

Monte Carlo Studies of Ternary Semiconductor Alloys: Application to the $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ System

P. C. Kelires

Physics Department, University of Crete, P.O. Box 1470, 714 09 Heraclion, Crete, Greece
and Foundation for Research and Technology-Hellas (FORTH), P.O. Box 1527, 711 10 Heraclion, Crete, Greece
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The structural properties of Si-Ge-C alloys are studied using Monte Carlo simulations. The large size mismatch among the constituents is overcome by introducing atom-identity switches accompanied with neighbor-atom relaxations. A repulsive interaction between carbon atoms is found, so no clustering is observed. No formation of Ge-C bonds is foreseen. The lattice structural parameters show strong deviations from linear behavior.

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Understanding of the equilibrium properties of semiconductor binary alloys has progressed rapidly in recent years, instigated by the importance of these alloys in electronic devices. The prototypical example is offered by Si-Ge alloys and superlattices grown on various substrates. These have been studied extensively [1], both theoretically and experimentally. The crucial ingredient in the description of these epitaxial systems is the built-in strain due to the lattice mismatch with the substrate. This affects not only the good quality of the grown crystals (appearance of dislocations and other extended defects as a result of strain relaxation), but also the band structure, energy gap, and band offsets as well.

A promising possibility to tackle such problems is to introduce a third element in the binary mixture, hoping that in this way one will have good control over the structural and electronic properties of the strained material. Because of this idea, the ternary Si-Ge-C alloy system has attracted considerable attention recently. The possibility that the incorporation of carbon atoms in pseudomorphic $\text{Si}_{1-x}\text{Ge}_x$ layers, grown on Si substrates, can compensate the built-in compressive strain is quite appealing. A number of experimental reports are devoted to this subject [2-4], but a theoretical treatment is lacking.

Here, we report the first attempt to obtain the equilibrium structure of the ternary $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ alloys. Extensive Monte Carlo (MC) simulations shed light on various aspects of the problem. By introducing a novel technique of atom-identity switching, which is accompanied with nearest-neighbor-atom relaxations, we were able to explicitly show the dependence of Si and Ge concentrations on increasing C content, and trace the distribution of C atoms in the lattice, both in the bulk and in the surface regions. The possibility for the clustering of C atoms and for the formation of Ge-C bonds is studied. We also examine the response of the structural parameters of the system to C incorporation.

The main obstacle in simulating such a system is the huge size mismatch between C and the other two species. We would like to incorporate C atoms in the Si-Ge lat-

tice in a natural way, and not by inserting them randomly by hand. This process, involving atom-identity switches, requires a rather severe structural alteration in the neighborhood of the insertion. Of course, we accept that C atoms are entering into the network substitutionally [2,3]. We accomplish this task and obtain compositional equilibration by using a continuous-space MC algorithm in the semigrand canonical ensemble [5], used successfully before [6,7], but with a significant modification in order to overcome the large formation energies and barriers for diffusion.

In this approach, one requires that the total number of atoms N , the pressure P , and the temperature T remain fixed, while allowing fluctuations Δn in the number of atoms of each species, driven by the appropriate chemical potential differences ($\Delta\mu = \mu_i - \mu_j$, $i, j \equiv \text{Si, Ge, C}$, in the present case). In practice, one models this ensemble by having, besides the usual random atomic displacements and volume changes, simple flips which convert the identity of a randomly chosen atom into one of the other possible identities of the system. The probability of accepting such a trial move is given by

$$P_{\text{acc}}(i \rightarrow i') = \text{Min}(1, \exp\{[\mu_{\text{Si}}\Delta n_{\text{Si}} + \mu_{\text{Ge}}\Delta n_{\text{Ge}} + \mu_{\text{C}}\Delta n_{\text{C}} - \Delta U(s^N)]/kT\}), \quad (1)$$

where $\Delta U(s^N)$, a function of the $3N$ scaled atomic coordinates s , is the change in potential energy due to the move. For systems with small atomic size mismatch among the constituents, equilibration within this ensemble is straightforward. When the atomic size mismatch, however, is large as in the present case, very few MC flips involving formation or elimination of a C site will be accepted, due to the generation of severely strained bonds with the neighboring atoms, and equilibration is impossible to achieve.

