Trivalent atoms defect-complexes induced defect levels in germanium for enhanced Ge-based device performance

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Abstract

Defect-complexes have significant impacts on the structural, electronic, optical, and electrical properties of semiconductors. Several defect-complexes formed by the n-type and p-type atoms in Ge has been implemented for the development of improved modern microelectronic devices. However, there is no reported study on the substitution-interstitial defect-complexes formed by trivalent atoms in Ge. In this paper, the hybrid density functional theory study of the structural, electronic, formation and defect levels induced by the trivalent substitution-interstitial ($B_{Ge}B_i$, $Al_{Ge}Al_i$, $Ga_{Ge}Ga_i$ and $In_{Ge}In_i$) defect-complexes in Ge are presented. The formation energy results showed that the trivalent substitution-interstitial defect-complexes in Ge formed with relatively low energies. The $Ga_{Ge}Ga_i$, under equilibrium conditions is the most energetically favourable, with a formation energy of 3.95 eV. All trivalent atoms are bound with their respective substitution and interstitial atoms without dissociation. With respect to their ability to form as a defect cluster, the $In_{Ge}In_i$ is the most stable defect-complex, with a binding energy of 2.91 eV. Except for the $Ga_{Ge}Ga_i$, all studied defect-complexes are electrically active. The $B_{Ge}B_i$ and $Al_{Ge}Al_i$ induced single acceptor level, while the $In_{Ge}In_i$ induced active donor levels. The acceptor defect level induced by the $B_{Ge}B_i$ is deep and that of the $Al_{Ge}Al_i$ is shallow, close to the conduction band. The results of this study are important as they provide theoretical insights into the experimental characterisation of the substitution-interstitial defect-complexes formed by trivalent impurities in germanium, which could help to improve Ge-based microelectronic devices.

Keywords: Germanium, formation energy, binding energy, defect level, substitution-interstitial, defect-complexes, DFT

1 Introduction

Recent developments in nanoelectronics, optoelectronics and microelectronics have led to significant interest in the improvement of modern semiconductor technology [1, 2]. Several semiconductors including those of the Si and Ge [3] have been developed for advancement applications in microelectronics. Amongst the group IV semiconductors, Ge stands out as a gateway material for the development of semiconductor transistor [4] and fully complementary metal oxide semiconductor (CMOS). Ge has a higher low-field carrier mobilities compared to Si [3]. However, the performance of Ge-based devices may be influence by the presence of impurities such as point defects or extended defects [5].

Point defects are sometimes unintentionally introduced into their hosts during metal-organic chemical vapor deposition (MOCVD) [6] or synthesis [7–9]. For example, carbon impurity can be easily introduced into a semiconductor during MOCVD, which may act as a source of yellow luminescence [10, 11]. The ion implantation technique introduces controlled defects into crystal lattice of a material. This process involves directing high-energy ions at the crystal, causing lattice damage and the introduction of defects [12, 13]. High-energy particles, such as electrons, protons, or ions, are used to irradiate germanium crystal, leading to the formation of defects. Such defects may migrate, annihilate, or aggregate during annealing. The introduction of large isovalent dopants such as Sn can influence interactions in Ge and Si [14]. Via fabrication and defect processes, high-quality Ge-based direct band gap semiconductor can be realized [15, 16]. Trivalent atoms have been used to doped materials for the realization of *p*-type semiconductors. The trivalent impurities introduced as interstitial significantly enhance diffusion activities in Si [17]. Study revealed that the electron transport and recombination properties of SiC nanotube [18] is influenced by the presence of trivalent atoms. Doping group IV atoms (Si, Ge) with trivalent atoms boron (B), indium (In), and gallium (Ga)) increase the number of holes in Si and Ge [19]. Furthermore, the trivalent doping has been used to established the energy and spatial distribution of intrinsic hole traps in dry thermal silicon dioxide [20] as well as, used as charge compensating defects in Ge [21].

Point defects can exist in crystalline materials such as interstitials, substitutions, antisites, or vacancies. These individual point defects can combine in a material, leading to the formation of defect complexes [22, 23]. Several studies that reported the formation of defect-complexes in semiconductor, including Ge or Si have been documented [24–26]. For instance, the nitrogen substitution and vacancy-complex in SiC is a defect-complex which has been identified as a strong candidate for application in quantum technologies [27, 28]. The monovacancy defect-complexes in

Ge have been observed to remain thermodynamically stable, even following high-temperature annealing. The nucleation and thermal evolution of these monovacancy defect-complexes holds significant importance for the manufacturing of future Ge-based electronic devices [29]. Defect-complexes of vacancy-donor pairs in n-type Ge doped with As, P, and Sb have been reported [30]. While defect-complexes with fewer P atoms exhibit negative charge, the introduction of Sb into Ge creates the presence of multiple competing traps in the positron trapping process [30].

