Equilibrium Alloy Properties by Direct Simulation: Oscillatory Segregation at the Si-Ge(100) 2×1 Surface

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We study surface and bulk equilibrium in Si-Ge alloys by direct simulation. The composition at a reconstructed (100) surface varies with depth in a complex oscillatory way. Lateral ordering occurs even in the fourth layer, driven by the local stress field. The bulk phase diagram is well described by regular solution theory.

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Theoretical understanding of the equilibrium properties of semiconductor alloys has progressed rapidly in recent years,[1] spurred in part by the increasing importance of such alloys in electronic devices. However, until now these studies have been restricted to homogeneous bulk systems; and the theoretical methods employed, such as the cluster-variation method[2] (CVM), offer little immediate prospect of going beyond such systems.

Because of the important role of reconstructed surfaces in modern epitaxial growth techniques, it is particularly desirable to understand how the properties of alloys are modified in such inhomogeneous environments. Here we report what is apparently the first calculation of equilibrium segregation at a semiconductor surface, using a variant of the grand-canonical Monte Carlo method introduced by Foiles[3] to study metal surfaces.

We find surprising results for the 2×1 dimer reconstruction of the (100) surface of an Si-Ge alloy. Strong *oscillatory* variations with depth are found in the equilibrium composition profile near the surface. Even the fourth layer shows striking deviations from bulk behavior, with a marked inequivalence between the two atoms in the unit cell, which reflects the strain induced by the reconstruction.

The method used here is a type of direct simulation. Simulations which allow each site to be either Si or Ge, with an Ising-type Hamiltonian, are quite standard; but the evaluation of the appropriate effective interactions, incorporating the effects of strain implicitly, has only been feasible in the simple bulk situation. On the other hand, methods such as molecular dynamics (MD), which permit arbitrary atomic displacements, and which incorporate strain explicitly, cannot, in practice, reach equilibrium for solid solutions because of the large barriers to atomic diffusion and the short simulation times which are feasible.

Foiles[3] pointed out that the advantages of both approaches could be combined by using a continuous-space Monte Carlo (MC) algorithm, which incorporates two kinds of MC "moves." The simulation includes small random atomic displacements, as well as moves which convert Si atoms into Ge and vice versa, allowing compositional equilibration. This approach may be viewed as a specialized case of the grand-canonical Monte Carlo method, which has been extensively discussed.[3]

An equilibrium distribution is obtained in the usual way, accepting trial moves with a probability

$$\exp[(\mu_{\rm Si}\Delta n_{\rm Si}+\mu_{\rm Ge}\Delta n_{\rm Ge}-\Delta U)/kT]$$

(but not more than 1), where ΔU is the change in potential energy due to the move, μ is the chemical potential for a given species, and Δn is the change in the number of atoms of that species. The total number of atoms remains fixed, so only the difference $\Delta\mu=\mu_{\rm Si}-\mu_{\rm Ge}$ is relevant.

In order to make the simulation tractable, we use an empirical interatomic potential[4] to model the interactions. Although less accurate than state-of-the-art quantum-mechanical calculations, this approach has been extensively tested.[4-6] It is well suited to the present problem because it describes both the surface dimerization and the elastic properties reasonably well.

Before addressing the surface problem, we illustrate the method by considering the bulk Si-Ge phase diagram, which has also been treated recently by Qteish and Resta.[7] Since the primary driving force for segregation here is the atomic size mismatch, this problem provides a stringent test of our ability to equilibrate both the spatial and chemical degrees of freedom simultaneously and consistently.

We map out the phase boundaries in the natural way. For each temperature, we equilibrate a periodically repeated cubic cell of 216 atoms, at zero pressure, over a range of values of the chemical-potential difference $\Delta\mu$. The presence of a first-order transition with $\Delta\mu$ indicates a miscibility gap at that temperature, and the alloy compositions just before and after the transition represent the miscibility limits. Such a calculation is illustrated in Fig. 1.

Because of the finite cell size, the cell can fluctuate between Si-rich and Ge-rich phases. As a result, the transition is broadened, and the average cell composition is, strictly speaking, a continuous function of $\Delta\mu$ at all tem-

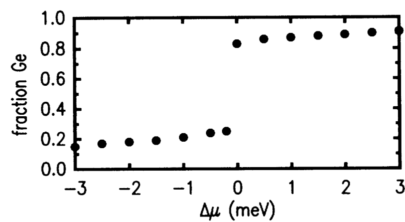

FIG. 1. Alloy composition vs chemical-potential difference (relative to an arbitrary origin) at 150 K.

