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Theoretical investigation of extended defects and their interactions with vacancies in $\mathbf{Si}_x\mathbf{Ge}_{1-x}$

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An *ab initio* investigation of the electronic and structural properties of the intrinsic stacking fault (ISF) in $\mathrm{Si}_x\mathrm{Ge}_{1-x}$ is presented. We also studied the interaction of vacancies with the ISF. The formation energy, per unit area, of the ISF is 2.1, 3.0 and 3.3 meV/Å^2, in pure Si, $\mathrm{Si}_{0.5}\mathrm{Ge}_{0.5}$ and pure Ge, respectively. Also it is shown that the ISF does not alter locally the randomness of the of the $\mathrm{Si}_{0.5}\mathrm{Ge}_{0.5}$ alloy. As far as the interaction of vacancies with the ISF is concerned, we show that the ISF acts as a sink to vacancies in Ge and in $\mathrm{Si}_{0.5}\mathrm{Ge}_{0.5}$, similarly to what was known to happen in Si. The formation of vacancies close to the ISF is energetically favorable, by about 0.2 eV, in comparison with the formation of vacancies in bulklike environments. Similarly to what happens in bulk $\mathrm{Si}_x\mathrm{Ge}_{1-x}$, the formation energy of the vacancies near the ISF depends strongly on the number of Si and Ge atoms in its nearest neighborhood.

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I. INTRODUCTION

$\mathrm{Si}_x\mathrm{Ge}_{1-x}$ alloys have great potential for technological applications in microelectronics. Since the width of the fundamental energy band gap and the electronic band offset can be tuned as a function of the alloy concentration (x), the main interests are to band-gap engineering for optical electronics and Si/SiGe heterojunction bipolar transistors. Although there are a large number of experimental works addressing the electronic and structural properties of $\mathrm{Si}_x\mathrm{Ge}_{1-x}$,[1–3] there are just a few theoretical works dedicated to the $\mathrm{Si}_x\mathrm{Ge}_{1-x}$ alloys. Recent theoretical study clarified the atomistic structure of the $\mathrm{Si}_x\mathrm{Ge}_{1-x}$ alloys,[4] where the Si/Ge atomic arrangement were obtained randomly, based upon the special quasirandom structure (SQS) approach proposed by Wei *et al.*[5] Very recently, using the same theoretical framework, the formation of vacancies in $\mathrm{Si}_x\mathrm{Ge}_{1-x}$ and the vacancy mediated Ge diffusion have been studied in detail.[6,7]

For many applications $\mathrm{Si}_x\mathrm{Ge}_{1-x}$ films are grown pseudomorphically in Si substrates, and consequently, they are strained. One possible mechanism for the release of strain is the formation of extended defects.[8] It is known that extended defects play an important role in electrical and mechanical properties of semiconductors. For instance, these defects normally introduce electrically active levels in the energy gap, and also vacancies can be segregated, gathering in the proximity of dislocations.[9] On the other hand, the formation of stacking faults plays an important role in the structural and dynamic properties of dislocations. In 1970 Ray and Cockayne,[10] using weak-beam electron microscopy, verified the formation of stacking faults due to the dissociation of dislocations in Si and Ge, while Chou *et al.*[11] performed an *ab initio* total energy study of the formation of stacking faults in Si. Antonelli *et al.*[12] performed a theoretical study of the vacancy-stacking fault interaction in Si. Their total energy calculations indicate an energetic favorability of the formation of vacancy near to the fault plane, compared with the formation of vacancy in the perfect crystal. Similarly, the formation of stacking faults in the $\mathrm{Si}_x\mathrm{Ge}_{1-x}$ alloys, as a function of the alloy concentration, and its interaction with point defects (e.g., vacancy) are important issues to be addressed based on *ab initio* calculations.

In this article, we present a theoretical investigation of the electronic and structural properties of the ISF in $\mathrm{Si}_x\mathrm{Ge}_{1-x}$. We also studied the interaction of vacancies with the ISF. The calculations were done in the framework of *ab initio* density functional theory.[13]

The outline of this paper is as follows. In Sec. II we present the calculation procedure, in Sec. III we present the results and discussion, and in Sec. IV we summarize our main conclusions.

