First-principles calculations of structural, electronic and optical properties of Zinc-blende $Si_xGe_{1-x}C$ alloys

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Abstract

We present first-principles calculations of the structural, electronic and optical properties of zinc-blende $Si_xGe_{1-x}C$ alloys by application of the full potential linearized augmented plane wave (FP-LAPW) method. In this approach, the generalized gradient approximation was used for the exchange-correlation energy which is based on the optimization of total energy and corresponding potential. The effect of composition on lattice constants, bulk modulus, band gap, real part of the dielectric function $\varepsilon(0)$ and refractive index $n(0)$ was investigated. These parameters were found to depend nonlinearly on alloy composition x, except the bulk modulus and the lattice parameter, which follows Vegard's law. Using the approach of Zunger et al, the microscopic origin of the gap bowing is also elucidated. It is concluded that the energy band gap bowing is primarily due to chemical charge-transfer effect. Contribution of volume deformation and structural relaxation to the gap bowing parameter is found to be very small.

Key Words: Alloys, Lattice parameter, Bulk modulus, Electronic structure, Band-gap, Gap bowing, Optical properties.

1. Introduction

Theoretical studies have been fundamental in the development of new materials and new devices for diverse industrial applications. In the last few years, the electronic properties of some SiC polytypes have been calculated [1–4]. Further studies went deep into the elastic [5] and the optical properties [6], and the high-pressure behaviour [7, 8]. Furthermore, molecular dynamics simulations have been carried out to study the thermomechanical properties of SiC [9]. However, there is a group of ternary compounds (SiGeC) that has

demonstrated much potential for use in column IV Heterojunction Bipolar Transistors (HBT's) [10, 11] and high hole mobility MOSFETs [12, 13]. Like its more common counterpart, silicon germanium (SiGe), SiGeC is a narrow bandgap semiconductor that is compatible with most silicon-based processing. Its bandgap is adjustable, approximately according to Vegard's law and depending mainly on germanium content [14]. What distinguishes SiGeC from SiGe is the potential strain compensating effect of substitutional carbon. Another possible IV-IV compound is GeC. Also, experimental works have been devoted to this compound [15–17]. Moreover, there have been relatively few theoretical studies of the electronic and structural properties of this material [16] compared with SiC and SiGe. The existence of this material in its zinc-blende form has been reported. First *ab initio* investigation [18] shows that GeC, like SiC, is a wide-gap semiconductor with an indirect band gap.

In order to help understand and control the material and behavior of bowing and related properties, we have investigated the effect of the Si concentration on the structural, electronic and optical properties of the $Si_xGe_{1-x}C$ alloys in zinc-blende structures with Si contents between 0 and 1 using the full potential-linearized augmented plane wave (FP-LAPW) method. Various quantities, including lattice parameters, bulk modulus and its pressure derivative, band gap and optical bowing, were obtained for this alloy. The article is organized as follows: in the first section we give a description of the ab initio theoretical method. In Section two, results and discussion for structural, electronic properties and optical properties are presented. In the final section, we present our conclusions.

2. Calculation method

First-principles calculations are performed by employing a full-potential linear augmented plane wave (FP-LAPW) approach [19, 20] based on density functional theory (DFT) [21] and implemented in Wien2k [22] code. The exchange-correlation contribution is described within generalized gradient approximation based on Perdew et al. (GGA96) [23]. The energy of separation between the valence and core states is -6.0 Ryd. The valence wave functions inside the muffin-tin spheres are expanded in terms of spherical harmonics up to $l_{\max} = 10$, and in terms of plane waves with a wave vector cutoff $K_{\max}$ in the interstitial region. We set the parameter $R_{mt} \cdot K_{\max} = 7$ for SiC and GeC and ternary alloy, where R_{mt} is the smallest muffin-tin radius, and $K_{\max}$ is a cutoff wave vector. The binary compounds crystallize in the zinc-blende structure SiC, GeC ($F\bar{4}3m$), the disordered ternary alloy is modelled using a supercell with 8 atoms in the (P) structure. The iteration process was repeated until the calculated total energy of the crystal converge to less than 1 mRyd. Total of 7 iterations was necessary to achieve self-consistency.

