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FP-LMTO method to calculate the structural, thermodynamic and optoelectronic properties of Si$_x$Ge$_{1-x}$C alloys

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RESEARCH ARTICLE

FP-LMTO method to calculate the structural, thermodynamic and optoelectronic properties of Si$_x$Ge$_{1-x}$C alloys

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The structural and electronic properties of the ternary Si$_x$Ge$_{1-x}$C alloys have been calculated using the full-potential linear muffin-tin-orbital (FP-LMTO) method based on density functional theory within both local density approximation (LDA) and generalised gradient approximation (GGA). The calculated equilibrium lattice constants and bulk moduli are compared with previous results. The concentration dependence of the electronic band structure and the direct and indirect band gaps are investigated. Using the approach of Zunger and co-workers, the microscopic origins of the band gap bowing are investigated also. Moreover, the refractive index and the optical dielectric constant for Si$_x$Ge$_{1-x}$C are studied. The thermodynamic stability of the alloys of interest is investigated by means of the miscibility. This is the first quantitative theoretical prediction to investigate the effective masses, optical and thermodynamic properties for Si$_x$Ge$_{1-x}$C alloy, and still awaits experimental confirmations.

Keywords: SiC; GeC; FP-LMTO; alloys; bowing parameter

1. Introduction

Despite their possible technological promises, IV–IV semiconductor compounds such as SiGe, SiC and GeC have received considerably less attention than the elemental group-IV materials as C and Si [1–24]. Immediate consideration in these compounds is their stability towards decay into their elemental constituents or into random alloys. Theoretical studies have fundamental aspects in the development of new materials and devices for different industrial applications. In the last few years, the electronic properties of some SiC polytypes have been calculated [15–18]. Further studies went deep into elastic [19], optical and high-pressure [25,21] properties. Furthermore, molecular dynamics simulations have been carried out to study the thermomechanical properties of SiC [26]. Another IV-IV compound is GeC. Several experimental works have been devoted to this compound [27–29]. Otherwise, there are relatively few theoretical studies of electronic and structural properties of this material [28] compared with SiC, SiGe [30] and Si [31]. The existence of this material in its zinc-blende structure has been reported. A first principle investigation [32] has show that GeC, like SiC is a wide-gap semiconductor with an indirect band gap.

There is another ternary IV-IV alloy, namely SiGeC, that has demonstrated much potential for use in Heterojunction Bipolar Transistors (HBT's) [33,34] and high hole mobility MOSFETs [35,36]. Like the more common counterparts, silicon germanium carbide SiGeC is a narrow band gap semiconductor that is compatible with most silicon-based processing. Its band gap is adjustable, approximately according to Vegard's law and depending mainly on the germanium content [37]. The SiGeC alloy has potential to the strain compensating effect of carbon substitution. In such alloys, the major limitation of their formation is the large difference in their covalent radii. Another one is that the diamond structure is stable at room temperature and normal pressure for Si and Ge but metastable for C. For these reasons a careful optimisation of the growth parameters is required to obtain a material suitable for device applications. Several attempts to grow SiGeC films on Si using molecular beam epitaxy (MBE), chemical vapour deposition (CVD) and C implantation followed by solid-phase epitaxial regrowth have been reported [38–44] (see also reference [45] and references therein). The optical and electronic properties of SiGeC alloys grown on Si substrates have been studied by Kolodzey and coworkers [46] using X-ray photoelectron spectroscopy and optical transmission measurements. Their study of optical transmission measurements showed that the absorption edge of thick layers is increased to higher energies with increasing carbon
fraction, and revealed that the presence of SiC and GeC vibrational modes in the infrared. The X-ray photoelectron spectroscopy indicated that the valence band energy maximum is increased with the C fraction relative to that of SiGe alloys of similar composition. On the theoretical side, many efforts have been made using various theoretical methods to study the physical properties of the SiGeC alloy. The electronic structure of the ordered Si$_{0.75}$Ge$_{0.25}$C alloy has been studied by Chen and coworkers [47] using the plane-wave pseudopotential method. The change in band gaps and valence band offsets (VBO) of strained SiGeC/Si(001) heterojunctions has been examined by Wu et al. [48] and Jörg Osten [49] using the first-principles pseudopotential method and the solid theory model, respectively. They have found that the valence band offsets (VBOs) of the compressively and tensilely strained SiGeC/Si(001) heterojunctions have decreased and increased, respectively, as the carbon fraction increases and the germanium fraction is kept constant. Ornar and Kolodzey [50] have performed linear combination of atomic orbitals on the band structure of SiGeC alloys. They found that for all compositions x and y the alloys have an indirect gap along the direction chosen and the gap shows a nonlinear composition dependence. A combined experimental and theoretical study on the lattice parameter of the SiGeC random alloys with different Ge and C concentration has been done by De Salvador et al. [51]. They found that $a_{\text{SiGeC}}(x,y)$ is in good agreement with the theoretical predictions and a strong deviation from Vegard’s law is derived. The structural properties of SiGeC alloys have been studied by Kelires [52] using Monte Carlo simulations. He has demonstrated how to obtain equilibrium properties of ternary semiconductor alloys, composed of atoms with a large size mismatch. A repulsive interaction between carbon atoms and a strong deviation from linear behaviour of the structural parameters is found. Windlt et al. [53,54] have investigated the structural and electronic properties of SiC and SiGeC random alloys using empirical pseudopotentials as well as local orbitals and plane wave density-functional calculations. They have focused on the strain-composition relation and band gap/deep level properties of the alloys, and found from the band structure calculations that the carbon-induced states are highly localised and could form a deep level in the band gap of silicon.

