

Surface and bulk equilibrium structures of silicon-germanium alloys from Monte Carlo simulations

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The technologically important alloy of silicon and germanium is known to have no long-range order in the bulk. Whether there is any short-range order in the bulk and the nature of the structure of the surface and near-surface regions remains the subject of some debate. We present a method of Monte Carlo simulation that is effective for studying the equilibrium structural properties of the bulk and strained-superlattice alloys. The simulations of the bulk alloy indicate that there is no short-range order and that the Si-Ge alloy is a true random alloy at room temperature and above. The surfaces of these alloys experience segregation of germanium to the surface, with no long-range order observed in the slightly silicon-rich subsurface layers, in agreement with recent experiments.

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I. INTRODUCTION

There has been a resurgence of interest in silicon-germanium alloys for fabricating electronic and optical devices.^{1,2} At room temperature and above, silicon and germanium are miscible at all compositions³ and the band gap can be varied from 0.66 eV for pure germanium up to 1.08 eV for pure silicon.⁴ Additionally, since the Ge lattice constant is only 4.2% larger than that of silicon, strained Si-Ge alloys can be grown on either silicon or germanium substrates. These superlattice systems have generated excitement because of their potential for creating various devices.^{1,2}

It has long been known that there is no long-range order in the bulk alloys, however, it is still unclear as to whether any short-range ordering exists, with some experiments suggesting it^{5,6} while others do not.^{7,8} Furthermore, little is known about the structure of the (100) surface of the alloy. Recent high-resolution electron-energy-loss spectroscopy (HREELS) studies^{9,10} indicate that segregation of Ge to the surface occurs.¹¹ A low-energy electron-diffraction (LEED) study of this surface shows a $p(2 \times 1)$ unit cell, suggesting that the surface atoms dimerize, as seen for either pure Si or Ge.

Most previous simulations have involved the study of superlattices,¹²⁻¹⁵ however, Kelires and Tersoff¹⁶ did study the equilibrium properties of the bulk and (100) surface of the alloy with a potential developed by Tersoff.¹⁷ They used a special grand canonical (constant chemical potential μ , temperature T , and pressure P) Monte Carlo (MC) simulation where the MC move consisted of either conventional random atomic displacements or a change of atomic species. This method allowed them to study equilibrium structural properties that could not be examined with conventional MC or molecular dynamics (MD) because of the very long annealing time that would be required for the atoms to diffuse. The calculated phase diagram indicated that all compositions of the alloy are stable down to the critical temperature of $T_c \approx 170$ K, after which segregation starts to occur for certain compositions. The surface, which

was simulated at constant volume rather than constant pressure, was found to segregate, producing a germanium-rich surface. By contrast, the second layer was silicon rich, while the third and fourth layers had the bulk composition but with a strain-induced ordering.

In this study, we present an alternative method of MC simulation where the equilibrium structures can also be determined without high-temperature annealing. The surface simulations here were carried out in the NPT ensemble, which lifts the constant volume restriction of previous work.¹⁶ We observe no long- or short-range ordering above T_c . We also see germanium segregation to the surface, with a relatively constant composition subsurface exhibiting some strain-induced ordering. These results agree well with experiment, indicating that this method of simulation should be an effective tool for studying superlattice structures or other mixed systems.

II. MONTE CARLO SIMULATION METHOD

A constant-temperature, constant-pressure, and constant number of particles MC simulation¹⁸ was employed in this study. In a constant-pressure simulation, the size of the simulation box is allowed to vary and the changes are accepted with a probability P of

$$P_{V_{\text{old}} \rightarrow V_{\text{new}}} = \exp\{-\beta[\delta U + P_{\text{ext}}\delta V - N\beta^{-1} \ln(V_{\text{new}}/V_{\text{old}})]\}, \quad (1)$$

