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AB INITIO STUDY OF TRANSITION METALS IMPURITIES AND STABILITY OF COMPLEXES IN GERMANIUM (Ge)

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ABSTRACT

By means of density functional theory, we present results of an *ab initio* calculation of vacancy-interstitial complexes (T_{Ge}-$V_{nGe}I_T$, for n = 1, 2, 3 and T: Cr, Mo, W, Mn and Fe) in Ge. The projector-augmented wave pseudo-potential within the generalized gradient approximation was used for all calculations. Structural properties and formation energies of the T_{Ge}-$V_{nGe}I_T$ for the neutral charge state were obtained. Our results show that under equilibrium conditions, vacancy-interstitial complex T_{Ge}-$V_{nGe}I_T$ formed with formation energies not higher than –1.00 eV. The formation energy result showed that the T_{Ge}-$V_{nGe}I_T$ is energetically more favourable for n = 1 and 2 than n = 3. The stabilities of the vacancy-interstitial complexes were obtained from their binding energies. For all T, the binding energies of the T_{Ge}-$V_{Ge}I_T$ are stable. For the T_{Ge}-$V_{2Ge}I_T$ and T_{Ge}-$V_{3Ge}I_T$, their binding energies lie between 1.79 and 6.10 eV and defect complexes are stable.

Keywords: Density functional theory, vacancy-interstitial, formation energy, impurities

INTRODUCTION

Due to low level of impurity and high electron-hole mobility of germanium (Ge), its application in semiconductor material technology has been promising and attracting attention (Claeys and Simoen, 2011; Chui *et al.*, 2003). Several studies on point defects in Ge have been studied either by experimental technique or theoretical modelling (Nyamere *et al.*, 2008; Fage-Pedersen *et al.*, 2000). Recently, it was revealed that some impurities form as complexes in Ge (Chroneos *et al.*, 2007; Chroneos and Bracht, 2014). Chroneos *et al.*, 1999, by using the generalized gradient approximation (GGA), predicted that except for boron (which mediate fast through interstitial in Ge), the group III impurities atoms are stable and formed vacancy-complexes in Ge. However, boron defect in Ge is found to be stable in the interstitial-complex. As a result, interest has been rekindled to find out if other impurities apart from interstitial-complexes are stable in Ge. Study on transition metal vacancy-interstitial complexes in silicon (Si) reveals that iron (Fe), which is one of the known detrimental metal impurities, causes depletion of charge migration in metal oxide semiconductor devices and thus acts as an effective minority carrier (Chroneos, 2010). Other studies on transition metal defects in Si and other semi-conducting materials have been reported in literature (Istratoy and Weber, 2002). For instance, Derlet *et al.*, 2007 reported that the binding energy between the second nearest neighbour vacancies in ferromagnetic bcc Fe is more favourable than those of the nearest neighbour configuration. However, to the knowledge of the authors, transition metals (such as Cr, Mo, W, Mn and Fe) related vacancy and interstitial-complexes in Ge have not been reported. Therefore, this study aims at investigating the structure and energetics of "Frenkel like" vacancy-interstitial complexes (T_{Ge}-$V_{nGe}I_T$, for n = 1, 2, 3) in Ge. In addition, this study provides a frontier insight for the proper understanding of T_{Ge}-$V_{nGe}I_T$ complexes in Ge. By means of density functional theory (DFT), we present an *ab initio* calculation of vacancy-interstitial complexes (T_{Ge}-$V_{nGe}I_T$, for n = 1, 2, 3 and T: Cr, Mo, W, Mn and Fe) in Ge. Our calculations employed the projector-augmented wave (PAW) pseudopotential within the generalized gradient approximation (GGA). Structural properties and formation energies of the T_{Ge}-$V_{nGe}I_T$ for the neutral charge state were obtained. The binding energies of the T_{Ge}-$V_{nGe}I_T$ complexes were predicted.