To achieve a high quality Ge-based electronic device, the influence of defect-complexes in the host materials must be well understood and controlled [25, 28, 31]. Despite several studies that reported important results of defect-complexes in Ge, there is lack of information on the trivalent atoms substitution and interstitial defect-complexes in Ge. Furthermore, considering the applicability of Ge in modern electronic devices, it is important that a detailed study of the trivalent atoms substitution and interstitial defect-complexes be carried out to provide information of their induced defect levels and how they may be controlled during device fabrication. Herein, we present computational studies which enable the understanding of electrically active defect levels induced by trivalent atoms substitution and interstitial defect-complexes in Ge.

In this study, results of the various defect levels induced by the trivalent atoms substitution-interstitial defect-complexes in Ge were presented. The defect-complexes studied are $B_{Ge}B_i$, $Al_{Ge}Al_i$, $Ga_{Ge}Ga_i$ and $In_{Ge}In_i$. Where $B_{Ge}B_i$ is a defect-complex consisting of B atom in Ge lattice position (B_{Ge}) and B atom in an interstitial position (B_i). The density functional theory (DFT) calculations with the Heyd, Scuseria and Ernzerhof (HSE06) [32] hybrid functional were used to predict the most energetically favorable trivalent atoms substitution-interstitial defect-complexes and their stability in Ge. We showed that the trivalent substitution-interstitial defects in Ge are stable. Strong induced electrically active defect level were observed for the $Al_{Ge}Al_i$, $B_{Ge}B_i$

and $In_{Ge}In_i$. Finally, we provided a crucial understanding of the electrical active defect levels induced by the trivalent atoms substitution-interstitial defect-complexes in Ge, which could be courted for application in improved germanium-based microelectronic devices.

2 Method

First-principle calculations were performed using the DFT as implemented in the Vienna *Ab-initio* Simulation Package [33, 34]. The projected augmented wave method was used to describe the core electron interactions. The s^2p^1 was used as the valence electrons for the group III (trivalent) atoms and the s^2p^2 was used as the valence electrons for the Ge. The HSE06 hybrid functional with the PBE of the generalized gradient approximation (GGA) was used as the exchange correlation. The HSE which is a mixture of the PBE and Hartree-Fock has been successfully used to predict accurate band gap of the semiconductors and provides an improved defect levels of various point defects in semiconductors [23, 35, 36]. This is in contrast to the local density approximation and GGA, which are known to underestimate the band gap of semiconductor materials, and hence, inadequately predict the defect levels in semiconductors [37–39]. In our calculations, we used a default mixing parameter of 25% and screening parameter of 0.2 $Å^{-1}$ as implemented in the HSE. It is important to point out that our choice of the HSE is guided by its capacity to accurately reproduce the experimental band gap of Ge [40]. To model the various defect-complexes in Ge, in particular, their formation, electrical and electronic properties, we constructed a supercell of size $2 \times 2 \times 2$ which has 64 atoms. The supercell is then optimized using the conjugate gradient algorithm with an atomic force convergence criterion lower than 0.01 eV/Å. We integrated the Brillouin zone using the Monkhorst-Pack scheme with a grid of $2 \times 2 \times 2$ **k**-points for both the pristine and defective supercell. However, we used a denser k-point grid of $20 \times 20 \times 20$ to calculate the density of states.

The well converged energy cut-off of 400 eV has been previously used to model the electronic and defect properties of impurities in Ge, and consequently produce results that are consistent with experimental data [41]. Thus, in this study, the energy cut-off for all the calculations was set to 400 eV, and the minimum total energy difference convergence criteria was set to below 10^{-5} eV.

The formation energy ($E^F(defect-complex,q)$) of a defect-complex in its charge state q as a function of the Fermi energy (ε_F) is defined as

$$E^F(defect-complex,q) = E(defect-complex,q) - E(pristine) + \sum_i \triangle(n)_i\mu_i, + q[E_V + \varepsilon_F] + E^q_{FNV}, \quad (1)$$

where the $E(defect-complex,q)$ is the total energy of the supercell with a defect, the $E(pristine)$ is the total energy of the pristine supercell. The chemical potential of the ith-type atom which represents the Gibbs free energy when an isolated atom exchange with the heat reservoir is represented as μ. The n is the number of atoms that are added or removed from the defective supercell. The chemical potentials of the trivalent atoms were calculated as the total energy per number of impurity atoms. The E_V is the energy of the valence band maximum (VBM). The E^q_{FNV} according to Freysoldt, Neugebauer and Van de Walle method [42] is the energy correction term, which accounts for the errors due to the finite size of the supercell and defect-defect interactions problems.