II. THEORETICAL APPROACH

The ISF can be obtained by removing a pair of atomic layers from the perfect crystal. In the diamond structure, the atomic planes follow the $\ldots AaBbCcAaBbCcAa\ldots$ stacking pattern along the [111] direction. If a pair of atomic layers (e.g., Aa) is removed, an ISF is created with the following stacking sequence: $\ldots AaBbCcBbCcAa\ldots$. Figure 1(a) exhibits the atomic arrangement of the ISF in the $\mathrm{Si}_{0.5}\mathrm{Ge}_{0.5}$ disordered alloy. Because we use periodic boundary conditions we need at least 6 atomic layers to represent the systems without the ISF and at least 10 atomic layers to represent the systems with the ISF. In our calculations each atomic layer is formed by 16 atoms, thus we have supercells with $N_{\mathrm{ISF}}=160$ and $N_{\mathrm{bulk}}=96$ atoms, for the calculations with and without the ISF, respectively.

$\mathrm{Si}_x\mathrm{Ge}_{1-x}$ is a substitutionally disordered alloy and, here, we model it by means of periodically repeated, finite supercells. In order to do that, we used the SQS approach.[5] A summarized description of this approach follows. 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

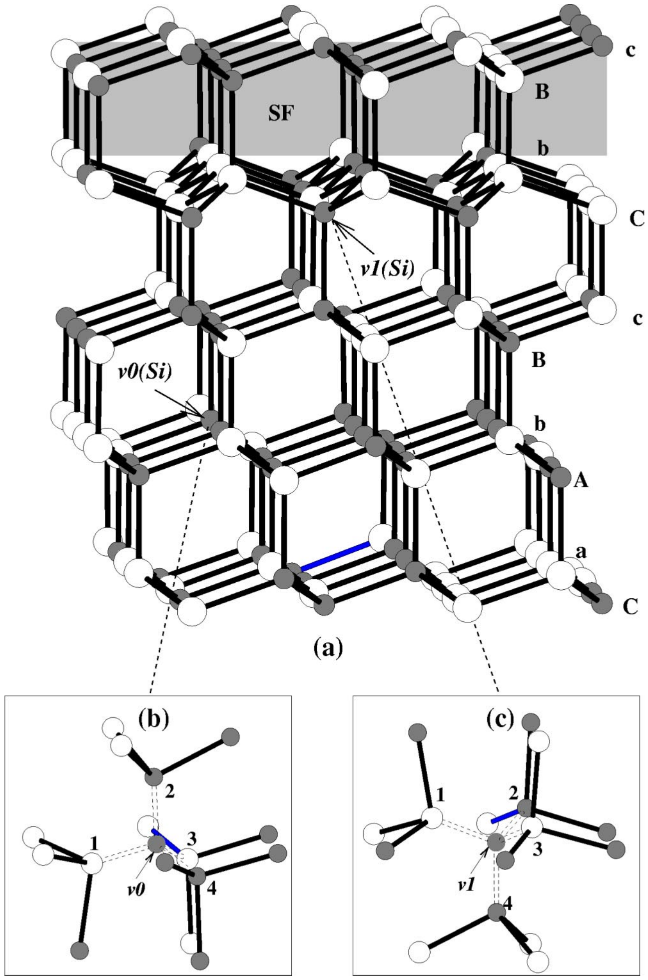

FIG. 1. (a) Structural model of the ISF in $Si_{0.5}Ge_{0.5}$. Si (Ge) atoms are represented by filled (empty) circles. The vacancies were created in the v_0 and v_1 sites. Atomic structure up to the SN of the vacancy, (b) $v0$ site (far from the ISF), (c) $v1$ site (close to the ISF).

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

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. We search for alloy configurations that obey the following criteria:[14] $\delta\Pi_m(\sigma)=0$ for $m=1$, 2 and 3, and $\delta\Pi_m(\sigma)\leqslant 0.001$ for $m=4$ and 5.