COMPUTATIONAL DETAILS

In this report, DFT electronic structure

calculations were performed using the Vienna ab initio Simulation Package (VASP) (Kresse and Furthmu¨ller, 1996). The projector-augmented wave (PAW) method, as implemented in the VASP code was used to separate the inner core electrons from the chemically active valence electrons (Kresse and Joubert, 1999; Kresse and Furthmu¨ller, 1996; Bl¨ochl, 1994). All calculations were carried out using the generalized gradient approximation (GGA), functional of Perdew, Burke, and Ernzerhof (PBE) Perdew*et al.*, 1996). DFT calculations based on the local density approximation (LDA) and GGA results have shown to underestimate the band gap properties and formation energies of most defects in Ge (De´ak *et al.*, 2010; Igumbor *et al.*, 2016; Igumbor *et al.*, 2015; Igumbor and Meyer, 2016). However, previous studies have demonstrated the efficacy of using the GGA exchange correlation functional to predict the binding energies of defects in Ge by comparison with other experimental study (Chroneos *et al.*, 2007). In addition, in this report, we focused only on the geometric structures of the complexes and binding energies which are determined from differences in defects formation energies. As a result, we expect that our results will be less sensitive to the exchange-correlation function.

We used a 64-atom super cell as the pristine. For the defects, a number of vacancies were created, and a transition metal atom was substituted in place of Ge atom. In addition, a transition metal atom was placed in an interstitial site in the 64-atom supercell. Both for the pristine and the defects, we used 2^3 Monkhorst-Pack special k-points Brillouin zone sampling scheme, achieving convergence of the total energy by setting the energy cut-off of the wave function expansion to 400 eV. In all the calculations, the structural optimization continued until both the total energy and forces were less than 10^{-5} eV and 0.01 eV/°A, respectively. Since the energy of formation of a system is strongly dependent on the spin-orbit coupling (SOC) due to the presence of relativistic effects in heavy atomic systems, the scalar relativistic effect has been taken into consideration by incorporating into the PAW potential the mass-velocity and Darwin correction terms. In addition to the scalar relativistic effect that was taken into account, spin orbit coupling was also taken into account for all calculations. To calculate the formation energy (E^f) of a defect, we calculated the total energy E(d) for a supercell containing the optimized defect d. The defect formation energy E^f (d) is given as (Zhang and Northruo, 1991; Christoph *et al.*, 2014)

$$E^f(d) = E(d) - E(pure) + \sum_i \Delta(n) \quad (1)$$

where E (pure) is the total energy of a supercell without a defect, Δ(((Δ(n)<, when an atom is added and Δ(n)> when an atom is removed) is the difference in the number of constituent atoms of type i between the pristine super cell and the super cell containing the defect, and μ_i is the chemical potential of type i th atom. The binding energy E_b which is defined as the energy required to split up defect cluster into well separated non-interacting defects is given as (Zollo*et al.*, 2004)

$$E_b = E^f_{(V_{Ge})} + E^f_{(T_{Ge})} + E^f_{(I_T)} - E^f_{(defect-complex)} \quad (2)$$

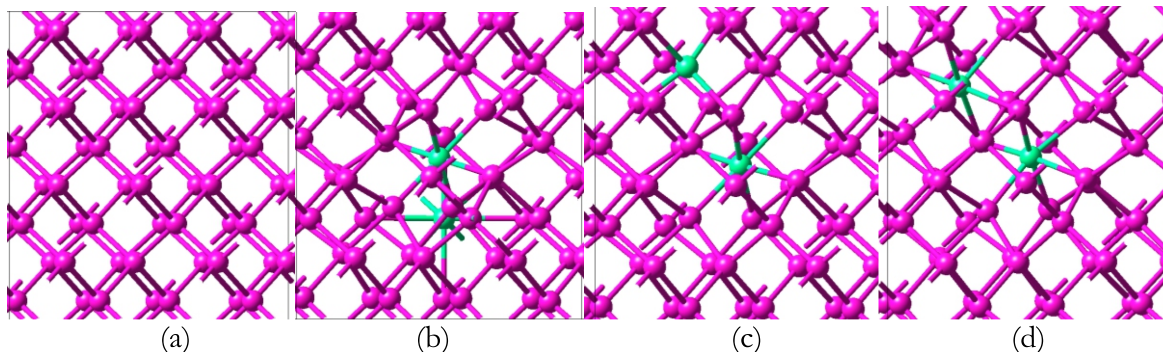
where the $E^f_{(V}$, $E^f_{(T}$, E and $E^f_{(defect-complex)}$ are the

formation energies of V_{Ge}, T_{Ge}, I_T and T_{Ge}-$V_{nGe}I_T$, respectively. Eq. 2 could be interpreted as the energy released from the bonded structure with respect to the isolated components.

