Electronic properties and defect levels induced by group III substitution-interstitial complexes in Ge

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Abstract In this report, we used the hybrid density functional theory to systematically investigate the formation of substitution-interstitial complex defects formed by group III (B, Al, Ga and In) atoms in Ge for charge states -2, -1, 0, $+1$ and $+2$ as a function of the Fermi level. Under equilibrium conditions, the substitution-interstitial complexes in Ge formation energies were found to be relatively lower than 7.00 eV and stable with respect to their binding energies. For the neutral charge state, the $Al_{Ge}Ga_i$ complex (where Al_{Ge} and Ga_i represent Al substitution in Ge and Ga interstitial, respectively) is the most stable defect with

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a binding and formation energies of 2.41 and 4.14 eV, respectively. Substitution-interstitial complexes induced defect levels in the band gap of Ge. Whereas the shallow donor defects are the $B_{Ge}Al_i$ and $In_{Ge}Ga_i$, the deep acceptor defects are $Ga_{Ge}B_i$, $B_{Ge}Ga_i$, $Al_{Ge}B_i$ and $B_{Ge}Al_i$. The $In_{Ge}Ga_i$ acts as a shallow single donor defect, the $In_{Ge}Al_i$ and $Al_{Ge}In_i$ induced only donor levels. The substitution-interstitial defects do not only alter the known electronic properties of the pristine host but also provide a new interesting character.

1 Introduction

Semiconductor material such as Ge, has great advantageous higher carrier mobilities, low dopant activation temperature and smaller band-gap properties relatively to Si. Ge is becoming increasingly important for applications in the field of microelectronics [1–5]. The high carrier mobility unique property of Ge enhances its use for a device where high electron-hole mobility is required [1]. Ge has a narrow experimental band gap (0.78 eV) and could also be highly doped with impurities. Doping of Ge with impurities and their electrical defect levels have been documented in literature [2, 6–9]. Numerous studies have predicted the structural, electronic and electrical defect levels of several point defects in Ge [2, 6–9]. This is motivated from the fact that the characteristics and performances of devices are impacted by defects. As a result, it is required that thorough understanding of the properties of point defects in Ge, combined with the knowledge of how to control them is essential. A foremost knowledge of how to control the activities of defect in Ge could help to improve the quality of its device for future applications [2, 6]. Studies reveal that defects if not controlled, can lead to the deterioration of

its yield, which consequently impact the quality of the devices. This is due to the fact that defects introduced in a material in most cases, alter the electrical and optical parameters of such material. Furthermore, the presence of these impurities in Ge could determine the lifetime of its carriers. This is mainly owing to the fact that the modified electronic properties of the crystal will give rise to defect levels within the band gap. Some of the well known point defects in Ge that are electrically active are the interstitials, vacancies, defect-complexes and substitutions [2,4,5,10–12]. The above listed defects exist in Si as well, and induced defect levels in its band gap [13–17]. Despite the huge effort made so far towards the study and understanding of point defect processes in several materials, they remain undiscovered defects which have not been investigated, and hence the defect levels are not known. Defect-complexes in semiconductor are well known to induce active defect levels in their host [2,18–22]. For example, in SiC and diamond, the nitrogen-vacancy (NV) centre is a well known defect-complex which has great application in qubit [18,23,24]. Amongst the notable defect-complexes pair are the FeAl and FeGa, which have been reported to induced deep donor levels in Si [25]. The influence of C_iC_{Si}, C_iO_i, B_iB_{Si}, FeGa in Si have been investigated and their defect levels predicted [19,26,25,27]. Boron interstitial (B_i) is known to be highly active in the formation of radiation defects. This give rise to the diffusing of B_i atom which is free to interact with one another forming a complex like B_iB_i defects. The activation energy of B_iB_i under annealing has been suggested to be lower than 2.00 eV as reported by Makarenko *et al* [27]. Furthermore, B_i can also be trapped by a substitutional boron, oxygen or carbon impurities in Si to form complex defects such as B_iB_{Si}, B_iO_i and and B_iC_{Si} [20]. While some results of the defect levels induced by the substitution-interstitial complexes in Ge

have been reported [2–5], the substitution-interstitial complexes ($X_{Ge}Y_i$: where X_{Ge} and Y_i represent X substitution and Y interstitial in Ge, respectively) including the $Ga_{Ge}B_i$, $Ga_{Ge}In_i$, $In_{Ge}B_i$, $In_{Ge}Al_i$, $Al_{Ge}In_i$ and $In_{Ge}Ga_i$ defect levels induced in Ge are not yet understood, hence the motivation of this report. The electronic properties and defects levels induced by In, Ga, Al and B substitutional-interstitial complexes in Ge, were predicted using the Heyd, Scuseria and Ernzerhof (HSE06) [28] hybrid functional within the framework of the density functional the-ory (DFT). The structural properties and the stability of the defects for charge states -2, -1, 0, $+1$ and $+2$ as a function of the Fermi level were predicted. The formation and binding energies as well as the charge state transition energies of the substitution-interstitial complexes were calculated. Our results show that these defects behave as *p*-type materials and do not show characteristics of spin polari-sation. However, strong orbital hybridization was observed. We further show that the point defects are all electrically active, showing tendency to induced energy levels that are either close to the valence band maximum (VBM) for the case of shallow donor, or close to the conduction band minimum (CBM), for the case of shallow acceptor levels.