In order to understand and control the material and the behaviour of bowing and related properties, we have investigated the effect of Si concentration on the structural, thermodynamic and optoelectronic properties of Si$_x$Ge$_{1-x}$C alloys in the zinc-blende structure by varying the Si content from 0 to 1 using the full potential muffin-tin orbital (FP-LMTO) method. Various quantities, including lattice parameters, bulk modulus and its pressure derivative, band gap and optical bowing, were obtained for this alloy. The organisation of the article is as follows: A brief description of the computational details and methodology is given in Section 2. We present the theoretical results and a discussion concerning the structural, electronic, optical and thermodynamic properties in Section 3. The conclusion is given in Section 4.

2. Method of calculations

The calculations reported here were carried out using the ab initio full-potential linear muffin-tin orbital (FP-LMTO) method [55–58] as implemented in the Lmtart code [59]. The exchange and correlation potential was calculated using the local density approximation (LDA) [60] and the generalised gradient approximation (GGA) [61]. The FP-LMTO is an improved method compared to previous LMTO techniques, and treats muffin-tin spheres and interstitial regions on the same footing, leading to improvements in the precision of the eigenvalues. At the same time, the FP-LMTO method, in which the space is divided into an interstitial regions (IR) and non-overlapping muffin-tin spheres (MTS) surrounding the atomic sites, uses a more complete basis than its predecessors. In the IR regions, the basis set consists of plane waves. Inside the MTS spheres, the basis is described by radial solutions of the one particle Schrödinger equation (at fixed energy) and their energy derivatives multiplied by spherical harmonics. The charge density and the potential are represented inside the MTS by spherical harmonics up to $l_{\text{max}} = 6$. The integrals over the Brillouin zone are performed up to 35 special $k$-points for binary compounds and 27 special $k$-points for the alloys in the irreducible Brillouin zone (IBZ) using Blöchl’s modified tetrahedron method [62]. The self-consistent calculations are considered to be converged when the total energy of the system is stable within $10^{-5}$ Ry. In order to avoid the overlap of atomic spheres, the MTS radius for each atomic position is taken to be different for each composition. We point out that the use of the full-potential calculation ensures that the calculation is not completely independent of the choice of sphere radii. The plane wave cut-off is varied to ensure the total energy convergence. The values of the sphere radii (MTS) number of plane waves (NPLW), used in our calculation are summarised in Table 1.

3. Results and discussions

3.1. Structural properties

The structural properties of the SiC, GeC binary compounds and their Si$_x$Ge$_{1-x}$C alloys in the cubic structure are calculated by means of the full-potential LMTO method. As for the ternary semiconductor alloys with the type of $B_{3}A_{1−x}C$, we have started our FP-LMTO calculations of structural properties with the zinc-blende structure and let the atoms move to their equilibrium positions according to the calculated forces. We have chosen the basic cubic cell as the unit cell. In this unit cell, there are four C anions, three A and
Table 1. The number of plane waves number PW, cut-off energy (in Ry) and muffin-tin radius (MTS) (in a.u.) used in our calculations for binary GeC and SiC and their Si\textsubscript{x}Ge\textsubscript{1-x} alloy in the zinc blende (ZB) structure.

<table>
<thead>
<tr>
<th>X</th>
<th>PW</th>
<th>Ecut total (Ry)</th>
<th>MTS (a.u)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LDA</td>
<td>GGA</td>
<td>LDA</td>
</tr>
<tr>
<td>0</td>
<td>5064</td>
<td>12050</td>
<td>153.657</td>
</tr>
<tr>
<td></td>
<td>Ge</td>
<td>2.011</td>
<td>2.064</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>1.713</td>
<td>1.758</td>
</tr>
<tr>
<td>0.25</td>
<td>33400</td>
<td>65266</td>
<td>217.239</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>1.993</td>
<td>2.063</td>
</tr>
<tr>
<td></td>
<td>Ge</td>
<td>1.993</td>
<td>2.063</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>1.698</td>
<td>1.687</td>
</tr>
<tr>
<td>0.50</td>
<td>33400</td>
<td>65266</td>
<td>222.294</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>1.970</td>
<td>1.997</td>
</tr>
<tr>
<td></td>
<td>Ge</td>
<td>1.970</td>
<td>1.997</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>1.678</td>
<td>1.701</td>
</tr>
<tr>
<td>0.75</td>
<td>33400</td>
<td>65266</td>
<td>227.763</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>1.946</td>
<td>1.973</td>
</tr>
<tr>
<td></td>
<td>Ge</td>
<td>1.946</td>
<td>1.973</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>1.658</td>
<td>1.680</td>
</tr>
<tr>
<td>1</td>
<td>5064</td>
<td>12050</td>
<td>168.800</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>1.919</td>
<td>1.944</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>1.634</td>
<td>1.656</td>
</tr>
</tbody>
</table>

