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Ab initio determination of the atomistic structure of Si_xGe_{1-x} alloy

P. Venezuela, G. M. Dalpian, Antônio J. R. da Silva, and A. Fazzio
Instituto de Física, Universidade de São Paulo, CP 66318, CEP 05315-970, São Paulo SP, Brazil

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We have performed systematical *ab initio* studies of the structural properties of Si_xGe_{1-x} alloy. To simulate the disordered alloy we use supercells where the Si and Ge atoms are randomly placed with the constraint that the pair correlation functions agree with their values for a perfect random alloy within a given tolerance. We obtain that the Si-Si, Si-Ge, and Ge-Ge bond lengths dependence with composition varies only slightly for the different kinds of bonds, with topological rigidity parameters between 0.6 and 0.7.

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I. INTRODUCTION

In the past few years, Si_xGe_{1-x} has overcome the reputation of a promising new material to become a reality for the microelectronics industry.[1,2] That happened mainly because of growth technique improvements.[3] The interest in this alloy is due to the possibility of band-gap engineering, as well as the development of high-speed electronic devices based on Si/Si_xGe_{1-x} heterostructures.[1,3]

Usually Si_xGe_{1-x} is grown on a Si substrate.[2] Thus, there is a lattice mismatch of up to 4%, depending on Ge concentration. Traditionally, the alloy would be grown pseudomorphically up to a critical thickness, with biaxial stress in the directions perpendicular to the growth. Nowadays, Si_xGe_{1-x} alloy may also be grown fully relaxed, with the use of grading composition layering techniques.[4] In this work we focus on the relaxed alloy.

Knowledge of the atomistic structure of this alloy is a prerequisite for the determination of several other important properties of this material, for instance, electronic properties, optical properties, thermodynamical properties, defects properties, etc. However, despite several experimental and theoretical studies, detailed understanding of the local structure of Si_xGe_{1-x} alloy is still an open question. In thermodynamical equilibrium at room temperature, Si_xGe_{1-x} forms a model random alloy without any substitutional order. This means that Si-Si, Si-Ge, and Ge-Ge bonds coexist in the material in a $x^2:2x(1-x):(1-x)^2$ proportion. Equilibrium bond lengths and angles are determined by the competition between two mechanisms: (i) if bond bending is energetically favorable, the system tends to reach the Pauling limit,[5] where the bond lengths are the sum of the constituent-element atomic radii. As a consequence, they are composition independent. (ii) On the other hand, if bond stretching is energetically favorable, the system tends to reach the Vegard limit,[6] where all the bond lengths have the same value and vary linearly as a function of composition.

It is well established that the character of the bonds in Si_xGe_{1-x} is closer to the Pauling limit than to Vegard's.[7] However, theoretical and experimental results disagree about the details of the bond-length dependence on composition. Previous theoretical, non–*ab initio* studies indicate that all three bonds Si-Si, Si-Ge, and Ge-Ge have the same behavior as a function of composition. On the other hand, experimental results indicate that the dependence on composition varies strongly with the kind of bond. In particular, Aubry *et al.*[7] claim that the Si-Si bond length has almost no dependence on the alloy composition, whereas for the Si-Ge and Ge-Ge, the bond-length dependence on alloy composition is significant.

Here we report *ab initio*, quantum mechanical calculations, for the structural and thermodynamical properties of the Si_xGe_{1-x} alloy. As far as the structural properties are concerned, we focus on the variation of the bond lengths with composition for two reasons: (i) this property is very important for the determination of the structure of the alloy, and (ii) it is necessary to understand better the discrepancies described above between experiments and theory. In Sec. II, we show how we simulate a random alloy by means of a finite-size supercell, and we also describe the *ab initio*, electronic structure calculations framework. In Sec. III we present our results and discuss them in comparison with previous calculations and experiments, and finally in Sec. IV we summarize our main conclusions.

