The interstitial C_iO_i defect in bulk Si and $Si_{1-x}Ge_x$

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Abstract
The equilibrium geometries, phonon spectra, electronic structures and optical properties of the C_iO_i defect in bulk Si and $Si_{1-x}Ge_x$ systems are calculated using the *ab initio* plane wave density-functional method. We find that in a Ge-doped Si crystal it is more energetically favourable for the defect to stabilize in a configuration with no Ge atoms in the first sphere. Our calculations show that the vibrational properties of the defect in the $Si_{1-x}Ge_x$ alloy are similar to those in the pure Si bulk crystal and only one local vibrational mode is sensitive to the presence of the Ge substitutions. The effect of C, O, Si and Ge isotopes on the phonon spectra are also investigated and found to be in good agreement with available experimental data. It also follows from our calculations of the singlet–triplet splitting and a position of the gap state of the defect with respect to the top of the valence band that the optical energies of the C_iO_i defect are expected to increase due to Ge doping, which is in agreement with available experimental data.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Silicon–germanium ($Si_{1-x}Ge_x$) alloys attract considerable interest due to their extensive applications in microelectronic and optoelectronic devices. In these systems, point defects are mainly responsible for their unique properties and that is why investigation of vibrational and electronic properties of impurities in these semiconducting materials is still a major research area. Valuable information about the symmetry of many point defects can be provided by the vibrational spectra measurements since light impurities produce local vibrational modes (LVMs) which are well isolated from the frequency range of the host crystal.

One of the most stable defects is the interstitial carbon–oxygen centre, C_iO_i, which is formed when a carbon interstitial defect, C_i, which is very mobile at room temperatures, is trapped by an oxygen interstitial defect, O_i [1]. The C_iO_i centre is quite stable with an annealing temperature around 350–450 °C [2].

There have been some experimental and theoretical studies of the carbon–oxygen defect in Si and its structure is now well understood. It is believed that the carbon–oxygen interstitial forms a ring core structure [1, 3, 4] in which the neighbouring O and C atoms are each bound to the three nearest Si atoms. One of the most important characteristics of the defect is its vibrational spectrum. Four fundamental low temperature local vibrational modes (LVMs) associated with the C_iO_i defect were found which are located at 1116, 865, 742 and around 585 cm^{-1} [5, 2]. These were confirmed by a few *ab initio* theoretical calculations performed within the density functional theory (DFT) and a localized basis set using either a cluster [4] or periodic boundary conditions [3, 1] models.

However, to the best of our knowledge, there have been no first principles theoretical studies of the C_iO_i defect in the Si/Ge alloy system. Therefore, the aim of the present paper is to fill in this gap by studying the geometry, energetics, vibrational spectrum and electronic structure of the interstitial C_iO_i defect in a Si/Ge system in the limit of small Ge concentrations using an *ab initio* density-functional theory, plane wave basis set and the pseudopotential method.

The plan of the paper is as follows. In section 2 we briefly describe our DFT method. The results on geometry, and electronic and phonon structures of the C_iO_i interstitial defect in the Si bulk are briefly summarized in section 3 to verify our methodology. The results of our calculations are compared with previous DFT calculations [1, 3, 4] in which a localized basis set was used. The consideration in section 3 is also useful as it serves as a convenient reference system with which the C_iO_i defect in Si/Ge alloy can be compared. Essentially new results for the C_iO_i interstitial defect in the Si/Ge alloy system are presented in section 4. Finally, in section 5 we discuss our results and draw brief conclusions.

2. Method

The theoretical methods used in this paper are essentially the same as in our previous paper [6] in which the properties of the O_i interstitial defect were considered. We used DFT, within the generalized gradient approximation (GGA) [7], periodic boundary conditions and plane wave basis set as implemented in the Vienna *ab initio* simulation package (VASP) [8–10] to obtain the relaxed geometries, the electron density, and the Kohn–Sham energies as well as the Hellmann–Feynman forces on atoms. The latter are used for geometry optimization and the calculations of the vibrational spectra. To minimize the cost of the calculations, ultrasoft pseudopotentials [11, 12] have been used for all species. All the calculations reported here are based on the periodic simple cubic cell containing 64 Si atoms, which was found to be of sufficient size in our previous work on the O_i defect [6]. When considering the C_iO_i defect in this cell, the $2 \times 2 \times 2$ Monkhorst–Pack **k**-point sampling [13] has normally been used. We have carefully checked that the relaxed geometry is well converged with respect to the **k**-point sampling.