where δU is the change in potential energy, P_{ext} is the external pressure (which is set to zero for our purposes), N is the number of particles, and V_{old} and V_{new} represent the old and new volumes, respectively. This allows the system to take on its natural value of the lattice constant rather than artificially holding it fixed, as in the case of a superlattice. In addition to the constant-pressure MC moves, we allowed two additional types of moves. The first type was random atomic displacements (referred to as normal MC moves) over all of the atoms in the system and the second type was a switch of any pair of atoms in the system. Furthermore, after every attempted switch,

the neighbors and next-nearest neighbors of the atoms that were attempting to switch were subject to normal MC moves. This allowed the neighboring atoms to relax in the case where a Si atom and a Ge atom were exchanged (since each may have potentially moved into a site where the bond lengths were either too long or too short). The configurations during these relaxations were not included in the averaging of thermodynamic quantities, since they were potentially not part of a Markov chain, which is required for MC simulations.¹⁹ This method facilitates finding the equilibrium structures for specific compositions without explicitly allowing diffusion by long-time, high-temperature annealing, which is typically the experimental procedure that is carried out before experimental measurements can be performed.

A drawback of this method is that it is not suitable for studying phase separation at low temperature, unlike the method of Kelires and Tersoff.¹⁶ The reason for this is simply that, at low temperatures, it is very unlikely for a silicon and germanium to switch in the simulation since the atoms are already near a minimum in energy for whatever environment in which they might happen to be. By exchanging them, the change in potential energy is in general large and positive. At a low temperature, this move would rarely be accepted. A simple modification of the algorithm that would circumvent this problem would be to attempt a switch and then do regular MC moves on the neighboring atoms before computing δU for the switch. This would allow the atoms to relax to a new minimum energy structure and therefore the change in energy would be negative for a move which was truly favorable. This current limitation in the method is not important for our purposes, however, because we are mostly interested in the structure of materials grown at or above room temperature. For theoretical studies of low-temperature structures and associated phase transitions, the method of Kelires and Tersoff¹⁶ is a more appropriate choice.

The model system consisted of either 12 or 9 layers, for the bulk and surface studies, respectively. Each layer contained 32 atoms with periodic boundary conditions. For the surface studies, periodic boundary conditions are imposed only parallel to the plane of the surface, with the bottom layer held fixed in both lattice position and random composition to represent the bulk. Initially all bond lengths were set equal and determined by linear interpolation of the lattice constant from the given composition.

The Si-Si potential employed was the Stillinger-Weber²⁰ (SW) two- and three-body potential for condensed phases of silicon. The Ge-Ge interactions were modeled with a reparametrization of SW by Ding and Andersen (DA).²¹ Finally, the Si-Ge cross terms were taken to be the geometric means of the parameters in the SW and DA potentials, as suggested and investigated by Abraham.²² This set of parameters yields qualitatively reasonable agreement with other studies for the energetics of the system. For example, density-functional calculations of Martins and Zunger²³ find that the cohesive energy of the alloy (-4.91 eV/atom) is indeed the geometric mean of the pure phases (-4.65 and -5.19 eV/atom for germanium and silicon, respectively).

TABLE I. Chemical and microscopic strain contributions to enthalpy of mixing. All energies are in meV/atom.

		ΔE_{MS}	ΔE_{chem}	ΔH
Zinc-blend	SW ^a	0	+6	+6
	Tersoff ^b	0	+6	+6
	MZ (LDA) ^c	0	+9	+9
Disordered	SW	+3	+3	+6
	Tersoff	NA ^d	NA	+7
	MZ (LDA)	+9	+5	+14
	Expt. ^e	NA	NA	+7

^aSW denotes the Stillinger and Weber potential, Ref. 20.

^bTersoff denotes the Tersoff potential, Ref. 17.

^cMZ denotes density-functional calculations for zinc-blend structure and Keating-type potential calculation for disordered structure, from Martins and Zunger, Ref. 23.

^dNA denotes not available.

^eExperimental results from Ref. 25.