2 Computational details

The results reported in this article were carried out using the density functional theory (DFT) as implemented in the Vienna *ab-initio* Simulation Package (VASP) [29, 30]. The core and valence electrons of the participating atoms (impurities and host) were separated using the projector-augmented wave method [31]. While the $4p^2$, $4s^2$ of Ge was treated as the valence electrons, the $2s^2$, $2p^1$ for B; $3s^2$, $3p^1$ for Al;

$4s^2$, $4p^1$ for Ga and $5s^2$, $5p^1$ for In atom, were treated as valence electrons. The HSE06 functional which provides partial cancellation of self−interaction has been previously used to predict accurately, the structural, electronic properties and defect levels induced in several semiconductor materials [32,33]. This is in contrast to the local density approximation (LDA) or the generalised gradient approximation (GGA) which severely underestimates band gap of material, and thereby inaccurately predict the defect levels induced in a material [34–36]. The HSE06 with a default mixing parameter of 25% (fraction of exact Hartree-Fock exchange) and 0.2 $Å^{-1}$ screening parameter was sufficient to predict a band gap of 0.78 eV for Ge, which is in agreement with experimental value of 0.78 eV at 0 K as reported by Morin *et al.* [37]. For defect modelling, a primitive unit cell of Ge was constructed and relaxed with an energy cuttoff of 800 eV and an $8 \times 8 \times 8$ Monkhost-Pack k-points. Subsequently, a $2 \times 2 \times 2$ supercell containing 64 atoms of Ge (see Fig. 1) was constructed from the relaxed primitive unit cell. The Supercell was further relaxed with an energy cuttoff of 400 eV with a $2 \times 2 \times 2$ Monkhost-Pack k-points, which was used to integrate the Brillioun zone. We allowed all the forces acting on the atoms to relax until they were less than 0.01 eV/Å. In all calculations, the minimum total energy difference was set to 10^{-5} eV, and spin effect was taken into account by including the spin orbit coupling. The formation energy ($E^f(d,q)$) of a supercell containing the optimized defect d in its charge state q as a function of the Fermi energy (ε_F) is calculated based on the formulation of Zhang and Northrup as reported in Refs [2,38,39].

$$E^f(d,q) = E(d,q) - E(pure) + \sum_i \triangle n_i \mu_i + q[E_V + \varepsilon_F] + E^q_{FNV}. \qquad (1)$$

According to Eq. 1, $E(d,q)$ is the minimum energy of the defective supercell, the energy of a supercell without a defect is denoted as $E(pure)$, the $\triangle n_i$ is the difference of the number of constituent atoms of type ith between the pristine and defect supercells, and μ_i is the chemical potential of type ith atom. All the participating atoms chemical potentials μ, were calculated as the total energy per atom. The Al and B chemical potential were calculated from the Al face centred cube structure and α-rhombohedral boron respectively. The correction term E^q_{FNV} is calculated according to the Freysoldt, Neugebauer and Van de Walle (FNV) method [40]. The E^q_{FNV} is used to correct the problem of potential alignment between the charged defect and bulk at a point far from the defect, and defect-defect interactions in a supercell of finite-size. To obtain the defect level in the band gap of Ge, we calculated the defect charge state transition energy level $\epsilon(q/q')$, which is the Fermi energy for which the formation energy of two charge state q and q' are the same. This is expressed mathematically as

$$\epsilon(q/q') = \frac{E^f(d,q) - E^f(d,q')}{q' - q}. \tag{2}$$

Where $E^f(d,q)$ and $E^f(d,q')$ are calculated at $\varepsilon_F = 0$. The binding energy E_b of a substitution-interstitial complexes is defined as the energy required to split up the parent defect into well separated non-interacting defects. The binding energies of the substitution-interstitial complexes of Ge were calculated using the method of Ref [2].

3 Results and discussion

3.1 Structural properties

In order to understand the structural configuration of substitution-interstitial complexes of Ge, we performed the structural properties analyses. Table 1 displays the results of the calculated bond length (BL) of impurity atom with the nearest neighbour Ge atom or impurity atom with the nearest neighbour impurity, and the difference between BL and nearest neighbour Ge-Ge bond length (D). The calculated Ge-Ge nearest neighbour bond length of 2.48 Å is in agreement with previous results [3, 5]. For the substitution-interstitial complex of Ge formed by Ga and B, the bond length of Ga-B atoms when a Ga atom is occupying the Ge atom lattice site and B an interstitial atom is 0.43 Å relatively lower than the bond length of the nearest neighbour Ge-Ge atoms. However, when B atom is at the Ge lattice site and Ga is an interstitial atom, the nearest neighbour Ga-B atoms bond distance is 0.16 Å relatively higher than the nearest neighbour Ge-Ge atoms bond length. For the $Ga_{Ge}Al_i$ and $Al_{Ge}Ga_i$ defects, we observed a situation where the respective bond distance of Al-Ga atoms is 0.06 Å and 0.04 Å relatively lower than that of the nearest neighbour Ge-Ge bond length. We attribute the difference of the bond distance to the relatively different size of the impurity atoms. Furthermore, the bond distance formed by the nearest neighbour Ga-In atoms, when Ga is an interstitial atom and In a substitutional atom is 0.17 Å relatively higher than that of the bond length of Ge-Ge nearest neighbour. However, when an Ga atom is substituted for Ge and a In atom is an interstitial, the In-Ga bond length is 0.14 Å relatively higher than that of the Ge-Ge nearest neighbour bond distance. For the $In_{Ge}B_i$ complex, the nearest neighbour bond distance of In-B

