

Strain-induced ordering in silicon-germanium alloys

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The structural stability of ordered AB alloys on the diamond lattice is discussed from the point of view of the competition between bond-angle and heterogeneous bond-length constraints. An infinite number of layered structures are favored in the absence of applied strain. With uniaxial strain a special ordered structure, consistent with recent electron diffraction measurements, is stabilized.

Isostructural order-disorder transitions are a common phenomenon in metallic alloys, where below a critical temperature T_c different atoms preferentially occupy special sublattice sites. In contrast, the semiconducting alloy Ge-Si is generally regarded as a model random alloy in that no long-range order has been observed under extremely prolonged anneals at any temperature,¹ and that the solidus and liquidus curves are fitted very well by ideal solution theory.² Recent work on Ge-Si/Si strained superlattices (SSL's), which at first indicated short-range order,³ and then true long-range order,⁴ has thus come as a considerable surprise.

The SSL's studied by Ourmazd and Bean were grown by molecular beam epitaxy on (001) Si, consisting of 20 periods of 75 Å of $\text{Ge}_{0.4}\text{Si}_{0.6}$ and 225 Å of Si. Despite the large lattice constant mismatch (4%) between Ge and Si, the layers can be grown free of extended defects and possess commensurate interfaces. The strain is accommodated by a tetragonal distortion of the unit cell in the alloy layers.⁵ The structure inferred from the electron diffraction pattern consists of the ordering of $\{111\}$ planes in the sequence SiSiGeSeSi . . . , producing a doubling of the unit cell. The two possible structures consistent with this ordering are shown in Fig. 1. The extra diffraction spots characteristic of the ordered state could be made to appear and disappear reversibly by annealing at 450 or 550°C, respectively, which indicates a true order-disorder transition within this temperature range.⁴

Given the reversible nature of the ordering, and the absence of such behavior under similar conditions in bulk material, Ourmazd and Bean conjectured that the transition was strain driven and strain stabilized.⁴ In this paper, I shall attempt to quantify this suggestion within the framework of a simple model.

Traditional models for ordering in metallic alloys have employed concepts such as electronegativity differences and atomic size mismatch involving only two-body forces.⁶ Such a model would predict that an ordered unstressed $\text{Ge}_{0.5}\text{Si}_{0.5}$ alloy would have the cubic zinc-blende structure. The competition between stiff bond-length and softer bond-angle forces may lead to stability for special ordered structures with broken cubic symmetry. Such ideas have been employed by Phillips and Thorpe to discuss the structure of covalently bonded *glasses* on intermediate-length scales.⁷ Here I show that this competition favors a novel superlattice which is one of the two structures consistent

with the electron diffraction measurements of Ourmazd and Bean.⁴

It is instructive to imagine building an AB alloy on a pseudodiamond lattice with rigid bonds of three different lengths and with springs *between* bonds to maintain the bond angles close to the perfect tetrahedral angle of $\sim 109^\circ$. An inhomogeneous distribution of bond lengths on this lattice can always be accommodated by small bond-angle deformations; however, for certain periodic structures, the bond angles can remain undistorted, so that no internal strain exists in the solid. An obvious requirement for such a strain-free structure is that the individual puckered hexagonal units of the diamond lattice be unstrained. Generally this requires that each pair of parallel bonds in the hexagon be identical, and so there are five allowed hexagonal units: *AAAAAA*, *ABAAB*, *ABABAB*, *ABBABB*, and *BBBBBB*. In the diamond lattice, three nearest-neighbor atoms occur in two different hexagons. Consequently, the A_6 and B_6 units will stack only with

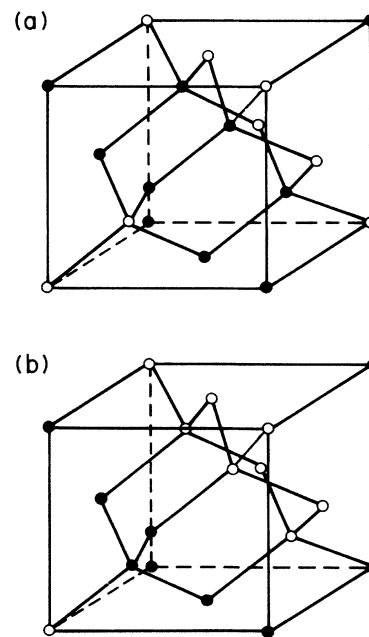


FIG. 1. The two ordered structures consistent with electron diffraction observations (Ref. 4).