one B, two A and two B, and one A and three B cations, for \( x = 0.25, 0.50 \) and 0.75, respectively. For the considered structures, we have performed the structural optimisation by calculating the total energies for different volumes around the equilibrium cell volume \( V_0 \) of the SiC and GeC binary compounds and their alloy. The calculated total energies are fitted to Murnaghan’s equation of state [63] to determine the ground state properties such as the equilibrium lattice constant \( a \) and the bulk modulus \( B \). The calculated equilibrium parameters \( (a \) and \( B) \) are given in Table 2 which also contains results of previous calculations as well as the available experimental data. Our calculated structural parameters are in good agreement with those obtained by first-principles methods within different approximations. The calculated lattice parameter for the SiC binary compound is in good agreement with other data, which ensures the reliability of the present first-principles computations. The computed lattice parameter slightly underestimates and overestimates the other data using LDA and GGA, respectively, which is consistent with the general trend of these approximations. As can be seen, the calculated lattice parameter for GeC \((x = 0)\) is larger than those of SiC \((x = 1)\); \( a_0 (\text{SiC}) < a_0 (\text{GeC}) \). As the anion atom is the same in both compounds, this result can easily be explained by considering the atomic radii of Ge and Si: \( R(\text{Ge}) = 1.52 \) Å, \( R(\text{Si}) = 1.46 \) Å, i.e. the lattice constant increases with increasing atomic size of the cation element. The bulk modulus for SiC is larger than that of GeC; \( B (\text{SiC}) > B (\text{GeC}) \); i.e. in inverse sequence to \( a_0 \) in agreement with the well-known relationship between \( B \) and the lattice constants: \( B \propto V_0^{-1} \), where \( V_0 \) is the unit cell volume. Furthermore, the values of the calculated bulk modulus using both approximations decrease in going from SiC to GeC, suggesting that the compressibility increases from SiC to GeC.

In the following paragraph we shed more light on the stability of the alloy and the two end compounds by

Table 2. Calculated lattice parameter \( a \) and bulk modulus \( B \) compared to experimental and other theoretical results of SiC, GeC and their Si\textsubscript{x}Ge\textsubscript{1-x} C alloys.

<table>
<thead>
<tr>
<th>Lattice constant ( a (\text{Å}) )</th>
<th>Bulk modulus B (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work.</td>
<td></td>
</tr>
<tr>
<td>x LDA</td>
<td>GGA</td>
</tr>
<tr>
<td>0</td>
<td>4.552</td>
</tr>
<tr>
<td>0.25</td>
<td>4.511</td>
</tr>
<tr>
<td>0.5</td>
<td>4.64</td>
</tr>
<tr>
<td>0.75</td>
<td>4.406</td>
</tr>
<tr>
<td>1</td>
<td>4.343</td>
</tr>
</tbody>
</table>

\footnote{\textsuperscript{a}Ref. [64], \textsuperscript{b}Ref. [65], \textsuperscript{c}Ref. [66], \textsuperscript{d}Ref. [26], \textsuperscript{e}Ref. [67], \textsuperscript{f}Ref. [68], \textsuperscript{g}Ref. [69], \textsuperscript{h}Ref. [70], \textsuperscript{i}Ref. [30], \textsuperscript{j}Ref. [71], \textsuperscript{k}Ref. [72], \textsuperscript{l}Ref. [73], \textsuperscript{m}Ref. [74].}
Table 3. Calculated enthalpy of formation $\Delta H$ (in eV/cell) using LDA and GGA for SiC, GeC and their Si$_x$Ge$_{1-x}$C alloys compared to other theoretical results.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$\Delta H$ – LDA</th>
<th>$\Delta H$ - GGA</th>
<th>Other cal.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.617</td>
<td>0.572</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>0.407</td>
<td>0.372</td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>0.038</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>0.75</td>
<td>$-0.103$</td>
<td>$-0.102$</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>$-0.439$</td>
<td>$-0.465$</td>
<td>$-0.36^a$</td>
</tr>
</tbody>
</table>

$^a$Ref. [75].