As such, muffin-tin radii of 1.8, 2.0 and 1.6 Bohr have been chosen for values for SiC, GeC, Si, Ge and C, respectively. For ternary compounds we have used muffin-tin radius of 1.45 Bohr for C, 1.65 Bohr for Si and 1.85 Bohr for Ge atoms.

The k-integration over the Brillouin zone is performed using the Monkhorst and Pack mesh [24]. A mesh of 37 special k-points for binary compounds and 17 special k-points for the alloy were taken in the irreducible wedge of the Brillouin zone.

Optical properties of a solid are usually described in terms of the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The imaginary part of the dielectric function in the long wavelength limit has been obtained directly from the electronic structure calculation, using the joint density of states (DOS) and the optical matrix elements. The real part of the dielectric function can be derived from the imaginary part by the Kramers–

Kronig relationship. The knowledge of both the real and the imaginary parts of the dielectric function allows the calculation of important optical functions. The refractive index $n(\omega)$ is given by

$$n(\omega) = \left[\frac{\varepsilon_1(\omega)}{2} + \frac{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)}}{2}\right]^{1/2}.$$

(1)

At low frequency $(\omega = 0)$, we get the relation

$$n(0) = \varepsilon^{1/2}(0).$$

(2)

In this paper, we also present and analyze the dielectric constant static $\varepsilon(0)$ of the dielectric function $\varepsilon(\omega)$ and the index of refraction $|\varepsilon_1(0)|^{1/2}$ at the frequency $\omega = 0$.

3. Results and discussion

3.1. Structural properties

Concerning the structural properties of this alloy, we determined its equilibrium parameters namely the lattice parameter, the module of compressibility and its derivative. In our calculations, we used approximation GGA for the determination of the potential of exchange and correlation. The other parameters used in calculations, namely the muffin-tin radius, $R_{mt} \cdot K_{\max}$ and $l_{\max}$ are presented in section 2. Integration over k in the zone of Brillouin was carried out by using the Monkhorst-pack scheme [24], 17 special points were used. The alloy was studied by using a primitive mesh of 8 atoms. We compute lattice constants, bulk modulus and their first derivatives by fitting the total energy versus volume according to the Murnaghan equation of state [25].

The values obtained for various concentrations of silicon are gathered in Table 1, we compare the calculated data with experiment and with results obtained from previous calculations. It is clear that our GGA results are in reasonable agreement with experimental values and other calculated values.

Furthermore, the calculated values of the bulks modulus, using the GGA approximation, decrease from SiC to GeC; from the lower to the higher atomic number. This suggests that GeC is more compressible than SiC. Variations of total energy as a function of the volume for these concentrations are shown on Figure 1.

The variation of the lattice parameter and bulk modulus as a function of the concentration, of alloy $Si_xGe_{1-x}C$ is illustrated on Figure 2 and Figure 3, respectively.

We note that the lattice parameter decreases linearly as a function of the concentration. Our calculations agree well with those calculated by Végard's law [26]:

$$a(AB_{1-x}C_x) = (1-x)a(AB) + xa(AC),$$

(3)

where $a(AB)$ and $a(AC)$ are the lattice parameters of binary compounds AB and AC; however, one may note a light deviation compared to the Vegard's law, due to the relaxation of the Si-C and Ge-C bond lengths to their equilibrium total energy minimizing value.

Hence, the lattice constant can be written as:

$$a(AB_{1-x}C_x) = (1-x)a(AB) + xa(AC) - x(1-x)b,$$

(4)

Table 1. The calculated lattice parameter a, bulk modulus B, and its pressure derivatives B' for $Si_xGe_{1-x}C$ and its binary compounds. Available experimental and theoretical data are also given for comparison.

	a (Å)	B (GPa)	B'	a (Å) Végard
GeC(P) Present work Other calculations	4.605 4.61[28] 4.61[30] 4.54[27] 4.43[31] 4.62[33]	173.652 200[28] 181[30] 203[27] 188[31] 200[33]	4.458 4.16[28] 4.20[30] 3.73[27] 3.45[31] 4.15[33]	4.605
$Si_{0.25}Ge_{0.75}C$	4.550	181.649	4.250	4.548
$Si_{0.5}Ge_{0.5}C$	4.494	193.162	4.107	4.491
$Si_{0.75}Ge_{0.25}C$	4.435	203.887	4.150	4.434
SiC(P) Present work Other calculations Expt	4.378 4.39[28] 4.40[30] 4.34[27] 4.32[9] 4.40[33] 4.36[32]	213.682 217[28] 206[30] 225[9] 227[29] 215[33] 225[32]	4.969 3.71[28] 5.30[30] 4.02[27] 4.11[9] 4.10[29]	4.378

where the quadratic term b is the bowing parameter.

