability of semiconductor alloys[5–7] have tacitly postulated that the enthalpy of mixing ΔH is always positive, neglecting all possibly attractive terms (e.g., charge transfers). For instance, in the delta lattice parameter (DLP) model of Stringfellow[5] it is postulated that the enthalpy H of *any phase*, ordered or disordered, is a convex function of its lattice parameter, i.e., $H = (-K/a^p)$ (where K is an empirical constant and $p > 0$). Hence, according to this model *any phase* with a lattice parameter obeying approximately Vegard's law[8] will necessarily have a *positive* enthalpy of mixing, proportional to the square of the lattice mismatch Δa of the end-point compounds, or $\Delta H = 0.5p(p+1)x(1-x)K(\Delta a)^2/a^{p+2}$. For example, the large lattice mismatch between diamond and silicon $\Delta a = 1.86$ Å (or 41% of the average lattice constant) suggests in the DLP model that $\Delta H[\text{SiC}] \gg 0$, yet SiC exists as a very stable "alloy." Similarly, in Van Vechten's model,[6] positive optical bowing accompanying compound formation is interpreted as a (destabilizing) upward shift of the valence-band energies, leading to $\Delta H > 0$ for disordered compounds if their band gaps are reduced relative to their average. The same argumentation can be extended to ordered alloys if we define optical bowing by analogy. However, for SiC, $\frac{1}{2}[E_g(\text{Si}) + E(\text{C})] - E_g(\text{SiC}) > 0$, yet SiC is far stabler than silicon + diamond. All strain-minimizing models[1,7] (including the DLP[5]) necessarily lead to $\Delta H > 0$, as the strain energy is positive definite and chemical interactions are ignored.

In the case of crystalline SiC, although the lattice mismatch is enormous, and the optical bowing b is large (the band gap of SiC is 0.6 eV lower than the average of the band gaps of silicon and diamond, hence $b = 2.4$ eV), one finds a large negative value of the experimental enthalpy of formation,[9] $\Delta H = -15.7$ kcal/mol. An analysis of the structure of cubic SiC shows that all bond angles are exactly tetrahedral and the lattice constant is such that the Si–C bond length can have any value it chooses (e.g., the sum of tetrahedral radii), therefore, *there is no strain in cubic SiC*. In this case the strain energy models for the random alloy are not applicable, and the DLP model, which owes its success in describing the enthalpy of mixing of random alloys to the fact that it has the same scaling as the lattice mismatch in the strain models,[10] fails completely, predicting that $\Delta H = +33$ kcal/mol. *Absence* of strain cannot explain why SiC has a large negative enthalpy of formation; other *chemical* interactions[2] must be introduced. However, simplistic models of chemical interactions also fail if the strain energy is neglected. In fact, if one uses a Pauling-like model of bonding to predict the stability of an alloy by supposing that the enthalpy of mixing is $\Delta H = -D(\chi_I - \chi_{II})^2$, where χ_I and χ_{II} are the electronegativities of the end-point compounds and D is an empirical constant, one obtains $\Delta H < 0$ for *all* alloys with an electronegativity mismatch. This contradicts experiment.[1,11]

We conclude that a reliable model for the stability of alloys should include both strain *and* chemical effects. Our *ab-initio* quantum mechanical calculations of the stability of ordered semiconductor alloys include such effects (strain, electronegativity, etc.) and are per-

