
https://doi.org/10.1063/5.0010311
Ab initio study of band gap properties in metastable BC8/ST12 Si$_x$Ge$_{1-x}$ alloys

Cite as: Appl. Phys. Lett. 117, 032105 (2020); https://doi.org/10.1063/5.0010311
Submitted: 09 April 2020 . Accepted: 05 July 2020 . Published Online: 22 July 2020

J. Wagner , and M. Núñez-Valdez

ARTICLES YOU MAY BE INTERESTED IN

High quality epitaxial thin films and exchange bias of antiferromagnetic Dirac semimetal FeSn
Applied Physics Letters 117, 032403 (2020); https://doi.org/10.1063/5.0011497

Perspective of self-assembled InGaAs quantum-dots for multi-source quantum implementations
Applied Physics Letters 117, 030501 (2020); https://doi.org/10.1063/5.0010782

Two-dimensional lateral surface superlattices in GaAs heterostructures with independent control of carrier density and modulation potential
Applied Physics Letters 117, 032102 (2020); https://doi.org/10.1063/5.0009462
High pressure modifications of silicon and germanium have seen substantial research in the last few decades as many of these modifications can be stabilized at ambient conditions and exhibit properties highly sought after in materials design. The cubic BC8 and tetragonal ST12 modifications are no exception and have seen a number of studies investigating their electronic structure and optical and thermoelectric properties.

Both modifications are obtained by pressure release at about 10–12 GPa from their respective primitive cell. Furthermore, we show that the indirect bandgap of the ST12 Ge bandgap is, in fact, slightly smaller than the indirect bandgap of DC Ge. BC8 Si has been synthesized within the compositional range of 0 \leq x \leq 1.12 It was found that upon pressure release, the ST12 structure is retained at least up to x \approx 0.25, whereas for x > 0.25, BC8 is formed. Other than this experimental study, we did not encounter other reports on the atomic structure or the electronic properties of these alloys as a function of composition x. We obtain the effective band structures of intermediate alloys by constructing special quasi-random structures (SQSs) and unfolding their band structure to the corresponding primitive cell. Furthermore, we show that the indirect bandgap of the ST12 Ge end-member can be tuned to become direct at x_{Si} \approx 0.16. Finally, our investigations also demonstrate that the BC8 modification, on the other hand, is insensitive to compositional changes and is a narrow direct bandgap semiconductor only for the case of pure Si.

Ab initio study of band gap properties in metastable BC8/ST12 Si_{x}Ge_{1-x} alloys

Cite as: Appl. Phys. Lett. 117, 032105 (2020); doi: 10.1063/5.0010311
Submitted: 9 April 2020 · Accepted: 5 July 2020 · Published Online: 22 July 2020

J. Wagner1,a) and M. Núñez-Valdez1,2,b)

AFFILIATIONS
1Helmholtz-Centre Potsdam GFZ, German Research Centre for Geosciences, Telegrafenberg D-14473 Potsdam, Germany
2Goethe University Frankfurt am Main, Altenhöferallee 1, 60438 Frankfurt am Main, Germany

a)Author to whom correspondence should be addressed: jowagner@gfz-potsdam.de
b)Electronic mail: mari_nv@gfz-potsdam.de