Defect level is described from the charge state transition energies. The energy needed for an atom or ion to change from one charged state to another is the charge state transition energy level [5]. A neutral atom can gain or lose electrons to change its charge from being positively charged to negatively charged. The transition of electrons between various energy levels within an atom occurs when an atom's charge state changes. To theoretically determine the positions of defect levels in the semiconductor

band gap, the width of the band gap must be known. For the pure Ge crystal, the band gap of 0.78 eV were previously obtained using the hybrid density functional [43], which agrees with experimental results of 0.78 eV as reported in Ref. [40]. The charge state transition energy level ($\epsilon(q/q')$) is the Fermi energy for which two charge states (q and q') in the band gap have the same energy. This is calculated as

$$\epsilon(q/q') = \frac{E^F(defect - complex, q) - E^F(defect - complex, q')}{q' - q}, \tag{2}$$

where the $E^F(defect - complex, q)$ and $E^F(defect - complex, q')$ are calculated at $\varepsilon_F = 0$. In this study, the considered charge states (q) are -2,-1, 0,+1and+2. Other charge states were not included as they are thermodynamically unstable.

The possibility of a defect-complex to disassociate into non-interacting defects under equilibrium conditions [23] needs to be understood. Hence, to provide information whether a defect-complex is energetically stable, it is imperative that the binding energy of such defect should be known. The binding energy is defined as the energy required to split a defect-complex into a non-interacting defect. In this study, the binding energy of a defect-complex is calculated using Eq. 3.

$$E_b = E^F_{\text{interstitial}} + E^F_{\text{substitution}} - E^F_{\text{defect}-\text{complex}}, \tag{3}$$

where $E^F_{\text{interstitial}}$, $E^F_{\text{substitution}}$ and $E^F_{\text{defect}-\text{complex}}$ are the formation energies of the interstitial, substitution and defect-complex of trivalent impurities in Ge, respectively. From Eq. 3, negative binding energy implies that a defect cluster formation is energetically unfavorable with respect to its constituent isolated components. Thus, the defect-complex is liable to dissociate with an amount of energy lower than its formation energy.

3 Results and discussion

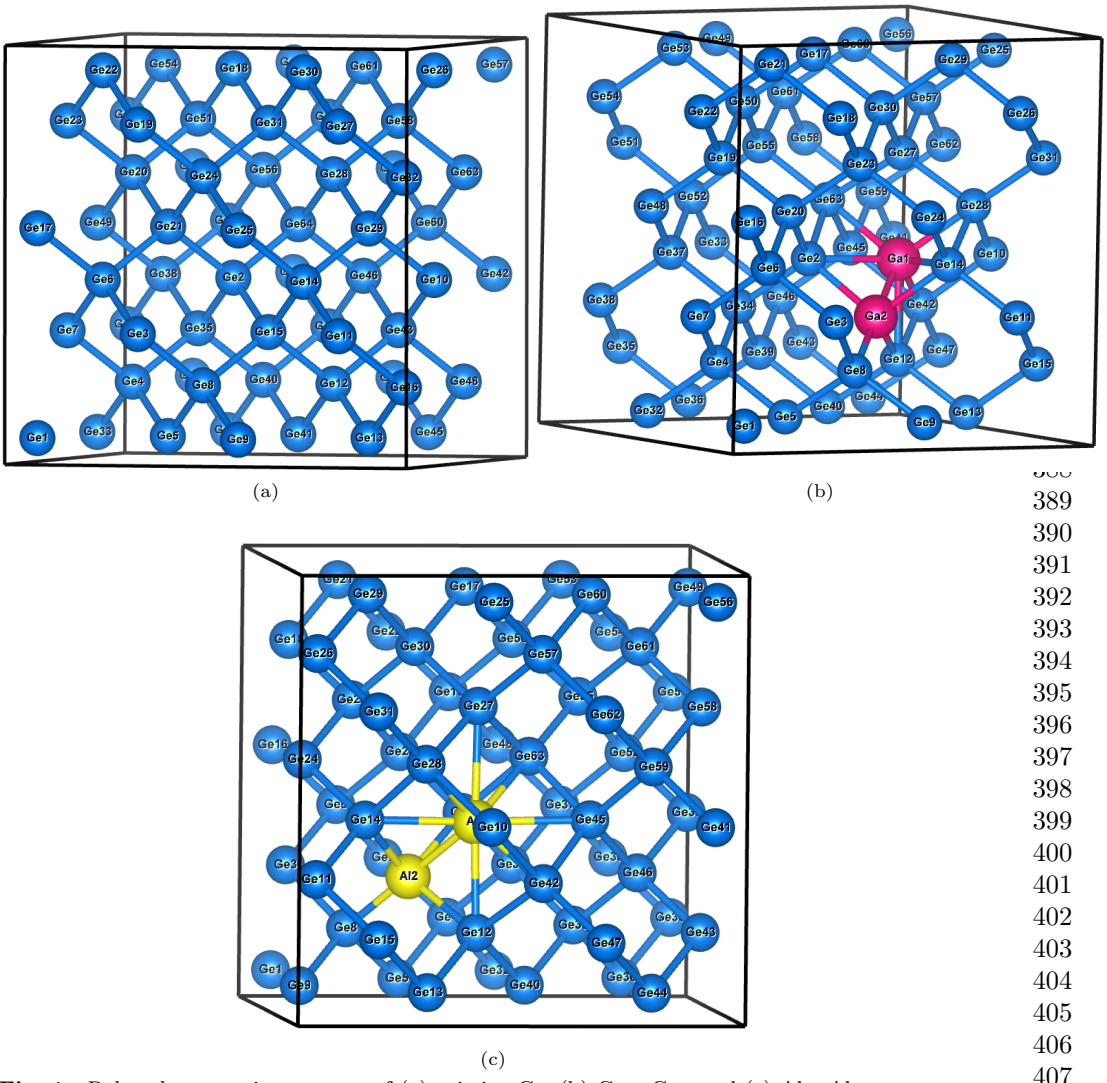
In this section, results of the structural and electronic properties, formation and stability of defect-complexes as well as the thermodynamically charge state transition levels in Ge were presented.