themselves and cannot be used in an alloy. The *AABAAB* (*ABBABB*) units will also stack only with themselves and the rigid constraints force them to form a planar structure consisting of four (111) planes (two puckered layers) where the outermost atoms are all *B* (*A*). These are precisely the double layers seen in the structure of Fig. 1(a). Because these double layers consist of two puckered layers containing only *AB* bonds, it is now clear that all the strain-free structures must be based on stacking with this “*AB*” layer as the basic unit.

Each puckered *AB* layer presents one type of atom on one side and the other atom on the opposite side; they can be stacked with either like or unlike bonds making connections. Stacking the layers with all *AB* connections produces the zinc-blende structure, and with all like bonds connecting (i.e., alternately *AA* and *BB*) produces the structure of Fig. 1(a). However, *arbitrary* (including aperiodic) stackings are also allowed. All of these strain-free structures have the composition $A_{0.5}B_{0.5}$. We note that the second structure which is consistent with the experimental measurements [Fig. 1(b)] is highly strained. If solely mechanical forces are operative, the strain-free structure will be the lowest in energy.

When a *uniaxial* strain is applied to this system (as in the SSL's), the bond angles will be deformed; if the bond-bending forces on the atoms are different, the degeneracy of the various strain-free structures will be broken. We can immediately see that the applied strain will favor the structure containing the maximum number of *like* bonds by considering a single chain of atoms in the (110) plane shown in Fig. 2. In the zinc-blende structure [Fig. 2(a)] the bond-angle deformation produced by compression is by symmetry identical on the two types of atom. In the dimerized chain [Fig. 2(b)] the bond-angle deformations on unlike atoms can be different. For a fixed strain, the dimerized chain will be of lower energy, because the strain can be principally accommodated on the softer atom. Thus, the structure with the lowest stored mechanical energy under strain will be that shown in Fig. 1(a).

In order to quantify these ideas we employ a valence-

force-field model,⁸ commonly and successfully used to model elastic properties. We use a simplified model with two constants α and β , representing the bond-stretching and bond-bending force constants, respectively.⁹ Then the energy for small distortions away from the equilibrium positions can be written

$$U = \frac{3}{2} \sum_{i>j} \alpha_{ij} (\delta l_{ij})^2 + \frac{1}{8} \sum_{ij>k} \beta_i (\delta \theta_{jik})^2 \quad (1)$$

The summations in Eq. (1) run over all sites i in the lattice and $\delta l_{ij}, \delta \theta_{jik}$ are the distortions from equilibrium of the bond lengths and bond angles between nearest-neighbor atoms. The equilibrium bond length can of course be chosen to be different between different atom pairs. The parameters α and β can be fit to the bulk and shear moduli of the pure materials, which yields $\alpha_{\text{Si-Si}} = 6.14$ eV; $\alpha_{\text{Ge-Ge}} = 5.34$ eV; $\beta_{\text{Si}} = 1.6$ eV; $\beta_{\text{Ge}} = 1.3$ eV. For the unlike bonds we used $\alpha_{\text{Si-Ge}} = 5.74$ eV, the average of the pure materials. The bond lengths were chosen in the ratio 1:1.02:1.04, assuming Vegard's law to hold on a microscopic scale.¹⁰ None of our results are sensitive to small changes in these values. The fitting of the parameters to the bulk and shear moduli underestimates the softness of bond bending in both Si and Ge; for example, this model will not reproduce the pronounced flattening of the TA phonon close to the zone boundary. Moreover, the distortions here are sizeable enough that anharmonic terms will be important, and we note that the Grüneisen constant for short-wavelength shear (i.e., L - or X -point TA phonons) is negative in both Si and Ge.¹¹ It is noteworthy that both period-doubled structures of Fig. 1 can be regarded as density waves coupled to the soft TA L -point phonon.

