

Ordering in Si-Ge superlattices

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We study RH1 ordering in Si-Ge superlattices using empirical potentials for the Si-Ge system, one of which incorporates long-range interactions and accurately reproduces the phonon spectra as well as equilibrium structures. Our simulations show that the energy difference between the RH1 and the disordered phase remains small over a wide range of situations, which cannot account for the high transition temperature and the reversibility of the former. We consider experimental evidence of further frustration in the disordered phase only; even so we show that it fails to stabilize the RH1 phase up to the observed temperature. Experimentally, ordering is observed by means of transmission-electron diffraction done on thin samples cut in the (110) plane. Our simulations show that the reconstructions on the (110) surface may provide the missing energy necessary to stabilize RH1 ordering.

In this work we apply recently developed empirical potentials to the study of long-range ordering in SiGe strained-layer superlattices. Clearly, it is necessary, in a study of strain effects, that the potential be satisfactory in the calculation of elastic properties, which is not the case with the potentials of Stillinger and Weber,¹ Biswas and Hamann,² and Tersoff,³ as has been pointed out by Cowley.⁴ The potentials used in this work⁵ arise from a class of potentials for Si, Ge, and Si-Ge that give elastic constants and their pressure derivatives, equilibrium states of Si-Ge strained-layer superlattices (SLS) grown in the [100] direction, and predict bulk phase stabilities that agree very well with experimental values and local density (LD) calculations.⁵⁻⁷ None of the potentials above, which are short ranged, can reproduce the TA flattening in the phonon spectra and at the same time give the correct elastic constants. In a previous paper,⁸ we extended our potential by introducing longer-range interactions like those considered in the valence-force-field (VFF) model of McMurry *et al.*⁹ Long-range interactions are important in the understanding of phonons of Si and Ge and their superlattices.¹⁰ This potential can be used to predict equilibrium structures accurately (which is a prerequisite for accurate phonon studies), in agreement with LD calculations, and at the same time calculate good phonon spectra. The results of this work⁸ confirm the validity of using our extended potentials for studies of phonon and thermodynamic properties of binary systems.^{6,11} In the work below, we first show that the energy difference between the ordered phase and the disordered phase is an order of magnitude too small to account for the stability of the former. This difference remains small (< 3 meV/atom) under a wide range of conditions. One way to increase this difference is to have the disordered phase additionally "frustrated." The ordered phase, which has been extensively studied with LD techniques, should not be similarly affected. We examine the experimental evidence for this and show that, within the constraints of this evidence, the energy difference does increase somewhat but not adequately. Finally, we note that the observation of ordering has only been reported

for thin samples cut in the (110) plane. We examine the possible influence of this plane on the stabilization of order. In particular, we speculate on the possibility of (110) surface reconstruction playing a role in the stability of the ordered phase.

Ordered RH1 and RH2 phases have been observed experimentally in SiGe systems grown in the [100] direction.¹²⁻¹⁵ In these phases the (111) planes, occupied by only one type of atom, are arranged in the order *AB-BA* and *BA-BA* respectively.¹² The mechanism of RH1 ordering has not been successfully explained despite much work.¹²⁻¹⁶ von Kanel and co-workers¹⁵ have found that only RH1 ordering is reversible after annealing to a high temperature of 1070 K. LeGoues and co-workers¹⁴ have discussed the mechanism of RH2 ordering; we have shown that it needs to be extended.¹⁷ Our simulations of RH2 ordering show it to be higher in energy than RH1 ordering, in agreement with LD results of Martins and co-workers.¹⁶ A similar model of ordering due to growth has been proposed by Jesson *et al.*,¹⁸ but this model does not explain the reversibility of the RH1 phase. In Table I we show the positions of peaks of Raman spectra obtained for the RH1 and RH2 phases and compare them with the experimental results of Lockwood and co-workers.¹³ It is clear that the experimental results are consistent with the presence of the RH1 phase and not the RH2. Lockwood and co-workers have also linked the modes at 255 and 435 cm^{-1} to the RH1 phase and have noted that they are very insensitive to annealing up to 1200 K. Our calculations⁸ show that the energy of the RH1 phase is, at best, only a few meV/atom lower than that of the random phase (see Table II), in agreement with LD results (Bernard and co-workers);¹⁶ the energy differences

TABLE I. Calculated and experimental positions of Raman spectra peaks in cm^{-1} .