The dynamical properties of the defective Si and Si/Ge systems have been studied using a method developed in [6] which is a modification of the direct (frozen-phonon) method [14, 15]. In our method only displacements of a finite set of atoms (a cluster) comprising the defect itself and a certain number of the host Si atoms have been accounted for in building up the dynamical matrix. It was found in [6] that all vibrational frequencies (apart from the lowest ones which cannot be considered reliable in this method) converge reasonably well with the cluster size. Diagonalization of the cluster dynamical matrix gives the vibration frequencies and the corresponding eigenvectors. The latter enable us to calculate the projected phonon density of states (DOS) and thus identify localized modes and resonances associated with the defect and/or Ge substitution. When plotting the phonon DOS, we smear out a finite discrete

set of local phonon levels calculated in our cluster approximation with a Gaussian of dispersion $\sigma = 10\,\text{cm}^{-1}$. In our phonon calculations a cluster containing 20 Si lattice sites has been used, which was found to be sufficient to converge all frequencies over $100\,\text{cm}^{-1}$.

To understand better the phonon DOS of a defect system in which some of the Si atoms are replaced by the Ge atoms, we also calculate the DOS for an artificial system in which atoms are positioned at the same sites as in the Ge-free system and the same force-constant matrix is assumed. However, the Si atoms which are supposed to be substituted by the Ge atoms are given the actual masses of the heavier Ge atoms. We call this system a 'fake' system [6]. Since Si and Ge atoms are chemically very similar, the fake system has all the essential features of the real defect system with Ge substitutions. Comparing the phonon DOS for the fake and actual systems one can learn a great deal about the effect of the Ge mass on the positions of the local phonon modes and thus separate out the effect of the chemical bonding. In addition, in some cases one can also approximately simulate the phonon spectrum of more complicated systems (containing several Ge atoms) without performing additional DFT calculations.

The charge density $\rho(\mathbf{r})$ of every cell has been analysed using the Lev00 package [16] by plotting the density along lines and in planes cutting through the cell as well as by calculating the amount of charge in spheres of different radii (see [17]). The electronic total and projected DOS have been calculated from the Kohn–Sham eigenstates using the method of tetrahedra [18, 19, 17].

The formation energies of the interstitial C_iO_i defect were calculated in a usual way by subtracting from the energy of the supercell containing the defect the chemical potentials μ_i of all individual species i [1, 20, 21, 6]. For Si, O and Ge we used the same values as in the previous paper: $\mu_{Si} = -5.427$ eV, $\mu_O = -9.19$ eV, $\mu_{Ge} = -4.35$ eV [6]. The chemical potential of C was chosen as the energy per atom in bulk diamond. Using a 4 $\mathbf{k}$-point and 128-atom supercell, this energy was calculated as $\mu_C = -9.117$ eV.

3. Interstitial carbon oxygen in silicon bulk

We carefully checked that the ring structure, shown in figure 1(a), suggested in [1, 3, 4] is the most energetically favourable defect geometry. The triplet electronic state of this defect is 0.57 eV higher in energy than the singlet state; note that ionic relaxation in the triplet state from the singlet state geometry is negligible. We find that the detailed geometry in the singlet state is slightly different from that reported previously in [4]. For instance, we found the Si–O distance between the O atom and the nearest out-of-ring Si atom to be 0.8 Å smaller, while two of the angles related to the O atom were found to be about 20° smaller. Those discrepancies are probably due to the local basis set and the cluster method used in the previous work. The formation energy of the ring structure defect we have calculated is 3.63 eV. Since the binding energy of the O_i defect was found in [6] to be 1.56 eV and the formation energy of the C_i interstitial calculated here is 3.74 eV, the binding energy between the two defects in the ring structure is obtained as 1.65 eV, in good agreement with the value of 1.7 eV [1, 3]. Note that the formation energy of a pair of nearest O_i and C_i defects (see figure 1(b)) is about 1 eV higher than that of the ring structure.