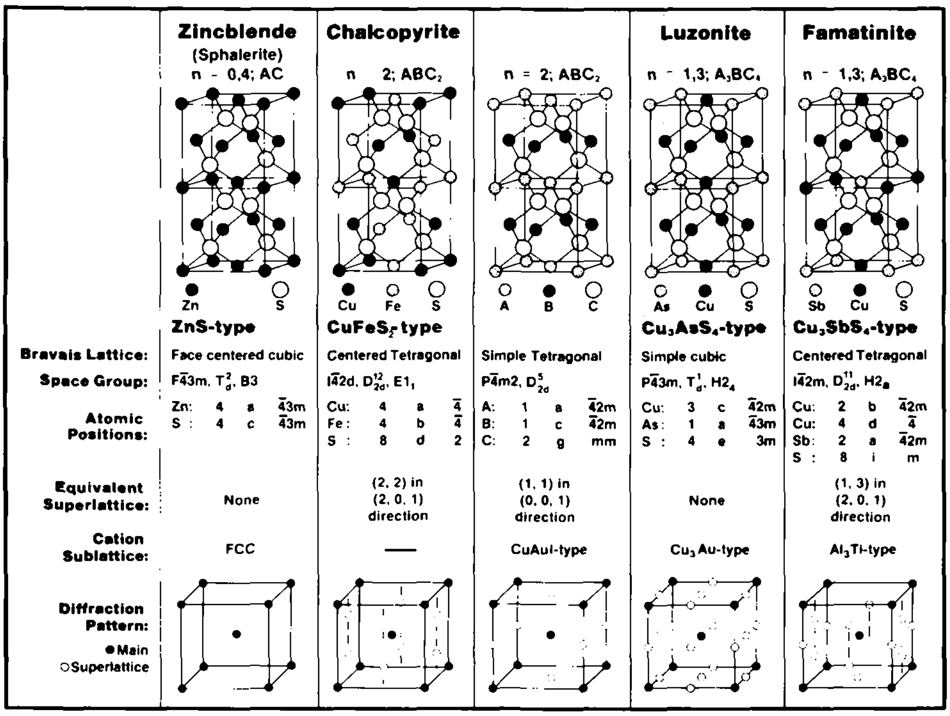
0003-6951/86/040523-04$01.75

formed within the pseudopotential local density formalism. Our calculation is based on a first-principles total energy minimization within the nonlocal pseudopotential representation of the local density formalism.[12] It uses an extensive plane wave basis set, including all plane waves with kinetic energies less than of 50 Ry for C and SiC, and 24 Ry for Si, Ge, and SiGe. For complex unit cells we use a cutoff of 18 or 12 Ry. Ten special **k** points are used for Brillouin zone integration for diamond or zincblende phases, and the **k** points obtained by folding two special **k** points of the fcc Brillouin zone are used in the other cases. The only empirical inputs are the atomic numbers and the crystal space groups.

For ordered (O) phases of alloys we first enumerate the tetrahedral adamantine space groups which are likely to occur using the Landau–Lifshitz theory.[13,14] We then calculate their total energy, including thereby both strain and chemical effects on the same basis, by performing a minimization of the total energy with respect to structural parameters.

The choice of ordered structures involves the use of the Landau–Lifshitz (LL) theory of structural phase transitions[13,14] which permits us to select a small number of structures with the following properties: (i) the order–disorder phase transition can be of second order[13] (but need not be). (ii) The ordered structures are stable with respect to antiphase boundaries.[14] (iii) They can occur over a wide concentration range in the phase diagram[14] (we notice that the observed ordered alloys[3,4] did not have the nominal stoichiometry of the phase). To find the LL structures in $A_{1-x}B_xC$ (or $AB_{1-x}C_x$) alloys we can ignore the sublattice with a single kind of atom (e.g., the C atom in $A_{1-x}B_xC$) and order the other sublattice as if it was a simple fcc structure. Figure 1 shows four (out of eight) of the structures obtained in this way, with information about their structural symmetries and diffraction patterns. These sets contain the three known structures of ternary semiconductors and one of an existing artificial structure (the CuAu-I structure[3]). In the case of the $A_{1-x}B_x$ semiconductor alloys (e.g., Si_xGe_{1-x}), the LL theory yields 32 structures with each sublattice occupied by one of the eight fcc patterns (enumerated by Khachaturyan[14]) plus the simple fcc lattice itself. According to Khachaturyan[14] both sublattices should have the same symmetry (e.g., the first three structures in Fig. 2, which include the observed CuPt ordering[4]), but we have also considered some structures where the symmetry of one sublattice is a subgroup of the symmetry of the other sublattice (e.g., the last two structures of Fig. 2). Notice that the two sublattices need not have the same composition and different structures can be built from the same pair of sublattices by changing their relative positions.

We have calculated the total energy of C, Si, Ge, SiC, and SiGe with a diamond or zincblende structure as a function of lattice constant; the results are summarized in Table I. Figure 3 shows the self-consistent electronic charge densities in the (110) plane, exhibiting a "camel's back" double-peak structure along the bond direction for diamond, but a flattening of the bond charge in Si and Ge, as the structures become less covalent and more metallic. Taking differences of the type $\rho(\mathrm{SiC}) - \frac{1}{2}[\rho(\mathrm{Si}) + \rho(\mathrm{C})]$, one observes a strong