calculating the enthalpy of formation using the following expression:

$$\Delta H (\text{Si}_x\text{Ge}_{1-x}\text{C}) = E(\text{Si}_x\text{Ge}_{1-x}\text{C}) - (1 - x)E(\text{Ge}) - xE(\text{Si}) - E(\text{C}) \quad (1)$$

The calculated values of the enthalpy of formation of the Si$_x$Ge$_{1-x}$C alloys is positive for the concentrations $x = 0.0, 0.25$ and $0.50$ (see Table 3); indicating that they are unstable for these concentrations and, thus, only for $x$ equal to or greater than $0.75$ they are suitable objects for synthesis and study. Our calculated value of the enthalpy of formation of SiC is in good agreement with that obtained by Yakoubi et al. [75] using the full potential linearised augmented plane wave plus local orbitals (APW + lo) method within the local density approximation (LDA).

Usually, for alloys for which the experimental data are rare, it is assumed that the atoms are located at the ideal lattice sites and the lattice constant varies linearly with composition $x$ according to Vegard’s law [76].

$$a(A_xB_{1-x}C) = xa_{AC} + (1 - x)a_{BC} \quad (2)$$

where $a_{AC}$ and $a_{BC}$ are the equilibrium lattice constants of the binary compounds AC and BC, respectively, and $a(A_xB_{1-x}C)$ is the lattice constant of the alloy. However, deviation from Vegard’s law has been observed in semiconductor alloys both experimentally [77] and theoretically [78–82].

Hence, the lattice constant can be written as:

$$a(A_xB_{1-x}C) = xa_{AC} + (1 - x)a_{BC} - x(1 - x)b \quad (3)$$

where the quadratic term contains the bowing parameter $b$.

Figures 1 and 2 show the variation of the calculated equilibrium lattice constant and bulk modulus as a function of concentrations $x$ for the Si$_x$Ge$_{1-x}$C alloy. The obtained results for the composition dependence of the calculated equilibrium lattice parameter almost follow Vegard’s law [76]. In going from GeC to SiC, when the Si-content increases, the values of the lattice parameters of the Si$_x$Ge$_{1-x}$C alloy decrease. This is due to the fact that the size of the Si atom is smaller than the Ge atom. On the opposite side, one can see from Figure 2 that the value of the bulk modulus increases as the Si concentration increases. The bowing parameters are determined by a polynomial fit. Using the LDA approximation, we obtained upward and downward bowing parameters equal to $0.056$ Å and $-41.77829$ GPa for the lattice and the bulk modulus, respectively. While the GGA approximation gives $-0.06514$ Å and $-64.10514$ GPa for the bowing lattice parameter and the bulk modulus, respectively. From Table 2, both approximations follow the tendency demonstrated by both experimental measurement and theoretical calculations.

3.2. Electronic properties

The calculated band structure of binary compounds as well as their investigated alloys using FP-LMTO within both LDA and GGA schemes yields an indirect band gap ($\Gamma \rightarrow X$) for the binary compounds of SiC and GeC. When the composition $x$ is varied, the valence band maximum (VBM) and the conduction band minimum (CBM) occur at the
Table 4. Direct Kohn-Sham band gap energy of $\text{SixGe}_{1-x}\text{C}$ alloys at different Si concentrations (all values are in eV).

<table>
<thead>
<tr>
<th>$x$</th>
<th>This work</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LDA</td>
<td>GGA</td>
<td>Exp.</td>
</tr>
<tr>
<td>0</td>
<td>3.508</td>
<td>2.572</td>
<td>3.50f</td>
</tr>
<tr>
<td>0.25</td>
<td>1.716</td>
<td>1.76</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>1.57</td>
<td>1.618</td>
<td></td>
</tr>
<tr>
<td>0.75</td>
<td>1.573</td>
<td>1.613</td>
<td>2.48f</td>
</tr>
<tr>
<td>1</td>
<td>6.733</td>
<td>6.138</td>
<td>7.59a</td>
</tr>
</tbody>
</table>

$^a$Ref. [83], $^b$Ref. [21], $^c$Ref. [84], $^d$Ref. [85], $^e$Ref. [32], $^f$Ref. [70], $^g$Ref. [47].