For small distortions away from the perfect diamond lattice positions, Eq. (1) reduces to a quadratic form. Given a choice of atomic configuration, Eq. (1) can be minimized with the boundary conditions of fixed average strain in the {001} planes (perpendicular to the growth direction), while the strain in the z direction is a free parameter. This corresponds to the experimental situation, where the layers are thin in comparison to their width (so that the strain is uniform) and also that the Si layers are much thicker than the alloy layers (so that the strain in the x - y planes is fixed by the Si lattice constant). For numerical calculations, I chose a pseudocubic unit cell containing 64 atoms with periodic boundary conditions. Equation (1) was then minimized for different atomic arrangements, both periodic and random within the unit cell. The results for a number of structures are shown in Fig. 3, with energy per atom plotted as a function of uniaxial strain. Table I shows a list of the structures plotted in the figure, together with calculated elastic moduli.

We force all the structures to be tetragonal, despite the fact that some of them (e.g., those of Fig. 1) could further lower their energy by rhombohedral or orthorhombic distortions. We suspect that the samples will be twinned on length scales short enough that individual domains will be unable to relax in this fashion.

Equation (1) and Fig. 3 represent only the *mechanical* energy of this system. Because different crystal structures have different arrangements of near neighbors, there should be differences in *chemical* energy between different

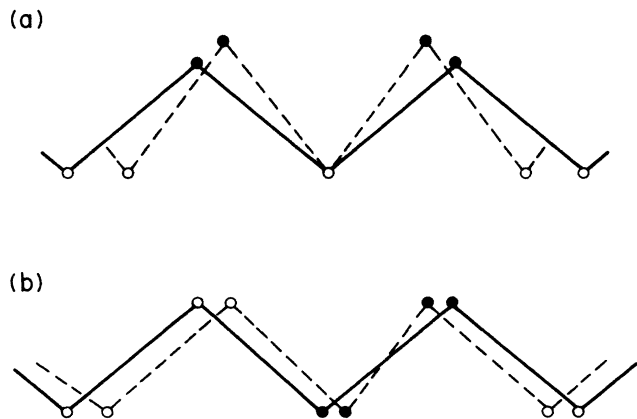


FIG. 2. Compressed chains of atoms in the (110) plane of the diamond structure. Only the dimerized structure (b) allows the bond-angle distortions produced by compression to be different on the two kinds of atom.

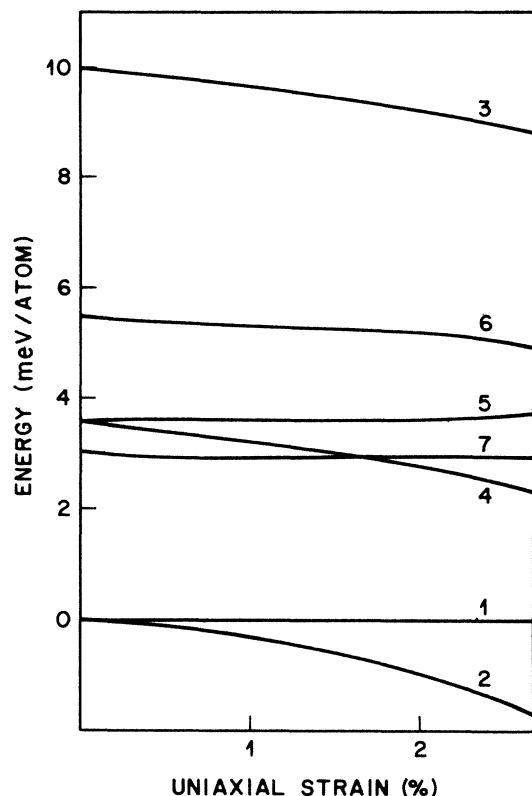


FIG. 3. Energy per atom of various arrangements of atoms in a 64-atom strained cube relative to that for the zinc-blende structure. The numbers refer to the labeling in Table I. Matching to the Si lattice constant corresponds to a value of the uniaxial strain of 2%.