Experiment ^a	235	290		445
RH1 (calculated)	255	295		435
RH2 (calculated)	210	280	350	450

^aReference 13.

TABLE II. Energies of RH1 and random phases in meV/atom for different Ge concentrations x , grown on Si and Ge substrates.

x	RH1(RH1)	c/a	Random	Modified random	$\Delta E_{\text{RH1S,M.Rand}}$	$\Delta E_{\text{RH1S,Rand}}$
Si substrate						
0.25	20.2	1.049	21.7	25.27	-5.1	-1.51
0.5	13.7(16.9)	1.035	15.5	20.0	-6.35	-1.84
0.75	6.7	1.018	8.3	11.8	-5.1	-1.56
Ge substrate						
0.25	5.6	0.983	6.7			-1.10
0.5	12.0	0.969	14.1			-2.15
0.75	21.74	0.953	23.0			-1.26

are an order of magnitude too small, when compared to the 30 meV/atom needed to explain the observed transition temperature of 900 K (von Kanel and co-workers¹⁵ and Koiller and co-workers¹⁶). In previous work we explored a range of parameter space which included⁸ (1) substantial incomplete and overrelaxations of the superlattice in the growth direction, (2) deviations of equilibrium interatomic distance, r_{SiGe} , of $\pm 1\%$ from that given by Vegard's law (Dismukes *et al.*¹⁹ have observed a small negative deviation of about 0.1%), (3) a large lattice mismatch with the substrate, and (4) nonelastic perturbations (i.e., keeping the bulk modulus B_0 and shear c' constant) to potential parameters F_r , f_{rr} , $F_{\phi\phi}$, $f_{r\phi}$, $f_{\phi\phi}$, and $f_{\phi\phi}^*$. In all these cases we have seen that there is a strong tendency for the energies of the ordered and disordered phases to track each other, despite substantial changes (well beyond what would be considered reasonable) from the equilibrium situation. Similar results are also obtained for the short-range potentials.¹⁶ From the results above, we see that if the RH1 phase is to be stabilized, a long-range potential, by itself, is not adequate and that, if the potentials are modified equally for the ordered and disordered phases, the energy differences will remain small when elastic constants are kept unchanged.

Bublik *et al.*²⁰ have obtained the excess energy and elastic constants of $\text{Si}_x\text{Ge}_{1-x}$ alloys using diffuse x-ray scattering. They obtained an excess energy of 9.54 meV, which agrees with the results of LD calculations (Martins and co-workers)^{16,21} and elastic constants of $c_{11} = 1.61$ (1.39), $c_{12} = 0.835$ (0.528), and $c_{44} = 0.855$ (0.706) 10^{11} N/m² for $x = 0.28$; the results are 16%, 58%, and 21% larger than the corresponding figures from a Vegard-like rule, where $c_{ij} = xc_{ij\text{Si}} + (1-x)c_{ij\text{Ge}}$ (in brackets), for elastic constants. The method of diffuse x-ray scattering is accurate for pure Si and Ge, for it gives elastic constants which agree to within 5.6% with values obtained by the ultrasonic method.²² However, Mendik *et al.*²³ have measured elastic constants for SiGe alloys and superlattices for $x = 0.49$ and 0.66 using the method of Brillouin scattering of Rayleigh waves and obtained values within 9.1% of those given by applying the Vegard-like law to the ultrasonic results. The velocity of sound waves measured by Brillouin scattering is systematically (about 5%) lower than that calculated using elastic constants from ultrasonic measurements and the reason is not understood.²⁴ In determining the elastic constants,

Mendik *et al.*²³ used a fitting procedure for the velocity of the Rayleigh wave, where variations of 4% in c_{11} (or c_{44} depending on the direction of the wave) give rise to a 1.6% change in the velocity, which would be detectable. The effect of changes in c_{12} is quite small; Karanikas and Sooryakumar²⁵ note that a change of 8% in c_{12} would still give a fit to within 0.2% of the measured velocities of surface waves of films grown on Si(111).

We now carry out simulations where we make changes only to the potential of the random phase; this will be done within the constraints of the experimental evidence of Bublik *et al.*²⁰ Here, we simply want to see if it is possible to find situations which will give energy differences large enough to account for the large transition temperature. The Raman spectra for SiGe alloys and superlattices have the general appearance of a three-mode behavior of a Si peak at 500 cm^{-1} , a Ge peak at 300 cm^{-1} , and a Ge-Si peak at 390–425 cm^{-1} .^{26,27} Dharma-wardana *et al.*²⁷ have modeled the spectra for superlattices in some detail and showed that the Ge-Si-like peak may not really be related to the Ge-Si zinc-blende peak but may actually be a Si slab mode weighed down by heavier Ge atoms at the edges of the slab; the frequency of this mode would then be largely determined by Si.