$\Gamma$-point, resulting in a direct band gap ($\Gamma \rightarrow \Gamma$) for the studied alloys. The calculated direct band gap ($\Gamma \rightarrow \Gamma$) values for $\text{Si}_x\text{Ge}_{1-x}\text{C}$ alloy are listed in Table 4, along with the available theoretical and experimental results. The computed direct band gaps of binary compounds are in good agreement with other results. For $\text{SiC}$, the calculated band gap is smaller than the experimental value. To best of our knowledge, there are no theoretical or experimental data on the energy band gaps for $x = 0.25, 0.5$ and $0.75$ available in literature to make a meaningful comparison. It is worthwhile to mention here that both LDA and GGA do not reproduce a perfect agreement with the experimental results because they do not take into account the quasi-particle self-energy to ground states properties [86] leading to errors in the band gap. It is important to note that the density functional formalism is limited (see [87]) and the derived band structure cannot directly be used for comparison with experimental band gaps. We consider that the experimental data are well reproduced by our calculations. One reason for deviations is that our theory is applied at $T = 0$ K, while experimental measurements were performed at room temperature ($T = 297$ K), and thus include the effect of thermal expansion. The above justification indicates that the $\text{Si}_x\text{Ge}_{1-x}\text{C}$ alloys may have a larger band gap than those indicated in Table 4.

The variation of the composition ($x$) versus the direct ($\Gamma \rightarrow \Gamma$) and indirect ($\Gamma \rightarrow X$) band gaps with both LDA and GGA approximations is shown in Figure 3. Following this figure we notice that for concentrations ($x$) ranging from $x = 0.08$ to 0.8, the alloy exhibits a direct band gap ($\Gamma \rightarrow \Gamma$) for both approximations. It is also seen that the direct and indirect band gaps show a nonlinear behaviour with increasing silicon concentration providing a positive and negative band gap bowing for the direct ($\Gamma \rightarrow \Gamma$) and indirect ($\Gamma \rightarrow X$) band gaps, respectively. Indeed, it is a general trend to describe the band gap of the $A_xB_{1-x}C$ alloy in terms of the energy gaps $E_{AC}$ and $E_{BC}$ of the binary compounds by the following semi-empirical formula:

$$E_g(x) =xE_{AC} + (1-x)E_{BC} - bx(1-x)$$  (4)

where $E_{AC}$ and $E_{BC}$ corresponds to the energy gap of $\text{SiC}$ and $\text{GeC}$ for the $\text{Si}_x\text{Ge}_{1-x}\text{C}$ alloy. From Table 4, it is clear that $E_g$ of $\text{SiC}$ using LDA is slightly larger than using GGA.

The calculated band gap versus concentration was fitted by a polynomial equation. The results are shown in Figure 3 and are summarised as follows:

$$\text{Si}_x\text{Ge}_{1-x}\text{C} \rightarrow \begin{cases} E_{\Gamma-\Gamma} = 3.76 - 13.53x + 16.06x^2 & \text{(LDA)} \\ E_{\Gamma-\Gamma} = 2.88 - 9.56x + 12.35x^2 & \text{(GGA)} \\ E_{\Gamma-X} = 1.67 + 9.62x - 9.75x^2 & \text{(LDA)} \\ E_{\Gamma-X} = 1.79 + 9.19x - 9.27x^2 & \text{(GGA)} \end{cases}$$  (5)
In order to understand the physical origins of bowing parameters in the A\textsubscript{x}B\textsubscript{1-x}C alloy, we follow the procedure of Bernard and Zunger [88], and decompose the total bowing parameter \( b \) into physically distinct contributions. The overall bowing coefficient at a given average composition \( x \) measures the change in the band gap according to the formal reaction

\[
x \ A(x)_C(a_{AC}) + (1 - x) B(x)_C(a_{BC}) \rightarrow A_x B_{1-x} C (a_{eq}) \quad (6)
\]

where \( a_{AC} \) and \( a_{BC} \) are the equilibrium lattice constants of the binary compounds and \( a_{eq} \) is the equilibrium lattice constant of the alloy with the average composition \( x \).

Equation (5) is decomposed into three steps:

\[
A(x)_C(a) + (1 - x) B(x)_C(a) \rightarrow A_x B_{1-x} C (a_{eq}) \quad (7)
\]

\[
x \ A(x)_C(a) + (1 - x) B_C(a) \rightarrow A_x B_{1-x} C (a_{eq}) \quad (8)
\]

\[
A_x B_{1-x} C (a) \rightarrow A_x B_{1-x} C (a_{eq}) \quad (9)
\]

The first step attributes the volume deformation (VD) effect on the bowing. The corresponding contributions \( b_{VD} \) to the bowing parameter represents the relative response of the band structure of the binary compounds \( AC \) and \( BC \) to hydrostatic pressure that arises from the change of their individual equilibrium lattice constants to the alloy value \( a = a(x) \). The second contribution, the charge exchange (CE) contribution \( b_{CE} \), reflects a charge transfer effect which is due to different (averaged) bonding behaviour at the lattice constant \( a \). The final step, the structural relaxation (SR), reflects changes in passing from the unrelaxed to the relaxed alloy by \( b_{SR} \). Consequently, the total bowing parameter is defined as

\[
b = b_{VD} + b_{CE} + b_{SR}. \quad (10)
\]

