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Interfacial stability and intermixing in thin-layer Si_n/Ge_n superlattices

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Using energies obtained from empirical-potential calculations, we study the relative stability between abrupt, ordered, and randomized interfaces in thin-layer superlattices. For most of the substrate parameter values, both ordered and randomized layers are more stable than the abrupt interface. The ordered geometries have even lower formation enthalpies than random structures. We examine the implications of these results in view of experimental studies of annealing and interdiffusion.

Interest in ultrathin strained-layer Si_n/Ge_m superlattices (SL's) has increased steadily over recent years, spurred by the potential applications of such systems in optoelectronic devices. The primary goal is to create direct-band-gap materials, as a result of zone-folding effects, which could be used as optical devices based on Si technology.[1] Theoretical efforts have been mainly focused on how strain effects, zone folding of the bands, and quantum confinement effects can influence the electronic structure of Si/Ge SL's.[2] However, little is yet known about the stability of abrupt interfaces in these SL's, and the possible intermixing of species near the boundary layers.

There are a number of issues related to interface roughness. Probably, the most intriguing phenomenon associated with the structure of Si/Ge SL's is the observed ordering of Si and Ge atoms in the boundary layers.[3,4] Roughness also takes place when the growth of Ge on Si changes from a two-dimensional to a nonplanar mode (islanding) after a certain thickness ($n \sim 6$ monolayers) is exceeded. It is reported that the use of surfactants[5] suppresses both the nonplanar growth as well as ordering. Still, one needs to know how sharp interfaces respond to *post-growth* thermal annealing. There is experimental evidence that substantial intermixing occurs even for short anneals.[6]

Here, we report a systematic study of the energetics and interfacial stability of thin-layer Si/Ge (100) SL's. There are conflicting theoretical predictions on this matter.[7,8] The extensive calculations are made tractable by using the empirical-potential approach. We find that for most of the substrate parameter values, thin alloyed layers (both ordered and randomized) are more stable than the abrupt interface. Ordered structures have lower formation enthalpies (by a small amount) than the randomized interface. We discuss this result in view of recent experimental findings.

Interdiffusion after thermal annealing can only be associated with thermodynamic instability of abrupt interfaces. This is in contrast to ordering mechanisms in *as-grown* samples, where highly *nonequilibrium conditions* exist. A way to visualize ordering in Si-Ge systems is by considering an alternating bilayer stacking of Si and Ge atoms in one of the four equivalent [111] directions. There are two rhombohedral bulk phases (RH1 and RH2) which are characterized by such stacking.[9]

Discussion about ordering in thin-layer SL's has been quite controversial. Recent experimental work,[3] based on Z-contrast scanning transmission electron microscopy, suggests that the ordering is irreversible and highly asymmetric (predominantly confined to the Si layers). It was earlier suggested[10] that Ge segregates to the SiGe(100) 2×1 dimerized surface because this lowers the enthalpy. The authors of Ref. 3 proposed that such Ge segregation at the rebonded edge configurations of the surface during growth is responsible for the ordering. This Ge-atom "pump model" naturally is a nonequilibrium growth mechanism.

A different picture emerged from earlier experiments,[4] in which various techniques were used to probe the distribution of species in the boundary layers. It was found that irrespective of the substrate lattice constant and the growth procedure, *as-grown* samples exhibit both RH1 and RH2 type of symmetric ordering. Moreover, annealing and subsequent cooling of these samples indicated the existence of a reversible *post-growth* order-disorder transition, with RH1 the thermodynamically stable phase. Thus, ordering is mostly attributed to bulk thermodynamics rather than to surface kinetics.

We believe that nonequilibrium growth models are plausible mechanisms to account for the observed ordering in *as-grown* samples. However, the questions of intermixing after thermal annealing, and of *post-growth* ordering need further consideration.

