THEORY OF INTERSTITIAL AGGREGATES IN GERMANIUM

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ABSTRACT

Ab initio methods are employed to examine the structure of the Ge self-interstitial and its aggregates. The energetics of the defects investigated here are broadly similar to the results found for the corresponding defects in Si. We report the predicted electronic structures of these defects.

INTRODUCTION

Much has been published regarding self-interstitials and their aggregates in diamond and silicon, but to date Ge has not received a great deal of attention. In diamond the single self-interstitial has been unambiguously detected in electron paramagnetic resonance (EPR), as have di- and tri-interstitial complexes, and (001)-platelets are also believed to be interstitial related. Unlike diamond, the existence of the single self-interstitial in Si and Ge has been confirmed in experiment only when they complex with impurities or aggregate to form extended defects. Interstitial aggregates are a source of transient enhanced diffusion, which makes a theory of interstitials in all group IV materials highly desirable, especially considering the recent developments in SiGe as an electronics material. Recently, some progress was made identifying the structures of interstitial aggregates in Si [1, 2]. In Ge the picture is much less clear, mainly because of a lack of clear experimental data. Only the hydrogenated self-interstitial has been identified [3]. Recent experiments claim to have provided some insight into the single interstitial [4].

In this paper we report preliminary results of the structures and electrical activity of the self-interstitial in Ge, and aggregates of up to four interstitials. We employ a local-density-functional approach using large, hydrogen terminated clusters [5], consisting of 132–308 atoms, relaxed via a conjugate gradient algorithm. The electrical levels were calculated using a technique described elsewhere [6]. The reference for the electrical levels was taken as Au or Se.

THE SINGLE INTERSTITIAL

For the neutral self-interstitial (I_1), in agreement with previous calculations [7], the $\langle 110 \rangle$ split-interstitial (Fig. 1(a)) was found to be lowest in energy.

The ⟨001⟩ split-interstitial, which is the ground state configuration for diamond, is about 1 eV higher in energy, although it is only stable under a D_{2d} symmetry constraint. An unconstrained relaxation leads to the ⟨110⟩ configuration. The symmetry-constrained T_d interstitial is also found to be ∼1 eV higher in energy. The hexagonal interstitial was found to be metastable at around 0.2 eV higher in energy, but relaxed in the atom centred cluster to a distorted ⟨001⟩ split interstitial (Fig. 1(b)). This geometry has C_{1h} symmetry and is about 0.3 eV higher in energy than the ⟨110⟩ geometry. This structure is important for di-interstitial models, described in the next section. As with Si, the bond-centred interstitial was found to be unstable and relaxed into the ⟨110⟩ configuration.

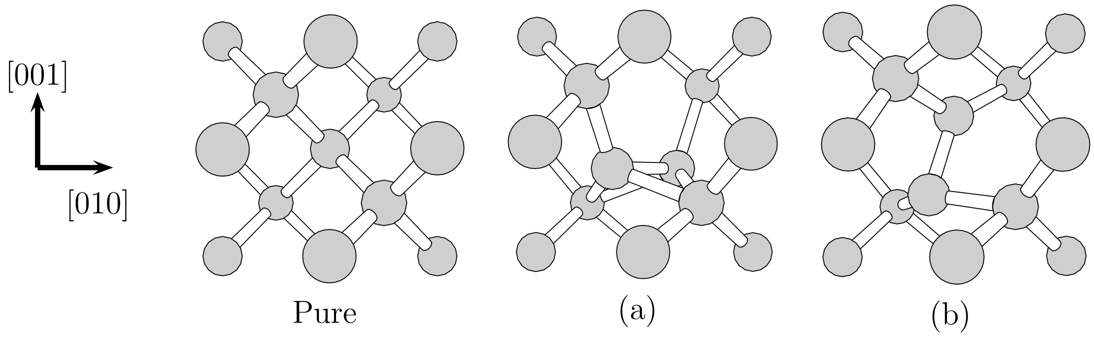

Fig. 1: Schematics of (a) the lowest energy neutral self-interstitial and (b) the approx. ⟨001⟩ split-interstitial related to the di-interstitial structures.

Haesslein *et al.* [4] identified the mono-vacancy in Ge using perturbed angular correlation spectroscopy (PACS) and deep level transient spectroscopy (DLTS). They also found another type of defect which they tentatively assigned to the self-interstitial close to the In probe. They concluded a donor level for the I_1 lying 0.04±0.02 eV below the bottom of the conduction band. However, da Silva *et al.* [7] calculated the (0/+) level for the ⟨110⟩ configuration to be 0.07 eV above the valence band, and they suggested that the PACS data shoud be re-interpreted in terms of a (0/−) level at E_v+0.31 eV which is 0.12 eV below their conduction band and a (0/+) level between 0.11 and 0.16 eV.