For all systems studied here, we determined the equilibrium atomic positions in two steps: (i) atomic relaxations within the valence force field (VFF) approach and (ii) refined full relaxations based upon *ab initio* total energy calculations. In the first step, the atomic relaxations were based on the elastic constants of Si and Ge, and there is no electronic charge transfer. Then, in the second step, we find the equilibrium atomic positions by performing *ab initio* total energy calculations starting with the atomic geometry obtained from the VFF calculation.

The *ab initio* total energy calculations were performed in the framework of the density functional theory,[13] within the local density approximation, using the Ceperley-Alder correlation[15] as parametrized by Perdew and Zunger.[16] The electron-ion interaction was treated by using norm-conserving, *ab initio*, fully separable pseudopotentials.[17] The wave functions were expanded in a plane wave basis set with a kinetic energy cutoff of 12 Ry. Equilibrium atomic positions were determined by relaxation within a force convergence criteria of 25 meV/Å. And the Brillouin zone was sampled by the Γ point.

The formation energy, per unit area, of the ISF is given by

$$E_F^{\mathrm{ISF}}=\frac{E_T^{\mathrm{ISF}}-\dfrac{N_{\mathrm{ISF}}}{N_{\mathrm{bulk}}}E_T^{\mathrm{bulk}}}{A}, \tag{4}$$

where E_T^{ISF} is the total energy of the supercell with the ISF and N_{ISF} atoms, E_T^{bulk} is the total energy of the defect-free system in a supercell with N_{bulk} atoms, and A is the area of the stacking fault (SF) plane.

We also investigated the interaction of a vacancy with an ISF in the alloy. The formation energy of a neutral vacancy $[E_F^{\lambda}(i)]$, surrounded by an atomic arrangement λ, can be written as

$$E_F^{\lambda}(i)=E_T^{\lambda}(i)-E_T^{\mathrm{Si_{0.5}Ge_{0.5}}}-\mu_i\,. \tag{5}$$

$E_T^{\lambda}(i)$ is the calculated total energy of the $Si_{0.5}Ge_{0.5}$ ISF with the vacancy i ($i=$Si or Ge), and $E_T^{Si_{0.5}\mathrm{Ge}_{0.5}}$ is the total energy of $Si_{0.5}Ge_{0.5}$ random alloy with an ISF, $Si_{0.5}Ge_{0.5}$-ISF [see Fig. 1(a)]. Since these two terms present different number of atoms, we have to include the chemical potential of the element i, μ_i.

Previous theoretical calculations[6] have shown that it is not important whether a Si or a Ge atom is removed from bulk $Si_{0.5}Ge_{0.5}$ to create the vacancy. Thus here we only consider Si vacancies.

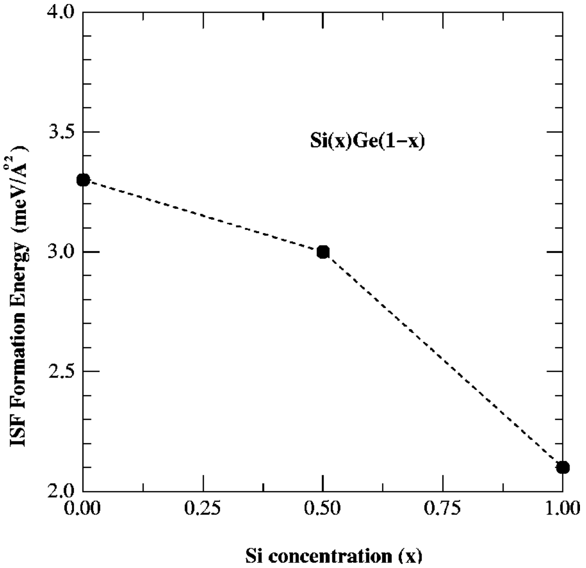

FIG. 2. ISF formation energy, per unit area, as a function of alloy concentration. The line is only a guide to the eyes.