atoms is 0.29 Å relatively lower than the nearest neighbour Ge-Ge atoms bond distance and the shortest bond distance of the In-B atoms is lower than the nearest neighbour Ge-Ge atoms bond distance by 0.05 Å. The bond lengths of the nearest neighbour Be-Al atoms for the case of $Al_{Ge}B_i$ and the $B_{Ge}Al_i$ defects are respectively 0.36 Å and 0.25 Å lower than that of the nearest neighbour Ge-Ge atoms bond distance. For the $Ga_{Ge}B_i$, $Ga_{Ge}In_i$, $In_{Ge}B_i$, $In_{Ge}Al_i$, $Al_{Ge}In_i$ and $In_{Ge}Ga_i$, the bond length of the substitutional atom and that of the nearest neighbour Ge atom is always the shortest bond distance.

3.2 Electronic properties

Generally, when a defect is introduced into a crystal, it may lead to alteration of the electronic properties, which could influence the performance of the material. As a result, the electronic properties of substitution-interstitial complexes of Ge were investigated. Fig. 2 displays the plot of the partial density of states (PDOS) of the substitutional-interstitial complexes in Ge. The electronic ground state orbitals induced in the band gap of Ge for the $Ga_{Ge}B_i$ are very close to the Fermi level from the VBM as shown in Fig. 2a. This suggests that the system behaves as a *p*-type material. The ground state orbitals observed for the $Ga_{Ge}B_i$ around the Fermi level were mainly contributed by the *p*-orbital of B and Ga atoms, with average contribution by the *s*-orbital of B and Ge atoms. Furthermore, additional sharp peaks were induced by the *p*-orbital of Ge close to the valence band. For the $B_{Ge}Ga_i$, we observed the presence of a sharp peak, which was contributed by the *s*-orbital of Ge atom. According to the charge transfer analysis, the s-orbital of Ge atom around the defects, gained electron from the s-orbital of the B and atoms.

Furthermore, the ground state orbital induced electronic states are lying above the Fermi level. For the $Ga_{Ge}Al_i$, the presence of a sharp peak is attributed to the strong presence of the *s*-orbital of Al atom. Succinctly speaking, the ground state orbitals are populated around the VBM, and close to the Fermi level. This same behaviour is observed for the $Al_{Ge}Ga_i$, where the ground states orbitals are 0.02 eV close to the Fermi level from the VBM (see Fig. 2a). These ground states are mainly contributions from strong presence of the *p*-orbital of the Al and Ge atoms. Charge transfer analysis results shows that there was a transfer of electrons from the *s*-orbitals of Al and Ga atoms to that of the Ge atom. Al atom loses electrons in this form $3s^2 \longrightarrow 3s^1$. Exploring the PDOS of the $In_{Ge}B_i$, we predicted that while the VBM is far from the Fermi level (the Fermi level was set to zero), the p-orbital of the In and Ge atoms induced ground state orbitals that are close to the Fermi level from the VBM as displayed in Fig. 2b. Furthermore, the *p*-orbital of the B atom is visibly seen at the CBM with a sharp peak which is 0.04 eV far away from the Fermi level. For the $B_{Ge}In_i$ and $Al_{Ge}In_i$, the respective sharp peaks observed are close to the VBM, which are mainly due to contribution from the strong presence of the *s*-orbital of In atom. For the $In_{Ge}Al_i$, the *s*-orbital of the In atom is very visibly and populated the valence band even up to the Fermi level. While the *s*-orbital of the In and Al atoms for the $Ga_{Ge}In_i$ and $B_{Ge}Al_i$ respectively are the dominating ground state orbitals around the Fermi level from the VBM, for the $Al_{Ge}B_i$ and $In_{Ge}Ga_i$ as shown by Fig. 2c, the *p*-orbital of Ge and *s*-orbital of Ga atoms are the participating ground state orbitals. Further exploring the PDOS of the defective system, we observed that the *s*-orbital of Ge atom around the defect atoms received electrons from the *s*-orbital of B and Al atoms. Succinctly speaking, the *s*-orbital of B atom loss an electron in this form

$2s^2 \longrightarrow 2s^1$. For the $Al_{Ge}B_i$, the s-orbital of the Al atom transferred electron to the surrounding atoms with the Ge atom benefited massively relatively to the B atom Substitutional-interstitial complexes in Ge behave as p-type materials and a strong presence of orbital hybridization was observed in all the systems as a result of the participating orbitals from the electron of the various atoms. In all the defects, the spin up and spin down are symmetrical suggesting the absent of spin polarisation. Based on the results of the charge transfer analyses, we found that the electron transfer from the s- and p-orbitals of the impurity atoms are usually transferred to the s- and p-orbitals of the host atoms.