An analysis of the electron density of the carbon–oxygen defect shown in figure 2 demonstrates clearly the formation of strong covalent bonding between C and O atoms of the ring structure with the four surrounding Si atoms. We find, by carefully analysing the electron density, that the Si atoms each contribute (as in the bulk silicon) a single electron to initiate the covalent bond. It can also be noticed that there is a very large electron density *between* the C and O atoms, which suggests that there is a covalent bonding between these atoms as well. This means that the picture of 'three coordinated C and O atoms' in the C_iO_i
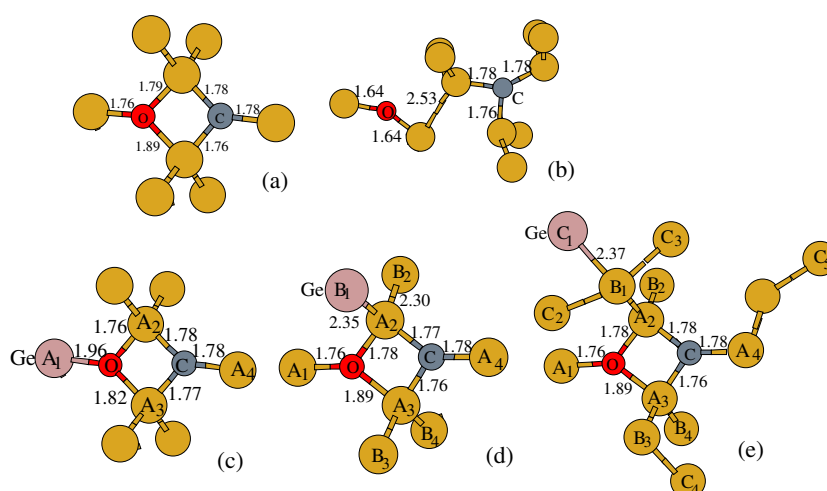
Figure 1. Different configurations for the interstitial carbon–oxygen defect in the Si and $Si_{1-x}Ge_x$ systems: (a) $Si_{64}CO$; (b) $Si_{64}CO$ with O in the second shell with respect to C; (c) the ring configuration for a system when a Ge atom is in the position marked A_1 which is nearest to the O atom; (d) a Ge atom in the second sphere around the C_iO_i defect in the position B_1; (e) a Ge atom in the third sphere in the position C_1. In all cases other possible substitutional sites for the Ge atom are also indicated as A_n, B_n and C_n with $n = 1, 2, \ldots$. The calculated bond lengths (in Å) are shown on the pictures as well.

defect suggested previously [1, 3, 4] is probably an oversimplification, and one has to rather talk about 'four coordinated C and O atoms'. Therefore, the model of the defect shown in figure 1 which implies a threefold coordination must be considered with caution.

We also find a double occupied gap state in the electronic DOS about 0.32 eV above the top of the valence band (VB). It represents a *lone pair* which is strongly localized on the C atom and has a dumb-bell shape with the lobes directed out of the C atom in the two directions perpendicular to the plane associated with the four atom ring. Note that a gap state lying 0.36 eV above the VB was also reported in [1, 3].

The calculated total and projected phonon DOS for the C_iO_i defect in silicon are shown in figure 3. We find four local vibrational modes (LVMs) around 1085.2, 831.9, 702.2 and 563 cm^{-1}. These are somewhat lower than those reported in [1] (likely due to the cluster approximation adopted here); however, the characterization of all the modes and their nature are the same, which is sufficient for our purposes. In particular, the 702.2 cm^{-1} vibration is associated mainly with the O atom. Finally, in general agreement with [1], there is also a defect related peak at around 517 cm^{-1} just at the top of the continuum composed of three oscillations at 512.1, 513.2 and 524.2 cm^{-1}.

We have also calculated the downward isotopic shifts for the LVMs and found them to be in very good agreement with previous theoretical calculations and the experiment [1].

4. Interstitial carbon oxygen in $Si_{1-x}Ge_x$

4.1. Energetics and geometry

To study the oxygen defect in the $Si_{1-x}Ge_x$ system, we considered the same 64 Si atom cell as above in which $n = 1, 2, 3$ Si atoms were substituted by Ge atoms. These calculations
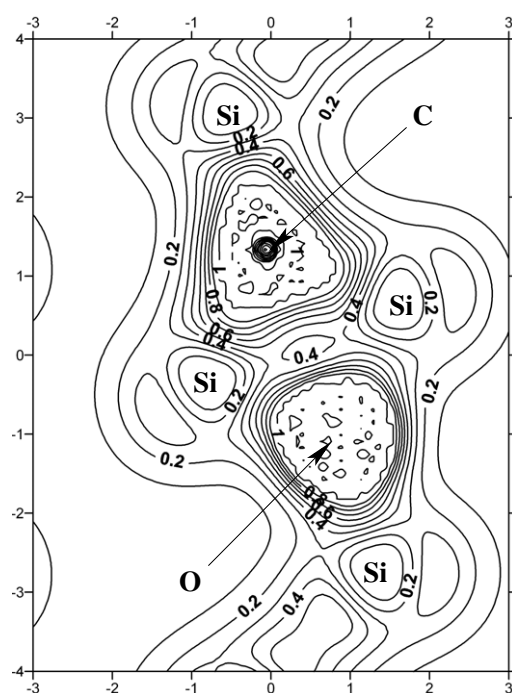
Figure 2. The valence electron charge density (in Å^{-3}) of the carbon–oxygen defect in Si plotted in the plane passing through the four atoms of the ring structure. The positions of the ring atoms are also indicated. The density was chopped at 1.0 Å^{-3}.
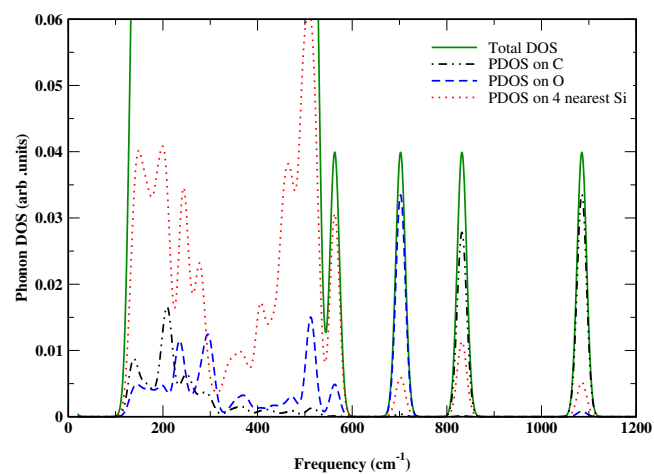
Figure 3. Total and projected phonon DOS for the C_iO_i defect in silicon.