	Zincblende (Sphalerite)	**Chalcopyrite**		**Luzonite**	**Famatinite**
	n = 0,4; AC	n = 2; ABC_2	n = 2; ABC_2	n = 1,3; A_3BC_4	n = 1,3; A_3BC_4
	● Zn ○ S	● Cu ○ Fe ○ S	○ A ● B ○ C	○ As ● Cu ○ S	○ Sb ● Cu ○ S
	ZnS-type	**$CuFeS_2$-type**		**Cu_3AsS_4-type**	**Cu_3SbS_4-type**
Bravais Lattice:	Face centered cubic	Centered Tetragonal	Simple Tetragonal	Simple cubic	Centered Tetragonal
Space Group:	$F\bar{4}3m$, T_d^2, B3	$I\bar{4}2d$, D_{2d}^{12}, $E1_1$	$P\bar{4}m2$, D_{2d}^5	$P\bar{4}3m$, T_d^1, $H2_4$	$I\bar{4}2m$, D_{2d}^{11}, $H2_a$
Atomic Positions:	Zn: 4 a $\bar{4}3m$ S : 4 c $\bar{4}3m$	Cu: 4 a $\bar{4}$ Fe : 4 b $\bar{4}$ S : 8 d 2	A: 1 a $\bar{4}2m$ B: 1 c $\bar{4}2m$ C: 2 g mm	Cu: 3 c $\bar{4}2m$ As : 1 a $\bar{4}3m$ S : 4 e 3m	Cu: 2 b $\bar{4}2m$ Cu: 4 d $\bar{4}$ Sb: 2 a $\bar{4}2m$ S : 8 i m
Equivalent Superlattice:	None	(2, 2) in (2, 0, 1) direction	(1, 1) in (0, 0, 1) direction	None	(1, 3) in (2, 0, 1) direction
Cation Sublattice:	FCC	—	CuAuI-type	Cu_3Au-type	Al_3Ti-type
Diffraction Pattern: ● Main ○ Superlattice					

FIG. 1. Four possible ordered structures and the zincblende structure of a semiconductor alloy $A_{1-x}B_xC$ or $AB_{1-x}C_x$. Structural information (space group, atomic positions according to the international Tables for Crystallography) is given in detail and the diffraction pattern is shown. We also indicate which artificially grown superlattice has the same structure as these phases, e.g., if one grows one layer of AC on top of one layer of BC in the (0,0,1) orientation [i.e. a (1,1) alternate monolayer superlattice] one obtains a "superlattice" whose structure is indistinguishable from that of the CuAu-I "compound."

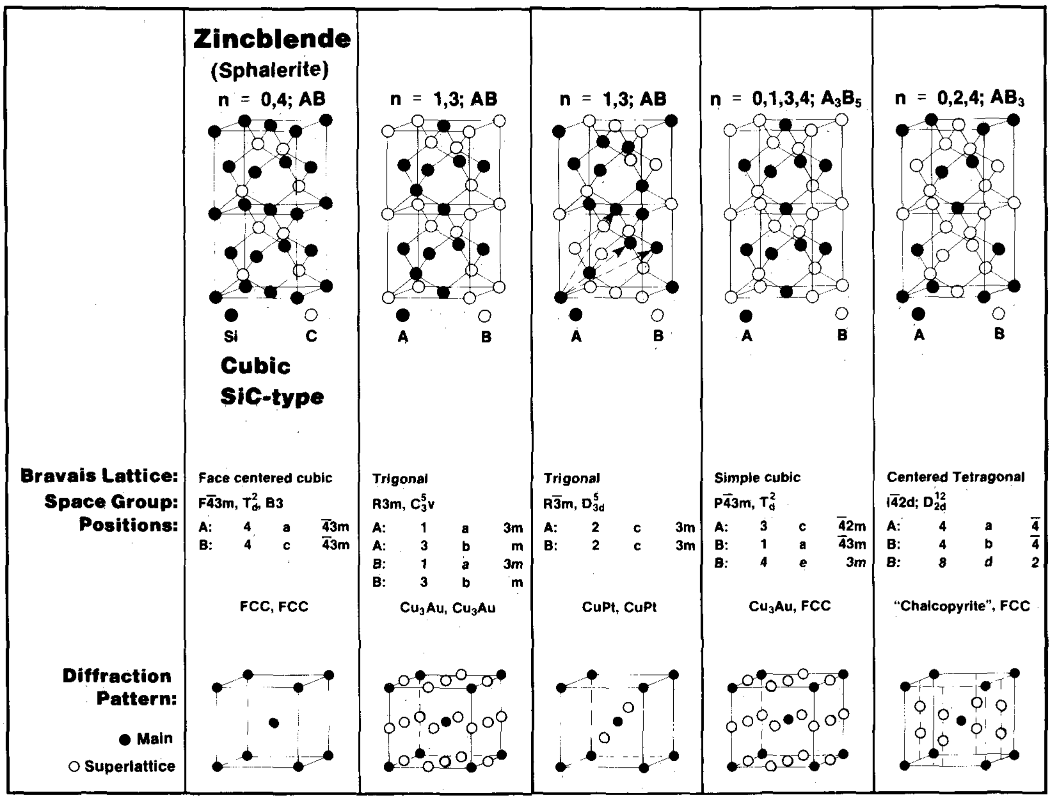


FIG. 2. Five possible ordered structures of a semiconductor alloy $A_{1-x}B_x$. Structural information is given in detail and the diffraction pattern is shown (see caption to Fig. 1).