ABSTRACT
The cubic Ia\textsuperscript{3} (BC8) and tetragonal P\textsubscript{4}2\textsubscript{1}2 (ST12) high pressure modifications of Si and Ge are attractive candidates for application in optoelectronic, thermoelectric, or plasmonic devices. Si\textsubscript{x}Ge\textsubscript{1-x} alloys in BC8/ST12 modifications could help overcome the indirect and narrow bandgaps of the pure phases and enable tailoring for specific use-cases. Such alloys have experimentally been found to be stable at ambient conditions after release from high pressure synthesis; however, their fundamental properties are not known. In this work, we employ ab initio calculations based on density functional theory (DFT) to investigate the electronic properties of these compounds as a function of composition x. We obtain the effective band structures of intermediate alloys by constructing special quasi-random structures (SQSs) and unfolding their band structure to the corresponding primitive cell. Furthermore, we show that the indirect bandgap of the ST12 Ge end-member can be tuned to become direct at x_{Si} \approx 0.16. Finally, our investigations also demonstrate that the BC8 modification, on the other hand, is insensitive to compositional changes and is a narrow direct bandgap semiconductor only for the case of pure Si.
position B. Atoms of type B form fourfold spiral chains, propagating parallel to the conventional c-axis [see Fig. 1(a)]. These spirals are linked by tetrahedra with an atom of type A in the center and a type B atom belonging to separate chains at each corner. A possible formation pathway from $\beta$-Sn $\rightarrow$ ST12 is a local bond twisting mechanism. This process results in strong deviations in tetrahedral bond angles as compared to the DC structure tetrahedron, while bond distances are preserved.

The BC8 structure [Fig. 1(b)], space group $Ia\overline{3}/C22_3$ (No. 7), has eight atoms in its primitive unit cell, forming a body-centered-cubic lattice. All atomic sites are symmetrically equivalent, and the structure is fully described by its lattice constant and one internal parameter. In BC8, bond distances are distorted as compared to the respective DC modification, while bond angles are more or less preserved. Thus, the structure can be viewed as an arrangement of highly distorted sixfold rings.

In this work, we chose a combined approach to model the $Si_xGe_{1-x}$ BC8 and ST12 alloys. First, to analyze order/disorder effects on phase stability and lattice parameters, we modeled all possible atomic site occupancies in the primitive cell of ST12 and BC8, using the package Site-Occupation-Disorder (SOD). By taking into account space group symmetry, we modeled a total of 362 configurations for $x = 0, 0.08, 0.16, 0.25, 0.33, 0.5, 0.66, 0.75, 0.84, 0.92, 1$ in the ST12 modification and a total of 475 configurations for $x = 0, 0.06, 0.125, 0.18, 0.25, 0.5, 0.75, 0.875, 1$ in the BC8 modification (eight and 16 atoms/cell). Second, we generated randomly distributed supercells for all intermediate compositions, as the experimentally synthesized alloys are expected to be fully disordered.

For all structural relaxations, we performed ab initio static calculations at zero pressure using the projector augmented wave (PAW) approach. For the exchange correlation energy, we employed the general gradient approximation in the revised Perdew–Burke–Ernzerhof (PBEsol) formalism as implemented in the VASP code. As these are identical to published data, we chose not to include them.

![FIG. 1. Conventional unit cells of ST12 Ge and BC8 Si end members. (a) In the ST12 Ge structure, additional atoms along the c-axis have been added to illustrate the spiral-chain arrangements formed by atoms at Wyckoff position B. Bonds to A atoms are not shown for simplification. (b) BC8 Si: The sixfold ring arrangement in the structure is shown by the thin black line (see the text).](image)

<table>
<thead>
<tr>
<th>ST12</th>
<th></th>
<th>BC8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>$c/a$</td>
<td>$E_{bg}$ (eV)</td>
</tr>
<tr>
<td>Ge</td>
<td>5.923</td>
<td>1.175</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>1.01</td>
</tr>
<tr>
<td>5.930</td>
<td>1.177</td>
<td>...</td>
</tr>
<tr>
<td>5.933</td>
<td>1.176</td>
<td>0.63$^b$</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>0.70</td>
</tr>
<tr>
<td>5.820</td>
<td>1.181</td>
<td>0.54</td>
</tr>
<tr>
<td>Si</td>
<td>5.635</td>
<td>1.194</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>0.04</td>
</tr>
<tr>
<td>6.605</td>
<td>0.01</td>
<td>HSE06$^a$</td>
</tr>
<tr>
<td>6.636</td>
<td>...</td>
<td>EXP$^a$</td>
</tr>
<tr>
<td>6.576</td>
<td>Metal</td>
<td>LDA$^a$</td>
</tr>
</tbody>
</table>

$^a$This work, HF: Hartree–Fock exchange mixing, and EXP: experimental study.