correspond to the value of x between $\frac{1}{64} \simeq 0.016$ and $\frac{3}{64} \simeq 0.047$. Then all atoms of the $Si_{64-n}Ge_nCO$ cell were allowed to relax to their mechanical equilibrium. Note that the Si and Ge atoms are nearly identical from the chemical point of view, the latter having slightly larger atomic radius. Therefore, we find very little additional atomic relaxation in the systems studied due to Ge substitutions.

Table 1. The formation, equation (1), and vertical singlet–triplet, ΔE_{ST}, energies of the C_iO_i interstitial defect in various Si/Ge systems (see figure 1).

One Ge atom			Two Ge atoms			Three Ge atoms		
Positions	E_f'	ΔE_{ST}	Positions	E_f'	ΔE_{ST}	Positions	E_f'	ΔE_{ST}
A_1	3.879	0.601	A_1A_2	4.77	0.414	$A_1B_4C_3$	3.849	0.617
A_2	4.449	0.467	A_1B_1	3.838	0.588	$B_3B_4C_1$	3.642	0.665
A_3	4.234	0.446	A_1B_2	3.822	0.608	$B_2B_3C_2$	3.601	0.659
A_4	4.069	0.553	B_1B_4	3.615	0.658	$C_1C_2C_3$	3.487	0.635
B_1	3.575	0.64	B_3B_4	3.536	0.645	$C_1C_4C_5$	3.638	0.648
C_1	3.576	0.639	B_1C_4	3.511	0.641			

A number of systems have been considered in which up to three Ge atoms have been positioned in various ways with respect to the C and O atoms in the defect as shown in figures 1(d) and (e). To simplify the forthcoming discussion, we have introduced the following nomenclature. There are four nearest neighbour Si positions to the C and O atoms which are indicated as A_1, A_2, A_3 and A_4. More positions exist in the second sphere, which are indicated as B_1, B_2, etc; similarly, in the third sphere the positions are denoted as C_1, C_2 and so on. Due to a quite large number of systems possible, only a limited number of them have been studied; we, however, believe that the particular systems we have considered are representative enough to make the necessary qualitative conclusions concerning the effect of the Ge substitutions (at rather small concentrations) on the defect properties.

The formation energies of the C_iO_i defect,

$$E_f'(C_iO_i) = E_{Si_{64-n}Ge_nCO} - (E_{Si_{64-n}Ge_n} + \mu_O + \mu_C), \tag{1}$$

are calculated with respect to the corresponding $Si_{64-n}Ge_n$ cell in which the C and O atoms are removed ($n = 1, 2, 3$). These energies are shown in table 1. Recall that the formation energy of the C_iO_i defect in Si has been found to be 3.63 eV.

As in the case of the C_iO_i defect in silicon discussed in the previous section, we found that the ring structure is the most energetically favourable structure. This is to be expected due to the chemical similarity of the Si and Ge atoms mentioned earlier. The calculated formation energies and geometrical parameters of the defect in the cases when one or more Ge atoms are positioned in the second and/or third spheres are found to be extremely close to each other and to the values found for the same defect in silicon (cf table 1, figure 1 and the discussion below).

It should be mentioned that the actual geometry optimization has not been performed for all systems in which Ge atoms were positioned in the second and/or third spheres with respect to the C and O atoms. This is because we have found, by studying a limited number of such systems, that the relaxation energies and the actual atomic displacements associated with each substitution Si $\rightarrow$ Ge are extremely small and are all comparable with those for the substitution in the silicon bulk (about 0.001 eV relaxation energy for every substitution). Therefore, we decided that in all other cases additional geometry optimization was not necessary and thus it was not performed.