We model the energetics of thin-layer SL's, by using two different interatomic potentials for Si-Ge systems.[11,12] In this way, we make sure that the results (at least qualitatively) do not depend on the particular choice of the potential. We believe that both treat strain and heteronuclear bonding reasonably accurately. As in our previous work on SiGe systems[10] we use the model potential of Tersoff,[11] the form of which is a direct generalization of that for the elemental systems Si and Ge. This potential has been discussed in detail elsewhere.[11]

The second model potential used here is that proposed by Stillinger and Weber[12] (SW). There are two parametrizations of this functional form, namely, for pure Si,[12] and for pure Ge as proposed by Ding and Andersen.[13] For the cross interactions and in analogy to the Tersoff potential, we utilize the following forms for the two-body $v_2(\vec{r}_{ij})$ and three-body $v_3(\vec{r}_i, \vec{r}_j, \vec{r}_k)$ terms of the SW potential:

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$$v_2(\vec{r}_{ij}) = \epsilon_{ij} f_2(\vec{r}_{ij}/\sigma_{ij}) ,$$

$$f_2(\vec{r}_{ij}) = \begin{cases} A_{ij}[B_{ij}(r_{ij}/\sigma_{ij})^{-4} - 1]\exp[(r_{ij}/\sigma_{ij} - a)^{-1}] & \text{for } r_{ij}/\sigma_{ij} < a \\ 0 & \text{otherwise,} \end{cases}$$

and

$$v_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) = \epsilon_{ijk} f_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) ,$$

$$f_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) = h(r_{ij}, r_{ik}, \theta_{jik}) + h(r_{ji}, r_{jk}, \theta_{ijk}) + h(r_{ki}, r_{kj}, \theta_{ikj}) ,$$

$$h(r_{ij}, r_{ik}, \theta_{jik}) = \begin{cases} \lambda_{jik} \exp[\gamma(r_{ij}/\sigma_{ij} - a)^{-1} + \gamma(r_{ik}/\sigma_{ik} - a)^{-1}] (\cos\theta_{jik} + \frac{1}{3})^2 & \text{for } \frac{r_{ij}}{\sigma_{ij}}, \frac{r_{ik}}{\sigma_{ik}} < a \\ 0 & \text{otherwise,} \end{cases}$$

$$A_{ij} = (A_i A_j)^{1/2},\ B_{ij} = (B_i B_j)^{1/2},\ \sigma_{ij} = (\sigma_i + \sigma_j)/2,\ \epsilon_{ij} = \chi_{ij}(\epsilon_i \epsilon_j)^{1/2},$$

$$\epsilon_{jik} = (\epsilon_{ij}\epsilon_{ik})^{1/2},\ \lambda_{ij} = (\lambda_i \lambda j)^{1/2},\ \lambda_{jik} = (\lambda_{ij}\lambda_{ik})^{1/2}.$$

The labels i, j, k run over the atoms of the system, r_{ij} is the length of the bond among atoms i and j, and θ_{jik} is the angle having i as the vertex atom. The parameter χ_{ij} ($\chi_{ii} = 1$, $\chi_{ij} = \chi_{ji}$), as in the Tersoff potential, strengthens or weakens the heteropolar bonds. We fit its value ($\chi_{\text{Si-Ge}} = 1.002\,01$) so that it reproduces the enthalpy of formation ($\Delta H = 8.9$ meV/atom) of the hypothetical zinc-blende (ZB) compound, as given by Martins and Zunger.[7] The parameter values of the elemental potentials are given elsewhere.[12–14] A similar construction of a mixed Si-Ge SW potential has been recently given by Karimi *et al.*,[15] but without the enhancement parameter χ_{ij}.

We have extensively tested the accuracy of the two potentials. Energies of various bulk Si-Ge phases are in good agreement with *first-principles* calculations.[7] In Table I, we display the calculated elastic constants for Si, Ge, and SiGe alloys. Values for Si and Ge agree rather well with experimental[16] and local-density approximation values.[7] For the ZB and the $Ge_{0.72}Si_{0.28}$ random alloy, the constants are about equal to the corresponding averages of Si and Ge. Thus, none of the potentials nor the more accurate pseudopotential method[7] can describe the observed[16] "bowing" of the elastic constants with alloy composition. Even the addition of a long-range term to the potentials would not correct this flaw.[17] In any case, it was shown[18] that the effect from stiffening the force constants in the random alloy is small.