$^b$Conductivity measurements.
focus on our PBEsol results, which reproduce the available experimental data much better (see below). As a compromise between efficiency and accuracy, a plane wave cutoff of 500 eV was chosen. Full structural relaxations of the cell volume and atomic positions for all configurations were performed with $10^{-4}$ eV and $10^{-5}$ eV convergence criteria in force and energy, respectively. To maintain the results comparable across different compositions, we chose a consistent $Γ$-centered $k$-point mesh with a sampling rate of 0.2 Å$^{-1}$. For density of states (DOS) and band structure calculations, we decreased the spacing to at least 0.07 Å$^{-1}$. These criteria led to $6 \times 6 \times 6$ and $16 \times 16 \times 16$ $k$-point meshes for structural relaxation and DOS calculations, respectively. For the much larger SQS, the respective meshes had to be reduced to $4 \times 4 \times 4$ and $9 \times 9 \times 9$. Finally, we investigated the electronic band structure of end members and intermediate compositions represented by the SQS. Note, however, that electronic band structures are only well defined for periodic crystals where Bloch’s theorem is valid. Naturally, this is not the case for random alloys where space group symmetry is formally broken. To overcome this, we followed the effective band structure approach (EBS). Any SQS supercell is geometrically linked to the corresponding PC by simple lattice vector translations. This enables the unfolding of any SC band structure to the Brillouin zone of the PC. During band unfolding, each state in the PC is assigned a spectral weight that reflects how well that state is preserved in the random SC. In this work, unfolding of selected Si,Ge$_{1-x}$ SQS has been performed using the BandUP code. The bandgap energy ($E_{bg}$) and position were determined using the SUMO code.

In a recent study of BC8 Si, simulations in the Heyd–Scuseria–Ernzerhof (HSE) formalism were performed to accurately reproduce the measured experimental bandgap. In order to better compare with these results, we also performed additional HSE06 calculations to give an estimate of its impact on the $E_{bg}$ values.

Table I lists lattice parameters and bandgap energies of the Si/Ge pure phases, comparing literature values and results of this work. After relaxation of ST12 Ge, we found the lattice parameter $a = 5.923$ Å and the ratio $c/a = 1.175$, which are in excellent agreement with experimental values (see Table 1). For ST12 Ge, we found an indirect bandgap of 0.436 eV (direct 0.443 eV) with the conduction band minimum (CBM) at [0.35, 0.35, 0.00] and the valence band maximum (VBM) at [0.34, 0.34, 0.00]. This is in good agreement with previous DFT studies. For density of states (DOS) and accuracy, a plane wave cutoff of 500 eV was chosen. Full structural relaxations of the cell volume and atomic positions for all configurations were performed with $10^{-4}$ eV and $10^{-5}$ eV convergence criteria in force and energy, respectively. To maintain the results comparable across different compositions, we chose a consistent $Γ$-centered $k$-point mesh with a sampling rate of 0.2 Å$^{-1}$. For density of states (DOS) and band structure calculations, we decreased the spacing to at least 0.07 Å$^{-1}$. These criteria led to $6 \times 6 \times 6$ and $16 \times 16 \times 16$ $k$-point meshes for structural relaxation and DOS calculations, respectively. For the much larger SQS, the respective meshes had to be reduced to $4 \times 4 \times 4$ and $9 \times 9 \times 9$. Finally, we investigated the electronic band structure of end members and intermediate compositions represented by the SQS. Note, however, that electronic band structures are only well defined for periodic crystals where Bloch’s theorem is valid. Naturally, this is not the case for random alloys where space group symmetry is formally broken. To overcome this, we followed the effective band structure approach (EBS). Any SQS supercell is geometrically linked to the corresponding PC by simple lattice vector translations. This enables the unfolding of any SC band structure to the Brillouin zone of the PC. During band unfolding, each state in the PC is assigned a spectral weight that reflects how well that state is preserved in the random SC. In this work, unfolding of selected Si,Ge$_{1-x}$ SQS has been performed using the BandUP code. The bandgap energy ($E_{bg}$) and position were determined using the SUMO code.