The general representation of the composition-dependent band gap of the alloys in terms of binary compound energy gaps of \( E_{AC}(a_{AC}) \) and \( E_{BC}(a_{BC}) \), and the total bowing parameter \( b \) is

\[
E_g(x) = x E_{AC}(a_{AC}) + (1 - x) E_{BC}(a_{BC}) - b x (1 - x) \quad (11)
\]

This allows a division of the total bowing \( b \) into three contributions according to:

\[
b_{CD} = \frac{E_{AC}(a_{AC}) - E_{AC}(a)}{1 - x} + \frac{E_{BC}(a_{BC}) - E_{BC}(a)}{x} \quad (12)
\]

\[
b_{CE} = \frac{E_{AC}(a)}{1 - x} + \frac{E_{BC}(a)}{x} - \frac{E_{ABC}(a)}{x(1 - x)} \quad (13)
\]

\[
b_{SR} = \frac{E_{ABC}(a) - E_{ABC}(a_{eq})}{x(1 - x)} \quad (14)
\]

All these energy gaps mentioned in (11)–(13) have been calculated for indicated atomic structures and lattice constants. Table 5 shows the calculated optical band gap bowing \( b \) for three different molar fractions \( x = 0.25, 0.5 \) and 0.75. The LDA (GGA) calculated band gap bowing \( b \) is found to be equal to \(-0.3185 \) (-0.7746), \(-0.073 \) (0.0214) and \(-0.0169 \) (0.0053) eV for \( x = 0.25, 0.5 \) and 0.75, respectively. From Table 5, we notice that the structural relaxation effect is negligible for the studied compositions \( x = 0.25, 0.50 \) and 0.75 and the main contribution to the band gap bowing is essentially due to the charge exchange (CE) contribution for \( x = 0.25 \) and 0.75. For \( x = 0.5 \), the band gap bowing is due to near equal contribution of the volume deformation (VD) and the charge exchange (CE) effects. Figure 4 shows a variation of the band gap bowing versus concentration. It is shown that the optical bowing remains linear and varies slowly in going from 0.25 to 0.5, and beyond 0.5 it increases rapidly, which checked the evaluation of the band gap according to concentration. To the best of our

<table>
<thead>
<tr>
<th>( x )</th>
<th>Optical bowing LDA</th>
<th>GGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>(-0.1130)</td>
<td>(-0.1607)</td>
</tr>
<tr>
<td>(-0.1964)</td>
<td>(-0.182)</td>
<td></td>
</tr>
<tr>
<td>(-0.0090)</td>
<td>0.0181</td>
<td></td>
</tr>
<tr>
<td>(-0.3185)</td>
<td>(-0.3246)</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>(-0.1372)</td>
<td>(-0.073)</td>
</tr>
<tr>
<td>(-0.1282)</td>
<td>0.0668</td>
<td></td>
</tr>
<tr>
<td>(-0.0204)</td>
<td>0.0276</td>
<td></td>
</tr>
<tr>
<td>0.0784</td>
<td>0.0214</td>
<td></td>
</tr>
<tr>
<td>0.75</td>
<td>0.2142</td>
<td>(-0.671)</td>
</tr>
<tr>
<td>(4.2528)</td>
<td>(4.3265)</td>
<td></td>
</tr>
<tr>
<td>(-0.0169)</td>
<td>0.0053</td>
<td></td>
</tr>
<tr>
<td>(4.0222)</td>
<td>(3.6608)</td>
<td></td>
</tr>
</tbody>
</table>

Table 5. Decomposition of optical bowing into volume deformation (VD), charge exchange (CE) and structural relaxation (SR) contributions (all values are in eV).

Figure 4. The calculated optical bowing parameters as a function of Si concentration within LDA and GGA.
knowledge, there are no theoretical or experimental data on the band gap bowing to check our predicted results.

### 3.3. Effective masses

Knowledge of the electron and hole effective mass values is indispensable for the understanding of transport phenomena, exciton effects and electro-hole in semiconductors. Excitonic properties are of great interest for semiconductor applications, and it is worthwhile to estimate the electron and hole effective mass values for Si$_x$Ge$_{1-x}$C alloys at different compositions. Experimentally, the effective masses are usually determined by cyclotron resonance, electron reflectance measurements or from analysis of transport data or transport measurements [89]. Theoretically, the effective masses can be estimated from the energy band curvatures. Generally, the effective mass is a tensor with nine components, however for the much idealised simple case, where the \( E-k \) diagram can be fitted by a parabola \( E = \hbar^2 k^2 / 2m^* \), the effective mass becomes a scalar at a high symmetry point in the Brillouin zone. We have computed the electron effective mass at the conduction band minima (CBM) and the hole effective mass at the valence band maxima (VBM) for the composition ranging from 0 to 1.0 for the Si$_x$Ge$_{1-x}$C alloys. The electron effective mass value is obtained from the curvature of the conduction band near the X-point for GeC and SiC and near the \( \Gamma \)-point at the CBM for \( x = 0.25 \), 0.5 and 0.75. The hole effective mass value is calculated from the curvature near the \( \Gamma \)-point at the VBM for all concentrations. The calculated electron and hole effective mass values for Si$_x$Ge$_{1-x}$C alloys are mentioned in Table 6. It is worth mentioning that the hole (heavy and light) effective masses strongly vary with composition; especially from \( x = 0 \) to 0.25 and from 0.75 to 1.0. This could be attributed to the change in the position of the conduction band minimum (CBM). The electron and hole effective masses are quite isotropic for different compositions. Since a small effective mass yields a high conductivity, the conductivity should be larger for \( x = 0 \) and 0.5. Table 6 lists the calculated electron and hole effective mass values for the studied compositions. From this table we can outline that for all compositions the electron effective mass is much smaller than that of the hole effective mass, highlighting that the carrier transport in this alloy is dominated by electrons. Our calculated effective masses for SiC are found comparable to those obtained using the full potential liberalized augmented plane wave method [90].