RESULTS

Structural properties

The geometric structures of the relaxed T_{Ge}-$V_{nGe}I_T$ (where T_{Ge} is a transition metal substitutional impurity in Ge, V_{Ge} and I_T are Ge vacancy and T interstitial, respectively) are shown in Fig.1. Fig.1a represents the relaxed geometric structure of a 64-atom Ge supercell. While Fig.1b represents the relaxed geometric structure of the T_{Ge}-$V_{Ge}I_T$, Figs.1c and 1d show the relaxed geometric structures of T_{Ge}-$V_{2Ge}I_T$ and T_{Ge}-$V_{3Ge}I_T$, respectively.



(a) (b) (c) (d)

Fig. 1. The relaxed geometric structures of Ge and T_{Ge}-$V_{nGe}I_T$ (a) a 64-atom Ge supercell; (b) T_{Ge}-$V_{Ge}I_T$; (c) T_{Ge}-$V_{2Ge}I_T$ and (d) T_{Ge}-$V_{3Ge}I_T$. The colour atoms are the T impurities introduced into a 64-atom supercell of Ge.

The predicted average bond lengths separation between T and its nearest neighbours Ge atoms are shown in Table 1. Our theoretical calculation of the bond length of Ge-Ge atoms is 2.45 Å, which is in good agreement with experimental and other theoretical results reported in literature (Singh, 1968; Chroneos *et al.*, 2007). For the T_{Ge}-$V_{nGe}I_T$, in all T, the differences between the bond length (Δx) before and after geometric relaxation are between 0.25 and 0.09 Å. For the T_{Ge}-$V_{Ge}I_T$, the Fe and Cr related complexes experience more strain in their bond length than the other T related complexes. The Fe and Cr related complexes have Δ_a of 0.16 and 0.24 Å, respectively. While for the T_{Ge}-$V_{2Ge}I_T$, Mo and Fe related defects experience larger strain in the bond length than others, the T_{Ge}-$V_{3Ge}I_T$ follows the same trend as the T_{Ge}-$V_{Ge}I_T$ with Δ_c of 0.16 and 0.19 Å, for the Fe and Cr related complexes, respectively. Interestingly we found that while for all T after geometric relaxation, the average T-Ge bond lengths increases for the case of the T_{Ge}-$V_{Ge}I_T$, but for the case of the T_{Ge}-$V_{Ge}I_T$ it reduces.

Table 1. The predicted average bond lengths of T and its nearest neighbour Ge atoms distance in Å, β and a, are the T-Ge atoms bond length before and after geometric relaxations, respectively. The Δ_x is the difference between β and a, for $x = a, b, c$.

Defect(T)	T_{Ge}-V_{Ge}			T_{Ge}-$V_{2Ge}I_T$			T_{Ge}-$V_{3Ge}I_T$		
	β	a	Δ_a	β	a	Δ_b	B	a	Δ_c
Cr	2.46	2.70	0.24	2.69	2.53	0.16	2.47	2.68	0.19
Mo	2.46	2.56	0.10	2.69	2.50	0.19	2.47	2.38	0.07
W	2.45	2.54	0.09	2.68	2.53	0.13	2.44	2.47	0.03
Mn	2.45	2.53	0.08	2.68	2.58	0.10	2.44	2.58	0.14
Fe	2.45	2.29	0.16	2.68	2.43	0.25	2.45	2.29	0.16

Formation energy of the T_{Ge}-$V_{nGe}I_T$

The result of the calculated energy of formation for the various complexes are displayed in Table 2. Fig. 2 represents the plot of formation energies as a function of the transition metal. Since we are investigating the stability of the complexes, we have limited our calculations only to the neutral charge state. The formation energies of T_{Ge}-$V_{Ge}I_T$ for the Mn, Mo, Cr, W and Fe impurities are between −8.74 and –2.85 eV. The M_{nGe}-$V_{Ge}I_{Mn}$ has the lowest formation energy of −8.74 eV. The order of the sequence of formation energies is Mn<W<Mo<Cr<Fe, as shown in Fig. 2. For all T, the formation energies of the T_{Ge}-$V_{2Ge}I_T$ are lower than that of the T_{Ge}-$V_{Ge}I_T$. For the T_{Ge}-$V_{2Ge}I_T$, the