3.3 Formation and binding energies

Table 2 lists the formation energies as well as the binding energies of the substitutional-interstitial complexes in Ge. The formation energies of substitution-interstitial complexes formed by the Ga, Al, B and In atoms in Ge are all within the range of 4.14-7.44 eV. The $Al_{Ge}Ga_i$ has the least formation energy of 4.14 eV revealing that it is the most energetically favourable defect. The substitution-interstitial formed by Ga with Al, or Ga with In, is more energetically favourable when Ga is an interstitial atom ($Al_{Ge}Ga_i$, $In_{Ge}Ga_i$) than when Ga as a substitution atom ($Ga_{Ge}Al_i$ and $Ga_{Ge}In_i$). On the other hand, for the $Ga_{Ge}B_i$ and $B_{Ge}Ga_i$, when Ga is a substitution atom is always more energetically favourable with an energy of formation of 0.25 eV than when a B atom is replaced with a Ge atom. It is obvious that for the atoms with a smaller radius relative to the Ga atomic radius, the substitution-interstitial complex is always more energetically favourable than when atoms with small atomic radius occupy an interstitial position. However, for

the $In_{Ge}Ga_i$ and $Ga_{Ge}In_i$, the latter is more energetically favourable under equilibrium conditions than the former with at least energy of 0.79 eV. The positive binding energies displayed by Table 2 show that these defects can only dissociate into non-interacting defects at the expense of energy higher than the binding energy. The substitution-interstitial complexes are all stable with respect to their binding energies. The $Ga_{Ge}B_i$ has a binding energy of 0.95 eV which is lower than the 1.60 eV binding energy of the $B_{Ge}Ga_i$. This suggests that the energy required to split up $Ga_{Ge}B_i$ into non-interacting defects should be higher than the amount of energy required to split up $B_{Ge}Ga_i$. Furthermore, while the binding energy of the $Ga_{Ge}Al_i$ is lower than that of the $Al_{Ge}Ga_i$, the $In_{Ge}Al_i$ has the lowest binding energy of 0.11 eV. The $Al_{Ge}Ga_i$ is the most stable defect complex with a binding energy of 2.41 eV.

3.4 Charge state transition levels

To show the defect levels induced by substitution-interstitial complexes in Ge, we have plotted the graph of the formation energy as a function of the Fermi level as shown in Fig. 3. The intersection of the charge states i.e when the charge states have the same formation energy is the charge state transition level and the corresponding Fermi energy is the defect energy level. A charge state transition level is accessible if it posses a donor or acceptor level not resonant inside the VBM or the CBM. If this happens, the most energetically favourable charge state transition level is reported. Tables 3 and 4 display the charge state transition ($\varepsilon(q/q')$) levels above the VBM in eV. Deep defect levels were introduced in the band gap of Ge for various acceptor substitutional-interstitial complexes. The $Ga_{Ge}B_i$ and $B_{Ge}Ga_i$

are electrically active and induced only acceptor level. While the $Ga_{Ge}B_i$ single acceptor energy level is $E_C-0.15$ eV, for the $B_{Ge}Ga_i$, its single acceptor defect level is $E_C-0.14$ eV. The defect levels induced by the $Ga_{Ge}B_i$ and $B_{Ge}Ga_i$ are shallow, and close to the CBM. The $In_{Ge}B_i$ and $In_{Ge}Ga_i$ induced shallow single acceptor and donor levels, respectively. Whereas the acceptor level induced by the $In_{Ge}B_i$ is $E_V+0.71$ eV, the single donor level of the $In_{Ge}Ga_i$ is 10 meV far away from the VBM. The $Ga_{Ge}In_i$ and $B_{Ge}In_i$ on the other hand, induced three distinct defect levels in the band gap of Ge. The $\varepsilon(+2/+1)$ (hereafter written without the ε for all charge state transition levels) defect level induced by the $Ga_{Ge}In_i$ and $B_{Ge}In_i$ are deep level. Whereas the $(+2/+1)$ induced by the $Ga_{Ge}In_i$ is $E_V+0.19$ eV, for the $B_{Ge}In_i$ its $(+2/+1)$ defect level is $E_V+0.13$ eV. This suggests that the $Ga_{Ge}In_i$ and $B_{Ge}In_i$ can act as donors, which under certain conditions donate electrons to the conduction band with an activation energy comparable to the thermal energy. Another interesting feature of the $Ga_{Ge}In_i$ and $B_{Ge}In_i$ is the presence of a shallow single acceptor level. While the $(0/-1)$ defect level induced by the $B_{Ge}In_i$ is $E_C-0.08$ eV, for the $Ga_{Ge}In_i$, it is closer to the CBM than that of the $Ga_{Ge}In_i$ with an energy of $E_C-0.02$ eV. As shown by Fig 3a, the $In_{Ge}B_i$, $B_{Ge}Ga_i$, $Ga_{Ge}B_i$ and $In_{Ge}Ga_i$ show that the neutral charge state dominate almost all over the Fermi level, however, for the $B_{Ge}In_i$ and $Ga_{Ge}In_i$, the +2, +1 and neutral charge states are almost evenly distributed across the Fermi level. The +1 charge state of the $In_{Ge}Ga_i$ is the most stable charge state close to the VBM, as the Fermi energy is varied further from away from the VBM, the neutral charge state becomes the most stable charge state. For the $B_{Ge}Ga_i$, $Ga_{Ge}B_i$ and $In_{Ge}B_i$, the neutral charge state is the most stable charge state close to the VBM. However as the Fermi energy is varied close to the CBM, the -1 charge state becomes more stable than