In a crystalline solid structure, the location and distribution of defects may be random. Therefore, when modeling defects in a solid crystal structure, it is important to take into consideration the various possible defect sites in order to obtain the most energetically favorable defect configurations. In this study, we adopted the method used by Igumbor *et al* [41] to ascertain the most energetically defect-complex configuration. According to Ref. [41], two different defect configurations were considered: these are when both the substitution and interstitial atoms are (i) nearest neighbour; and (ii) not nearest neighbour. Igumbor *et al* [41] showed that both configurations (i) and (ii) are energetically favorable with relatively low formation energies. However, the substitution and interstitial atoms as nearest neighbour defect-complex was more energetically favorable. Hence, in this present study, we focused only on the defect-complex configuration where the substitution and interstitial atoms are nearest neighbor.

3.1 Structural properties

Fig. 1 shows the relaxed geometric structure of pristine Ge, $Ga_{Ge}Ga_i$, and $Al_{Ge}Al_i$. Table 1 shows the various relaxed bond lengths of the impurity and Ge atoms for the defect-complexes. The bond lengths of the X_{Ge}-Ge for all impurity atoms are shorter than that of the X_i-Ge. Except for the B-Ge, all the X_i-Ge bond distances are higher than the relaxed pristine Ge-Ge bond length. The various impurity atoms experienced different levels of strain in their bond lengths. The relaxed bond length of the X_{Ge}-Ge namely: B-Ge, Al-Ge, Ga-Ge and In-Ge are 0.51, 0.06, 0.07 and 0.02 Å, respectively, which are different from that of the pristine Ge-Ge. This suggests that

there is significant strain induced in the system, which could influence the amount of energy required for such defects to form in Ge.



(a) (b)

(c)

Fig. 1 Relaxed geometric structure of (a) pristine Ge, (b) $Ga_{Ge}Ga_i$, and (c) $Al_{Ge}Al_i$.

We also evaluated the bond order to ascertain whether a bond is formed between the defective atoms, as well as the host. A bond order of 1.34 was found between the two B atoms. This is an indication that the two B atoms are strongly bound to each

Table 1 The bond length of the trivalent interstitial (X_i) and substitution (X_{Ge}) atoms with their nearest neighbor Ge atoms. The trivalent-trivalent (X-X) atomic bond length is also listed. The radii of the impurity atoms used for this study are Al=1.84 Å, B= 0.85 Å, In=1.93 Å, and Ga=1.87 Å

	X-X (Å)		X_{Ge}-Ge (Å)	X_i (Å)
B-B	1.54	B-Ge	1.95	2.12
Al-Al	2.56	Al-Ge	2.40	2.50
Ga-Ga	2.51	Ga-Ge	2.53	2.62
In-In	2.71	In-Ge	2.48	2.72

other. The substitution B atom slightly shifted from its relaxed position to forming three bonds with its nearest neighbor three Ge atoms. In contrast, the B interstitial atom is strongly bound to one Ge atom. For the other defective systems, that is the $Al_{Ge}Al_i$, $Ga_{Ge}Ga_i$, and $In_{Ge}In_i$, we found bond order of 0.39, 0.43, and 0.48 for Al-Al, Ga-Ga, and In-In, respectively, between the substitution-interstitial atoms. The substitution atoms are more likely to form bonds with the host Ge atoms than their interstitial counterparts.