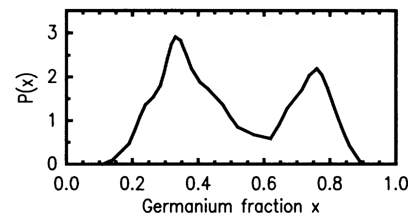

FIG. 2. Probability $P(x)$, in arbitrary units, for the simulation cell to have an instantaneous Ge fraction x, plotted vs x. Curve shown is for 160 K, at a value of $\Delta\mu$ around the transition value.

peratures. As seen in Fig. 1, the cell used here is large enough that the transition may be quite abrupt. Nevertheless, just below the minimum temperature for complete miscibility, T_c, such fluctuations can interfere with an accurate identification of the miscibility limits, or even of the existence of a transition.

In order to avoid this problem, we examine not only the average cell composition, but the probability distribution for this composition. As shown in Fig. 2, for a temperature just below T_c, this distribution is bimodal, as the cell fluctuates between phases. At a value of $\Delta\mu$ where the cell will be found in either of the two phases with nearly equal probability, the average compositions of the respective metastable phases give very good estimates of the miscibility limits. Moreover, the mere existence of such a bimodal distribution confirms that the temperature is below T_c. Above T_c, however broad the distribution, it should be unimodal.

Detailed simulations as a function of $\Delta\mu$ at a series of temperatures result in the phase diagram shown in Fig. 3. There is a small but systematic asymmetry in the phase diagram. Extrapolating by eye gives T_c around 165 or 170 K.

For comparison, regular solution theory predicts[8] that $T_c = 2\Delta H/k$, where ΔH is the enthalpy of mixing per atom for the 50-50 alloy, and k is the Boltzmann constant. Since the interatomic potential used here gives[4] an enthalpy of mixing (for the perfectly random alloy at $T=0$) of 7.3 meV/atom, T_c is predicted to be 170 K.

Thus the simulation results are in excellent agreement with regular solution theory, as expected for this nearly ideal solution. This agreement, in fact, provides a strong test of the accuracy of the MC equilibration. If the atomic positions did not relax sufficiently in response to atom switching, the effective mixing enthalpy (and hence T_c) would be much higher.

The enthalpy of mixing here is about 30% lower than that calculated by Qteish and Resta.[7] This difference may be due to inaccuracies in our empirical potential, such as the failure to describe the observed[9] "bowing" of the elastic constants with alloy composition. On the other hand, it may be due to the fact that fully relaxed geometries are used here, whereas only partial relaxation was included in Ref. 7. In either case, the associated uncertainty is only 2–3 meV/atom, and so will prove unimportant in the surface studies below, where the relevant energy scale is an order of magnitude larger.

Alloy surfaces have been extensively studied for metals,[3,10,11] but not for semiconductors. Experimentally, it is now possible to measure the composition site by site, using atom-probe techniques or low-energy electron diffraction.[10] Not only is enrichment of one constituent generally observed at metal surfaces, but in some cases [e.g., Pt-Ni or Pt-Rh(100)] the composition varies nonmonotonically with depth.[10] Theoretical approaches[11] for metal surfaces (other than that of Ref. 3) have generally not included the local strain effects associated with atomic size mismatch or surface reconstruction, and so are not applicable to the case of Si-Ge alloys.

The Monte Carlo approach described above is now applied to the problem of a semiconductor surface. The simulation cell used here is a 24-layer (100) slab, with 288 atoms per cell (12 per layer) periodically repeated in two dimensions. The two surfaces are prepared in the 2×1 dimer reconstruction,[12] which is known to occur (with minor variations) for both Si and Ge(100).

We begin by considering a relatively low temperature, 300 K. It is presumably not possible experimentally to equilibrate the alloy at such a low temperature, but this case provides a natural starting point for discussing higher temperatures.

For simplicity, the surface lattice constant is fixed at the pure Si value. Since Si-Ge alloys are often grown

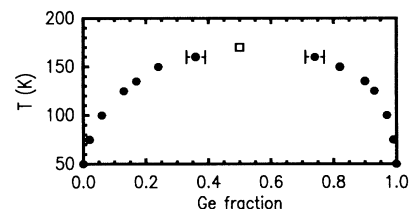

FIG. 3. Calculated phase diagram of Si-Ge alloy. Solid circles are pointed on the phase boundary, below which segregation occurs. Statistical error bars are negligible except where shown. The open square is the result of regular solution theory, based on calculated enthalpy of mixing for the perfectly random 50-50 alloy at $T=0$.

epitaxially on Si substrates, this case is as physically relevant as that in which the alloy takes its natural lattice constant. In any case, tests indicate that, at temperatures above T_c, such small variations in the surface lattice constant have little effect. At lower temperatures, the epitaxial constraint suppresses segregation,[1,13] permitting us greater freedom in the choice of alloy composition. A convenient value of $\Delta\mu$ is used here, which yields (with the constrained surface lattice constant) a bulk alloy composition of about 50% Ge.