Srivastava, Martins, and Zunger²⁴ proposed that the enthalpy of mixing is composed of a microscopic strain (MS) and chemical (chem) contribution, i.e., $\Delta H = \Delta E_{MS} + \Delta E_{chem}$. The chemical term contains contributions due to chemical bonding, while the strain term comes about by the three different optimal bond lengths adopting nonoptimal bond angles when these bond lengths are distributed randomly. A comparison of the energetics of this potential with those of others is presented in Table I and it can be seen that this choice of potential is in reasonable agreement with available information.^{17,20,23,25}

A variety of temperatures and compositions were investigated for both the bulk and surface alloys. One thousand random atomic displacement (normal MC) moves were attempted on randomly chosen atoms, after which a constant-pressure move and an atom-atom switch were attempted. These moves then were followed by 100 normal MC moves over the nearest and next-nearest neighbors of the pair of atoms that may have switched. This cycle of moves was repeated for 1 000 000 or more normal MC moves.

III. RESULTS AND DISCUSSION

A. Low-temperature structures

As discussed above, we would not expect low-temperature segregation to be achieved from a randomly mixed initial structure. However, at 0 K, the lowest energy structure would be a fully phase-separated system. This is because a Si-Ge bond is weaker than $\frac{1}{2}U_{Si-Si} + \frac{1}{2}U_{Ge-Ge}$, where U_{A-A} is the strength of an $A-A$ bond. Thus, the lowest-energy structure would be one that maximized homoatomic bonds, even though this creates a strain at the interface of the two phases. This system was briefly investigated by starting the system in a segregated state. At 0 K, the system stayed segregated as expected. As the temperature was increased to 50 K, a

few switches were accepted so that occasionally silicon atoms would embed themselves in the germanium phase and vice versa. This shows that, as the temperature is increased from absolute zero, silicon and germanium become miscible in small proportions up to some T_c , above which temperature they are completely miscible at all compositions. By 100 K, the system seems to mix completely after a long enough simulation time, indicating that T_c for the SW-DA potential is lower than that for Tersoff's potential.¹⁷

The silicon-germanium alloy is often referred to in terms of solution theory, where the atoms are assumed to be sites on a regular lattice. An ideal solution is one in which the mixture of the species is governed purely by entropic effects, i.e., the potential energy of such a system is independent of the local positions of the silicon and germanium atoms. However, this is not true for Si-Ge alloys. A regular solution is a better description here because the assumption of position independence of the total energy is removed, although any dependence on the microscopic strain is ignored. In such a system, the segregation transition is now driven by both energetic and entropic effects. Using a mean-field solution, such as the Bragg-Williams approximation, the critical temperature for a fourfold coordinated lattice is found to be²⁶

$$T_c = 2 \Delta U / k_B \quad (2)$$

at $\chi_{\text{Si}} = \chi_{\text{Ge}} = \frac{1}{2}$, where $\Delta U = \frac{1}{2}\epsilon_{AA} + \frac{1}{2}\epsilon_{BB} - \epsilon_{AB}$ (ϵ_{AA} is the A - A bond energy). For the SW-DA potential, $\Delta U = 5.7$ meV/atom so that regular solution theory (RST) predicts a $T_c \approx 130$ K, whereas Tersoff's potential yields a $T_c \approx 170$ K from RST. Recent density-functional theory with MC sampling²⁷ also predicts a $T_c \approx 170$ K, while local-density-approximation (LDA) results of Martins and Zunger²³ produced a $T_c \approx 210$ K. The μ PT MC simulations of Kelires and Tersoff are in excellent agreement with the Tersoff RST critical temperature, with a segregation T_c from MC ≈ 170 K. By contrast, the present simulations exhibit mixing below the predicted RST value of T_c for the SW-DA potential. One possible explanation is that the current method of simulation is producing a metastable structure in these regions. Alternatively, we may be observing a phase analogous to a supercooled fluid, in which the phase mixing is frozen in at $T < T_c$. However, when the temperature is lowered to 75 K, the $\text{Si}_{0.5}\text{Ge}_{0.5}$ alloy does start to segregate, indicating that whatever the cause of the metastability, it is not very large. In actuality, attempts to grow crystals of the alloy at such a low temperature experimentally would probably result in the formation of an amorphous, inhomogeneous mixture anyway, due to kinetic barriers to diffusion. Given that actual materials growth and operation will occur at higher temperatures, the rest of the simulations in this study were at room temperature and above.