In the simulations below, we will focus our attention on superlattices since they have been better studied, especially with regards to ordering and to Raman spectra.^{15,27} If we increase VFF parameters by 20% for Si, Ge, and SiGe for the disordered phase, we obtain energy differences of 1–2 meV/atom higher for values of $x = 0.25 - 0.75$. Results of Bublik *et al.*²⁰ show a 35% increase in the bulk modulus of the random phase of $x = 0.28$, over the value given by the Vegard-like rule, while the shear c' is essentially unchanged. Dharma-wardana's²⁷ results show that the positions of the three Raman modes are largely determined by the parameters of Si and Ge only. So for the next simulation, we modify only the parameters of SiGe to keep the three Raman modes where they are. Assuming, for convenience, that the same increase in the bulk modulus applies to the random phase of $x = 0.25$, we increase the quantity $F_r + 6f_{rr}$ for the potential of SiGe [see Eq. (1)] by a factor of 8/3 (since 3/8 of the bonds in this random phase are SiGe bonds), to increase the bulk modulus of random $\text{Ge}_{0.25}\text{Si}_{0.75}$ by 35%. Since we have an extra degree of freedom and noting that, at the Γ point, the optical

phonon frequency of the (ordered) zinc-blende form of SiGe is given by⁹

$$\omega^2 = \frac{8}{3m} \left(F_r + 8F_\phi + -2f_{rr} - 8\sqrt{2}f_{r\phi} + 16f_{\phi\phi}^* \right), \quad (1)$$

we can require $F_r - 2f_{rr}$ to be constant; the results reported below are not much affected by this condition. We show in Table II, the results for this modified random phase. We also display the energies of a modified RH1 phase (designated RH1S), where the number of SiGe bonds per atom is reduced from three to two, with a resulting gain in energy of 2–3 meV/atom. The typical atomic configuration of the RH1 phase has the zigzag Si-Si-Ge-Ge chains, as shown in Fig. 1(b) in the (110) planes, say, and the zinc-blende Si-Ge-Si-Ge chains in the orthogonal $(1\bar{1}0)$ planes. The RH1S phase is obtained from the RH1 phase by sliding, in the $[1\bar{1}0]$ direction by one lattice spacing, every alternate pair of (110) planes. The configuration in the $(1\bar{1}0)$ planes will then be like that in the (110) planes, except that the chains will run in alternating directions. The energy differences $\Delta E = E_{\text{RH1S}} - E_{\text{random}}$ have increased from 2 to 6 meV/atom for the hardened potential, for $x = 0.25, \dots, 0.75$, but are still inadequate to explain the high transition temperature. The results are similar for superlattices.

Similar energy differences can also be obtained if we change the shear modulus only, as we have shown recently,⁸ but the size and types of these changes required are not supported by the measurements of Bublik *et al.*²⁰ We note that as far as superlattices are concerned, the elastic constants we have used for the SiGe phase may not be inconsistent with the elasticity results of Mendik

*et al.*²³ They carried out experiments on superlattices with periods of about 10 layers. If we assume that inter-diffusion (which is less than 7%) is confined to about two monolayers at the interface (von Kanel and co-workers¹⁵ and Dharmawardana *et al.*²⁷), then the effective elastic constants of a thick sample of the superlattice, using the modified potential, would fall within the errors of the surface-wave experiments.

We consider now a different possible mechanism for RH1 ordering. In the experiments referred to above,^{12–15} diffraction patterns were obtained by transmission electron microscopy (TEM) on thin samples cut in the (110) plane. We will show that it is possible for this surface to stabilize RH1 ordering. The clean Si(110) surface is known to reconstruct in the 16×2 structure, made up of alternating upper and lower (110) terraces, separated by monolayer $[\bar{1} \ 1\bar{2}]$ steps.²⁸ Each terrace is eight unit cells wide in the $[110]$ direction. Because the 16×2 unit cell is so much larger than the RH1 cell, we will not specifically take it into account in our computations below; our results, which will be obtained for the plain (110) surface, should remain valid even for the reconstructed surface.