The results of the simulation are summarized in Fig. 4, which shows the site-by-site composition in equilibrium. The most obvious effect is the strong segregation of Ge to the surface. Ge has a lower surface energy than Si, about 0.07 eV/atom lower for the (100) 2×1 with this potential, so segregation of a layer of Ge to the surface reduces the enthalpy.

A surprising feature of the results is that the Ge concentration is strongly *reduced* in the second layer, relative to the bulk. Thus the concentration profile at the surface is oscillatory. Stranger still, the third and fourth layers show strong deviations from bulk composition, tending towards one Si and one Ge on the respective sites of the 2×1 cell at low temperatures.

The striking behavior of these deeper layers can be easily understood, using the concept of an atomic stress tensor,[14] or more specifically its trace, which defines a local compression. Heuristically speaking, some atoms may be viewed as under compression, if their bonds are shorter than the sum of covalent radii, while other atoms are under tension. This can be quantified by considering a uniform expansion of the system. Then by analogy with the macroscopic pressure, we define an atomic compression

$$p_i = -dE_i/d\ln V\,, \qquad (1)$$

where E_i is the energy of atom i, and V is the volume. This compression can be converted into units of pressure by dividing by an appropriate atomic volume.

The decomposition of the total energy into atomic contributions is, in principle, not unique, but may often be made in practice. In particular, this decomposition is specified explicitly in the definition of the interatomic potential used here.[4] The value of such a decomposition in understanding atomic-scale behavior of complex systems has already been demonstrated.[15]

Examining the (100) 2×1 surface of pure Si in this way, we find that the second layer is under a large compression, about 0.4 eV/atom, corresponding roughly to a pressure of 30 kbar. Substituting a Ge atom, which is larger than Si, would obviously tend to raise the energy of site under compression, but would lower the energy of a site under tension.

Since the logarithm of the volume ratio of bulk Ge and Si is 0.12, the above compression can be converted into an estimate of the energy gained or lost by substituting Ge for Si, by multiplying the compression (1) by 0.12. For the second layer, this yields an estimate of 0.04 eV/atom, which is very significant on the scale of thermal energies.

In the fourth layer, the two atoms per cell are inequivalent. One atom is directly below the dimer, and is under a compression of about 0.3 eV, while the other is between dimers, and is under a tension of similar magnitude. Thus the former site is driven towards being pure Si at low temperatures, and the latter towards pure Ge. A similar effect is seen in the third layer, but is a bit weaker.

For the surface dimer layer, the compression is very weak, consistent with the relatively unconstrained geometry. The surface composition is driven by the reduction of surface energy associated with the dangling bond, and not by atomic compression.

Understanding the room-temperature equilibrium structure, and the effects which cause it, we now wish to get an overview of the behavior with increasing temperature. For this purpose we adopt a somewhat simpler approach. Instead of calculating the chemical potential at each temperature for the bulk composition of interest, we fix the number of Ge and Si atoms. Only moves which switch a Ge and a Si simultaneously are considered, thus permitting diffusion while conserving the cell composition.

Figure 5 shows the resulting site-by-site composition, for the first four layers of a slab with 50-50 composition,

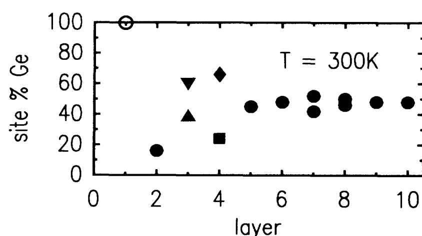

FIG. 4. Composition vs layer number, for fixed slab composition at 300 K, as described in text. For layers with inequivalent sites, both sites are shown.

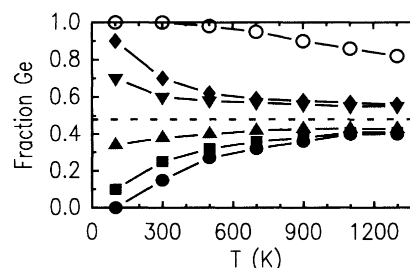

FIG. 5. Composition of individual sites vs temperature, for fixed slab composition, as described in text. As in Fig. 4, open circles are surface layer, filled circles are second layer, triangles and inverted triangles are third layer, and diamonds and squares are fourth layer.

as a function of temperature. The enhancement of Ge concentration at the surface remains strong even at high temperature because of the large lowering of the surface energy. Composition variations in deeper layers are reduced, but still moderately large. Even the lateral composition modulation in the fourth layer is almost 20%, easily large enough to observe experimentally, up to the highest temperatures considered, and probably up to the melting point.

In conclusion, we have demonstrated that it is feasible to calculate equilibrium properties of semiconductor alloys by direct simulation, even for the case of a reconstructed surface. This approach is applicable to a range of important problems, including segregation at semiconductor interfaces, grain boundaries, and other defects.

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