B. Structure for room temperature and above

Experimentally, no long-range order (LRO) is observed in the bulk alloy at any temperature or composition. However, alloys grown using molecular beam epitaxy

(MBE) exhibit LRO along (111) planes,^{28–30} which is destroyed by annealing at 700 K.³⁰ The bulk alloys in these simulations also did not show LRO. However, when a surface is formed, long-range ordering is induced at the surface, as discussed later.

The issue of short-range ordering (SRO) in the bulk alloys is more controversial than that of long-range ordering. This is partly due to difficulties in interpreting the experimental measurements, making computer simulation an effective alternative tool for examining this question. The degree of SRO was analyzed in two ways, the first being an examination of the neighbor distribution, i.e., the coordination number of an atom to a different type of atom. Figure 1 shows the theoretical example for a purely random system of a 50%-50% alloy and the results from simulations of a 50%-50% alloy at 298 and 500 K for the silicon-atom neighbor distribution. Note that all three distributions are reasonably symmetric. If there was a tendency for like atom to cluster together, then the peaks on the left-hand side would increase while those on the right-hand side would decrease. Other compositions show essentially the same behavior, i.e., they follow the random alloy distribution. However, the shapes of the distributions were found to be sensitive to the lattice constant, indicating that growth on lattice-mismatched substrates could lead to very different structures than those of the bulk alloy. Another method of measuring the tendency to cluster is that due to Cowley,³¹ where a degree of order, α , is defined by

$$\alpha_i = 1 - (P_i^{AB} / \chi_B), \quad (3)$$

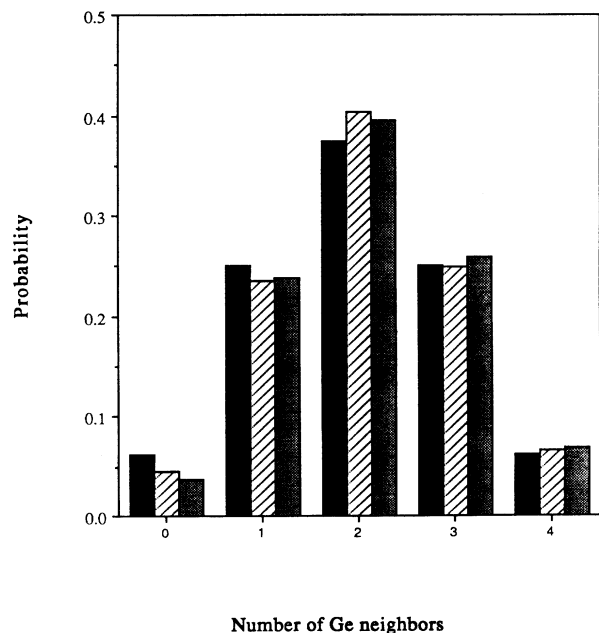


FIG. 1. Neighbor distribution for Si atoms in the $\text{Si}_{0.5}\text{Ge}_{0.5}$ bulk alloy. The number of Ge neighbors is along the horizontal axis. Solid bars show a theoretical random distribution, striped bars are MC results for $T = 298$ K, and shaded bars are MC results for $T = 500$ K. The standard deviation of this data does not exceed 0.03.