the other charge states. Suggesting that the positive charge states (+2 and +1) despite being accessible, are not stable as the Fermi energy is varied from the VBM to the CBM. The $Ga_{Ge}In_i$ on the other hand, is stable for the +2, +1, 0 and −1 charges states. While the single acceptor level induced by the $Ga_{Ge}In_i$ is at $E_C-0.02$ eV, for the double and single donor, the defect levels are 0.19 and 0.44 eV, respectively far from the VBM. Interestingly, the $In_{Ge}Ga_i$ is only stable at +1 and 0 charge states, and induced a donor level at $E_V+0.10$ eV. The (+1/0) charge state transition defect level induced by the $In_{Ge}Ga_i$ is closer to the VBM relatively to that of the $Ga_{Ge}In_i$. While the (+1/0) defect level induced by the $Ga_{Ge}In_i$ is deep, for the $Ga_{Ge}In_i$, its (+1/0) charge state transition energy level is shallow.

As listed in Table 4, the $Ga_{Ge}Al_i$ is stable in the +2, +1, 0 and −1 charges states. This gives rise to the double (+2/+1), single (+1/0) donor levels and single (0/−1) acceptor level, which has an energy of $E_V+0.13$, $E_V+0.42$ and $E_C-0.06$ eV respectively. Close to the VBM, the +2 charge state is the most stable, however, as the Fermi level is varied across the band gap of Ge, the +1 and 0 become most stable at distinct Fermi energy. Further varying the Fermi energy close to the CBM, the −1 charge state becomes most stable. The donor levels induced by the $Ga_{Ge}Al_i$ suggest the ability of the defect to donate electrons whereas the acceptor levels suggest the ability of the defect to acceptor electrons. The $Al_{Ge}Ga_i$ is electrically active and induced a single acceptor level at $E_C-0.06$ eV. The $Al_{Ge}Ga_i$ induced defect level is shallow and close to the CBM. This is however in contrast to the $Ga_{Ge}Al_i$ which we have shown that it acts as both a donor and acceptor at different charge state transition level. For the $Al_{Ge}Ga_i$, the positive charge states are not always stable despite the fact that they are accessible. The $In_{Ge}Al_i$ and $Al_{Ge}In_i$,

are unique, they both induced the same defect levels in the band gap of Ge. The (+2/+1) and single (+1/0) donor levels are all deep for the $In_{Ge}Al_i$ and $Al_{Ge}In_i$. As displayed by Fig. 3b, the $In_{Ge}Al_i$ is energetically more stable than the $Al_{Ge}In_i$ for al charge states. However, $In_{Ge}Al_i$ and $Al_{Ge}In_i$ charge states of +2, +1 and 0 are evenly distributed across the band gap as the Fermi energy is varied. This suggests that the negative charge states are not always stable. Furthermore, the $B_{Ge}Al_i$ induced a shallow double donor level at E_V+0.07, this is in addition to the single acceptor and donor levels of the $B_{Ge}Al_i$. Whilst the acceptor level is at E_C−0.13 eV, the single donor level is deep lying at E_V+0.38 eV. This is however not the same for the $Al_{Ge}B_i$ which induced only a single acceptor defect level. This acceptor level has an energy of of 0.65 eV from the VBM. While the $B_{Ge}Al_i$ defect levels are deep, the same is applicable to the $Al_{Ge}B_i$. We observed that whereas the +2 and +1 charge states of the $Al_{Ge}B_i$ are not stable, for the $B_{Ge}Al_i$, they are stable and accessible.

4 Summary

The electronic properties, formation and binding energies of In, Ga, Al and B substitution-interstitial complexes in Ge were predicted using the HSE06 within the framework of DFT. This report shows that the substitution-interstitial complexes are always stable with respect to their binding energies. Under equilibrium conditions, for the neutral charge, the $Al_{Ge}Ga_i$ is energetically favourable with a binding energy of 2.41 eV. We have shown that under equilibrium conditions, the charge states of the $B_{Ge}In_i$ and $In_{Ge}B_i$ are the least stable with energy relatively higher than 6.00 eV. The $Al_{Ge}Ga_i$ and $Al_{Ge}Ga_i$ with energy relatively lower than

4.5 eV are the most stable defects for charge states +2, +1 and 0, −1, respectively. While defects such as the $B_{Ge}In_i$, $Ga_{Ge}In_i$, $Ga_{Ge}Al_i$, $In_{Ge}Al_i$, $Al_{Ge}In_i$ and $B_{Ge}Al_i$ act as double donors, the $Al_{Ge}Ga_i$, $Al_{Ge}B_i$, $Ga_{Ge}B_i$, $B_{Ge}Ga_i$ and $In_{Ge}B_i$ behave as acceptors. Whereas the shallow donor defects are the $B_{Ge}Al_i$ and $Ga_{Ge}In_i$, the deep acceptor defects are the $Ga_{Ge}B_i$, $B_{Ge}Ga_i$, $Al_{Ge}B_i$ and $B_{Ge}Al_i$. The $In_{Ge}Ga_i$ acts as a shallow single donor defect and the $In_{Ge}Al_i$ and $Al_{Ge}In_i$, induced defect levels are donors.