We examine the interfacial stability of the superlattice, grown on a given substrate, in terms of its enthalpy of formation defined as the energy per atom taken with respect to the energies of equivalent amounts of its crystalline constituents Si and Ge at their bulk equilibrium lattice constants:

$$\Delta H(\text{Si}_n/\text{Ge}_n) = E(\text{Si}_n/\text{Ge}_n) - \tfrac{1}{2}[E(\text{Si}, a = a_{\text{Si}}) + E(\text{Ge}, a = a_{\text{Ge}})].$$

Alternatively, one can consider the epitaxial formation enthalpy δH which is taken with respect to Si and Ge, both coherent with the substrate. We are interested in relative values of ΔH (or δH) among different configurations. These are more accurate than absolute values (as is the case for *ab initio* calculations as well).

We begin by considering the stability of the Si_4/Ge_4 (100) SL. We use a supercell of 128 atoms with periodic boundary conditions. It is generated from an orthorombic unit cell of eight (100)-(2 × 1) layers with 8 Si and 8 Ge atoms, used also earlier[8] and shown in Fig. 1. Relaxations of atomic positions and of the supercell volume to the lowest-energy configuration are carried out using the Monte Carlo method. We consider three strain con-

TABLE I. Calculated elastic constants in comparison with experimental values and *first-principle* results. All values are in Mbar.

	Si	$Ge_{0.5}Si_{0.5}$ (ZB)	$Ge_{0.72}Si_{0.28}$	Ge
c_{11}	1.66[a]		1.61	1.28
	1.50[b]	1.42	1.39	1.37
	1.51[c]	1.47	1.44	1.38
	1.59[d]	1.48		1.31
c_{12}	0.64		0.84	0.48
	0.80	0.58	0.52	0.45
	0.76	0.64	0.59	0.51
	0.64	0.56		0.48
c_{44}	0.79		0.85	0.67
	0.70	0.69	0.67	0.67
	0.56	0.60	0.58	0.59

[a]Experimental value from Ref. 16.
[b]Using the Tersoff potential.
[c]Using the SW potential.
[d]*Ab initio* result from Ref. 7. Similarly for all other entries.

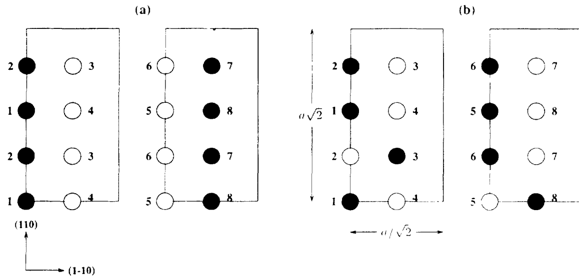

FIG. 1. The (2 × 1) orthorombic unit cell projected on the (001) plane. Numbers identify the layers from bottom to top (the upper four are shown separately). (a) The ideal SL; sharp interfaces are between layers 2/3 and 6/7. (b) Two interdiffused, ordered layers ($q = 2$) at each interface.

ditions. The "free-floating" case $a_s = a_{SL}$ (i.e., the SL is allowed to take its natural lattice constant), and the two limiting epitaxial conditions $a_s = a_{Si}$ and $a_s = a_{Ge}$. We limit interdiffusion to two monolayers. Ordered layers are generated by interchanging Si and Ge atoms across the boundary, in the way shown in panel (b) of Fig. 1. Note that in the case of thin-layer Si_n/Ge_m ($n, m < 8$) SL's we do not have the full extent of ordered bulk phases but fractional unit cells.