where i is the neighbor shell (i.e., $i=1$ for the nearest neighbors, $i=2$ for the next-nearest neighbors, etc.), P_i^{AB} is the probability of an atom of type B being a neighbor of an atom A , and χ_B is the mole fraction of B . α varies from $+1$ to a negative value of $1 - (1/\chi_B)$, with positive values correlated with a tendency for like atoms to cluster and a value of zero indicating a purely random distribution. For all compositions examined and at all temperatures of 298 K and above, we found α to be close to zero, as seen in Table II. Thus, even for disparate mixtures (unequal compositions) we observed no tendency to cluster. To test that this was not a function of the starting configuration, the system was started either from a random mixture or a system where the germanium atoms were initially clustered. In both cases, the system would mix randomly by the end of the simulation. As a severe test of this, Table II lists the values of α_i for a $\text{Si}_{0.95}\text{Ge}_{0.05}$ system, where we see α remains close to zero. The only exception is at low temperatures where some clustering is evident (vide supra), which is also shown in Table II for contrast.

A simple estimate for the lattice constant of an alloy can be obtained from Vegard's law, which assumes a simple linear relationship between the two pure substance's lattice constants. Experimental³² and theoretical^{27,33} studies have shown that Si-Ge alloys follow Vegard's law quite closely with only a small negative deviation. Figure 2 shows the lattice parameter as a function of composition for the system at 298 K, compared to Vegard's law and experimental results.³² The lattice parameter also expands smoothly with temperature, with values of 5.534, 5.546, and 5.562 Å for $T=0, 298,$ and 500 K, respectively. Interestingly, we find that the lattice constant only started changing in the simulations after the system mixed completely and the bond lengths relaxed, even though such fluctuations were allowed throughout the simulations.

The structure of the (100) surface of the alloy is not well understood. In the only previous simulations of which we are aware, Kelires and Tersoff¹⁶ indicated that Ge segregated to the surface, with a silicon-rich second layer and a bulk composition for all other layers. HREELS studies⁹⁻¹¹ found that annealing a $\text{Si}_{0.60}\text{Ge}_{0.40}$ alloy at 700 K produced an almost pure Ge surface. For a composition $\text{Si}_{0.80}\text{Ge}_{0.20}$, the surface was found to be about 75% Ge with a Si-rich subsurface. In our simulations, germanium also segregates to the surface leaving silicon-enriched subsurface layers. A simple rationalization for this observation is that Ge segregates to the surface because it has weaker bonds than silicon. Thus, the

TABLE II. Cowley's order parameter as a function of temperature and composition.

% Si	% Ge	T (K)	α_1	α_2
50	50	298	-0.03	-0.02
50	50	500	-0.01	-0.02
75	25	298	-0.05	-0.03
95	5	298	-0.03	0.03
95	5	50	0.26	0.14

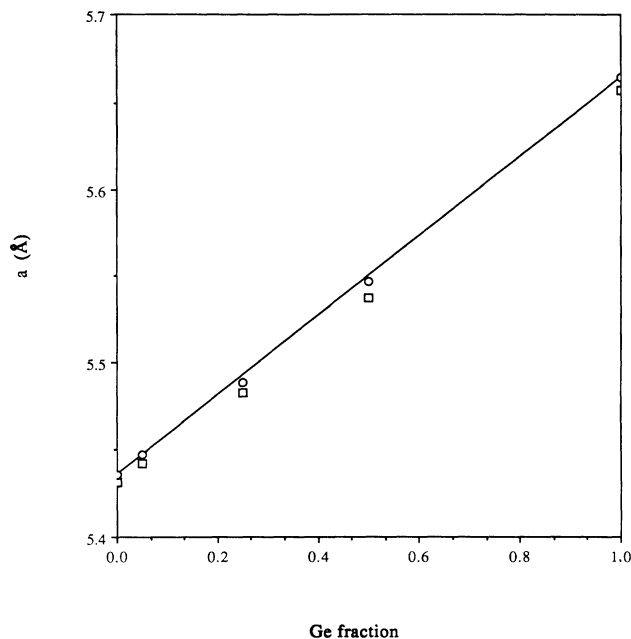


FIG. 2. Lattice parameter as a function of composition. The solid line represents Vegard's law, the open circles are the simulation results, and the squares are experimental results from Ref. 32.