charge redistribution: in SiC, charge is accumulated preferentially on the C atom (as indeed its higher electronegativity would suggest). Since the C–C bond has a higher cohesive energy than the Si–Si bond, this direction of charge transfer promises to stabilize SiC over Si + C, as indeed observed. (Note that since Ge is more electronegative than Si but has weaker bonds, the same argument suggests SiGe to be *less stable* than Si + Ge.) We also include in Table 1 results for three other structures of $Si_n Ge_m$ shown in Fig. 2. Cubic SiC is found to have a large *negative* enthalpy of formation $\Delta H^{(O)} = -15.2$ Kcal/mol, while zincblende SiGe has a very small *positive* enthalpy of formation $\Delta H^{(O)} = 0.41$ kcal/mol; similarly other $Si_n Ge_m$ structures have a small *positive* enthalpy of formation. The main reason that *disordered* alloys have $\Delta H^{(D)} > 0$ is that[2] a distribution of different bond lengths and angles is quenched into these samples. This then leads to a large strain energy, overwhelming chemical effects. Hence, when comparing ordered alloys to random alloys, in the latter we must add a strain energy term because of microscopic composition fluctuations. This strain energy is estimated[10] as $\Delta H^{str} = 0.4$ kcal/mol for the 50%–50% composition of SiGe, and 32 kcal/mole for "random" SiC. (These values were obtained with a valence force field model,[10] where only the *elastic* energy associated with straining bond lengths or bond angles is taken into account.) We conclude that *even when bulk ordered alloys are unstable with respect to disproportionation into pure compounds (i.e., $\Delta H^{(O)} > 0$), they are nevertheless stabler than the disor-*

TABLE I. Calculated and experimental lattice constants a, bulk moduli B, and enthalpies of formation ΔH of: diamond, cubic SiC, Si, zincblende SiGe, Ge, and two other Landau-Lifshitz phases $SiGe_3$ and Si_5Ge_3. Their structures are shown in Fig. 2.

Compound		a(Å)	B(GPa)	ΔH (kcal/mole)
C	calc.	3.516	503	···
(O_h^7)	expt.	3.566	442	···
SiC	calc.	4.318	234	− 15.2
(T_d^2)	expt.	4.358		− 15.7
Si	calc.	5.378	95.3	···
(O_h^7)	expt.	5.430	98	···
SiGe	calc.	5.472	87.3	+ 0.41
(T_d^2)				
SiGe	calc.			+ 0.32
(D_{3d}^5)				
Ge	calc.	5.573	77.5	···
(O_h^7)	expt.	5.657	76	···
$SiGe_3$	calc.			2×0.23
(D_{3d}^5)				
Si_5Ge_3	calc.			4×0.53
(T_d^2)				