<table>
<thead>
<tr>
<th>X</th>
<th>LDA</th>
<th>GGA</th>
<th>LDA</th>
<th>GGA</th>
<th>Other cal.</th>
<th>LDA</th>
<th>GGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (( \Gamma-X ))</td>
<td>0.0016</td>
<td>0.0018</td>
<td>0.767</td>
<td>0.786</td>
<td>0.110</td>
<td>0.130</td>
<td></td>
</tr>
<tr>
<td>0.25 (( \Gamma-\Gamma ))</td>
<td>0.0057</td>
<td>0.0057</td>
<td>1.178</td>
<td>1.224</td>
<td>0.290</td>
<td>0.314</td>
<td></td>
</tr>
<tr>
<td>0.50 (( \Gamma-\Gamma ))</td>
<td>0.0054</td>
<td>0.0055</td>
<td>0.873</td>
<td>0.981</td>
<td>0.230</td>
<td>0.255</td>
<td></td>
</tr>
<tr>
<td>0.75 (( \Gamma-\Gamma ))</td>
<td>0.0054</td>
<td>0.0054</td>
<td>2.064</td>
<td>1.982</td>
<td>0.420</td>
<td>0.430</td>
<td></td>
</tr>
<tr>
<td>1 (( \Gamma-X ))</td>
<td>0.0018</td>
<td>0.0018</td>
<td>1.154</td>
<td>1.725</td>
<td>1.11$^a$, 1.15$^a$</td>
<td>0.160</td>
<td>0.280</td>
</tr>
</tbody>
</table>

$^a$Ref. [90].

The refractive index and dielectric constants are very important to determine the optical and electric properties of a crystal. Advanced applications of alloys can significantly benefit from the knowledge of accurate index data. The use of fast non-destructive optical techniques for epitaxial layer characterisation (determination of thickness or alloy composition) is limited by the accuracy with which refractive indices can be related to alloy composition. These applications require an analytical expression or known accuracy to.
Table 7. Refractive index of Si$_x$Ge$_{1-x}$C alloys for different compositions $x$.

<table>
<thead>
<tr>
<th>Composition</th>
<th>This work LDA</th>
<th>This work GGA</th>
<th>Other calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeC</td>
<td>1.920</td>
<td>2.002</td>
<td>2.65$^a$</td>
</tr>
<tr>
<td>Si$<em>{0.25}$Ge$</em>{0.75}$C</td>
<td>1.933</td>
<td>1.938</td>
<td></td>
</tr>
<tr>
<td>Si$<em>{0.5}$Ge$</em>{0.5}$C</td>
<td>1.904</td>
<td>1.953</td>
<td></td>
</tr>
<tr>
<td>Si$<em>{0.75}$Ge$</em>{0.25}$C</td>
<td>1.891</td>
<td>1.893</td>
<td></td>
</tr>
<tr>
<td>SiC</td>
<td>1.825</td>
<td>1.858</td>
<td>2.70$^a$</td>
</tr>
</tbody>
</table>

$^a$Ref. [97].

relate the wavelength dependence of the refractive index to alloy composition, as determined from simple techniques as photoluminescence. Different theoretical models relate the refractive index to the energy band gap as mentioned for a large set of semiconductors [94–96].

Table 7 summarises the calculated values of the refractive index for the alloy under investigation, obtained using the FP-LMTO method. Comparison with the available data has been made where possible. As compared with other calculation [97], it seems that the values of $n$ obtained from the FP-LMTO method for the end-point compounds (i.e., SiC and GeC) are in good agreement with previous theoretical results.

