Bondlengths and Phase Stability of Silicon-Germanium Alloys under Pressure

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Bondlengths of Si–Si, Si–Ge, and Ge–Ge pairs in Silicon-Germanium alloys were determined as a function of hydrostatic pressure using \textit{ab initio} electronic structure calculations. A series of ordered structures was selected to represent the various atomic environments in actual alloys. Enthalpies of formation computed for these structures were used to model the phase stability under hydrostatic pressure.

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Germanium-silicon alloys form completely miscible solid solutions with the diamond structure during solidification from the melt.\(^1\) The electronic, optical and mechanical properties of these alloys derive in part from the 4.2\% difference in the lattice parameters of Si and Ge. Therefore, Ge–Si alloys have become important materials for bandgap engineering. In order to better understand these materials, and to facilitate modeling of material properties, a detailed knowledge of the bondlengths is important. However, experimental studies using extended X-ray absorption fine structure (EXAFS) measurements have given contradictory results. It remains controversial whether bondlengths in Ge–Si alloys vary with composition. With one notable exemption,\(^2\) measurements may have been affected by large bias stresses inherent in epitaxially grown alloy. Therefore, an \textit{ab initio} calculation of Ge–Si alloys might shed light on these matters, by providing bondlengths as a function of composition and local environment, and by providing information on the degree of short range order that occurs at thermodynamic equilibrium.

In addition, as bandgap engineering exploits the ability to select the atomic configuration of alloys by deposition techniques, it would be of interest if layered structures could be obtained by alternate methods. In Nature heterostructures commonly occur as a result of ordering phenomena. Therefore, in this work the effect of pressure on the tendencies toward the formation of ordered superstructures has been examined. Only moderate pressures have been considered because at pressures over 10 GPa the diamond lattice becomes unstable and a structural phase transformation takes place.\(^3\) While it is not at all unlikely that at very high pressures layered and other ordered structures might be stabilized, it is unlikely that such superstructures would be of practical use, because upon return to ambient pressure the material would become highly defected when it passes through a structural transition.

A series of ordered structures were selected to study the bondlengths and thermodynamic properties of Si–Ge alloys. The ordered structures were generated by distributing Si and Ge atoms within a single diamond cube. As such a cube contains 8 sites, there are \(2^8 = 256\) possible configurations, however, many of these configurations are related by symmetry, so that there are in fact 16 distinct structures only, see Fig. 1. Equilibrium atomic positions in these structures were calculated using a quasi Newton-Raphson algorithm for minimizing the atomic forces as computed \textit{ab initio} with a plane wave pseudopotential method employing ultrasoft pseudopotentials.\(^4\) The cutoff energy in all cases was set to 188.3 eV and the cutoff for the augmentation of the charge was set to 241.9 eV. The local density approximation of the density functional theory was used, with the exchange-correlation potential of Ceperly-Alder as fitted by Perdew and Zunger.\(^5\) Reciprocal space integrations were carried out using a mesh of \(10 \times 10 \times 10\) Monkhorst-Pack \textquoteleft special\textquoteright k-points.\(^6\) For all structures the periodic cell selected was the cubic diamond cell with 8 atoms, even for those structures which have a smaller unit cell. Calculations were repeated for various hydrostatic pressures in which both unit cell lattice parameters and angles, as well as internal degrees of freedom were optimized. The stress was in all cases converged to better than 0.01 GPa, and atomic forces were less than 10 meV/\(\text{Å}\). Results of the calculations at zero pressure are listed in Table 1. It is apparent that in spite of the structural optimization most structures remain rather close to the original cubic cell. The formation enthalpies are positive for all structures, indicating the phase separating nature of the alloy. The formation enthalpies are very small, in part because Ge–Si is isoelectronic meaning that chemical interactions are very weak. Therefore, the positive enthalpies of formation reflect mostly the relaxation enthalpy associated with the size difference of the Ge and Si atoms.