To overcome this problem, we introduce appropriate relaxations of first-nearest-neighbor atoms following each

attempted move. The potential-energy part of the Hamiltonian now reads

$$\Delta U(s^N) = E_{\text{cluster}} \left(i \rightarrow i', \sum_{k=1}^{\text{nn}} \sum_{j=1}^3 \Delta s_k^j(r_{0k}^j) \right) - E_{\text{cluster}}^0, \quad (2)$$

where the energy is estimated over the cluster of atoms affected by the move and the relaxations, instead of over the whole system, before and after the move. Each nearest neighbor is relaxed away or towards the central atom (which changes identity from i to i' and is labeled 0) in the bond direction \vec{r}_{0k} . This means that every scaled coordinate s^j is altered according to the scheme

$$\Delta s_k^j(r_{0k}^j) = A_{\text{bond}} r_{0k}^j, \quad (3a)$$

$$A_{\text{bond}} = \{b_{0k}[i'(0), i(k)] - |\vec{r}_{0k}| \} \chi_{\text{rel}} / |\vec{r}_{0k}|, \quad (3b)$$

where b_{0k} is the bulk equilibrium bond length among atoms 0 (after the flip) and k . The relaxation parameter χ_{rel} , ranging from 0.0 to 1.0, decides how large the relaxation (expressed by A_{bond}) should be. We find that intermediate values of χ_{rel} make the best effect. This is illustrated in Fig. 1, which shows the drastic increase of switch-success rate, relative to null relaxation, as a function of χ_{rel} . For values approaching unity, i.e., when the bond relaxes to its ideal bulk value, the success rate drops (but still remains higher than for $\chi_{\text{rel}} = 0.0$) due to straining of the backbonds in the neighboring atoms. We hope to further improve this scheme by extending the relaxations to more distant neighbors. We should also point out that the success rate of flips involving C sites is much lower than for Si or Ge (at least at the low C concentration limit). This is consistent with, though not directly linked to, the high formation and diffusion activation energies of C substitutionals in Si [8,9].

To model the interatomic interactions and calculate the energies entering in Eq. (2) we use a well-tested [7]

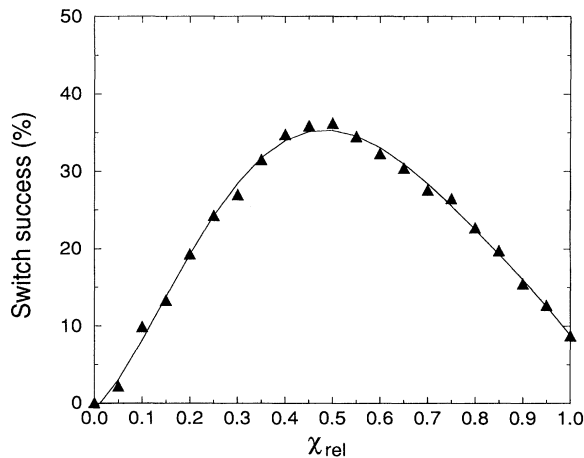


FIG. 1. Variation of switch success as a function of the relaxation parameter (see text). The zero of the y axis corresponds to the success rate with null relaxation.

empirical potential [10], which we extended to the case of a ternary system. It starts with potentials for elemental Si, Ge, and C; then the cross interactions are determined from the elemental parameters by an interpolation scheme. Here, in order to model the unknown Ge-C interactions, we have fitted the potential to the enthalpy of formation ($\Delta H \approx 0.2$ eV/atom) of the hypothetical zinc-blende Ge-C alloy, calculated using the pseudopotential-density-functional method [11]. The large positive value of ΔH means that Ge and C are immiscible at zero pressure under equilibrium conditions. Sankey *et al.* [12] also arrived at a similar value for ΔH .

For the simulations we use cubic supercells of 512 atoms with periodic boundary conditions. We start with well-equilibrated $\text{Si}_{1-x}\text{Ge}_x$ random alloys, above the critical temperature for phase separation $T_c \approx 170$ K [7] (most simulations are done at 300 K). The composition x is obtained by a suitable choice of $\Delta\mu_{\text{Si-Ge}}$. Then we vary the carbon chemical potential μ_C (referred to μ_{Si} or μ_{Ge} ; there are only two independent chemical potentials-fugacities in the system), in order to obtain the desired C content in the cell.