We report the behavior of the bulk modulus as a function of Si-composition x for $Si_xGe_{1-x}C$ compounds. Our results show a small deviation from the linear concentration dependence (LCD). With a quadratic fit, we find a small downward bowing parameter of $b = 3.21$ GPa. The small bowing parameter is due to the bulk modulus of GeC which is 18.73% smaller than SiC. We are satisfied to discuss only our results considering the absence of experimental and theoretical studies on this alloy.

3.2. Electronic properties

In study of the electronic properties of this alloy, interest is precisely in the structure of energy bands. For each concentration, the band structure was calculated using the lattice parameter obtained during structural optimization. Energy bands structures for various concentrations of silicon are shown in Figure 4.

For alloy $Si_xGe_{1-x}C$, calculations of the band structures for all concentrations of silicon gave a direct gap at the Γ point.

Values of the direct and indirect gap, for various concentrations of silicon, are given in Table 2. The variation of the direct and indirect gap of alloy $Si_xGe_{1-x}C$ as a function of concentration is shown in Figure 5. Polynomial fit of the curves shows a nonlinear behavior of the variation of the gaps:

$$E_{\Gamma \to X} = 3.371 + 0.986x - 0.329x^2, \tag{5}$$
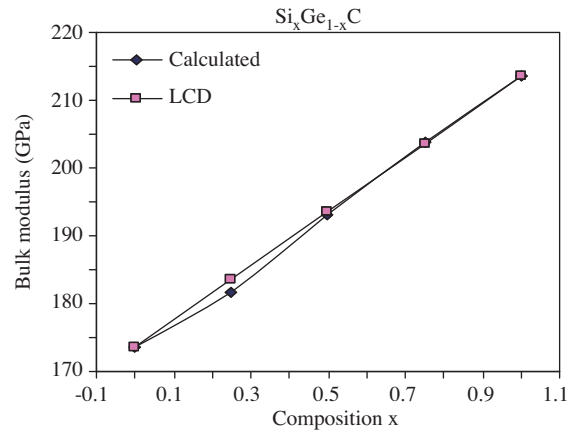
$$E_{\Gamma \to \Gamma} = 1.646 - 0.054x - 0.234x^2. \tag{6}$$
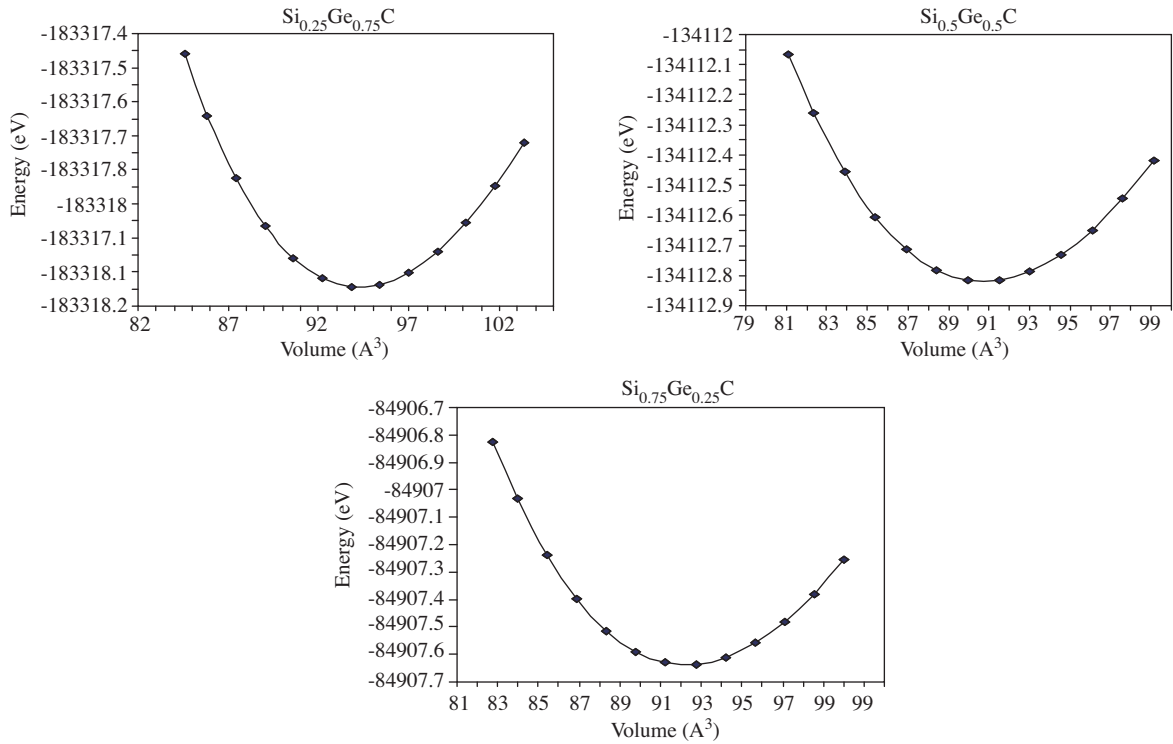
Figure 1. Total energy as a function of the volume with GGA calculation for $Si_xGe_{1-x}C$ alloy.
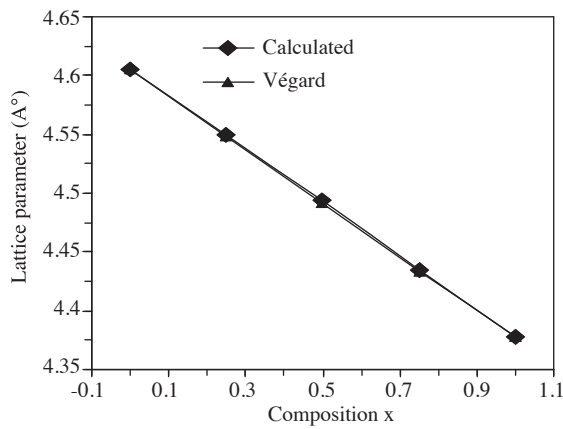