3.2 Electronic properties: partial density of states

To comprehend the impact of trivalent defect-complexes on the electronic structure of Ge, we obtained the partial density of states (PDOS) as depicted in Fig. 2. In contrast to Fig. 2a, the $B_{Ge}B_i$ induced notable orbital ground states in the band gap of Ge as shown in Fig. 2b. While the *p*-orbital of the B atom is predominantly visible in the conduction band minimum (CBM), the *p*-orbital of the Ge atom is predominantly observed at the VBM. In addition, the sharp peak from the *s*-orbital of the B atom contributed to the orbital ground states near the VBM. For the $Al_{Ge}Al_i$ as shown in Fig. 2c, we observed a different pattern from that of the $B_{Ge}B_i$. The *s*-orbital of the Al atom generated a peak near the Fermi level, mainly dominated by the Al atom's *s*-orbital. Other defects that induced sharp peak close to the Fermi level

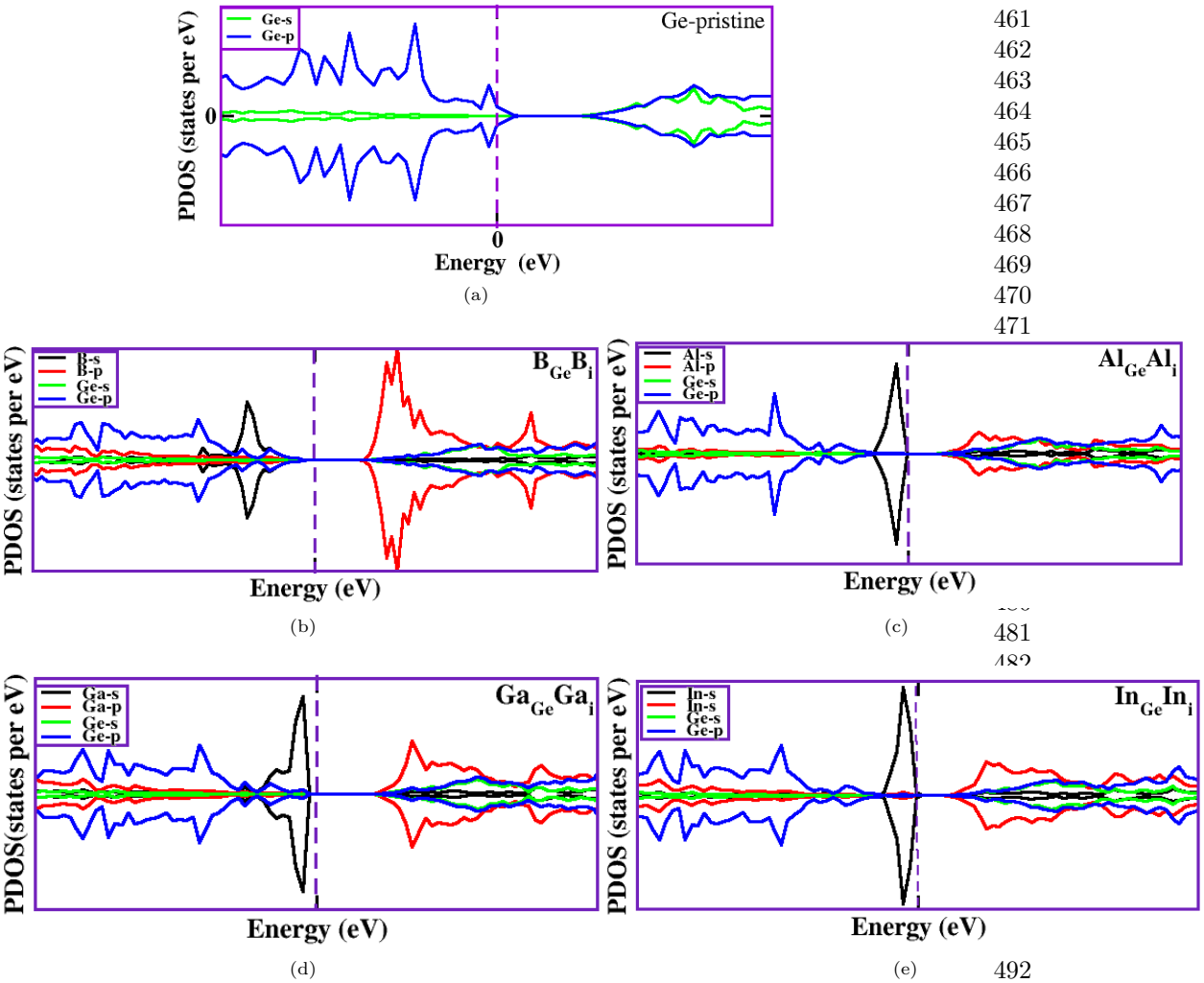


Fig. 2 Plots of partial density of states (PDOS) of the trivalent atom substitution-interstitial defect-complexes in Ge: (a) pristine Ge; (b) $B_{Ge}B_i$; (c) $Al_{Ge}Al_i$; (d) $Ga_{Ge}Ga_i$ and (e) $In_{Ge}In_i$. The Fermi level is set to zero and is represented by the dash line.

are the $Ga_{Ge}Ga_i$ (Fig. 2d) and $In_{Ge}In_i$ (Fig. 2e). In all, the positions of the Fermi-level for the defective systems are the same as that of the pristine Ge, however, the energy levels of induced orbital states differed from each defective system. For all the defective systems significant contribution of the peaks in the uppermost conduction band comes from the *p*-orbitals of the impurity and Ge atoms. The valence band of the defective systems are highly populated by the *s*-orbital of the respective impurity

atoms. Obvious overlapping of p-orbital of Ge/Al atoms for the $Al_{Ge}Al_i$, Ge/Ga atoms for the $Ga_{Ge}Ga_i$ and Ge/In atoms of the $In_{Ge}In_i$ were observed.