Summarizing, if Ge atoms do not appear as the nearest neighbours of the C and O atoms, the C_iO_i defect can be viewed as a Si–C–Si_2–O–Si molecule which is only slightly perturbed by the Ge atoms surrounding it.

However, the situation becomes rather different if one or more Ge atoms are positioned next to the carbon and oxygen atoms, i.e. in the positions from A_1 to A_4. As one can see from the data in table 1, the formation energy of the defect is by only about 0.3 eV higher if a single Ge atom replaces the Si atom in the position A_1 which is next to the O atom; from 0.5 to 0.9 eV

higher formation energies are found for the other three positions A_2, A_3 or A_4. On the whole, the formation energies are relatively higher if at least one Ge atom is positioned in the first sphere of the O and C atoms. Similarly to the case of the O_i defect in the Si/Ge system [6], a larger Ge atom in the first sphere of the C_iO_i defect costs considerable penalties in the defect elastic energy and is thus not energetically favourable.

Interestingly, the situation is opposite to the case when a Ge atom has a dangling bond (and is not bonded in one direction, i.e. is at an open end) which may happen at vacancies or at surfaces of the Si/Ge alloys. *Ab initio* DFT calculations [22, 23] showed that in these situations the Si–Ge bond is *stronger* than the Si–Si one (e.g. by about 0.25 eV for vacancies) because there is enough space in the system to accommodate a larger Ge atom and reduce the positive elastic energy. This effect explains the segregation of Ge atoms near vacancies and at surfaces and surface defects observed experimentally in Si/Ge alloys (see [22, 23] and references therein).

We thus conclude that the most energetically favourable configurations of the C_iO_i defect in the Si/Ge alloy are obtained with four Si atoms completely surrounding the C and O atoms, i.e. when Ge atoms are not positioned in the first sphere.

The point about only small perturbation of the C_iO_i defect due to the Ge substitution for systems in which Ge atoms are positioned in the second and third spheres can also be illustrated by the following simple calculation (see [6]). The *total* formation energy of the C_iO_i defect (with respect to the silicon lattice) in those systems,

$$E'_f(C_iO_i; Ge_n) = \left(E_{Si_{64-n}Ge_nCO} + n\mu_{Si}\right) - \left(E_{Si_{64}} + n\mu_{Ge} + \mu_O + \mu_C\right) \tag{2}$$

can formally be written as a sum of the formation energies of the carbon–oxygen defect in the Si/Ge system, equation (1), and the energy

$$E_s(Ge_n) = \left(E_{Si_{64-n}Ge_n} + n\mu_{Si}\right) - \left(E_{Si_{64}} + n\mu_{Ge}\right) \tag{3}$$

required to substitute n Si atoms with Ge atoms in the CO-free system. If the C_iO_i interstitial and the Ge substitutions are independent of each other, the formation energy $E'_f(C_iO_i)$ in the Si/Ge system should be very close to the formation energy $E_f(C_iO_i) = 3.63$ eV in the Ge-free system. As follows from the data available in table 1, this is indeed the case for the systems in which Ge atoms are positioned in the second and third spheres, as expected. The perturbation caused by the Ge atom(s) in the first sphere is substantial so that the two formation energies are no longer similar.

We have also looked at the electronic DOS of the C_iO_i defect in various Si/Ge systems. In this section we shall only mention a single system in which a Ge atom is in the A_1 position. No considerable differences have been found in the DOS except for a slightly shifted up position of the gap state (0.34 eV above the valence band maximum). Similarly, there is no noticeable change found in the electron distribution in the defect region in comparison with the reference Ge-free defect system. We have also studied the electronic DOS for several systems which contain two and three Ge atoms in the second and third sphere, respectively. These are discussed in section 4.3.