III. RESULTS AND DISCUSSIONS

A. Si_xGe_{1-x} intrinsic stacking fault

For the $Si_{0.5}Ge_{0.5}$ alloy, after the initial VFF relaxation process, we performed the *ab initio* relaxation in the way described in the last section. In the *ab initio* relaxation process the total energy decreases only by about 1 meV/atom, for the alloys with and without the ISF. It means that the VFF calculations model the structure of these systems quite accurately, and thus, we can infer that the elastic effects are dominant for the relaxations in both cases. For the alloy with the ISF, in particular, the VFF model is accurate because this defect does not produce significant changes in bond distances and angles in comparison with the perfect crystal.

Figure 2 shows the formation energy of the ISF, per unit area, calculated by Eq. (4), as a function of the alloy concentration. For pure Si ($x=1.0$) we obtained a formation energy of 2.1 meV/Å^2. For pure Ge ($x=0.0$) the formation energy is 1.2 meV/Å^2 larger than that obtained for the pure Si ($E_F^{\mathrm{ISF}}=3.3$ meV/Å^2). In the $Si_{0.5}Ge_{0.5}$ alloy the formation energy of the ISF is 3.0 meV/Å^2, being slightly smaller than the formation energy of the Ge ISF. These results imply that, it is significantly less likely to find an ISF in Si_xGe_{1-x} than it is in pure Si.

As far as the atomistic structure is concerned, in pure Si, the Si-Si equilibrium bond lengths far from the fault plane are the same as that obtained for the Si bulk 2.33 Å. On the other hand, in the SF plane, the Si-Si bonds are stretched by 0.7% along the [111] direction, when compared with the Si-Si bonds far from the SF plane. These results, as well as, the formation energy of the ISF in pure Si, are in good agreement with previous *ab initio* calculations by Chou *et al.*[11]

Similarly, for pure Ge, the equilibrium bond lengths at the SF plane are stretched by 0.6% along the [111] direction, relatively to the Ge-Ge bonds far from the fault region, and for $Si_{0.5}Ge_{0.5}$ the bond lengths at the fault plane are stretched by 0.8% (Si-Si), 1.0% (Si-Ge), and 0.6% (Ge-Ge), along the [111] direction, compared with the bonds far from the fault plane. We have also verified that the calculated bond lengths for the $Si_{0.5}Ge_{0.5}$ alloy confirm the Pauling limit for such structure,[4] even near the SF plane.

We represent the $Si_{0.5}Ge_{0.5}$ alloy with the ISF by the SQS model. It means that we have assumed an ideal randomness of the alloy even in the vicinity of the fault. However, in principle, a defect could alter locally the randomness of the alloy, and as a consequence we should verify whether there are any preferential bonding configuration near the SF plane. Thus, we have calculated the formation energy of the $Si_{0.5}Ge_{0.5}$-ISF alloy considering a full Si-Ge atomic swap in our supercell sites (Si↔Ge), i.e., all the Si sites become occupied with Ge atoms and vice versa. Therefore, the calculated statistical correlation is still the same, however, the atomic concentration of the Si and Ge atoms at the fault plane is exchanged. In the original cell, the relative concentration between Si and Ge at the fault plane was, [Si]/[Ge] =2/3, and after Si↔Ge swap it becomes [Si]/[Ge]=3/2, increasing (reducing) the number of Si-Si bonds (Ge-Ge bonds) at the SF plane. Our calculations show that the formation energy of the ISF in $Si_{0.5}Ge_{0.5}$ changes by only 0.13 meV/Å^2 due to the full Si↔Ge swap, thus there is no significant preferential bonding arrangement for Si and Ge near the SF plane. That is, the SQS model is still valid at the SF region.