Figure 2. Lattice parameter as a function of composition x for $Si_xGe_{1-x}C$ compounds.

Figure 3. Bulk modulus as a function of composition x for $Si_xGe_{1-x}C$ compounds.

It is clear from the above equations that the direct $\Gamma \rightarrow \Gamma$ and indirect $\Gamma \rightarrow X$ band gaps, versus concentration, exhibit a nonlinear behavior. The direct gap $\Gamma \rightarrow \Gamma$ exhibits a downward bowing with a value of -0.234, while the indirect gap $\Gamma \rightarrow X$ has an upward bowing of -0.329 within the range of x investigated.

To analyze the physical origin of the gap bowing, we follow the approach of Zunger et al. [34]. In this approach, gap bowing coefficient b is assumed to be independent of composition x and is decomposed into three components. The overall bowing coefficient at $x = 0.5$, measures the change in band gap in the formal
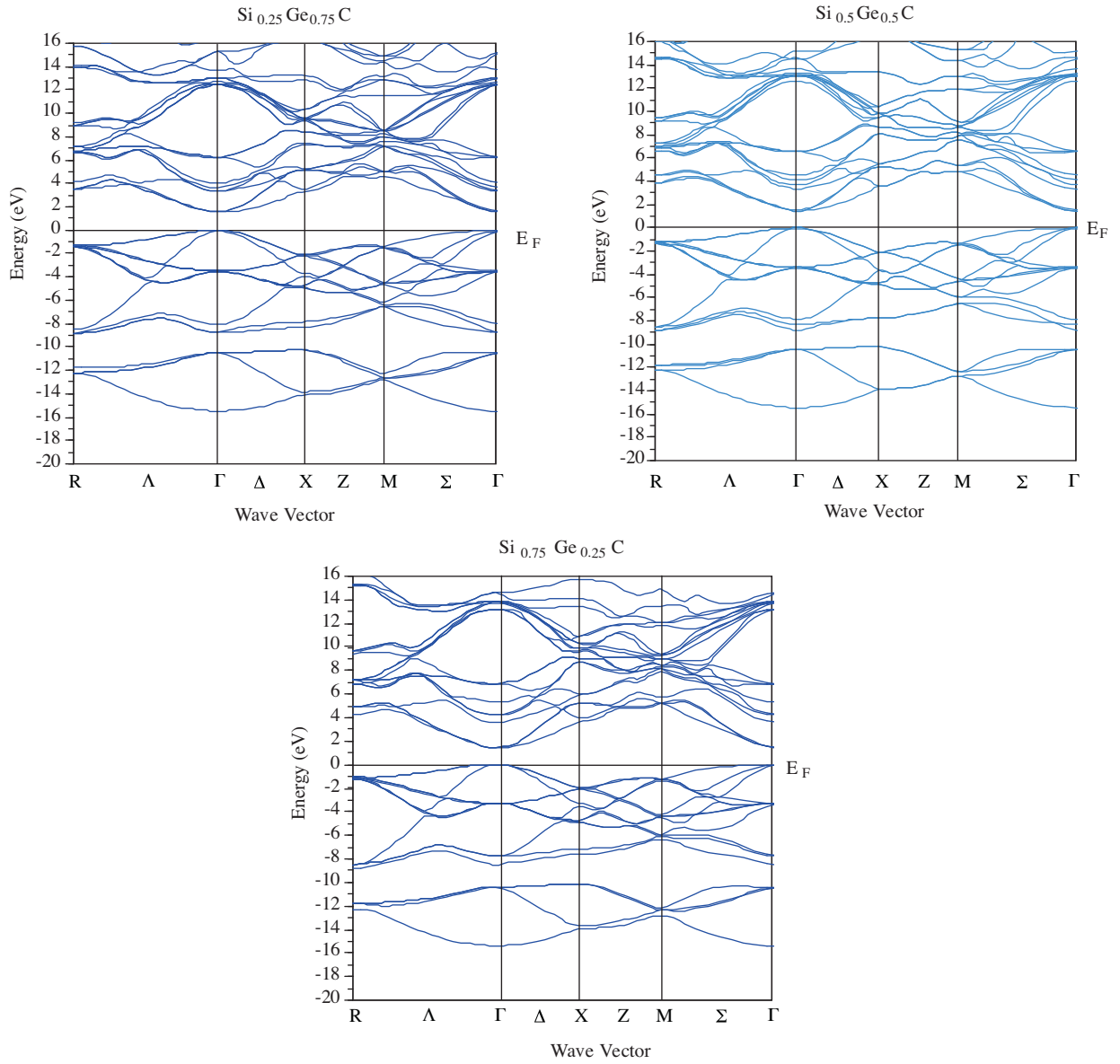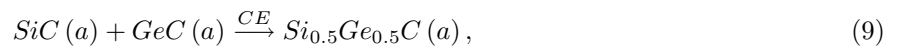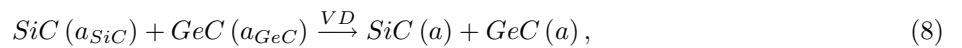
Figure 4. Band structure of the ternary alloy $Si_xGe_{1-x}C$.

reaction:

$$SiC\left(a_{SiC}\right) + GeC\left(a_{GeC}\right) \rightarrow Si_{0.5}Ge_{0.5}C\left(a_{eq}\right), \tag{7}$$
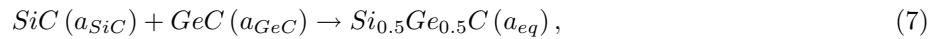
where a_{SiC} and a_{GeC} are the equilibrium lattice constants of the constituent parents SiC and GeC, and a_{eq} is the equilibrium lattice constant for $Si_xGe_{1-x}C$ alloy with $x = 0.5$. Reaction (7) is decomposed into three component reactions:

$$SiC\left(a_{SiC}\right) + GeC\left(a_{GeC}\right) \xrightarrow{VD} SiC\left(a\right) + GeC\left(a\right), \tag{8}$$

$$SiC\left(a\right) + GeC\left(a\right) \xrightarrow{CE} Si_{0.5}Ge_{0.5}C\left(a\right), \tag{9}$$

Table 2. The calculated direct ($\Gamma \to \Gamma$) and indirect ($\Gamma \to X$) band gaps for $Si_xGe_{1-x}C$ alloy.