We first examine how Si and Ge respond to the incorporation of C into the network. We generate a series of samples with increasing C content χ_C , either epitaxial or bulk, in the way explained above (we keep $\Delta\mu_{\text{Si-Ge}}$ fixed). Strictly speaking, these samples are in “quasiequilibrium”; we go well above the solid solubility of C in Si ($\leq 2 \times 10^{-3}$ at. %, even lower in Ge), so the material is metastable, but it can be obtained experimentally by nonequilibrium techniques (molecular beam epitaxy [2], solid phase epitaxy [3], etc.). The results of these extensive calculations are shown in Fig. 2. The most prominent effect is the steady elimination of Ge atoms from the lattice as χ_C increases (see both panels of Fig. 2), evidence for the strong repulsive Ge-C interaction. C atoms substitute almost solely at Ge sites. From Eq. (1), it follows that, in general, two factors have control over the alloy compositions. The chemical-potential part enforces C over Si or Ge, as μ_C increases, but on equal terms ($\Delta\mu_{\text{Si-Ge}}$ fixed). So, the driving force for Ge elimination is chemical-bond preference (favoring Si-C bonds over Ge-C bonds), which dominates the potential energy part $\Delta U(s^N)$.

Very few Ge-C bonds are found ($\leq 5\%$), and only when equilibrating the samples at high T 's (~ 1000 K), and at high χ_C . At low C concentrations Ge-C bonds are completely absent, in agreement with Raman measurements [2]. It is instructive to look at the distribution of C atoms in the lattice, in the most technologically interesting case, i.e., for $\chi_C \leq 0.03$. Figure 3 shows the radial distribution functions $g(r)$ for a typical sample strained on Si(100). In the total function, we easily identify the Si-C peaks, but no first-neighbor C-C peak is observed. A closer look at the C-C partial $g(r)$ reveals that C atoms stay at least 4.0 Å apart. This indicates a large repulsive interaction

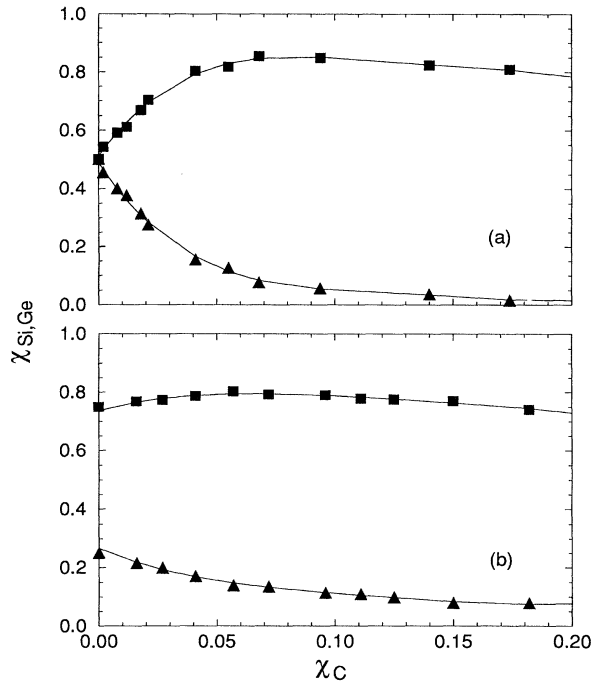


FIG. 2. Equilibrium Si and Ge concentrations as a function of C content. Squares stand for Si, triangles for Ge. (a) Bulk alloy, starting from $\text{Si}_{0.5}\text{Ge}_{0.5}$. (b) Strained alloy on Si(100), starting from $\text{Si}_{0.75}\text{Ge}_{0.25}$.

between substitutional carbons (Ref. [9] estimates a first-neighbor C defect interaction energy of 1.3 eV in Si). Thus clustering of C in the real material is quite unlikely. Obviously, the driving force keeping C atoms away is minimization of strain energy. Only for χ_{C} exceeding 0.2 do C-C homopolar bonds appear.