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Table 1 The calculated bond distance (BL) of impurity atom with the nearest neighbour Ge atom or the nearest neighbour impurity and the difference between BL and Ge-Ge bound length (D). The calculated Ge-Ge bond distance is 2.48 Å, which is in agreement with previous results [3,5]. The Ge-Ge bond length was calculated with respect to the nearest neighbour Ge atoms.

Defect		BL (Å)	D (Å)	Defect		BL (Å)	D (Å)
$Ga_{Ge}B_i$	B-Ga	2.05	0.43	$B_{Ge}Ga_i$	B-Ga	2.32	0.16
	Ga-Ge	2.52	0.04		Ga-Ge	2.59	0.11
	B-Ge	2.10	0.38		B-Ge	2.13	0.35
$Al_{Ge}Ga_i$	Al-Ga	2.54	0.06	$Ga_{Ge}Al_i$	Al-Ge	2.52	0.04
	Ga-Ge	2.63	0.15		Ga-Ge	2.38	0.10
	Al-Ge	2.39	0.07		Al-Ge	2.63	0.15
$Ga_{Ge}In_i$	Ga-In	2.62	0.14	$In_{Ge}Ga_i$	Ga-In	2.65	0.17
	Ga-Ge	2.37	0.11		Ga-Ge	2.65	0.17
	In-Ge	2.70	0.22		In-Ge	2.49	0.01
$In_{Ge}B_i$	In-B	2.19	0.29	$B_{Ge}In_i$	In-B	2.43	0.05
	In-Ge	2.63	0.15		In-Ge	2.67	0.19
	B-Ge	2.09	0.39		B-Ge	2.09	0.39
$In_{Ge}Al_i$	In-Al	2.65	0.17	$Al_{Ge}In_i$	In-Al	2.62	0.14
	In-Ge	2.49	0.01		In-Ge	2.70	0.22
	Al-Ge	2.65	0.17		Al-Ge	2.38	0.10
$Al_{Ge}B_i$	Al-B	2.12	0.36	$B_{Ge}Al_i$	Al-B	2.23	0.25
	Al-Ge	2.38	0.10		Al-Ge	2.59	0.11
	B-Ge	2.40	0.08		B-Ge	2.14	0.34

Table 2 The energy of formation (E^F) and binding energy (E_B) in eV for substitutional-interstitial complexes of Ge at zero Fermi energy. The values listed here are for the neutral charge state.

Defect	E^F	E_B	Defect	E^F	E_B
$Ga_{Ge}B_i$	5.43	0.95	$Al_{Ge}Ga_i$	4.14	2.41
$B_{Ge}Ga_i$	5.68	1.60	$Ga_{Ge}Al_i$	4.24	0.59
$B_{Ge}In_i$	7.44	1.91	$In_{Ge}Al_i$	5.44	0.11
$In_{Ge}B_i$	6.35	0.75	$Al_{Ge}In_i$	6.16	1.21
$Ga_{Ge}In_i$	6.06	1.10	$Al_{Ge}B_i$	5.48	1.07
$In_{Ge}Ga_i$	5.27	0.57	$B_{Ge}Al_i$	5.78	1.20

Table 3 The defect levels induced by substitution-interstitial complexes in Ge. Charge state transition ($\varepsilon(q/q')$) energy levels were calculated with reference to VBM and are all in eV

Defect	$(+2/+1)$	$(+1/0)$	$(0/-1)$
$Ga_{Ge}B_i$	-	-	0.63
$B_{Ge}Ga_i$	-	-	0.64
$In_{Ge}B_i$	-	-	0.71
$Ga_{Ge}In_i$	0.19	0.44	0.76
$In_{Ge}Ga_i$	-	0.10	-
$B_{Ge}In_i$	0.13	0.43	0.70

Table 4 The charge state transition ($\varepsilon(q/q')$) levels above the VBM in eV induced by Al related substitution-interstitial complexes in Ge.