Mn_{Ge}-$V_{2Ge}I_{Mn}$ has the lowest formation energies of –10.29 eV. For the T_{Ge}-$V_{2Ge}I_T$, as it is observed for the case of the T_{Ge}-$V_{Ge}I_T$, Fe related defects have the highest formation energies. For the T_{Ge}-$V_{3Ge}I_T$, the formation energies are between −9.60 and −4.63 eV. The sequence of the formation energy is the same as that of the T_{Ge}-$V_{Ge}I_T$. From the results of the formation energy, it is obvious that for all T and *n*, the Mn related defect under equilibrium condition is energetically the most favourable and the Fe and the Cr related defects are energetically less favourable. For the T_{Ge}-$V_{3Ge}I_T$, T_{Ge}-$V_{2Ge}I_T$ and T_{Ge}-$V_{Ge}I_T$, except for Cr which is energetically most favourable in T_{Ge}-$V_{Ge}I_T$, the Mo, W, Mn and Fe are energetically most favourable in the T_{Ge}-$V_{2Ge}I_T$. The difference in formation energies could be as a result of the level or amount of strain experienced by the bond lengths when defect was introduced into the supercell.

Table 2. Predicted formation energies E_f in eV of T_{Ge}-$V_{nGe}I_T$ (for *n*=1, 2, and 3) complexes in Ge. The lowest formation energy for a transition metal in each complexis written in bold.

Defect (T)	T_{Ge}-$V_{3Ge}I_T$	T_{Ge}-$V_{2Ge}I_T$	T_{Ge}-$V_{Ge}I_T$
Cr	–5.53	–6.12	–6.25
Mo	–6.67	–6.87	–6.28
W	–6.80	–6.81	–7.59
Mn	–8.74	–10.29	–9.60
Fe	–2.85	–4.53	–4.63

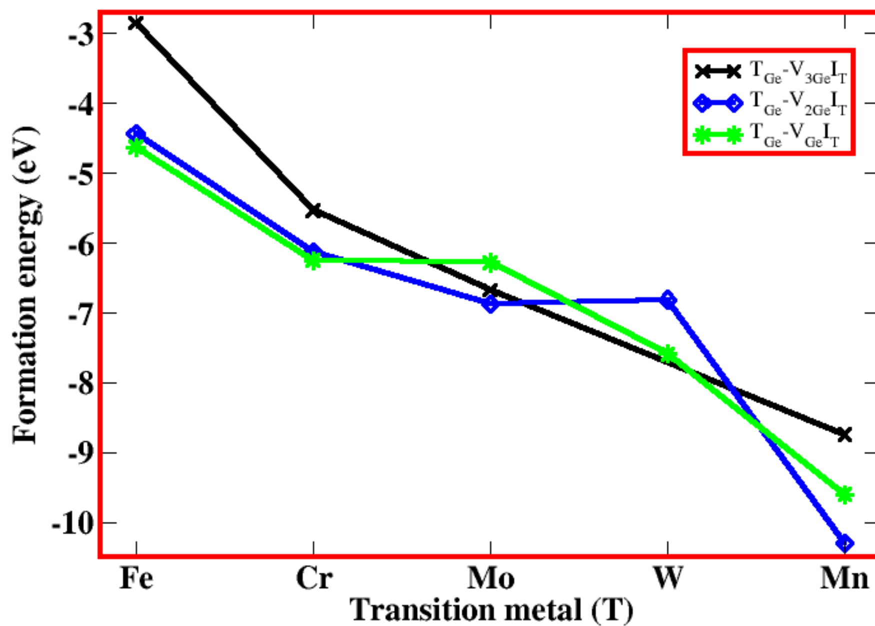


Fig. 2. The plot of formation energy as a function of transition metal.

Stability of transition metals impurity and complexes in Ge

The stability of vacancy-interstitial complexes is well understood from their binding energies E_b. The result of the binding energies for the T_{Ge}-$V_{nGe}I_T$ is listed in Table 3. Fig. 3 represents the plot of binding energies as a function of the transition metal. According to the definition of the E_b in Eq. 2, positive binding energy means that the defect complex can form without dissociation. Based on the definition, we found that for all T and n, T_{Ge}-$V_{nGe}I_T$ is positive. The implication of this is that Cr, Mo, W, Mn and Fe impurities form vacancy-interstitial complexes in Ge that are stable. While the W, Cr and Fe related defects are more stable for the T_{Ge}-$V_{Ge}I_T$ (as shown in Fig. 3) with bind energies of 6.88, 5.07 and 3.57 eV, respectively, the Mn and Mo are more stable for the T_{Ge}-$V_{2Ge}I_T$ with binding energies of 5.73 and 5.60 eV, respectively. For Cr, Mo, W, Mn and Fe related defects, the

difference between the most stable and the next most stable complexes in terms of binding energies are 0.13, 0.20, 0.78, 0.69 and 0.10 eV. This shows that the complex defects under investigation cannot dissociate into smaller fragments, unless at the expense of energy.