There have been reports [4,13] that for C concentrations of $\sim 4\%$ the epitaxial films develop stacking defects, and at $\sim 11\%$ become amorphous. Although our cells are small for the study of extended defects, we were able to detect the onset of amorphization, by monitoring the ring statistics of samples strained on Si(001). We find that significant disorder appears in the network for $\chi_{\text{C}} \geq 0.15$, in the form of odd-membered rings (mainly fivefold and sevenfold). Also, in a short-range picture, we observe a rather unusual overcoordination of Ge ($n_{\text{Ge}} \sim 4.3$). Si shows a similar trend, but in a much lesser degree ($n_{\text{Si}} \sim 4.03$), while C remains fourfold coordinated. The role of tensile stress in the production of such disorder is presently examined.

We have also looked at the possibility for segregation of C to the surface of the material. Earlier work [7] had predicted that, in equilibrium, the SiGe(100)-(2 \times 1) reconstructed surface is Ge rich, even at high T 's, while the profile in subsurface layers varies with depth in an oscillatory way. This picture has been recently verified by photoemission measurements [14]. Here, it is found

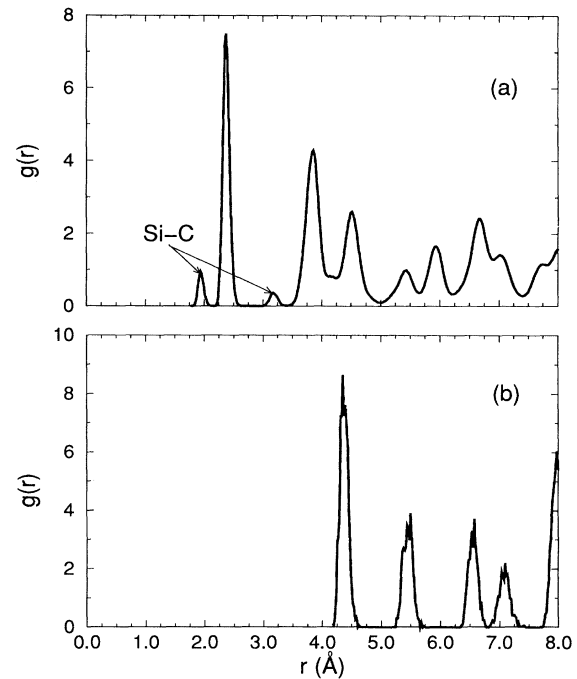


FIG. 3. Radial distribution functions of a $\text{Si}_{0.73}\text{Ge}_{0.24}\text{C}_{0.03}/\text{Si}(100)$ alloy at 300 K. (a) Total function. (b) Partial C-C function.

that for low concentrations, C is preferentially found in the bulk (in agreement with experiment [2]). This is a typical example of an alloy exhibiting competition among the solute elements, a case well studied for metal alloys [15]. If Si is the base element and Ge and C are the solute elements, then Ge being the more surface-active element will repel C from the boundary, due to their strong repulsive interaction. It might even lead to the enhancement of Ge surface segregation. At higher concentrations ($>10\%$), however, some C is also found on the topmost layer forming Si-C dimers. Obviously in this case, the repulsion among C substitutionals, aided also by the strong driving force for Si-C bond formation, overwhelms the Ge-C interaction.

Finally, we study how C incorporation compensates the compressive strain in $\text{Si}_{1-x}\text{Ge}_x/\text{Si}(100)$ films. Succeeding to reduce this epitaxial strain will effectively increase the critical thickness above which dislocations appear. The crucial point here is the amount of carbon needed for this purpose, given a certain Ge content. In earlier analyses of experimental data [2-4], it was assumed that the structural parameters of the alloy obey a linear interpolation scheme of the elemental parameters (Vegard's law). To the contrary, here we find significant deviations from such linear behavior. We demonstrate the degree of deviation, and its consequences, for alloys with fixed Ge composition, $\chi_{\text{Ge}} = 0.25$. In the case of pseudomorphic epitaxial growth (without dislocations), the macroscopic

theory of elasticity (MTE) predicts that the perpendicular lattice constant of the alloy is given by the expression