II. THEORETICAL PROCEDURES

We performed *ab initio*, total energy calculations in order to determine the most stable microscopic configurations of Si_xGe_{1-x}. In order to do that, it is necessary to model the alloy by means of periodically repeated, finite supercells. First, we discuss how we generate a truly random distribution of Si and Ge atoms in the cells. The procedure we used is related to the special quasirandom structure (SQS) model proposed by Wei *et al.*[8]

For a supercell with a given number of sites, we generate a configuration σ where all the cell sites are occupied by the components of the alloy. Then, we calculate the pair correlation functions, given by

$$\Pi_m(\sigma)=\frac{1}{Z_m N}\sum_{i,j}\Delta_m(i,j)S_iS_j\,. \tag{1}$$

Here Π_m is the mth-order pair correlation function, Z_m is the number of mth-order neighbors to a site, N is the number of atoms in the cell, $\Delta_m(i,j)$ is 1 if sites i and j are mth-order neighbors and zero otherwise, and S_i is a variable taking values -1 if site i is occupied by Si and $+1$ if it is occupied by Ge. For a perfectly random (R) infinite alloy, the pair correlation function does not depend on m,

$$\Pi_m(R)=(2x-1)^2, \tag{2}$$

where x is the Si concentration. For a given configuration we calculate the deviation from randomness as

$$\delta\Pi_m(\sigma)=|\Pi_m(\sigma)-\Pi_m(R)|. \tag{3}$$

The quantity above indicates how random the σ configuration is. Our protocol to generate an acceptable configuration is the following: (i) we place the Si and Ge atoms in a N-atom supercell at random, with a specified composition ($N_{Si}/N=x$); (ii) we calculate $\delta\Pi_m(\sigma)$ for that configuration; (iii) if it is large, the configuration is not statistically independent. Then, we generate a new configuration as in (i) and repeat the process until the calculated $\delta\Pi_m(\sigma)$ are smaller than a chosen tolerance ε. For the 128-atom supercells, we search for alloy configurations that obey the following criteria: $\delta\Pi_m(\sigma)=0$ for $m=1$, 2, and 3 and $\delta\Pi_m(\sigma) \leqslant 0.001$ for $m=4$ and 5. For the 16-atom supercells, we search for alloy configurations that obey $\delta\Pi_m(\sigma)=0$ for $m=1$, 2, and 3.

After selecting the random configurations using the procedure described above, we performed first-principles, total energy calculations,[9] based on the density functional theory[10] with the local density approximation[11] (LDA) for the exchange-correlation potential. The electron-ion interactions are described using the norm-conserving pseudopotentials of Bachelet, Hamann, and Schlüter[12] in the Kleinman-Bylander[13] form. A plane-wave basis set was used with an energy cutoff (E_{cut}) of 12 Ry for the 128-atom cells and 20 Ry for the 16-atom cells. For the 128-atom cells the Brillouin zone (BZ) was sampled using the Γ point, and for the 16-atom cells it was sampled with 10 special k points.[14]

We always begin the calculations with the atoms sitting in the sites of a diamond lattice. Then, the total energy of the cell is minimized by allowing all atoms to move in the direction of the forces, until all force components are smaller than $0.025\ \text{eV/Å}$.

The systems which we calculated could, in principle, be trapped in metastable configurations. So we have done some tests in order to rule out this possibility. Beginning with the relaxed cell, we introduced random displacements in the atomic positions and let the system relax again. For random displacements amplitudes up to 15% of the average bond length, the system always relaxes back to the same configuration it had before. Therefore, it is unlikely that the configurations we have determined are trapped in a local minimum of the total energy.

After this procedure is done for several alloy compositions, we can plot the average bond length between atoms i and j, as a function of the Si composition (x). The slope of these curves (θ_{ij}) are related to the rigidity of the lattice. The topological rigidity parameter (a^{**}) can be defined as[15]

$$a_{ij}^{**}=1-\frac{\theta_{ij}}{(R_{Si}^0-R_{Ge}^0)}, \tag{4}$$

where R_{Si}^0 and R_{Ge}^0 are the equilibrium bond lengths for bulk Si and Ge, respectively. If $a^{**}\rightarrow 1$, the system reaches the Pauling limit, whereas if $a^{**}\rightarrow 0$, the system reaches the Vegard limit.

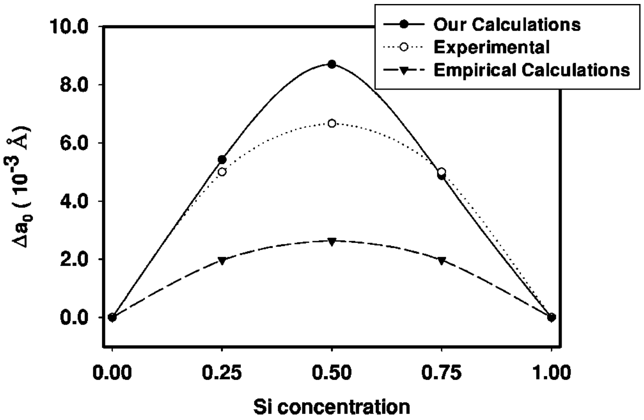

FIG. 1. Deviation from linearity of the lattice parameter, as defined in Eq. (5). Solid circles are our calculations, open circles are experimental results from Ref. 16, and triangles are empirical potential results from Ref. 20.