4.2. Vibrational properties

To investigate how the Ge doping perturbs the vibrational properties of the C_iO_i defect, we have calculated the phonon DOS for some of the Si/Ge systems featured in table 1. The phonon DOS for the system in which a single Ge atom is in position C_1 is extremely similar to that for the Ge-free system shown in figure 3. The Ge substitution resulted only in a resonance around 140 cm^{-1} and a relatively small upward shift of the first of the local peaks by 23 cm^{-1}; the other three local vibrational modes stay in practically the same positions of 1080, 826 and
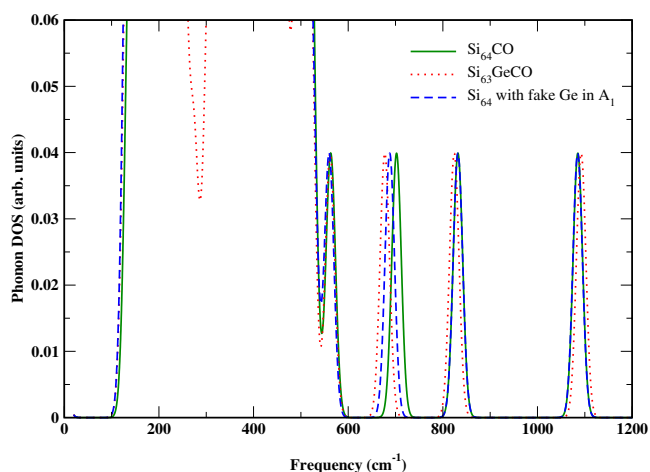
Figure 4. Calculated total DOS for the C_iO_i defect in silicon (solid curve), with a single Ge atom in position A_1 (dotted curve) and for the same fake system (dashed curve).
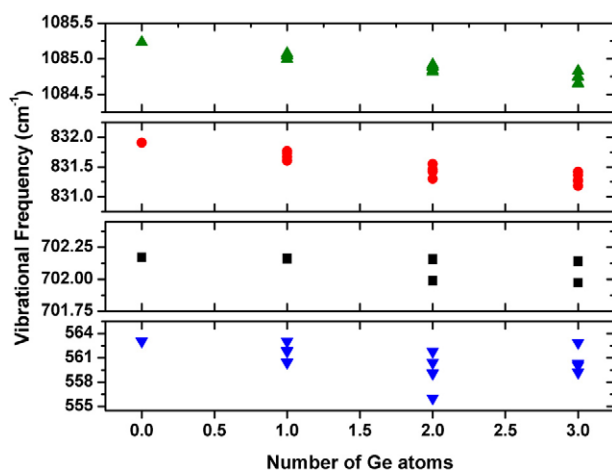
Figure 5. Calculated positions of the four local vibrational peaks in the phonon DOS for fake Si/Ge systems containing the C_iO_i defect as a function of the number of Ge atoms in the cell.

702 cm^{-1}. These results are consistent with our earlier conclusion based merely on energetic arguments that the systems in which Ge atoms are not located in the first sphere with respect to the C and O atoms can be treated as consisting of an independent Si–C–Si$_2$–O–Si molecule and Ge substitution defects.

The phonon DOS for the defect system in which a single Ge atom is in position A_1 is shown in figure 4. The two highest carbon related local peaks shift insignificantly to 821 and 1092 cm^{-1}. The second peak experiences a downward shift by 24 to 678 cm^{-1}. There is no noticeable change in the position of the first phonon peak. Note, however, that the contribution of the O atom into the first peak is more significant than for the Ge-free system.

It is also seen from the same picture that qualitatively the phonon DOS for the same defect with the Ge atom can be well reproduced by considering the corresponding 'fake' system (section 2). Similar analyses have also been performed for other systems. The

Table 2. Calculated downward isotopic shifts for LVMs (in cm^{-1}) for systems containing ^{72}Ge atom in the positions A_1 and C_1. Left panel: C and O isotopic shifts. Right panel: isotopic shifts due to ^{30}Si atom at four positions.

$^{12}C^{16}O$		$^{13}C^{16}O$		$^{12}C^{18}O$		$^{13}C^{18}O$		^{30}Si at A_1	^{30}Si at A_2		^{30}Si at A_3		^{30}Si at A_4	
A_1	C_1	A_1	C_1	A_1	C_1	A_1	C_1	Ge at C_1	Ge at A_1	C_1	Ge at A_1	C_1	Ge at A_1	C_1
1092.3	1080.5	36.5	35.7	1.1	1.2	37.7	37.1	0.03	1.0	1.1	1.0	0.98	2.6	2.6
821.1	826.9	21.3	22.7	0.03	0.05	21.5	22.8	0.005	2.3	2.4	5.2	5.4	0.04	0.03
677.4	707.3	0.3	0.3	31.1	33.8	31.3	34.0	1.8	3.0	1.37	0.9	0.1	0.2	0.14
561.8	586.2	0.1	0.1	3.6	7.5	3.7	7.7	1.0	9.2	6.3	3.6	2.7	1.1	0.3
520.8	524.5	0.1	0.3	0.2	0.3	0.3	0.6	0.005	0.3	3.7	9.1	2.9	0.01	0.02
514.3	521.0	0.4	0.2	15.2	7.1	15.8	7.3	0.9	1.6	3.1	3.2	2.96	1.6	3.1
496.5	512.3	0.01	0.01	0.01	0.0	0.03	0.0	0.003	0.0	5.4	0.0	6.9	8.3	0.01

positions of the four LVMs calculated for all the systems studied using their corresponding fake images are shown in figure 5. Only systems which do not have Ge atoms in the first sphere (positions A_1–A_4) have been used since these are energetically more favourable. One can see that the two highest modes shift very slightly downward with the increase in the number of Ge atoms; the other two modes remain in the same position. However, one may expect some broadening of the vibrational peak corresponding to the first mode (around 563 cm^{-1}) with the increase of the Ge concentration. A general conclusion can be drawn that the Ge substitutions have very little effect on the phonon spectrum of the C_iO_i defect in the Si/Ge system.