$$a_{\perp}(x, y) = a_0(x, y) \left[1 - \frac{2c_{12}(x, y)}{c_{11}(x, y)} \frac{a_{\text{Si}} - a_0(x, y)}{a_0(x, y)} \right], \quad (4)$$

where $c_{11}(x, y)$ and $c_{12}(x, y)$, the elastic constants of the alloy, as well as the equilibrium lattice constant $a_0(x, y)$, are obtained by a linear interpolation to those of bulk Si, Ge, and C. Panel (a) of Fig. 4 shows the deviation of the MC results for a_{\perp} from the predicted values, $\Delta a_{\perp} = a_{\perp}^{\text{MTE}} - a_{\perp}^{\text{MC}}$, as a function of C content. At $\chi_{\text{C}} = 0.0$ ($\text{Si}_{0.75}\text{Ge}_{0.25}$), there is already a small deviation from Vegard's law ($\Delta a_{\perp} \approx 4 \times 10^{-3} \text{ \AA}$), noticed also before [16,17]. Deviations increase rapidly with C content, and even for $\chi_{\text{C}} = 0.03$, Δa_{\perp} becomes an order of magnitude larger. Interestingly, the variation of Δa_{\perp} is not linear. We are presently investigating the response of the elastic constants to alloying with C, in order to understand this inharmonic effect [18].

These deviations from elasticity theory have a profound effect on strain compensation. This is demonstrated in panel (b) of Fig. 4, showing how epitaxial strain, defined as $\epsilon_{\perp} = (a_{\perp} - a_{\text{Si}})/a_{\text{Si}}$, is reduced with increasing C content. If MTE holds, then more than 3% of C

is needed to compensate the strain for $\chi_{\text{Ge}} = 0.25$. On the other hand, the MC results show that less C ($\approx 2\%$) is enough to accomplish this. Such a difference in the critical χ_{C} is not unimportant. Adding this extra carbon amount could drive the system above the threshold for breakdown in crystallographic perfect layer growth (generation of stacking defects). In fact, a very sensitive and even abrupt dependence of disorder on χ_{C} is found experimentally [4,13]. The details of the lattice elastic response to the carbon amount added definitely needs further consideration.

In conclusion, we have demonstrated in this paper how to obtain equilibrium properties of ternary semiconductor alloys, composed of atoms with large size mismatch. The relevant MC method is applied here to the $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ alloy, but it could be as easily used to treat other systems, where the appropriate interatomic interactions are known.

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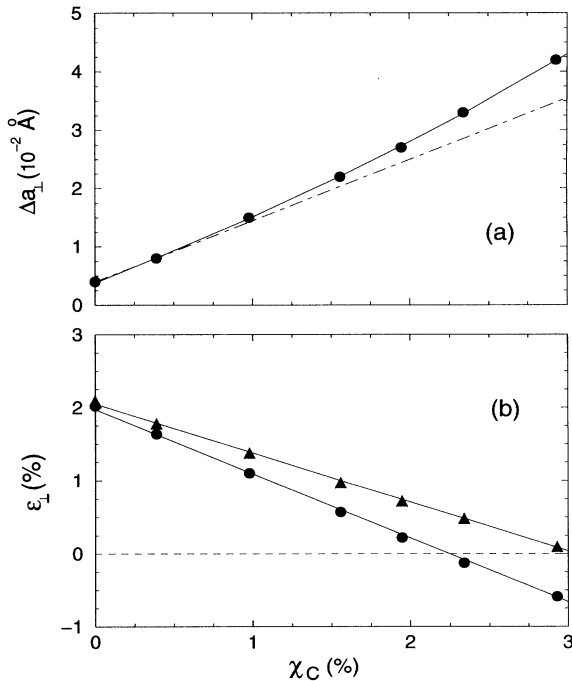


FIG. 4. Response of lattice parameters of $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y/\text{Si}(100)$ ($x = 0.25$) alloys, at 300 K, to C incorporation. (a) Deviation of MC results for a_{\perp} from the predictions of MTE (see text). Dot-dashed line shows a hypothetical linear variation of Δa_{\perp} . (b) Strain compensation. Triangles denote MTE predictions; circles are the MC results.

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