The results of our calculations are given in Table II. Both potentials predict that for $a_s = a_{Si}, a_{SL}$ substrates the ordered interface ($q = 2$) is more stable than the abrupt interface ($q = 0$). We say that the two interfaces (per cell) are attractive. By partitioning the total energy of the system into bond energies (or equivalently into atom energies[10]) we are able to trace the energy differences. The ordered SL of Fig. 1(b) involves a variety of local geometries. It is a mixture of Si-Si_3Ge, Ge-Ge_3Si clusters (locally reminiscent of RH2 stacking), and of Si-Ge_4, Ge-Si_4 units (locally ZB), besides Si-Si_2Ge_2 and Ge-Si_2G_2 geometries. On the other hand, the ideal SL involves only Si-Si_2Ge_2 and Ge-Si_2Ge_2 clusters, along with Si-Si_4 and Ge-Ge_4 units. The energy gain is a result of a delicate trade-off among these bonding environments. For example, the average of atom energies in Si-Si_4 and Ge-Ge_4 units (when $a_s = a_{Si}$ and referring to the central atoms) is $-(4.630+3.813)/2=-4.222$ eV with the Tersoff potential. By replacing these units with Si-Si_3Ge and Ge-Ge_3Si, with average $-(4.477+3.971)/2=-4.224$ eV, one gains 2 meV. For a Ge substrate, abrupt and ordered interfaces become almost degenerate. There is a small deviation in the predictions of the two potentials, possibly due to the slightly different treatment of elastic energies.

TABLE II. Enthalpy of formation ΔH (in meV/atom) of the Si_4/Ge_4 superlattice constrained on various substrates. The number of ordered monolayers is denoted by q; r denotes randomized layers (averages over five configurations). The first entry in each case is the result with the Tersoff potential; the second refers to the SW potential.

	$a_s = a_{Si}$	$a_s = a_{SL}$	$a_s = a_{Ge}$
$q = 0$	17.5	7.9	14.4
	17.5	8.4	16.0
$q = 2$	16.2	7.3	14.7
	16.5	7.7	15.7
$r = 2$	16.8	7.7	15.0
	17.0	8.2	16.2

The randomized interface (r=2, two monolayers with random distribution of species) has also lower energy than the abrupt SL, but higher than the ordered structure. However, the energy differences involved are only ~ 0.5 meV. This seems too small to stabilize thin-ordered layers at finite temperatures, thinking in equilibrium theory terms, because of the larger configurational entropy of the random alloy. It could only happen if, once ordering is formed, diffusion is so slow that it is unable to destroy it. There is experimental evidence that diffusion at the interface is rapid only at the very early annealing stages,[6] after which it diminishes. In such a case, contributions from configurational entropies might be minor. (In fact, equilibrium theory predicts that Si and Ge will freely dissolve into each other, giving a random alloy structure, but this is not the case seen in practice.)

Figure 2 shows the variation of the difference in ΔH between abrupt and ordered interfaces as a function of SL thickness. Appropriate supercells, similar to that of Fig. 1, are used for each case. For $n > 4$, as in Si_6/Ge_6 SL, there is the possibility for intermixing four monolayers at the interface. We either generate ordered layers ($q = 4$) by interchanging 2 Si and 2 Ge atoms, in a manner similar to that in Fig. 1(b), or random alloyed layers ($r = 4$). The ordered SL now involves mainly Si-$SiGe_3$ and Ge-$GeSi_3$ units (locally RH1), plus fewer RH2-type units. The gain in energy for $q = 4$ is even larger than for $q = 2$, with respect to $q = 0$ (abrupt), for $a_s = a_{Si}, a_{SL}$ substrates, but the ordered structure seems to be unstable on a Ge substrate for both potentials. This is possibly due to a larger cost in elastic energy. Ge