Table 3. The predicted binding energies (E_b) of T_{Ge}-$V_{nGe}I_T$ (for n = 1, 2, and 3) vacancy- interstitial complexes in Ge. The E_b are all in eV.

Defect (T)	T_{Ge}-$V_{3Ge}I_T$	T_{Ge}-$V_{2Ge}I_T$	T_{Ge}-$V_{Ge}I_T$
Cr	4.35	4.94	5.07
Mo	5.40	5.60	5.00
W	6.10	5.37	6.88
Mn	4.18	5.73	5.04
Fe	1.79	3.47	3.57

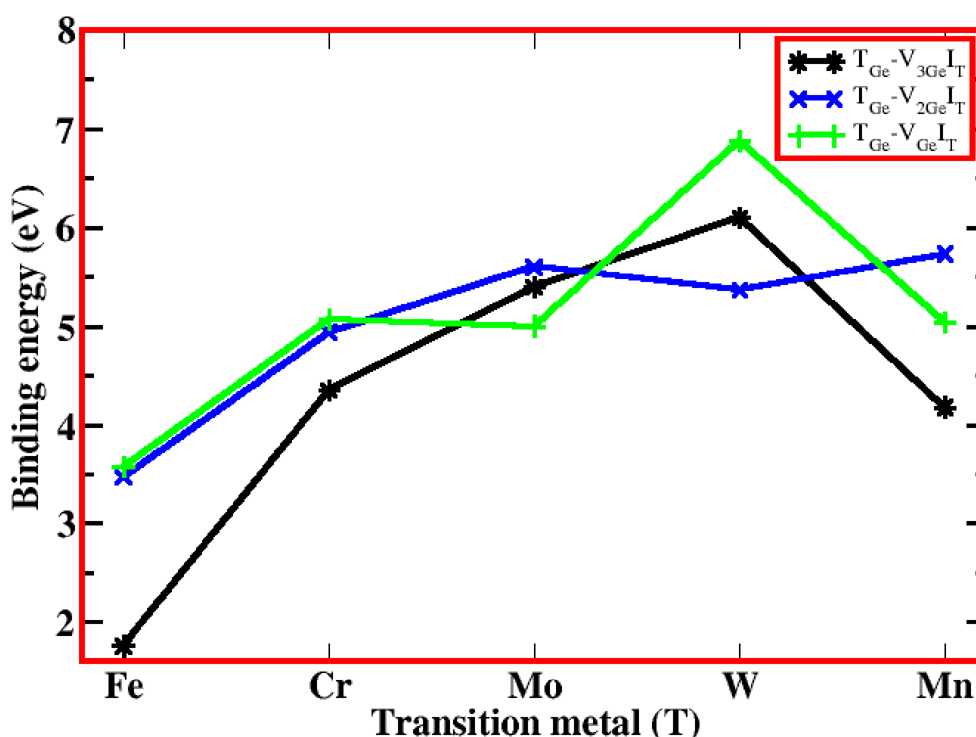


Fig. 3. The plot of binding energies as a function of transition metal.

CONCLUSION

In conclusion, we have presented DFT *ab initio* calculated results of interactions between T (T: Cr, Mo, W, Mn and Fe) vacancy-interstitial complexes in Ge. Our calculations employed projector-augmented wave (PAW) pseudopotential within the generalized gradient approximation (GGA). The structural property and formation energies of the T_{Ge}-$V_{nGe}I_T$ for n = 1, 2, 3 in the neutral state were obtained. The result of our calculation shown that T related vacancy-interstitial complexes in Ge formed with low formation energies between −10.29 and -2.85 eV. For all T, and n, the Mn related a defect complex is energetically most favourable. The stability of T_{Ge}-$V_{nGe}I_T$ defects was also predicted. The calculated binding energy results shown that for all T and n, the Cr, Mn, W, Mo and Fe formed "Frenkel like" complexes that are stable in Ge with binding energies between 1.70 and 6.88 eV. The result of this report will provide a frontier insight for experimental investigation of T_{Ge}-$V_{nGe}I_T$ complexes in Ge.

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