The isotopic shifts of the phonon frequencies of the C_iO_i defect calculated for two systems in which Si atoms in positions A_1 and C_1 were replaced by Ge atoms are shown in table 2. Only a limited number of isotopic combinations has been studied, as shown. Different Ge isotopes have a very small effect on all the LVMs and are thus not shown. On the other hand, the mass of the C atom significantly affects the two highest vibrational frequencies, while the mass of the O atom affects the 677.4 and 514.3 modes which is in line with our results for the Ge-free system. Since we know from the results on the energetics of the C_iO_i defect in the Si/Ge alloy that it is more energetically preferable for the Ge atoms not to be in the first sphere with respect to the C and O atoms, we can conclude that, at least for small Ge concentrations in which the effect of the lattice expansion due to Ge substitution is not significant, one should not expect any significant change in the phonon spectrum due to different Ge isotopes. On the other hand, the phonon local peaks due to C and O isotopes shift in the same way as in the Ge-free system.

4.3. Optical properties

It is known from photoluminescence (PL) measurements [24] that the zero-phonon line (C-line) associated with the C_iO_i defect shifts towards higher energies with increasing Ge content, x. This transition is assigned to occur between the donor level of the defect (the gap state in the electronic DOS) and the excited energy level represented by an effective-mass state near the bottom of the conduction band. The latter is assumed to be much less sensitive to the Ge content, x, than the position of the gap state with respect to the valence band. Therefore, it was concluded in [24] that the gap state should move linearly towards the valence band with increasing x.

Two types of calculations have been done here in order to understand these experimental results. First, we have calculated the position of the gap state with respect to the top of the valence band (i.e. the hole ionization activation energy) for two systems, B_1B_4 and $C_1C_4C_5$, containing two and three Ge atoms in the second and third spheres, respectively. The position

of the gap state has been found to be 0.265 and 0.260 eV, respectively. This is to be compared with the gap position of 0.32 eV found for the Ge-free system in section 3. Thus, the position of the gap state is found to be reduced with the Ge content in agreement with the experiment. The amount of the reduction is also very similar to that observed experimentally [24].

Second, we have attempted to estimate directly the vertical optical transition energies for the C_iO_i defect. It is well known that the DFT technique we use in this study is not directly suitable for the calculations of the optical transition energies. We believe, however, that some qualitative conclusions can be still made if the vertical singlet–triplet transition energies, ΔE_{ST}, are calculated for every system studied. In order to calculate ΔE_{ST}, we used the relaxed singlet structures and then calculated the total energy of the triplet state keeping the same geometry (i.e. the vertical transition). Note that due to the negligible atomic relaxation in the triplet state mentioned in section 3, the vertical transition energies may also be considered as the energy differences between the minima of the singlet and triplet potential energy surfaces.

The transition energies calculated in this way are shown in table 1. These are to be compared with the vertical energy of 0.64 eV found for the same defect in the Ge-free system (section 3). First of all, it can be seen that the transition energies are up to 0.2 eV smaller if there is at least one Ge atom in the first sphere. However, these systems which have higher formation energies are to be considered only if the concentration of Ge is high. On the other hand, if Ge atoms are located in the second and/or third spheres, then it follows from our calculations that the transition energies experience a slight increase.

Thus, we conclude that, at least at small Ge concentrations, the general trend is that the transitions energies should slightly increase with the increase of the Ge content, x.

5. Discussion and conclusion

In this paper we reported first-principles DFT calculations of the interstitial C_iO_i defect in Si and Si/Ge systems. In both cases we studied the geometry and energetics as well as the vibrational and optical properties of the defect.

Chemically, the C_iO_i atoms establish strong covalent bonding with the neighbouring Si atoms which donate an electron each to form the Si–C–Si$_2$–O–Si molecule. Our calculations for the carbon–oxygen defect in silicon agree reasonably well with the existing experimental data [5, 1] and previous calculations [1]. In particular, we confirm that the ground state of the defect has a ring structure and that the vibrational spectrum contains four peaks associated with local vibrations which are around 1085, 831, 702 and 563 cm^{-1}. We also agree with the previous work that the highest frequency local mode is carbon rather than oxygen related.