Figure 2 displays the equivalent-cubic lattice parameters of the 16 structures in Fig. 1. It should be noted that the Si (Ge) lattice parameter is about 0.8 (0.6)\% smaller than the experimentally determined value, which is within a typical error range for LDA type calculations. The lattice parameter of Ge–Si alloys is almost a linear function of composition, with but a slight negative deviation of about 0.14\% at equiatomic composition, in agreement with experimental evidence.\(^7\) This result is in contrast to an earlier \textit{ab initio} calculation which found a positive deviation.\(^8\) Possibly, the small positive deviation in the earlier work results from the approximations involved in limiting the chemical interactions to pairwise terms. The deviation, in any case, is very small, less than 0.001 nm at equi-atomic composition. Moreover, the configurational dependence of the lattice parameter is exceedingly small. The symbols in Fig. 2 at composition 0.25, 0.375, 0.5, 0.625, and 0.75 show multiple data points which are so closely spaced that they cannot be discerned on the scale of the plot. This suggests that short-range order in this
Fig. 1 Structures used for the determination of the bondlengths and phase stability. Note that structures labeled a-f exist with both Si-majority and Ge-majority variants, making for a total of 16 structures. cubic: (a), (b), (e), (g); tetragonal: (c), (j); orthorhombic: (f), (h); trigonal: (d), (i).

Table 1 Structure and formation enthalpy ($\Delta H_{\text{form}}$) of Si–Ge structures shown in Fig. 1.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Composition</th>
<th>$a$ (nm)</th>
<th>$b$ (nm)</th>
<th>$c$ (nm)</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>$\Delta H_{\text{form}}$ (meV/atom)</th>
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<tr>
<td>a</td>
<td>Ge$_8$</td>
<td>0.5623</td>
<td>0.5623</td>
<td>0.5623</td>
<td>90</td>
<td>90</td>
<td>90</td>
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<td>Ge$_7$Si</td>
<td>0.5590</td>
<td>0.5590</td>
<td>0.5590</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>7.08</td>
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<td>0.5558</td>
<td>0.5557</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>12.93</td>
</tr>
<tr>
<td>d</td>
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<td>0.5558</td>
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<td>90.03</td>
<td>90.03</td>
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<td>e</td>
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<td>0.5527</td>
<td>0.5527</td>
<td>0.5527</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>17.75</td>
</tr>
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<td>f</td>
<td>Ge$_3$Si$_3$</td>
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<td>0.5528</td>
<td>0.5527</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>13.97</td>
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<td>0.5497</td>
<td>0.5496</td>
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<td>90</td>
<td>90</td>
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<td>h</td>
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<td>0.5499</td>
<td>0.5499</td>
<td>0.5496</td>
<td>90.03</td>
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<td>90.03</td>
<td>14.01</td>
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<td>0.5497</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>15.90</td>
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<td>0.5498</td>
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<td>90</td>
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<td>0.5469</td>
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<td>17.17</td>
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<td>90</td>
<td>12.00</td>
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<td>90.03</td>
<td>90.03</td>
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<td>0.5414</td>
<td>0.5414</td>
<td>90</td>
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<td>90</td>
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<tr>
<td>p</td>
<td>Si$_8$</td>
<td>0.5387</td>
<td>0.5387</td>
<td>0.5387</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Fig. 2 Lattice parameter of structures shown in Fig. 1. The dashed line is a straight line between the terminal points, according to Vegard’s law.

alloy cannot cause changes in the lattice parameter.

The calculations show that the bondlengths of Si–Si, Si–Ge, and Ge–Ge nearest neighbor pairs depend on the alloy composition in a rather linear fashion as is shown in Fig. 3. However, the three types of bondlengths differ considerably at all compositions indicating that bondbending occurs. These results agree rather well with those recently measured with EXAFS by Yonenaga and Sakurai$^{25}$ in Czochralski grown Si–Ge alloys. In particular, they find that the Ge–Ge and the Si–Ge bondlengths decrease each by 0.000040 nm/atomic percent Si, whereas our calculation gives 0.000035 and 0.000031 nm/atomic percent Si, respectively. Our calculation also predicts a decrease of the Si–Si bondlength of 0.000027 nm for every atomic percent Si added to the alloy.