	$E_{\Gamma\Gamma}$ (eV)	$E_{\Gamma X}$ (eV)
GeC	1.650	3.366
$Si_{0.25}Ge_{0.75}C$	1.609	3.622
$Si_{0.5}Ge_{0.5}C$	1.572	3.738
$Si_{0.75}Ge_{0.25}C$	1.470	3.960
SiC	1.359	4.019
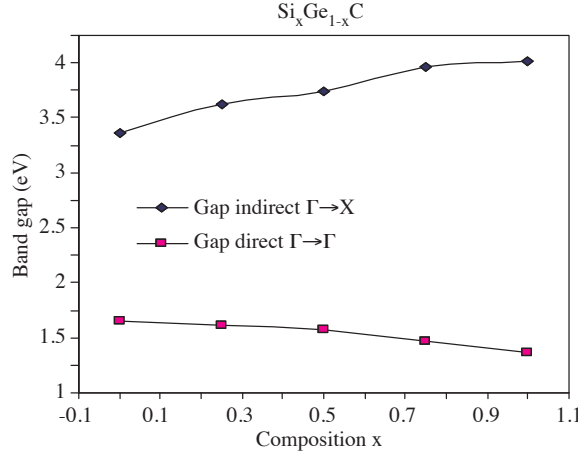
Figure 5. Composition dependence of the direct ($\Gamma \to \Gamma$) and indirect ($\Gamma \to X$) band gaps in $Si_xGe_{1-x}C$ alloy.

$$Si_{0.5}Ge_{0.5}C\,(a) \xrightarrow{SR} Si_{0.5}Ge_{0.5}C\,(a_{eq}). \tag{10}$$

The first step measures the effect of volume deformation (VD) on the energy gap bowing. The corresponding contribution to the bowing, b_{VD}, is responsible for the variation of the band gap width in the individual components, SiC and GeC, to hydrostatic pressure of the solid solution. The second step, due to charge-exchange (CE) contribution b_{CE}, the relaxation of the interatomic bond lengths in the superlattice was not carried out. In this case, there occurs a charge redistribution between the Si-C and Ge-C bonds, which results in changing the arrangement of the electron energy bands. The final step, the "structural relaxation" (SR), measures changes in passing from the unrelaxed to the relaxed alloy by b_{SR}. Consequently, the total gap bowing parameter is defined in [34] as

$$b = b_{VD} + b_{CE} + b_{SR}, \tag{11}$$

$$b_{VD} = 2\left[\varepsilon_{SiC}\,(a_{SiC}) - \varepsilon_{SiC}\,(a) + \varepsilon_{GeC}\,(a_{GeC}) - \varepsilon_{GeC}\,(a)\right], \tag{12}$$

$$b_{CE} = 2\left[\varepsilon_{SiC}\,(a) + \varepsilon_{GeC}\,(a) - 2\varepsilon_{Si_{0.5}Ge_{0.5}C}\,(a)\right], \tag{13}$$

$$b_{SR} = 4\left[\varepsilon_{Si_{0.5}Ge_{0.5}C}\,(a) - \varepsilon_{Si_{0.5}Ge_{0.5}C}\,(a_{eq})\right], \tag{14}$$

where ε is the energy gap which has been calculated for the indicated atomic structures and lattice constants. All terms in expressions (11)–(13) have been calculated separately via self-consistent band structure calculations FP-LAPW. Three contributions to the direct gap bowing ($\Gamma \to \Gamma$) have been calculated using GGA-PBE scheme

and the results are given in Table 3. It is clear that the main contribution to total gap bowing of $Si_{0.5}Ge_{0.5}C$ alloy is due to the charge exchange effect represent by b_{CE}.