The above observation indicates the presence of strong orbital hybridization between the p-orbital of the host and impurity atoms. Succinctly speaking, all the defects considered exhibit a $p-$type semiconducting characteristic and their Fermi levels are situated close to the valence band. Therefore, the majority carriers are mainly hole. The majority and minority spins are symmetrically aligned suggesting lack of spin polarisation. Hence, such defects in Ge may not be courted for device applications where spin dependent is required.

3.3 Formation energies of defect-complexes

The formation energies of point defects are crucial in determining the energetics and stability of defects [5]. Fig. 3 displays the formation energies of the neutral charge state of the trivalent interstitial-substitution defect-complexes in Ge. The $B_{Ge}B_i$, $Al_{Ge}Al_i$, $Ga_{Ge}Ga_i$ and $In_{Ge}In_i$, under equilibrium conditions were energetically favorable. However, the most energetically favorable is the $Ga_{Ge}Ga_i$ with formation energy of 3.95 eV. The above results is relatively lower than di-interstitial of Ge which has a formation energy of 6.52 eV [43] for its most energetically favorable configuration. The $B_{Ge}B_i$ is the least energetically favorable with a relatively higher formation energy of 7.39 eV. The ordering of the formation energy is therefore $B_{Ge}B_i$>$In_{Ge}In_i$> $Al_{Ge}Al_i$>$Ga_{Ge}Ga_i$. The impurity atoms used for this study have different radii (Al=1.84 Å, B= 0.85 Å, In=1.93 Å, Ga=1.87 Å) [44]. Therefore, when different sizes of the participating trivalent atoms are introduced into a pristine Ge supercell, we expect a distortion in the volume of the pure Ge crystal structure. This alteration can give rise to considerable amount of strain induced in the lattice as experienced by the bond length formed by the impurity and the nearest neighbor Ge atoms. The extent of strain experienced in the bond length could influence the formation energies required for a defect-complex

to form. For instance, defect complexes involving the Al ($Al_{Ge}Al_i$) and Ga ($Ga_{Ge}Ga_i$), formed with a relatively lower formation energies.

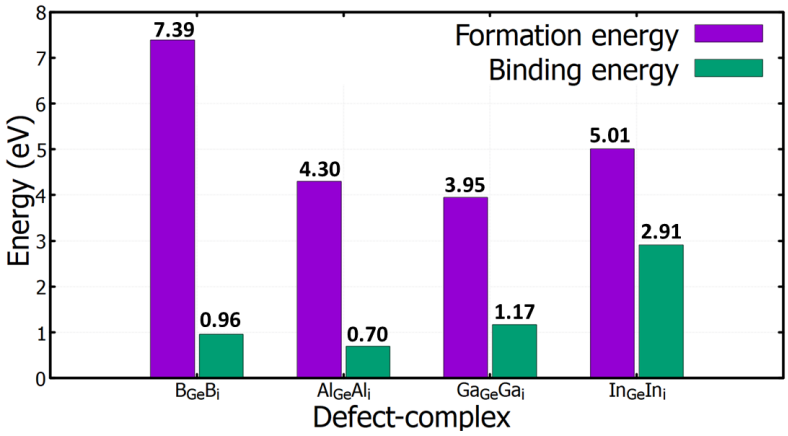


Fig. 3 The energy of formation and the binding energy in eV of the trivalent atoms substitution-interstitial defect-complexes in Ge at $\varepsilon_F = 0$.

3.4 Binding energies of defect-complexes

The binding energy provides information about the stability of defect-complexes relative to their constituents [5]. To ascertain if the defect-complex will dissociate into non-interacting constituents, we calculated the binding energies of the trivalent atoms defect-complexes in Ge. As shown in Fig 3, all the trivalent impurities are stable due to their positive binding energies. This suggests that the substitution and interstitial of the B, Al, Ga and In atoms bound with Ge atom as complexes. Therefore, for the defect-complex $Ga_{Ge}Ga_i$ to dissociate into a non-interacting Ga_{Ge} or Ga_i, it will require an energy at least higher than 5.12 eV; and this can only happen if external energy of similar amount is applied to the Ge bulk containing the defect-complex. The most stable defect-complex is the $In_{Ge}In_i$ with a binding energy of 2.91 eV. Despite the high diffusion rate of B interstitial in semiconductors [45], the $B_{Ge}B_i$ with a high formation energy is relatively stable with a binding energy of 0.96 eV. The least energetically stable defect-complex is the $Al_{Ge}Al_i$. While the binding energy of the B atoms

pair is higher than that of Al atom pair by 0.26 eV, the binding energy of the $In_{Ge}In_i$ is higher than that of the $Ga_{Ge}Ga_i$ by 1.74 eV. Our results show that the stability of trivalent defect-complexes increases with respect to the increasing atomic radius of the participating atoms. Based on Eq. 3, at the ambient temperature, separating the defect-complexes into their isolated non integrating defects will occur at the expense of an external perturbation of similar energy value.