Other EXAFS studies$^{9,10}$ have given a somewhat smaller Ge–Ge bondlength change of 0.000030 nm/atomic percent Si, but in that work MBE grown Si–Ge alloys were used which might suffer from strain effects.$^{25}$ An elastic network model$^{11}$ with force constants fitted to experimental data has given comparable results: a decrease of the Ge–Ge, Si–Ge, Si–Si bondlengths of 0.000037, 0.000034, and 0.000030 nm/atomic percent Si, respectively. Another ab initio study$^{7}$ has given somewhat smaller changes in the bondlengths, with an average for the Ge–Ge, Si–Ge, and Si–Si bonds of approxi-
ultimately 0.000025 nm/atomic percent Si. The variation of the bondlengths with composition is much less than the variation of the lattice parameter with composition. The lattice parameter changes by 0.000236 nm/atomic percent Si, or almost an order of magnitude greater than the Ge–Ge, Si–Ge, and Si–Si bondlengths.

As Figure 3(a) indicates, there is very little variation in the bondlength between structures at the same composition. In particular the structures at equiatomic composition (structures g, h, i, and j in Fig. 1) represent various atomic environments, yet the bondlengths are the same to within about 0.1 percent. However, in other simulations a significant spread in the bondlengths was computed. This apparent contradiction is readily resolved when it is realized that the bondlength is very sensitive to the local composition and that in the large cells modeled in the other work more realistic composition fluctuations occur which then naturally give rise to a more or less gaussian distribution of bondlengths.

One might expect that, due to the 28% greater bulk modulus of Si as compared to Ge, pressure might significantly change the differentiation between bondlengths, and their composition dependence. Application of pressure would reduce the atomic size of the softer Ge more than Si, so that lattice parameters and bondlengths become more similar.

In Fig. 3(b) the bondlengths as a function of composition are shown at a hydrostatic pressure of 3 GPa. It is apparent that the Ge–Ge, Ge–Si, and Si–Si bondlengths are very clearly distinct and differ much from each other at all alloy compositions. However, the composition dependence of the bondlengths is reduced at a pressure of 3 GPa as compared to the 0 GPa case. The Ge–Ge, Si–Ge, and Si–Si bondlengths decrease each by 0.000026, 0.000024, and 0.000021 nm/atomic percent Si, respectively, which is noticeably less than at 0 GPa, as was expected on the basis of the argument above.

Figure 4 shows that in contrast to the bondlengths, there is a wide variety of bondangles centered around the ideal tetrahedral angle of 109.4712 degrees. The bondangles are very sensitive to the local configuration. The range in bondangles is greatest around equi-atomic composition. It should be noted that in concentrated alloys the Ge–Ge–Ge angles tend to be significantly smaller than the Si–Si–Si angles. This can be understood on the basis of the bondlengths. Ge–Ge bonds are longer than average, so that a Ge triangle is forced in a too small a space. This forces the two extremal Ge atoms to approach each other closer than according to the ideal tetrahedral bondangle. Conversely, Si–Si bonds are shorter than average, so that a Si triangle is stretched to connect with the surrounding atoms. This makes the tetrahedron more ‘linear’ than the ideal tetrahedral bondangle. Similar conclusions were drawn from the elastic network model.

To address the question whether layered structures might form spontaneously by ordering under pressure, the Si–Ge phase diagram has been computed as a function of pressure. Under hydrostatic pressure bondlengths are more similar, which reduces the relaxation enthalpy and the formation enthalpy.