In order to model a carbon–oxygen interstitial defect in a Si/Ge alloy system, we substituted up to three Si atoms around the C and O atoms by Ge atoms and then relaxed the total energy of the each system. These calculations correspond to a rather low concentration of Ge atoms in the alloy $Si_{1-x}Ge_x$ (x between 0.016 and 0.048). Our main conclusions coming from these calculations can be summarized as follows. First, it is energetically more favourable for the Ge atoms not to be directly connected to the C and O atoms in the C_iO_i defect. Note that the same effect was found in our recent *ab initio* calculations of the O_i defect in the $Si_{1-x}Ge_x$ alloy [6]. Therefore, at rather low Ge concentrations the C_iO_i defects are most likely to form Si–C–Si$_2$–O–Si ring core structures similar to that formed in silicon; these molecules may, however, have Ge atoms in their neighbourhood. The formation energies are very weakly affected by the presence of the Ge atoms in the second and/or third spheres. Second, the effect of the Ge atoms on the geometry and vibrational properties of the Si–C–Si$_2$–O–Si molecules is very small. Third, at higher Ge concentrations one has also to consider a possibility of forming Si–C–Si$_2$–O–Si molecules in which one or more Si atoms are replaced by Ge atoms.

We predict that in those cases the vibrational spectrum of the defect is somewhat distorted. In particular, we find that the 702 cm^{-1} peak moves downwards by several tens of cm^{-1}.

We have also calculated the position of the gap state associated with the defect for a number of systems with different numbers of Ge atoms and found that it moves towards the top of the valence band. In addition to that, we have also calculated the vertical singlet–triplet energy differences, ΔE_{ST}, for all the systems studied and found that those increase with the Ge content. It has been assumed in both cases that Ge atoms substitute Si atoms only in the second and third spheres. These results are in close agreement with the available PL data [24].

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References

[1] Coutinho J, Jones R, Briddon P R, Oberg S, Murin L I, Markevich V P and Lindstrom J L 2001 *Phys. Rev.* B **65** 14109
[2] Davies G and Newman R 1994 *Handbook on Semiconductors* vol 3B (Amsterdam: North-Holland) chapter 21, p 1557
[3] Coutinho J, Jones R, Briddon P R, Oberg S, Murin L I, Markevich V P and Lindstrom J L 2001 *Physica* B **308–310** 305
[4] Jones R and Oberg S 1992 *Phys. Rev. Lett.* **68** 86
[5] Davies G, Oates A S, Newman R C, Wooley R, Lightowlers E C, Binns M J and Wilkes J G 1986 *J. Phys. C: Solid State Phys.* **19** 841
[6] Hao S, Kantorovich L and Davies G 2004 *Phys. Rev.* B **69** 155204
[7] Perdew J P, Chevary J A, Vosko S H, Jackson K A, Pederson M R, Singh D J and Fiolhais C 1992 *Phys. Rev.* B **46** 6671
[8] Kresse G and Hafner J 1993 *Phys. Rev.* B **47** 558
[9] Kresse G and Furthmüller J 1996 *Comput. Mater. Sci.* **6** 15
[10] Kresse G and Furthmüller J 1996 *Phys. Rev.* B **54** 11169
[11] Kresse G and Hafner J 1994 *J. Phys.: Condens. Matter* **6** 8245
[12] Vanderbilt D 1990 *Phys. Rev.* B **41** 7892
[13] Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5188
[14] Kresse G, Furthmüller J and Hafner J 1995 *Europhys. Lett.* **32** 729
[15] Parlinski K, Li Z Q and Kawazoe Y 1997 *Phys. Rev. Lett.* **78** 4063
[16] Kantorovich L N 1996–2004 User-friendly visualisation program for ab initio DFT codes castep/siesta/vasp
[17] Kantorovich L N, Holender J and Gillan M J 1995 *Surf. Sci.* **343** 221
[18] Lehmann G and Taut M 1972 *Phys. Status Solidi* **54** 469
[19] Jepsen O and Andersen O K 1971 *Solid State Commun.* **9** 1763
[20] Pesola M, vonBoehm J, Mattila T and Nieminen R M 1999 *Phys. Rev.* B **60** 11449
[21] Coutinho J, Jones R, Briddon P R and Oberg S 2000 *Phys. Rev.* B **62** 10824
[22] Boguslawski P and Bernholc J 1999 *Phys. Rev.* B **59** 1567
[23] Boguslawski P and Bernholc J 2002 *Phys. Rev. Lett.* **88** 166101
[24] Hayama S *et al* 2003 *Physica* B **340–342** 823