It is well known that the formation of the ISF in pure Si perturbs the valence and conduction bands edges:[11] at the Γ point the ISF gives rise to an occupied defect state at ≈0.10 eV above the valence band maximum (VBM) and an empty state at ≈0.20 eV below the conduction band minimum (CBM). For the $Si_{0.5}Ge_{0.5}$ ISF, our calculated electronic structure also indicates a defect state at ≈0.09 eV above the VBM and an empty defect state at ≈0.13 eV below the CBM. The highest occupied state is mainly localized at the ISF region, along the bonds between two different pairs of atomic bilayers, e.g., *Cb* and *Bc*, see Fig. 3(b). Similar charge density distribution for the highest occupied state has been verified for the Si ISF.[11] The planar average of the charge density distribution of the highest occupied state, along the [111] direction, is shown in Fig. 3(c). A charge concentration in the SF plane is clearly observed.

B. Interaction of a vacancy with an ISF in Si_xGe_{1-x}

We have investigated the properties of vacancies in the $Si_{0.5}Ge_{0.5}$ ISF alloy, as well as in Si ISF and Ge ISF. To create the vacancy a Si atom was removed from two distinct sites: Far from the fault plane (v_0) and near the fault plane (v_1). The location of these sites in the supercell are shown in Fig. 1(a), while Figs. 1(b) and 1(c) depict the local atomic arrangement of the Si and Ge atoms, up to the second-neighborhood (SN) of the vacancies.

In Ref. 6, it is shown that the vacancy formation energy $[E_F^{\lambda}(i)]$ in bulk $Si_{0.5}Ge_{0.5}$ strongly depends on the Si/Ge relative population in the nearest-neighborhood (NN) of the vacancy. Nevertheless, the formation energy of the vacancy depends only weakly on the Si/Ge population in the SN of the vacancy. Thus, here we sample the several types of va-

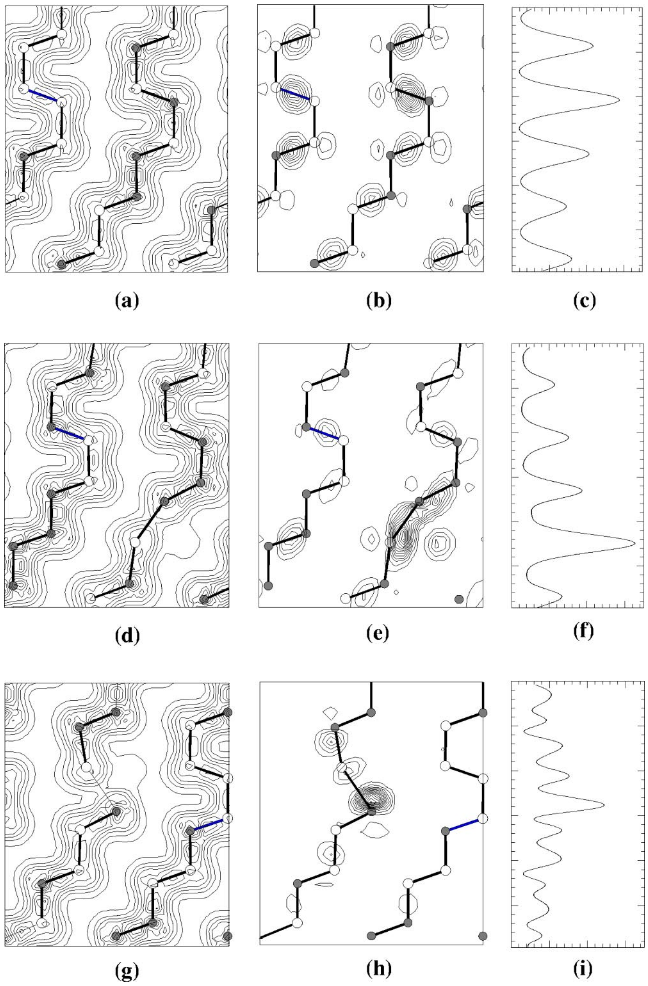

FIG. 3. Charge density contour plots at the $Si_{0.5}Ge_{0.5}$ ISF (a) total, (b) highest occupied level, and (c) planar average of the highest occupied level. For the vacancy far from the fault plane in $Si_{0.5}Ge_{0.5}$ (v_0 site) (d) total, (e) highest occupied level, and (f) planar average of the highest occupied level, and for the vacancy near the fault plane (v_1 site) (g) total, (h) highest occupied level, and (i) planar average of the highest occupied level. Si (Ge) atoms are represented by filled (empty) circles and the ISF is located where the atomic zigzag is shifted.

cancies in $Si_{0.5}Ge_{0.5}$ by considering only three different Si/Ge configurations in the NN, viz. 4-Ge/0-Si, 2-Ge/2-Si, and 0-Ge/4-Si, always with 6-Ge/6-Si in the SN.