A cluster expansion was used to represent the enthalpy of formation as a function of the correlation functions. It should be mentioned that the enthalpy, rather than the energy was used so that the expansion could be performed at various hydrostatic pressures. Formation enthalpies for the (relaxed) 16 structures shown in Fig. 1 were computed, so that in principal up to 16 effective cluster interactions (ECIs) could be determined. However, a cluster expansion using just 7 ECIs was found to reproduce the formation enthalpies to better than 16 μeV, and moreover gave a predictive error of less than 25 μeV. These extremely small errors in the cluster expansion are much less than the errors in the \textit{ab initio} data themselves.
Of course, formation enthalpies in the Si–Ge system are not large, the largest value of +22 meV/atom occurs for structure g (see Table 1). The cluster expansion consisted of a reference enthalpy (so-called empty cluster), an onsite enthalpy, the nearest and second nearest neighbor pair interactions represented by pairs 1-2 and 1-3 in Fig. 5(a), and three site ECI associated with the sites 1-3-4 and sites 1-3-5, and a five site ECI associated with sites 1-2-3-4-5. It should be mentioned that the ECIs associated with the last two clusters were much smaller than the other terms. The three site ECI associated with sites 1-3-4 was however, significant. De Gironcoli et al. found that unrelaxed Si–Ge alloys could be modeled with pair interactions up to the third neighbor shell only, but to correctly describe relaxed alloys pair interactions up to about twice the lattice parameter were needed. Possibly, such very long range pair interactions were needed because many-body interactions which properly can capture the angular nature of the bonding were not included in that work.

The cluster variation method was used to compute the phase diagram with 10-site and 5-site maximal clusters, shown in Fig. 5. These maximal clusters were generated according to the Vul-de Fontaine algorithm. A total of 85 correlation functions (including the empty cluster) occur in the disordered (diamond) structure, which were determined by minimization of the Gibbs free energy as a function of pressure, composition, and temperature using the Newton-Raphson method. The phase diagram, depicted at hydrostatic pressure of 0 and 3 GPa (see Fig. 6) shows a miscibility gap. At 0 (3) GPa pressure the maximal temperature $T_c$ is 223 (192) K, indicating that hydrostatic pressure lowers the miscibility gap. This is very reasonable, because as was mentioned pressure makes the Si–Si and Ge–Ge bondlengths more similar so that the energy of mixing which mainly derives from the relaxation energy, becomes less positive. At pressures of a few GPa the lowering of $T_c$ is quite linear, about 10 K/GPa. It is surprising and counter-intuitive that in other work a strong increase of the $T_c$ is found. The 0 GPa pressure $T_c$ found here (223 K) compares well with other work, such as the work based on an empirical potential by Kelires and Tersoff (170 K) and the ab initio work by de Gironcoli et al. (170 K), and slightly less well with that by Qteish and Resta (360 K).

The rather small pressure effect found in this work (10 K/GPa) is insufficient to eliminate the miscibility gap in the pressure range in which the diamond structure is stable.

Therefore, it is not possible to stabilize and form diamond-structure based ordered phases by application of hydrostatic pressure. The low value of $T_c$ indicates that Si–Ge alloys solidified from the melt, or annealed at high temperature have no short-range order, as was confirmed with CVM calculations. Of course, short or long range order can be induced by kinetic factors during the deposition process.

In conclusion, we have shown that Si–Ge alloys feature clearly distinct lengths for the Si–Si, Si–Ge, and Ge–Ge bonds. These bondlengths depend on composition, but not on how the neighboring Si and Ge atoms are arranged around the bond. The composition dependence of the bonds is similar to that found in other ab initio work, although the values reported here agree more closely with the EXAFS results of Yonenaga and Sakurai. The Si–Ge phase diagram is found to be a very weakly phase separating system with a $T_c$ of only 223 K. Application of hydrostatic pressure lowers the $T_c$ by about 10 K/GPa, which means that Si–Ge phase separates at all pressures at which the diamond structure is stable. Therefore no diamond-based ordered structures can be stabilized by pressurizing.

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REFERENCES