Defect	$(+2/+1)$	$(+1/0)$	$(0/-1)$
$Ga_{Ge}Al_i$	0.13	0.42	0.72
$Al_{Ge}Ga_i$	-	-	0.72
$In_{Ge}Al_i$	0.23	0.51	-
$Al_{Ge}In_i$	0.17	0.39	-
$B_{Ge}Al_i$	0.07	0.38	0.65
$Al_{Ge}B_i$	-	-	0.63

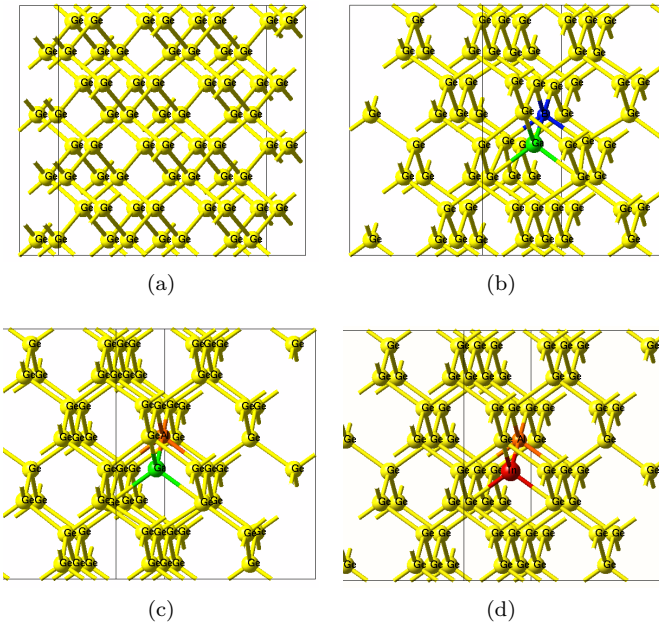
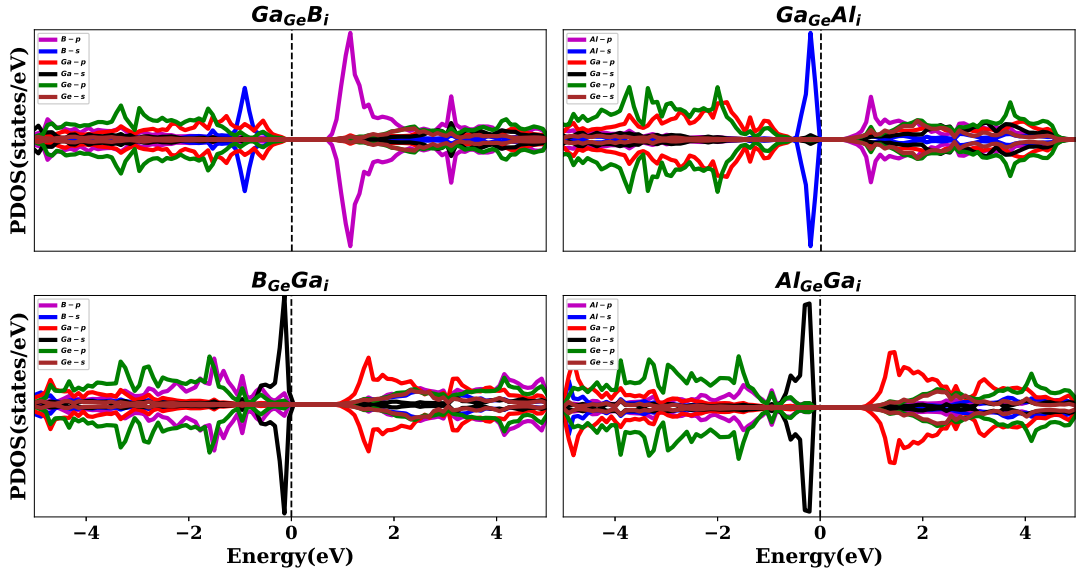
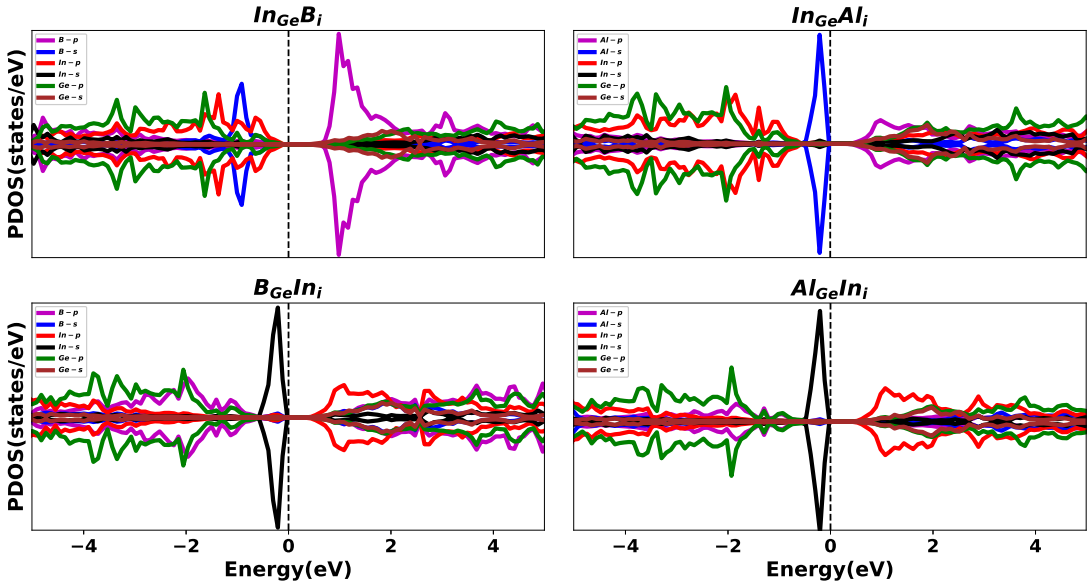


Fig. 1 The relaxed geometric structures of (a) pristine 64 atoms Ge, (b) $B_{Ge}Ga_i$, (c) $Al_{Ge}Ga_i$ and (d) $Al_{Ge}In_i$.