In a recent study of BC8 Si, simulations in the Heyd–Scuseria–Ernzerhof (HSE) formalism were performed to accurately reproduce the measured experimental bandgap. In order to better compare with these results, we also performed additional HSE06 calculations to give an estimate of its impact on the $E_{bg}$ values.

Table I lists lattice parameters and bandgap energies of the Si/Ge pure phases, comparing literature values and results of this work. After relaxation of ST12 Ge, we found the lattice parameter $a = 5.923$ Å and the ratio $c/a = 1.175$, which are in excellent agreement with experimental values (see Table 1). For ST12 Ge, we found an indirect bandgap of 0.436 eV (direct 0.443 eV) with the conduction band minimum (CBM) at [0.35, 0.35, 0.00] and the valence band maximum (VBM) at [0.34, 0.34, 0.00]. This is in good agreement with previous DFT studies.

In order to better compare with these results, we also performed additional HSE06 calculations to give an estimate of its impact on the $E_{bg}$ values.

Table I lists lattice parameters and bandgap energies of the Si/Ge pure phases, comparing literature values and results of this work. After relaxation of ST12 Ge, we found the lattice parameter $a = 5.923$ Å and the ratio $c/a = 1.175$, which are in excellent agreement with experimental values (see Table 1). For ST12 Ge, we found an indirect bandgap of 0.436 eV (direct 0.443 eV) with the conduction band minimum (CBM) at [0.35, 0.35, 0.00] and the valence band maximum (VBM) at [0.34, 0.34, 0.00]. This is in good agreement with previous DFT studies.

In order to better compare with these results, we also performed additional HSE06 calculations to give an estimate of its impact on the $E_{bg}$ values.

Table I lists lattice parameters and bandgap energies of the Si/Ge pure phases, comparing literature values and results of this work. After relaxation of ST12 Ge, we found the lattice parameter $a = 5.923$ Å and the ratio $c/a = 1.175$, which are in excellent agreement with experimental values (see Table 1). For ST12 Ge, we found an indirect bandgap of 0.436 eV (direct 0.443 eV) with the conduction band minimum (CBM) at [0.35, 0.35, 0.00] and the valence band maximum (VBM) at [0.34, 0.34, 0.00]. This is in good agreement with previous DFT studies.

In order to better compare with these results, we also performed additional HSE06 calculations to give an estimate of its impact on the $E_{bg}$ values.

Table I lists lattice parameters and bandgap energies of the Si/Ge pure phases, comparing literature values and results of this work. After relaxation of ST12 Ge, we found the lattice parameter $a = 5.923$ Å and the ratio $c/a = 1.175$, which are in excellent agreement with experimental values (see Table 1). For ST12 Ge, we found an indirect bandgap of 0.436 eV (direct 0.443 eV) with the conduction band minimum (CBM) at [0.35, 0.35, 0.00] and the valence band maximum (VBM) at [0.34, 0.34, 0.00]. This is in good agreement with previous DFT studies.

In order to better compare with these results, we also performed additional HSE06 calculations to give an estimate of its impact on the $E_{bg}$ values.

Table I lists lattice parameters and bandgap energies of the Si/Ge pure phases, comparing literature values and results of this work. After relaxation of ST12 Ge, we found the lattice parameter $a = 5.923$ Å and the ratio $c/a = 1.175$, which are in excellent agreement with experimental values (see Table 1). For ST12 Ge, we found an indirect bandgap of 0.436 eV (direct 0.443 eV) with the conduction band minimum (CBM) at [0.35, 0.35, 0.00] and the valence band maximum (VBM) at [0.34, 0.34, 0.00]. This is in good agreement with previous DFT studies.
The total energy of the alloy $E_{\text{Ge}}$ and $E_{\text{Si}}$ are the energies of the respective end-member compositions. If pressure $P$ is different from zero, $E_J$ becomes the enthalpy $H_J = E_J + PV$, and if $P$ and temperature $T$ are different from zero, the Gibbs energy $G_J = H_J - TS = E_J + PV - TS$, where $S$ is the entropy. At zero pressure and temperature, any thermodynamically stable phase against decomposition into other binaries or the elements is located on the convex hull. The stability for each alloy with different atomic configurations at each composition $x$ is quantified by the energy deviation $E_J$ from the thermodynamic convex hull.