The calculated formation energies, as a function of the vacancy position (v_0 or v_1) and the NN Si/Ge population (λ), are shown in Fig. 4. In this figure the values in the curve labeled as *crystal* (ISF) correspond to the formation energies of the vacancy in the v_0 (v_1) sites. For vacancies far from the fault plane, v_0 site, our calculations agree very well with the values in bulk $Si_{0.5}Ge_{0.5}$ (Ref. 6). As a consequence, it can be said that the v_0 site (far from the fault plane) mimics quite well a bulklike environment in the $Si_{0.5}Ge_{0.5}$-ISF alloy. The positive slope of the vacancy formation energy, as a function of the number Si atoms at the NN, can be attributed to the smaller dangling bond energy of a Ge atom when compared with a Si atom.

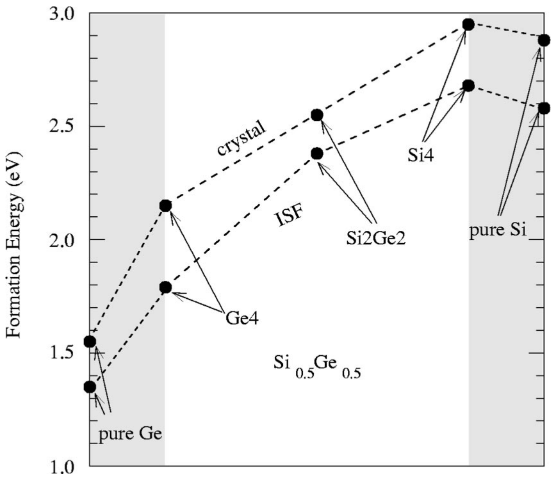

FIG. 4. Formation energy of the vacancies. The curve labeled as crystal (ISF) refers to vacancies far from (close to) the ISF. In the middle of the figure the formation energies in $Si_{0.5}Ge_{0.5}$ are shown, while in the left and right edge are shown the formation energies for Ge and Si, respectively. Lines are only guides to the eyes.

In pure Si, Antonelli *et al.*[12] obtained that the formation energy of the vacancy is reduced by 0.23 eV when it is close to the ISF, compared to a vacancy in a bulklike site. Here we have a similar value (0.30 eV), which is shown in the right edge of Fig. 4. In pure Ge and $Si_{0.5}Ge_{0.5}$ the formation energy of the vacancy is also reduced by similar values according to Fig. 4. Thus, the ISF acts as a sink to vacancies in Ge and in $Si_{0.5}Ge_{0.5}$, similarly to what was known to happen in Si.

We next have studied the energetic favorability of the vacancy near the fault plane (v_1). We have examined two aspects. (i) Strain relief process, since the network topology in the SN of the vacancy is different in the v_0 and v_1 sites [see Figs. 1(b) and 1(c)]. (ii) Comparison of the electronic perturbation, in the $Si_{0.5}Ge_{0.5}$-ISF random alloy, due to the creation of the vacancies. We have considered the vacancy with 2-Ge/2-Si atoms in the NN in this analysis.

In order to infer the effect of the atomic relaxation, we have compared the vacancy formation energies $E_F^{\lambda}(i)$ in the v_0 and v_1 sites, for (a) frozen geometry, i.e., the atomic positions of the $Si_{0.5}Ge_{0.5}$-ISF alloy are not allowed to relax after the vacancy creation, and (b) full atomic relaxation (values already shown in Fig. 4). In both cases the vacancy in the v_1 site is energetically favorable. The energy difference is 0.22 and 0.18 eV for the frozen geometry and full relaxed cases, respectively. Thus, the energetic favorability of the vacancy near the ISF plane can not be attributed to a better strain relief process in the v_1 site compared with the v_0 site.