Tight-binding calculations by Chadi²⁹ show that the plain (110) surface relaxes mainly by the tilting of bonds, $\sim 30^\circ$, between atoms on the top layer; there is charge transfer from the atom that relaxes inwards, towards the bulk, to the atom that moves outwards. The mechanism is the same for the buckling of dimers on the (001) reconstructed surface. Chadi's³⁰ tight-binding calculations for this surface give buckled dimers with atomic displacements in good agreement with the total energy results of Yin and Cohen.³¹ In recent work,³² we have seen that the buckling of dimers on the Si(001) surface leads to substantial energy gains over the unbuckled surface. The frustration of this buckling by stress or disorder or defects can cost much energy. In this work we have been able to tune our potential to the results of recent total energy calculations³³ for the missing dimer Si(001) surface. As there is no similar total energy calculation for the reconstruction of the (110) surface, we will use Chadi's tight-binding results²⁹ to modify the potential. In view of the success of Chadi's method in the (001) surface problem and the similarity of the mechanism for buckling for both surfaces, we expect this to be a good approach; as we shall see, the results below are not sensitive to the fitting parameters. We modify the potential used in previous work³² (see reference for form and details of the potential) in a simple way to reproduce the outward and inward shifts (buckling) as well as the lateral shifts of the first-layer atoms. We show in Fig. 1(a) the atomic configurations of the top two layers of the (110) surface and in Fig. 1(b) a side view of this surface. The equilibrium bond-bending angle θ_i (Ref. 32) for the top-layer atom, which relaxes outwards, is set at 80° , while that of the other atom which moves inwards remains at 120° . For the second-layer atom, we reset only one angle, that between the bonds that the atom forms with the first-layer atom and the third-layer atom. These equilibrium angles are set at 125° and 100° , respectively [see Fig. 1(b)]. With these equilibrium angle settings we are able to fit the vertical displacements of

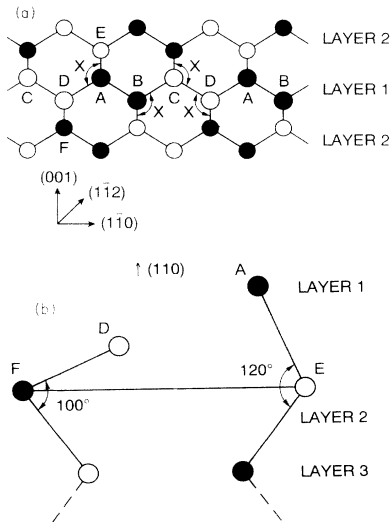


FIG. 1. (a) Atomic configurations of the top two layers of the (110) surface; on layer one, filled circles are atoms that relax outwards, while empty circles are atoms that move into the bulk; on layer two, filled (empty) circles are atoms with equilibrium angle of 100° (125°). (b) A side view of the surface. Atoms A, D, E, and F identify the same atoms as in (a).

first-layer atoms from unrelaxed positions to within 0.01 Å of Chadi's results.²⁹ The two simplest reconstructions of the (110) surface have the following bond tilting patterns: (1) atoms *B* and *D* in Fig. 1(a) relax outwards and *A* and *C* relax inwards, and (2) atoms *A* and *B* relax outwards while *C* and *D* move in. For the latter reconstruction, to make it more favorable in energy than the former, one equilibrium bond angle [marked × Fig. 1(a)] at each surface atom is reset to 90°.

In our simulations for SiGe systems, we use the angle settings for the second reconstruction; atoms on the surface layer that relax outwards are identified with Ge atoms, and those relaxing inwards are Si atoms. On the second layer, we consider two possibilities: (1) Ge atoms are assigned the 100° bond angle and Si atoms the angle of 125°, and (2) the angle of 100° (125°) is assigned to any atom that has a Si (Ge) atom above it on the top layer. Clearly the first assignment describes some correlation between an atom on the top layer, and the one directly below it in the second layer, while the second assignment does not have this correlation at all. The correlation may come about because electron transfer from a surface atom of a given type to another surface atom is affected by the specific type of atom linked to it on the second layer.