Figure 5 shows the variation of the calculated refractive index versus concentration for the alloys. One can notice that the refractive index decreases monotonically with increasing Si content over the entire range of 0–1 for the FP-LMTO method. The calculated refractive index versus concentration is fitted by a polynomial equation. The results are summarised as follows:

$$n(x) = 1.92 + 0.067x - 0.16x^2 \quad \text{FP - LMTO (LDA)}$$  \hfill (17)

$$n(x) = 1.99 - 0.115x - 0.018x^2 \quad \text{FP - LMTO (GGA)}$$  \hfill (18)

From these equations, we note the weak non-linear dependence of the refractive index of the alloys with concentration $x$. Interestingly, we note that on going from SiC to GeC the band gap of Si$_x$Ge$_{1-x}$C increases (see Figure 5) but the refractive index decreases. This is in agreement with the quantum-mechanics equation (n(E$_g$)) [98] which states that when the band gap $E_g$ increases, the refractive index $n$ decreases, and vice versa, but not linearly.

3.5. Thermodynamic properties

In this section we present a rigorous theoretical study of the thermodynamic properties of Si$_x$Ge$_{1-x}$C alloys, where the calculations carried out here are based on *ab initio* method within the GGA scheme. We calculate the Gibbs free energy of mixing $\delta G_m(x, T)$ which allows us to access the T–x phase diagram and obtain the critical temperature, $T_c$, for miscibility. Details of the calculations are given in references [99–101]. For alloys, the Gibbs free energy of mixing $\Delta G_m$ is expressed as:

$$\Delta G_m = \Delta H_m - T \Delta S_m$$  \hfill (19)

Where

$$\Delta H_m = \Omega x(1-x)$$  \hfill (20)

$$\Delta S_m = -R[x \ln x + (1-x) \ln (1-x)]$$  \hfill (21)

$\Delta H_m$ and $\Delta S_m$ are the enthalpy and entropy of mixing, respectively; $\Omega$ is the interaction parameter and depends on the material; $R$ is the gas constant and $T$ is the absolute temperature.

Indeed, an important contribution arises from the mixing enthalpy, which can be obtained from the calculated total energies as, $\Delta H_m = E_{Si_xGe_{1-x}C} - (1-x)E_{GeC} - xE_{SiC}$, where $E_{Si_xGe_{1-x}C}$, $E_{GeC}$ and $E_{SiC}$ are the respective energies of the Si$_x$Ge$_{1-x}$C alloy, and the binary compounds SiC and GeC. We then calculated $\Delta H_m$ to obtain $\Omega$ as a function of concentration. From a linear fit we obtained:

$$\Omega \text{ (Kcal/mol)} = 5.381 + 0.425x$$  \hfill (22)

which shows the marginal dependence of $\Omega$ on the concentration $x$ for Si$_x$Ge$_{1-x}$C alloys. Now, we first calculate $\Delta G_m$ by using Equations (19)–(21). Then we use the Gibbs free energy at different concentrations to calculate the T–x phase diagram which shows the stable, metastable and unstable mixing regions of the alloy. At a temperature lower than the critical temperature $T_c$, the two binodal points are determined as those points at which the common tangent line touches the $\Delta G_m$ curves. The two spinodal points are determined as those points at which the second derivative of $\Delta G_m$ is zero: $\partial^2 (\Delta G_m) / \partial x^2 = 0$. 

![Figure 5. Refractive index as a function of composition x for Si$_x$Ge$_{1-x}$C.](image-url)
Figure 6 shows the calculated phase diagram including the spinodal and binodal curves for the alloy of interest. We have calculated the phase diagram using the average value of the $x$-dependent $\Omega$, hence the phase diagram looks symmetric. We observe a critical temperature $T_c$ of 873K for $\text{Si}_x\text{Ge}_{1-x}\text{C}$ alloys. The spinodal curve in the phase diagram marks the equilibrium solubility limit, i.e. the miscibility gap. For temperatures and compositions above this curve a homogeneous alloy is predicted. The wide range between spinodal and binodal curves indicates that the alloy may exist as a metastable phase. Hence our results indicate that the $\text{Si}_x\text{Ge}_{1-x}\text{C}$ alloys are stable at relatively high temperature.

4. Conclusion
The (FP-LMTO) method is used to calculate the structural and electronic properties of zinc-blende SiC, GeC and their $\text{Si}_x\text{Ge}_{1-x}\text{C}$ alloy. We have found that the variation of structural parameters versus silicon concentration is nearly in agreement with Vegard's law. Our results of the electronic band structure show a nonlinear variation of the fundamental band gaps versus Si concentration. We have characterized the deviation from the linear behaviour by calculating the optical bowing parameter. The main contribution to the optical bowing is essentially due to the volume deformation effects. The obtained values of the effective masses indicate that the carrier transport in this alloy should be dominated by electrons.

We find that $n(E_g)$ of $\text{Si}_x\text{Ge}_{1-x}\text{C}$ alloys increases with a decreasing energy gap, in agreement with the quantum-mechanics equation. The investigation of the thermodynamic stability allowed us to calculate the critical temperature which is 873K.

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