Table 3. Decomposition of optical bowing, into contributions due to volume deformation (VD), charge exchange (CE) and structural relaxation (SR), compared with that obtained by a quadratic interpolation (all values in eV).

| Direct ($\Gamma \rightarrow \Gamma$)	Present work	Present work quadratic equation
b_{VD}	-0.048	
b_{CE}	-0.294	
b_{SR}	$+0.072$	
b	-0.270	-0.234

For the study of the optical properties of this alloy, we were interested in the variation of the static optical properties (real part of the dielectric function $\varepsilon(0)$ and index of refraction $n(0)$) as a function of the concentration. Values of the real part of the dielectric function $\varepsilon(0)$ and the index of refraction $n(0)$, for various concentrations of silicon, are given in Table 4. Variations of the static optical properties as a function of the concentration of silicon are illustrated in Figures 6 and 7.

Table 4. The calculated real part of the dielectric function $\varepsilon(0)$ and index of refraction n(0) for $Si_xGe_{1-x}C$ alloy.

	$\varepsilon(0)$	$n(0)$
GeC	7.836	2.799
$Si_{0.25}Ge_{0.75}C$	7.538	2.745
$Si_{0.5}Ge_{0.5}C$	7.275	2.697
$Si_{0.75}Ge_{0.25}C$	7.070	2.659
SiC	6.907	2.628
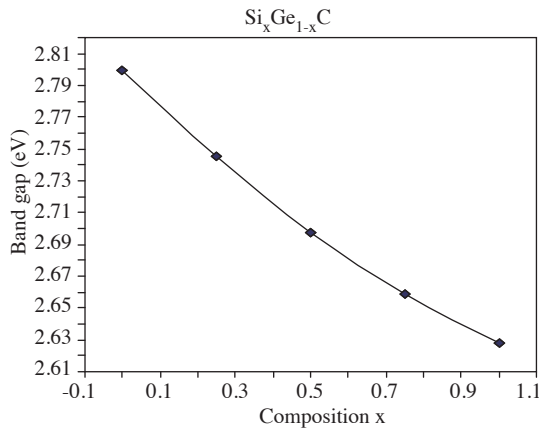
Figure 6. Variation of the index of refraction $n(0)$ with the concentration of silicon for $Si_xGe_{1-x}C$ alloy.
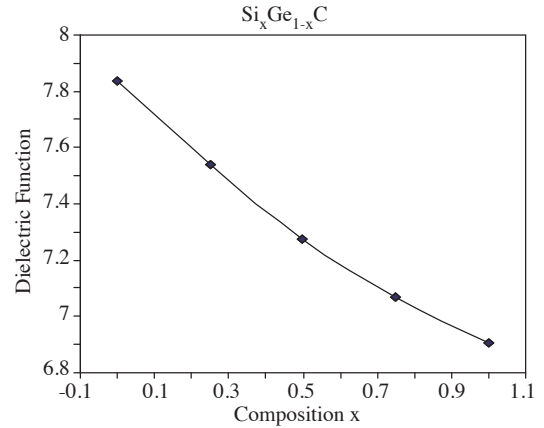
Figure 7. Variation of the real part of the dielectric function $\varepsilon(0)$ with the concentration of silicon for $Si_xGe_{1-x}C$ alloy.

These curves are given using a polynomial adjustment. This adjustment led us to the following expressions of ε and n:

$$\varepsilon = 7.837 - 1.305x + 0.374x^2 \tag{15}$$

$$n = 2.799 - -0.235x + 0.064x^2. \tag{16}$$

In light of these equations, we can note that there is no linearity of the dependence of the optical properties of this alloy within concentration x.

4. Conclusion

We have studied the electronic, structural and optical properties of $Si_xGe_{1-x}C$ ternary alloy by first principles FP-LAPW calculations. We have investigated the composition dependence of the lattice constant, bulk modulus, band gap, the real part of the dielectric function $\varepsilon(0)$ and refractive index $n(0)$. These parameters were found to depend nonlinearly on alloy composition x, except the bulk modulus and the lattice parameter, which follows Vegard's law. The calculated electronic properties of $Si_xGe_{1-x}C$ alloys for different silicon compositions x, show that the fundamental gap is direct and is along the direction $\Gamma \rightarrow \Gamma$. The band gap exhibits non-linear behavior or bowing effect with the change of concentration. The main contribution to the total bowing parameter comes from the charge transfer between anion and cation. We consider that the results obtained are only one predictive study, by hoping that our current work will stimulate even more work on these materials.

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