potential energy of the crystal is minimized by segregating Ge atoms to this reconstructed surface that is replete with one dangling bond per atom. In other words, the surface free energy of Ge is lower than that of Si. Additionally, moving a silicon atom from the surface to the bulk provides for more opportunities for the formation of strong Si-Si bonds. Figure 3 shows the (temperature-dependent) composition that we find for the $\text{Si}_{0.5}\text{Ge}_{0.5}$ alloy as a function of depth into the crystal. We only show the first six layers in Fig. 3 because layers 7 and 8 yield composition affected by the presence of fixed layer 9. Only the surface layer shows a large deviation away from the bulk composition. However, there does appear to be a slight depletion in the near-surface layers, although this effect is not as pronounced as in the previous simulations.¹⁶ Other stoichiometries also remain close to their corresponding bulk compositions except at the surface layer, which is always found to be Ge rich. As the temperature is increased, the fraction of Ge atoms on the surface decreases (due to entropy), contrary to what is seen experimentally. This is easily understood in terms of kinetic effects ignored in the simulation. At high temperatures during annealing experiments, Ge atoms can diffuse farther to get to the surface, while in the simulations, atoms can always be exchanged from anywhere within the system. Thus, we are examining the thermodynamically preferred structures while ignoring kinetic barriers that preclude diffusion of Ge to the surface at lower temperatures.

For all compositions examined, the Si and Ge atoms at the surface form dimer rows, as is now generally accepted for Si and Ge (100) surfaces.³⁴ In a $\text{Si}_{0.90}\text{Ge}_{0.10}$ alloy, we

find that the surface is not pure Ge but has some randomly distributed Si atoms on the surface. At such a composition, almost all of the Ge atoms would prefer to segregate to the surface to make a pure Ge surface, however, entropic effects prevent this. This makes physical sense also since, even under high-temperature annealing, it would be unlikely for atoms to work their way to the surface from deep within the crystal. The Ge atoms that segregate to the surface probably originally resided in a near-surface layer.

We do not observe the significant deviation from the bulk composition in the second layer that was seen in previous simulations,¹⁶ although there does appear to be

some silicon enrichment of the near surface layers, especially at 298 K. A major difference between our work and that of Kelires and Tersoff is that their simulations fixed the lattice constant at the value for silicon. Consequently, we carried out an additional simulation at 298 K where the lattice constant was held fixed at the silicon value. In this case, the second layer was significantly silicon enriched, 88% Si, as opposed to a bulk value of 50%. Thus, the constraint in their model is responsible for the observed substantial enriching behavior. This makes sense physically, since this external constraint would disfavor formation of Ge-Ge bonds, leading to a preference for the shorter Si-Ge bonds between surface