Focusing on the electronic aspects, we see that the creation of the vacancy in $Si_{0.5}Ge_{0.5}$, gives rise to occupied states in the band gap. However, as shown in Fig. 5, the positions of the single particle energy levels are different for the vacancy far and near the ISF plane. In this figure the levels are plotted taking as reference the levels introduced by the ISF, as discussed in Sec. III A. Far from the ISF plane [Fig. 5(b)], the highest occupied state lies at 0.11 eV above

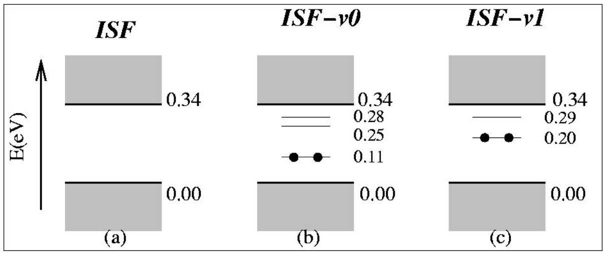

FIG. 5. Single particle energy levels for (a) $Si_{0.5}Ge_{0.5}$ alloy with an ISF, and vacancies at (b) v_0 (far from the SF) and (c) v_1 sites (near the SF). The energy references are the levels introduced by the ISF.

the VBM, with two empty orbitals at 0.25 and 0.28 eV above the VBM. While for the vacancy near the fault plane, the highest occupied vacancy level lies at 0.20 eV above the VBM, with a lowest unoccupied orbital at 0.29 eV above the VBM, see Fig. 5(c).

In Fig. 3 we show the total charge density of the systems without vacancies [Fig. 3(a)] and with vacancies at the v_0 and v_1 sites, Figs. 3(d) and 3(g), respectively. In Figs. 3(e) and 3(h) the highest occupied orbital charge densities of the systems with vacancies at the v_0 and v_1 sites are shown. As expected, these states have a significant localization near the vacancy sites. The planar average of the highest occupied orbital charge densities, Figs. 3(f) and 3(i), for the systems with vacancies at the v_0 and v_1 sites, respectively, depict the charge distribution of these states along the [111] direction. At the v_0 site, the pronounced peak in Fig. 3(f), indicates the localization of this electronic level near the vacancy site. And although there is a similar peak in Fig. 3(i), there is also for this case a different pattern of oscillation of the planar average away from the vacancy. Thus, we see that the electronic properties of the vacancy change significantly when it is close to the ISF, compared to a vacancy in a bulklike site.

IV. CONCLUSION

In summary, we have done a systematical theoretical investigation of the electronic and structural properties of the ISF in Si_xGe_{1-x} and its interaction with vacancies. The calculations were done in the framework of *ab initio* density functional theory.

In pure Si, we found that the formation energy, per unit area, of the ISF is 2.1 meV/Å^2, in agreement with previous calculations.[11] In $Si_{0.5}Ge_{0.5}$ and pure Ge, we found that the formation energy of the ISF are 3.0 and 3.3 meV/Å^2, respectively. Thus, it is significantly less likely to find this kind of defect in Si_xGe_{1-x} than it is in pure Si.

Our calculations also have shown that the randomness of the of the alloy is not affected locally by the presence of the ISF. As far as the interaction of vacancies with the ISF is concerned, we show that the ISF acts as a sink to vacancies in Ge and in $Si_{0.5}Ge_{0.5}$, similarly to what was known to happen in Si.[12] The formation of vacancies close to the ISF is energetically favorable, by about 0.2 eV, in comparison with the formation of vacancies in bulklike environments.

Similarly to what happens in bulk Si_xGe_{1-x},[6] the formation energy of the vacancies near the ISF depends strongly on the number of Si and Ge atoms in its nearest neighborhood.

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