structures. Chemical energies are almost always dominant over mechanical energies in determining crystal structure; only in special cases such as this where the atoms are so chemically similar can mechanical forces play an important role. In any case, the offsets between different curves in Fig. 3 cannot be taken to be reliable, but of all the structures studied, the dimer structure of Fig. 1(a) (structure 2 of Table I) has the lowest energy, although only by a small amount. Note that there is a continuum of curves lying in between the dimer structure (2) and the zinc-blende structure (1) which are longer period orderings of the basic

“AB” (111) layer. If chemical energies (such as the heat of mixing which might favor Ge-Si bonds over homopolar bonds) were large, (1) would be stabilized relative to (2) because the zinc-blende structure has all AB bonds (see Table I). Since the dimer structure has one less AB bond per unit cell than the zinc-blende structure, the ionic contribution to the bond energy must be less than 1 meV for the dimer structure to be favored. No measurements of the heat of mixing are available, but an analysis by Van Vechten¹² of the distribution coefficient of Si impurities in Ge found the ionic contribution to the heat of mixing to be zero (so that the solid phase should be an ideal solution). (The estimated¹² error is approximately ± 1 meV/atom).

The energy differences between different structures are small in comparison to thermal energies at the temperature of the experiments. However, at finite temperature, the dimer structure is further stabilized relative to the other ordered structures because it has softer phonons (see Table I) and therefore a larger phonon entropy. We have estimated the phonon entropy by calculating the vibrational modes of the 64 atom unit cell. At 300 K the phonon entropy contributes to a lowering of the free energy of the dimer structure (2) by about 1 meV/atom relative to the random case, and about 0.3 meV/atom relative to the zinc-blende structure (1).

The transition temperature to a disordered state can be estimated from the energy differences between curves 2 and 7 in Fig. 3 (about 4 meV). Even taking the phonon entropy into account, this yields $T_c \lesssim 100$ K. An alternative estimate can be made by calculating the energy of an isolated defect pair (interchanging two atoms) which we calculate to range between 20 and 30 meV per pair of atoms. This yields a somewhat higher estimate for $T_c \approx 150$ K, but still well below the observed $T_c \approx 750$ K. Our treatment of short-wavelength shear is not completely adequate, and we have neglected anharmonicity (both of which effects would raise our estimates of T_c). It is possible that inclusion of these effects might enable this model to account quantitatively for the high observed transition temperature, although the energy scale seems rather too small. The model is qualitatively successful in favoring the correct type of ordered structure (although present experiments have so far failed to distinguish between the structures 2 and 3 of Table I, this should be possible with x-ray diffraction).

In conclusion, I have shown that, in contrast to chemical

TABLE I. Bulk and shear moduli as well as the fraction of AB bonds for the structures whose energy is shown in Fig. 3. The disordered case (7) involves an average over 10 realizations and has an rms deviation of less than 5%.

Structure	Elastic moduli (10^{11} dyn cm ⁻²)		f_{AB}
	$(c_{11} + 2c_{12})/3$	$(c_{11} - c_{12})/2$	
1 Zinc blende	9.20	4.64	1.0
2 Double (111) [Fig. 1(a)]	9.09	4.54	0.75
3 Double (111) [Fig. 1(b)]	10.40	4.63	0.25
4 Double (001)	9.62	4.00 4.95	0.5
5 Double (100)	9.62	4.95 4.00	0.5
6 Double (110)	9.83	4.63 4.72	0.25
7 Random	9.60	4.62	0.5

interactions, the competition between bond-length and bond-angle forces can provide special stability to a novel ordered semiconductor alloy structure. In a 50% *AB* alloy based on the diamond lattice, a class of layered structures is preferred, and in the presence of applied uniaxial strain a dimerized structure is singled out.

After this work was submitted, I became aware of the very recent work of Martins and Zunger,¹³ in which they present total energy calculations of the enthalpies of formation of the zinc-blende and rhombohedral structures (1 and 2 of Table I). Their conclusions are very similar to those presented here. Remarkably, they found that the

chemical energy of forming a heteropolar bond was *positive* (~ 4 meV/bond), which provides further stability of the dimer structure (2) relative to zinc blende, but indicates that *all* mixed phases are metastable at low temperatures and will tend to disproportionate.

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