(a)



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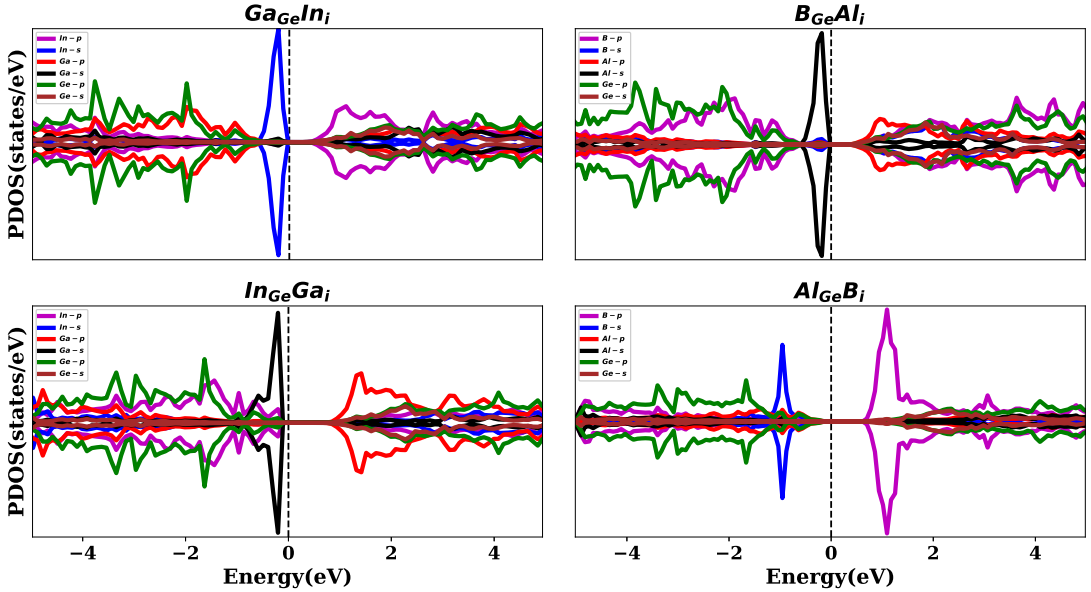
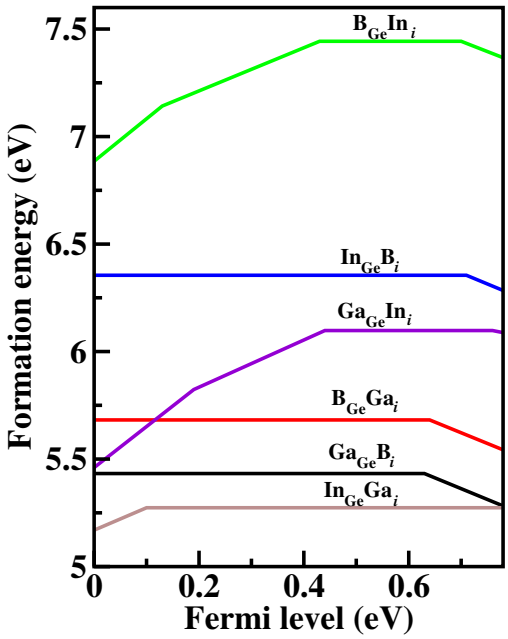
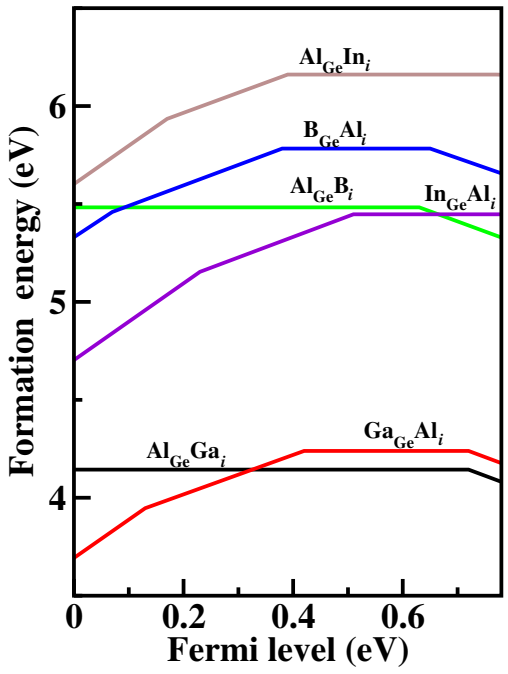


(c)

Fig. 2 Plots of partial density of states (PDOS) of substitution-interstitial complexes in Ge. The vertical dashed line represents the Fermi energy which is set to zero.



(a)



(b)

Fig. 3 Plot of formation energy as a function of the Fermi level. The slope of each plots corresponds to the transition charge state level (defect level).