3.5 Defect levels induced by defect-complexes

The theoretical prediction of active defect levels induced in the band gap is paramount to the identification of the electrical characteristics of defect-complexes [5]. Thus, the electrical characteristics, in particular the electrically active defect levels induced in Ge is essentially obtained from the charge state transition energy levels between the VBM and CBM [5]. For us to investigate the electrically active defect levels induced in the band gap of Ge by the substitutional-interstitial defect-complex of trivalent atoms, we plotted the graph of the formation energy as a function of the Fermi level as displayed in Fig. 4. Table 2 lists the charge state transition energy levels above the VBM. The $Ga_{Ge}Ga_i$ is not electrically active as the neutral charge state spreads across the band gap of Ge when the Fermi energy is varied from the VBM to the CBM. While the $Al_{Ge}Al_i$ and the $B_{Ge}B_i$ induced a single acceptor defect level, the $B_{Ge}B_i$ induced defect level is a single deep acceptor level with an energy of E_C-0.21 eV (E_C is the energy of the CBM). The $B_{Ge}B_i$ neutral charge state spread across the band gap as the Fermi energy is varied up to 0.57 eV. The $Al_{Ge}Al_i$ on the other hand, induced a single shallow acceptor level (E_C-0.02 eV), which is very close to the CBM. The proximity of the (0/-1) to the CBM of AlGeAli suggests that future experimental characterization of the defect should be conducted to confirm the existence of the induced defect level under ambient conditions, including increasing temperatures. Under equilibrium conditions, the (0/-1) charge state transition energy levels

Table 2 The charge state transition ($\varepsilon(q/q')$) defect energy levels induced by the trivalent substitution-interstitial defect-complexes in Ge. The values displayed are in eV and above the VBM.

Defect	$(+2/+1)$	$(+1/0)$	$(0/-1)$
$B_{Ge}B_i$	-	-	0.57
$Al_{Ge}Al_i$	0.11	0.32	0.76
$Ga_{Ge}Ga_i$	-	-	-
$In_{Ge}In_i$	0.29	0.57	-

of the $Al_{Ge}Al_i$ and $B_{Ge}B_i$ can ionized at relatively energy lower than 3 k_BT (k_B is the Boltzmann constant). The substitutional-interstitial defect-complex that induced donor levels are the $Al_{Ge}Al_i$ and $In_{Ge}In_i$. Both defects induced single and double donor levels. The +2 charge state of the $Al_{Ge}Al_i$ is more stable and close to the VBM, however, as the Fermi energy is varied towards the CBM, at energy of 0.32 eV, the +1 charge state becomes more thermodynamically stable. For the $Al_{Ge}Al_i$, the neutral charge state spreads almost 50% of the band gap. However, its (+2/+1) and (+1/0) change state transition defect levels are shallow and deep, respectively. The $Al_{Ge}Al_i$ (+2/+1) energy level is E_V+0.11 eV and that of the (+1/0) is E_V+0.32 eV. The origin of compensation centre as a result of radiative and non-radiative recombination centres in semiconductor materials is linked to the activities of defect levels induced in the host. The deep defect levels induced by the $Al_{Ge}Al_i$ are expected to decrease the radiative efficiency of Ge-based devices via recombination of excess electron-hole pairs [46]. For the $In_{Ge}In_i$, the energy level of the (+2/+1) is E_V+0.29 whereas that of the (+1/0) is E_V+0.57. The +2 and +1 charge states spread across 70% of the band gap from the VBM. The $In_{Ge}In_i$ deep defect levels ((+1/0) and (+2/+1)) may not have significant effect on the transport properties of carriers. However, they can act as recombination centers for electrons and holes. Consequently, the lifetime of non-equilibrium carriers is reduced. For the (+1/0) of the $Al_{Ge}Al_i$, the (+1/0) and (+2/+1) of the $In_{Ge}In_i$ increase in the concentration of electrons (holes) leads to an increase in the recombination rate. Therefore, the electrons (holes) are captured and