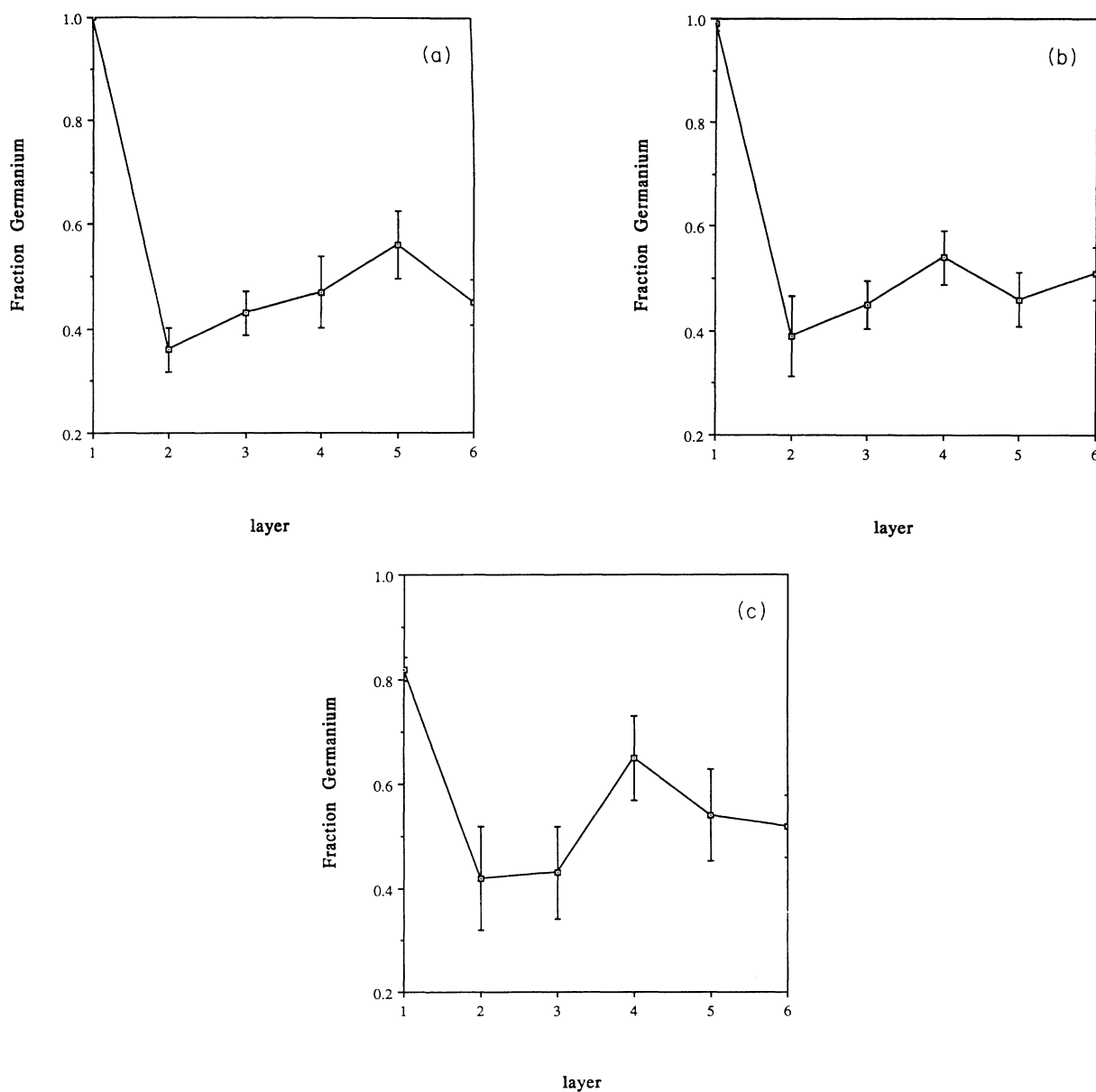


FIG. 3. Composition as a function of depth into the crystal for the $\text{Si}_{0.5}\text{Ge}_{0.5}$ alloy surface. Layer 1 is the surface layer. (a) is for $T=298$ K, (b) is for $T=500$ K, and (c) is for $T=1000$ K. At all temperatures, Ge segregates to the surface, with the other layers consisting of slightly Si-enriched layers. At higher temperatures, some disruption of Ge segregation to the surface occurs.

and second-layer atoms. Therefore, although previous simulations may be valid for superlattice structures where real constraints on the lattice constant exist, the current results are probably a more accurate description of the pure alloy's surface and near-surface structure. The previous simulations found a strain-induced ordering within the third and fourth layers, which we also observed in our constant-pressure simulations. This ordering occurs because the atoms are in two different types of environments because of the reconstruction on the surface. The sites are either strained by a compression (under the dimer rows) or an expansion (under the troughs between the dimer rows). This strain drives the larger germanium atoms to occupy the expanded sites while the silicon atoms prefer the compressed sites. Since this effect is seen in the constant-pressure simulations, it can be regarded as being a universal phenomenon that could exist in pure alloys as well as superlattices. These results are encouraging for the use of Si-Ge alloys as electronic devices that may need to operate at elevated temperatures. Our results indicate that for materials grown under MBE conditions, where diffusion may occur (and, hence, allow Ge atoms to segregate to the surface during growth), the structure of the surface is affected only at very high temperatures and that the near-surface layers remain random alloys, although they may be slightly silicon enriched. Although in these simulations this overall enrichment is partially a consequence of the reduction of the number of germanium atoms that have segregated to the surface, this phenomenon may be present in the true alloy, since diffusion is extremely slow and therefore the germanium atoms that segregate would have to come from the near-surface layers.