III. RESULTS AND DISCUSSIONS

A. Lattice parameter and alloy formation energy: Composition dependence

It is well established experimentally that the lattice parameter of $\mathrm{Si}_x\mathrm{Ge}_{1-x}$, as a function of x, presents a slight deviation from linearity.[16] The lattice parameter versus composition curve has a small, negative bowing. Therefore, we do not assume linearity, also known as Vegard's law,[6] but instead we determine the equilibrium lattice parameter for each composition studied. To perform such a task, we used the 16-atom cells, because at this size it is feasible to perform calculations that have total energies fully converged with respect to E_{cut} and BZ sampling.

For each composition studied, we calculated the total energy, as described above, for several volumes around the experimental volume. Then, the total energies obtained were fitted by the Murnaghan equation of state,[17] which resulted in the equilibrium lattice parameter $[a_0^{eq}(x)]$ for each composition. To quantify the bowing of the lattice parameter, we define its deviation from linearity as

$$\Delta a_0(x)=[xa_0^{Si}+(1-x)a_0^{Ge}]-a_0^{eq}(x), \tag{5}$$

where a_0^{Si} and a_0^{Ge} are the lattice parameters of bulk Si and Ge,[18] respectively. Notice that, according to the definition above, Δa_0 is positive when there is a negative bowing of the lattice parameter. In Fig. 1 we compare our results for Δa_0 with experimental results[16,19] and empirical calculations.[20] The agreement between our calculations and the experimental measurements is very good.[21] This gives us confidence that the modeling of the random alloy by the SQS procedure is a good approximation, even for a cell as

TABLE I. Alloy formation energy in meV/atom. x is the Si composition, and 16 and 128 refer to the size of the supercells used in our calculations.

x	16	128	Experimental[a]
0.25	3.0	3.5	-
0.50	4.7	4.8	6.5
0.75	2.3	3.2	-

[a] Reference 22.

small as 16 atoms. In all calculations with the 128-atom supercell, we use the lattice parameters determined by the procedure described above.

In Table I we show the alloy formation energy $\Delta E(x)$ defined as

$$\Delta E(x)=E_{Si_xGe_{1-x}}-[xE_{Si(bulk)}+(1-x)E_{Ge(bulk)}], \quad (6)$$

where $E_{Si_xGe_{1-x}}$, $E_{Si(bulk)}$, and $E_{Ge(bulk)}$ are the total energies per atom for the Si_xGe_{1-x} alloy and the Si and Ge bulk, respectively. As can be seen from Table I, our result for $x=0.5$ is in good agreement with the experimental result of Stringfellow.[22] Moreover, all our numbers are in fair agreement with previous theoretical calculations.[23,24]

As expected, the alloy formation energy is larger for $x=0.5$ than for $x=0.25$ and $x=0.75$. This is a consequence of a larger number of unlike bonds in the $x=0.5$ alloy. The small values of $\Delta E(x)$ (always smaller than $\simeq 5$ meV/atom) for Si_xGe_{1-x} imply a low critical temperature (T_c) for the decomposition of this alloy. The simplest way to calculate T_c is by equating $\Delta E(x)$ to $T_c\Delta S(x)$, where $\Delta S(x)$ is defined using an equation similar to Eq. (6) above, where the energy E is replaced by the entropy S. If we consider only the configurational entropy, $T_c\simeq 80$ K for $x=0.5$. This is the reason why, for most of the relevant temperatures, Si_xGe_{1-x} is a random alloy, as long as it is in thermodynamical equilibrium.

B. Bond lengths: Composition dependence

Recently, two experimental groups[7,25] have addressed the issue of the composition dependence of the bond lengths in Si_xGe_{1-x}. Aubry *et al.*[7] performed x-ray-absorption fine-structure measurements, and Ridgway *et al.*[25] performed extended x-ray-absorption fine-structure experiments. In Ref. 25, the Si-Si bond lengths were not measured. In Table II we show the values of the topological rigidity parameter (a^{**}) obtained in these experiments.