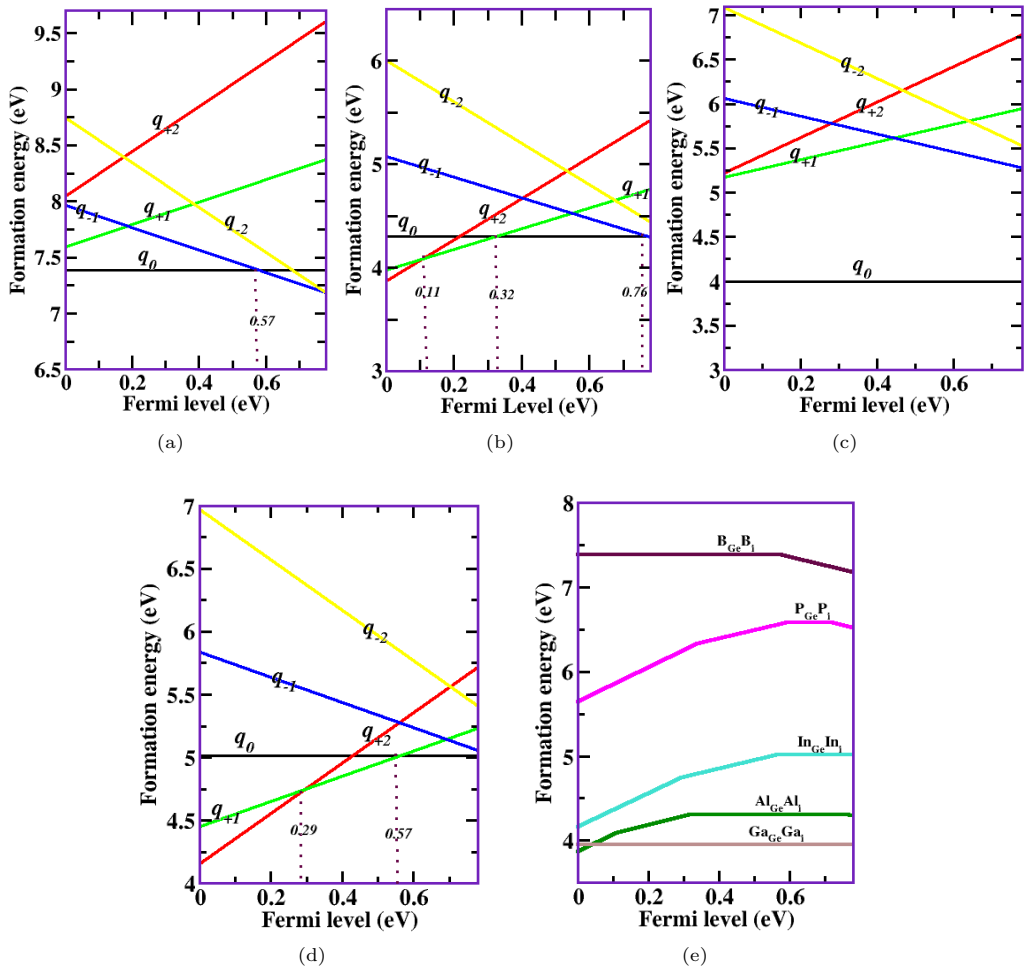


Fig. 4 Plot of formation energy as a function of the Fermi energy for the substitution-interstitial defect-complexes formed by the trivalent atoms in Ge: (a) $B_{Ge}B_i$; (b) $Al_{Ge}Al_i$; (c) $Ga_{Ge}Ga_i$; (d) $In_{Ge}In_i$; and (e) short representation of all the possible thermodynamic charge states transition levels. The slope of each graph corresponds to the different charge states (q_{-2}, q_{-1}, q_0, q_{+1} and q_{+2}). The dash vertical line represents the possible thermodynamic stable transition energy levels.

recombined with the holes (electrons), which reduces the lifetime carriers. Finally, this study's results show that defect-complexes are important, as they revealed how their formation in Ge could influence the electrical, electronic properties and the overall performance of Ge-based devices.

4 Conclusion

Density functional theory calculations using hybrid functionals were conducted to determine the formation energies, stability of defect-complexes, and the electrically active defect levels induced by trivalent substitution-interstitial pairs in Ge. Under equilibrium conditions, while the $Ga_{Ge}Ga_i$ is the most energetically favourable (energy of 3.95 eV) for the neutral charge state, the $B_{Ge}B_i$ is the least energetically favorable with a formation energy of 7.39 eV. The ability for the defect-complexes to form as a cluster of defects was established by calculating the binding energy. All the defect-complexes reported in this study are stable are stable with respect to their isolated defects constituting each of the defect complexes. The electronic structure results predict that the trivalent defect-complexes behave as *p*-type semiconductors. The electrically active defect levels were established from the defect levels induced in the band gap of Ge. The $Al_{Ge}Al_i$, $B_{Ge}B_i$, $In_{Ge}In_i$ are all electrically active, with noticeable induced defect levels in the band gap of Ge. Whereas the $Al_{Ge}Al_i$ and $In_{Ge}In_i$ induced single and double donor levels, the $B_{Ge}B_i$ induced a deep defect level. In addition, the $Al_{Ge}Al_i$ induced a shallow acceptor level close for the CBM. The result of this study provides useful theoretical insight into the formation and stability of defects complexes that may enable the application of Ge-based materials for important electronics applications.

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Declarations

Conflict of Interest: The authors declare that they have no conflict of interest.

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