IV. SUMMARY

In conclusion, a simple MC method involving volume fluctuations, atom switches, and two types of random atomic displacement makes an effective tool for studying the structure of Si-Ge alloys of fixed composition. No long- or short-range order is observed, lending credence to the theory that these alloys behave like regular solutions. At temperatures below 100 K, these alloys phase separate, although some nucleation of Ge clusters inside a Si phase (and the reverse) were observed at 50 K for a

Si_{0.50}Ge_{0.50} alloy. At room temperature and above, the (100) surface of the bulk alloy segregates Ge to the surface and the subsurface layers become silicon rich. In 50%-50% or Ge-rich alloys, the surface is pure germanium, except at very high temperatures. In silicon-rich alloys, the surface is not pure Ge, with some Si atoms dispersed randomly throughout the surface layer. The second- and third-layer compositions show a slight, temperature-dependent deviation from the rest of the subsurface layers in constant-pressure simulations. However, when the lattice constant is constrained to that of pure silicon, the second layer becomes predominantly silicon atoms. The previous constant-volume MC work¹⁶ probably predicts alloy structures appropriate for a superlattice, where the external constraint imposed on the lattice constant is realized. However, constant-pressure simulations that obtain an optimal lattice constant must be performed in order to correctly predict surface and near-surface structures for bulk alloys and thick films or large superlattice periods. This MC method seems to be effective for revealing structures at temperatures above the critical temperature. Structures predicted with this technique should be comparable to structures formed by MBE or following annealing cycles. Since the predicted structures for the bulk and surface pure alloys agree quite well with experiment, studies of the structures of Si-Ge superlattices using this simulation technique are now in progress.³⁵

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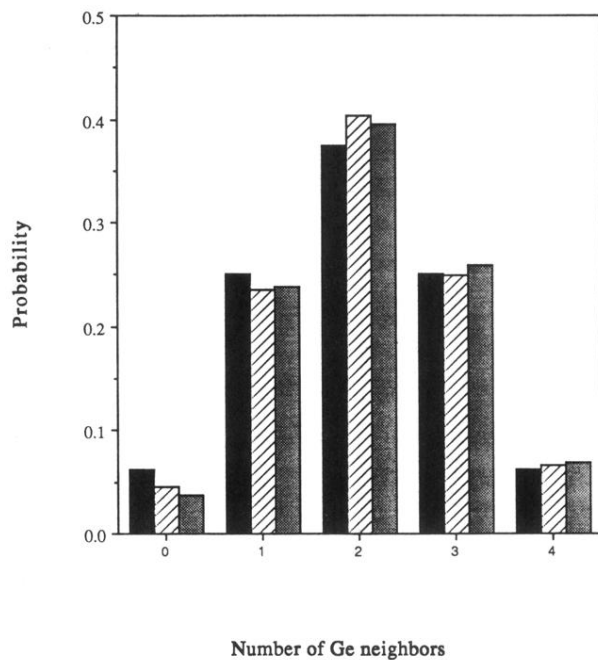


FIG. 1. Neighbor distribution for Si atoms in the $\text{Si}_{0.5}\text{Ge}_{0.5}$ bulk alloy. The number of Ge neighbors is along the horizontal axis. Solid bars show a theoretical random distribution, striped bars are MC results for $T = 298$ K, and shaded bars are MC results for $T = 500$ K. The standard deviation of this data does not exceed 0.03.