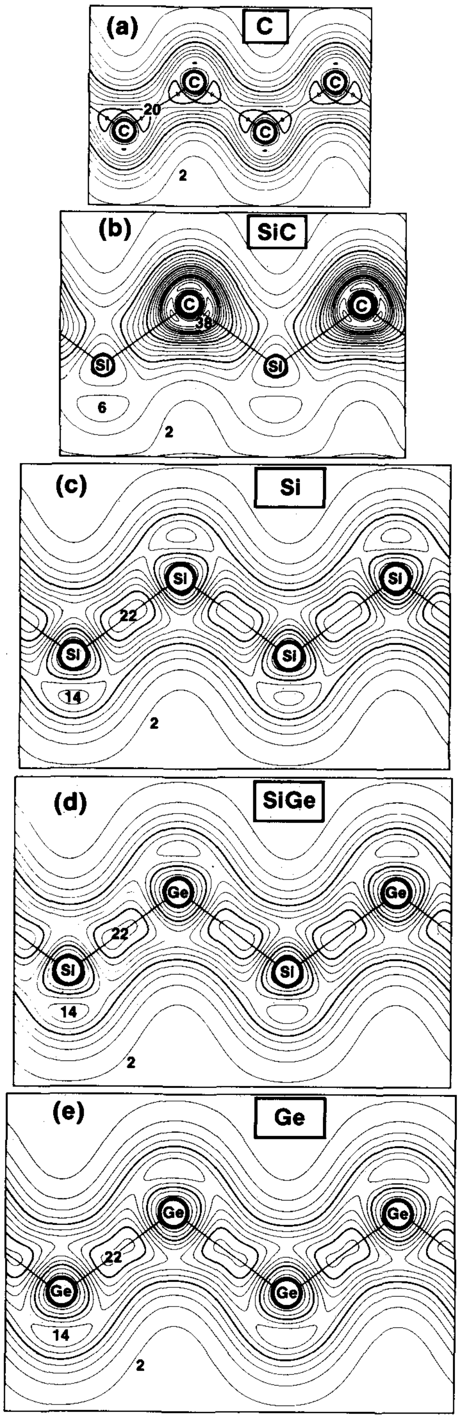


FIG. 3. Calculated charge densities in the (110) plane in electrons/cell. The correct proportion between the various lattice constants of these compounds is preserved.

dered alloys ($\Delta H^{(O)} < \Delta H^{(D)}$). This leads to an interesting possibility: if disproportionation is not permitted either for kinetic reasons (low diffusion rates) or by coherent strain effects[15] (i.e., activation barriers posed by different local concentrations with different local lattice constants, hence additional macroscopic strain), we expect to find at lower temperatures *ordering in a metastable phase*. Therefore, at low temperatures one can expect to find either truly stable ordered phases ($\Delta H^{(O)} < 0$), or metastably ordered phases ($0 < \Delta H^{(O)} < \Delta H^{(D)}$). According to our calculations of the enthalpy of ordered $\mathrm{Si}_n\mathrm{Ge}_m$ alloys, these phases should be metastable in bulk form, which is in agreement with the experimental observations[4] of ordering in $\mathrm{Si}_x\mathrm{Ge}_{1-x}$: the strongest superlattice diffraction peaks were observed after half an hour of annealing at 450 °C, but if the annealing was prolonged the order *decreased*, an effect attributed[4] to the diffusion of Ge from the alloy into the Si substrate. (Epitaxial SiGe/Si: is, however, predicted[2] to be stable.) A consistent picture of the metastability of ordered $\mathrm{Si}_n\mathrm{Ge}_m$ alloys emerges from both theory[16] and experiment.[4]

ACKNOWLEDGMENT

This work was supported in part by the Office Of Energy Research, Materials Science Division, U.S. Department of Energy, Grant No. DE-AC02-77-CHO-0178.

REFERENCES

[a] Present address: Department of Physics, University of California, Berkeley, California 94720.

[1] M. B. Panish and M. Ilegems, Prog. Solid State Chem. **7**, 39 (1972); F. Rosenberger, in *Cohesive Properties of Semiconductors Under Laser Irradiation*, edited by L. D. Laude (Nijhoff, The Hauge, 1983), p. 128; G. B. Stringfellow, J. Phys. Chem. Solids **34**, 1749 (1973); **33**, 665 (1972).

[2] G. P. Srivastava, J. L. Martins, and A. Zunger, Phys. Rev. B **31**, 2561 (1985).

[3] T. S. Kuan, T. F. Kuech, W. I. Wang, and E. L. Wilkie, Phys. Rev. Lett. **54**, 201 (1985).

[4] A. Ourmazd and J. C. Bean, Phys. Rev. Lett. **55**, 765 (1985).

[5] G. B. Stringfellow, J. Cryst. Growth **27**, 21 (1974).

[6] J. Van Vechten, in *Semiconductor Handbook*, edited by S. P. Keller (North-Holland, Amsterdam, 1980), Vol. 3, p. 1.

[7] P. A. Fedders and M. W. Muller, J. Phys. Chem. Solids **45**, 685 (1984).

[8] L. Vegard, Z. Phys. **5**, 17 (1921).

[9] D. D. Wagman, W. H Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Shumm, *National Bureau of Standards Technical Note 270* (United States Government Printing Office, Washington, DC, 1968).

[10] J. L. Martins and A. Zunger, Phys. Rev. B **30**, 6217 (1984).

[11] M. F. Gratton, R. G. Goodchild, L. Y. Juravel, and J. C. Woolley, J. Elect. Mater. **8**, 25 (1979).

[12] J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4409 (1979).

[13] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, Oxford, 1969), Chap. 14.

[14] A. G. Khachaturyan, *Theory of Structural Transformations in Solids* (Wiley, New York, 1983).

[15] G. B. Stringfellow, J. Elec. Mater. **11**, 903 (1982).

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