Finally, it can be observed that the formation energies of SQS supercells fall right within the spread of all PC configurations, indicating that the SQSs are indeed good representations of each ensemble. Experimental studies show that the synthesis and stabilization of intermediate metastable configurations are achieved with the addition of pressure and/or temperature for both BC8 and ST12 structures. To give a meaningful description of the band structure of intermediate compositions, we unfolded the SQS bands using the BandUP code. Then, we evaluated the bandgap energy as well as the CBM/VBM positions using the SUMO code. For the ST12 structure, we found that the increasing Si content in Ge ST12 gradually opens the gap, while at the same time, the CBM and VBM are slightly shifted, narrowing the already small difference between direct and indirect transition. This culminates in a direct bandgap at $x_{\text{Si}} \approx 0.16$ as shown in Fig. 4. To confirm this observation, we repeated the band structure calculation for this composition using a total of 1000 K-points in the region $M - \Gamma - Z$ with the same result. Further introduction of Si into ST12 Ge led to the retraction of the original CBM along the $\Gamma - M$ line and the formation of a new CBM at $Z$, resulting in an indirect bandgap (0.85 eV at $x_{\text{Si}} = 0.5$) steadily widening until the end-member composition was reached. For the ST12 alloys, SQS band calculations were not repeated in the HSE06 formalism as they are computationally extremely demanding. However, a qualitatively similar behavior as described above for ST12 end-member compositions is expected.

For all BC8 alloys, PBEsol calculations predicted a metallic nature throughout the compositional range. Simulations using the same HSE06 parameters as for the end-member compositions also resulted in indirect bandgaps for all intermediate compositions. Even the smallest addition of Ge that we modeled ($x_{\text{Si}} = 0.94$) resulted in an indirect bandgap. Increasing the Ge content did not change the overall band structure features all the way up to end member Ge.

In summary, we have shown that it should be possible to compositionally tune the bandgap in ST12 $\text{Si}_{x}\text{Ge}_{1-x}$ alloys to become direct at low Si concentrations ($x_{\text{Si}} \approx 0.16$). Given that samples with such compositions have already been synthesized following a well-established method, it should be possible to validate our predictions by further experiments. For the BC8 structure, we have demonstrated...
that widening the narrow bandgap of pure BC8 Si by alloying it with Ge is not possible. In this case, more traditional avenues for bandgap tuning (e.g., other dopants, inducing strain, and etching) may be more rewarding. From our overall results, we conclude that Si$_{1-x}$Ge$_x$ ST12 alloys with $0.1 \leq x \leq 0.2$ are viable candidates for direct bandgap materials based on a considerable percentage also exploiting readily available Si. Therefore, we suggest further experimental studies on these alloys to confirm our findings and to enhance more functional materials. For example, BC8 Si nanoparticles have already been considered for solar energy conversion, and a rich ST12 Si has been shown to have the capacity to exhibit superconducting properties.

The authors gratefully acknowledge the Gauss Centre for Supercomputing e.V. (www.gauss-centre.eu) for funding this project by providing computing time through the John von Neumann Institute for Computing (NIC) on the GCS Supercomputer JUWELS at the Jülich Supercomputing Centre (JSC) under project abinitio:modmatsgeo. J.W. and M.N.-V. were supported by the Helmholtz Association through funding of first-time professorial appointments of excellent women scientists (W2/W3).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon request.

REFERENCES