TABLE II. Topological rigidity parameter a^{**} as defined in Eq. (4). Our results compared with experiments.

Bond	Our results	Aubry *et al.*[a]	Ridgway *et al.*[b]
Si-Si	0.73	0.94	NA[c]
Si-Ge	0.69	0.84	0.88
Ge-Ge	0.65	0.70	0.72

[a] Reference 7.
[b] Reference 25.
[c] Not available.

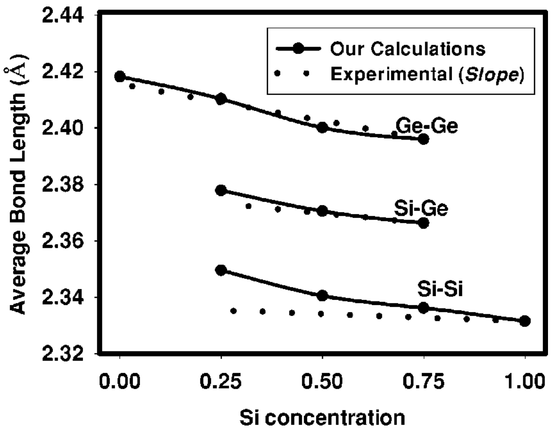

FIG. 2. Average bond lengths as a function of Si composition. Circles are our calculations (the solid line is just a guide to the eye), and the dotted lines correspond to the slope of experimental measurements of Ref. 7.

The same issue was studied by means of non–*ab initio* calculations.[15,26–28] In these works, different kinds of empirically fitted models were used, and they all reached similar conclusions. Depending on the theoretical approach, the values reported for a^{**} ranged from 0.60 to 0.71, and these values do not vary with the kind of the bond. This is in contrast to the experimental results, where one sees that the value of a^{**} depends on the type of bond, being larger for Si-Si and Si-Ge than the theoretical results.

Figure 2 shows the average lengths for each kind of bond as determined in our 128-atom supercell calculations. Since we use the LDA, the bond lengths are underestimated in comparison with the experimental values, and we may only compare the slope of our curves with the slope of the experimental curves. The dotted lines in Fig. 2 are the slope of the experimental results of Ref. 7. For $x=0$, the Ge-Ge bond length has its equilibrium value of Ge bulk. When Si atoms are added to the material, the lattice parameter decreases and so do the Ge-Ge bond lengths. The same behavior is seen for the other bonds (Si-Ge and Si-Si).

From the slope of the bond-length curves shown in Fig. 2, we can determine a^{**}.[29] In Table II we compare our values with the experimental results. From Fig. 2 and Table II we see that (i) differently from previous empirical calculations, our results show that the dependence of bond lengths with composition varies slightly with the kind of bond (however, the variation observed experimentally is significantly larger); (ii) our values for a^{**} are smaller than the experimental values for all kinds of bonds, particularly for the Si-Si bond; (iii) the results of Ref. 7 indicate that the Si-Si bond length is almost insensitive to the addition of Ge to the material, whereas we find a small but non-negligible increase.

In order to make a better comparison between our results and the experiments, it is important to mention the measurement uncertainties reported by Aubry *et al.*[7] For the Ge-Ge, Si-Ge, and Si-Si bond lengths versus composition curves, they find error bars in the range 0.005–0.02 Å, 0.01–0.03 Å, and 0.02–0.06 Å, respectively. Interestingly, the experimental error bars increase from Ge-Ge to Si-Si and also does the difference between our results and the experimental ones.

IV. CONCLUSION

In conclusion, we have performed a fully *ab initio* electronic structure calculation for the $\mathrm{Si}_x\mathrm{Ge}_{1-x}$ alloy, using supercells and an SQS-like method to simulate the randomly distributed configurations. For supercells as large as 128 sites, we obtain results for the behavior of the bond lengths with the composition slightly different from previous, non–*ab initio* calculations. All the bond lengths have their topological rigidity parameters close to each other and with values between 0.6 and 0.7. This is in disagreement with some recent experimental findings.[7,25] However, the uncertainties in these experimental results are significant. Given the large success of *ab initio* methods, such as the one used in the present work, to describe structural properties of solids, we believe that our disagreement with these measurements should motivate further, more sensitive experiments to be performed in order to resolve these discrepancies.

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