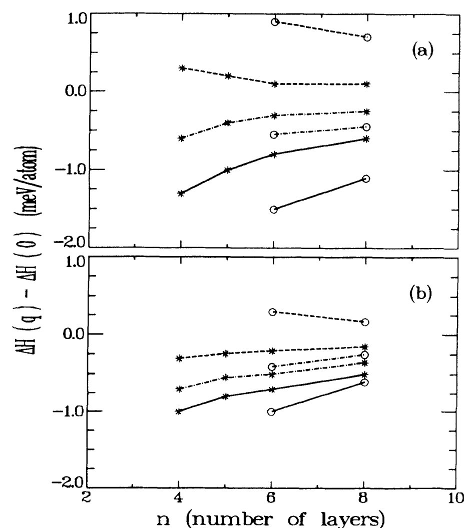

FIG. 2. The variation of the difference in ΔH among abrupt ($q = 0$) and ordered interfaces, as a function of SL thickness, for (a) the Tersoff potential, (b) the SW potential. Stars refer to $q = 2$, open circles refer to $q = 4$ (see text). Solid lines, Si substrate; dashed-dotted lines, free-floating SL; dashed lines, Ge substrate.

has softer moduli than Si (or SiGe), so it costs more to strain Si-Si and Si-Ge bonds on Ge rather than Ge-Ge bonds on Si. Also, the stability of ordered structures (both q=2,4) seems to weaken with increasing n (weakly interacting interfaces). Random alloyed layers are still stable (except on Ge) and have higher energies than the $q=4$ structure, but again $\Delta H(r=4)-\Delta H(q=4)\simeq 1$ meV.

In a previous work, Bernard and Zunger[7] found no tendency for thin-ordered, or even randomized, layers to be more stable than the abrupt interface on any substrate. Although one might expect that the instability of the ordered bulk SiGe phases is possibly not overcome by interface effects, the finding of a stable abrupt interface (with respect to at least some randomization, and on all substrates) is rather unexpected, taking into account the tendency of the Si-Ge system towards randomness. Their calculations were based on an anharmonic valence-force-field (VFF) model to treat the elastic energies and on cluster expansions for the chemical energies. In a similar approach (a harmonic VFF is used instead), Mäder, von Känel, and Baldereschi[8] found that thin-ordered layers could be stable with respect to the ideal SL. However, their energy differences are much too small (≤ 0.2 meV) to draw definitive conclusions. Besides, they have not considered the relative stability among ordered and randomized interfaces. They also find higher stability of interdiffused structures on Ge(001) substrates, in contrast to the tendency for reduced stability that was found here and explained above. [Similarly, we find that the RH1 bulk phase is epitaxially unstable on Ge(001), in agreement with *first-principles* calculations,[7] while Mäder, von Känel, and Baldereschi[8] find it stable on Ge(001). This might indicate an erroneous treatment of the elastic energies by their VFF model.]

Substantial post-growth intermixing, even for the shortest anneals, has been experimentally observed.[6] Initially, the number of Si-Ge bonds increases drastically. Upon further annealing it continues to increase but at a much lower rate, consistent with a low diffusion constant. Quite interestingly, two LO peaks (near 255 and 435 cm^{-1}) in the Raman spectra have been associated with ordering. These initially weak LO peaks increased sharply in intensity after a lengthy anneal. It is not clear whether these observations are relevant to our results. Assuming that these peaks truly indicate ordering (doubts have been raised about it[19]), we still need to know what diffusion mechanisms lead to an ordered structure, and what potential barriers prevent the randomization of thin layers.

Finally, similar arguments apply to the case of the reported[4] reversible *post-growth* order-disorder transition. It was observed that after high-T (≥ 1070 K) annealing and subsequent rapid cooling, all ordered domains vanish. However, upon *slow cooling* ordering reappears. Presumably, in this *quasistatic* process the system has the opportunity to move from the state of disorder ($\Delta S_{\rm conf}$ dominates) to a deeper minimum in the free energy (order). Again, we need to assume that at this temperature range, where order survives, $\Delta S_{\rm conf}$ is minor. Obviously, a realistic and quantitative estimate of configurational entropies, in connection with actual diffusion mechanisms, is needed to test this hypothesis.

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