In Table III we show the results of simulations for situation (1). The axial ratio, c/a , of a SiGe superlattice grown on a Si(Ge) substrate, fully relaxed in the [001] growth direction, has a value of about 1.035(0.969). The energy differences between RH1 ordering and random (averaged over 15 samples) show that the former is more favorable by 39–51 meV/surface atom for (three relaxed and one unrelaxed) superlattices grown on Si, SiGe, and Ge substrates. RH1S ordering would improve this even more. This is a substantial energy difference, sufficient to stabilize RH1 ordering for the top few layers until the transition temperatures observed by von Kanel and co-workers.¹⁵ In Table IV we show the cumulative energy differences for the top n layers, $n = 1, \dots, 8$, which have been stabilized by the sixth layer, with the main contribution coming from the top two layers. Takayanagi *et al.*³⁴ have shown that it is possible to observe ordering confined to a few top layers by means of TEM and transmission electron diffraction (TED) when they used these techniques to study the Si(111)-7 × 7 reconstruction. When we vary the fitting angles, marked × above, by ±5°, the energy differences change by ±2.5 meV/surface atom. Results are similarly insensitive to variations of the other fitting angles.

For situation (2), energy differences still favor RH1 over random, but by reduced amounts of 11–31 meV/surface atom. These results indicate that the conclusion of ordering, induced by the (110) surface recon-

TABLE IV. Cumulative energy differences between RH1 and random phases in meV/(110) surface atom for the top n layers of SiGe superlattices grown on Si substrates.

n	1	2	3	4	5	6	7	8
ΔE	14.6	53.6	53.2	38.5	44.8	50.6	50.8	50.8

struction, is quite robust. Our results also show that ordering occurs independently of whether or not the superlattice is epitaxially strained, which is consistent with the experimental observations of Lockwood and co-workers¹³ and von Kanel and co-workers.¹⁵ It would also be consistent with the observation that TED spots are much fainter¹⁵ after annealing the sample, as this ordering is essentially a (110) surface phenomenon. While reversible RH1 ordering has been seen by Ourmazd and Bean¹² and extensively investigated by von Kanel and co-workers,¹⁵ recent experiments by Kesan *et al.*³⁵ do not find this reversible phase change even after prolonged annealing at high temperatures. This disagreement in findings is initially puzzling; however, it may have some connection to the way TEM samples are prepared for observation. If indeed (110) surface reconstruction is responsible for reversible RH1 ordering, then the nature of the sample surface will determine how strongly the ordering appears. One could then conceivably see some sample-to-sample variations in the nature of ordering, depending on the quality of the (110) surface.

In conclusion, we have considered two possible mechanisms for the high transition temperature of the RH1 phase.¹⁵ Our simulations, using an empirical potential, which give both phonon spectra and structure correctly, show that energy differences between RH1 and the disordered phase track each other over a large range of situations, with magnitude less than 3 meV, which is an order of magnitude too low to explain this stability. This is also true of the short-ranged potentials.¹⁶ Experimental evidence indicates the possibility that the phases, RH1 and random, may have different elastic constants. Since the RH1 with its small unit cell has been extensively investigated using LD calculations,^{16,21} the frustration we argue for the random phase should not affect it. While the evidence for further frustration of the random phase is not incontrovertible, our simulations incorporating it within the constraints of the experimental data show that it is still inadequate to explain the transition temperature of the RH1 phase. Observations of RH1 ordering have been done essentially by means of TEM on thin samples cut in the (110) plane; we have considered the effect of reconstructions of this surface on stabilizing the ordering. The (110) surface reconstructs by bond-tilting or buckling, gaining a substantial amount of energy in the process. It is the frustration of this buckling by disorder that may provide a possible mechanism for the stability, until high temperatures, of RH1 ordering for the top few layers of the (110) surface. We see that the results are robust, being relatively insensitive to fitting parameters; RH1 would still have a lower energy than random even in the (unlikely) no correlation case of situation (2). This

TABLE III. Energy differences between RH1 and random phases in meV/(110) surface atom for SiGe superlattices grown on Si, SiGe, and Ge substrates.

Substrate	Ge	SiGe	Si	Si
c/a	0.969	1.00	1.035	1.0 (unrelaxed)
ΔE	39	41	42	51

type of surface induced ordering is in agreement with experimental observations of Lockwood and co-workers¹³ and von Kanel and co-workers,¹⁵ and may well explain why it is not observed in the experiments of Kesan *et al.*³⁵ More experimental work is clearly needed before this proposed (possible) role of the Si(110) surface reconstruction in the stabilization of the ordered phase can be

unambiguously established.

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