We have also examined the energetics for the ionised interstitial. For the 1+ and 2+ charge states the ordering of the energies is reversed. The tetrahedral interstitial is found to be the lowest in energy with the ⟨110⟩-split much higher. The tetrahedral interstitial is calculated to have a double donor level close to the conduction band.

THE DI-INTERSTITIAL

For the di-interstitial, four energetically competitive structures were found. Two of these models were already proposed for Si by Kim [8] and Coomer [1]. The new models (Fig. 2) have C_2 symmetry. The Kim, Coomer and Fig. 2(a) structures are very similar in terms of bonding and can be transformed into each other by only displacing the central atoms by a small amount. These three models all have several over-coordinated Ge atoms, and consequently the barrier to reorientation is likely to be small.

The C_{2h}-symmetry nearest-neighbour di-⟨001⟩-split interstitial model that is responsible for the R1 EPR centre in diamond [9] is around 1 eV higher in energy. However, a similar structure (Fig.2(b)) was found to be nearly as stable as the three low energy models. This geometry is atypical of low energy structures found thus far in that there are two *under-coordinated* Ge atoms. The 'dangling-bonds' lead to empty states in the band gap that could give rise to optical activity. The filled Kohn-Sham levels of all the low-energy structures are similar. The Kim model is predicted to possess a single donor level close to the valence band top, and no acceptor level. It is anticipated that the other models would possess similar electrical levels.

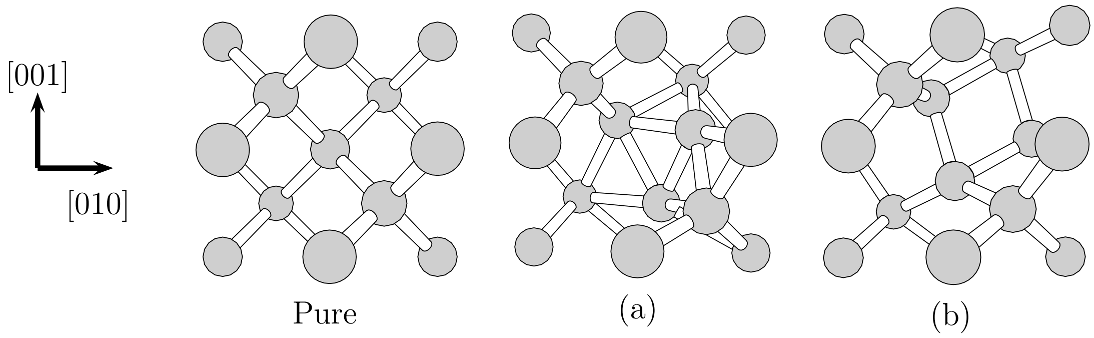

Fig. 2: Schematics of C_2 di-interstitial models.

Several further models for I_2 were considered. The relaxed C_2 configuration formed by two ⟨001⟩ split-interstitials at next nearest-neighbour sites was found to be stable but 0.6 eV higher in energy. Two bond-centred interstitials placed on opposite sides of the hexagonal ring is also a stable structure, lying 0.5 eV above the ground state. The model proposed in Ref. [10] was found to be unstable, in agreement with previous calculations for the same defect in Si [1].

THE TRI-INTERSTITIAL

Four different configurations of the tri-interstitial are considered. First is that responsible for the O3 EPR centre in diamond [9]. Second is a structure proposed for the W-line in Si [1] consisting of three bond-centred interstitials surrounding a T_d interstitial site. These reconstruct to form a three-fold ring at the centre of the defect, leaving all atoms fully-coordinated. Finally two models are considered consisting of four atoms sharing a single lattice site proposed for Si by Colombo [11] and Gharaibeh *et al.* [12] with T_d and C_{3v} symmetry respectively. The calculations cannot distinguish in energy between the Colombo and Gharaibeh defects, which are both lower in energy than the Coomer and O3 models by about 0.6 and 1.5 eV respectively. Again, the Kohn-Sham levels suggest that there are filled and empty states in the gap that may give rise to localised optical transitions. I_3 is expected to be a donor although an estimate of the position of the level is pending.

THE TETRA-INTERSTITIAL

For the I_4, a large cluster centred at the tetrahedral-interstitial site was used ($Ge_{188}H_{120}$). A number of initial configurations have been relaxed consisting of I_3 models with an additional interstitial. All of them were more than 1.9 eV higher in energy than the D_{2d} model originally suggested by Humble for diamond [13], and subsequently by Arai for Si [14]. This model consists of four $\langle 001\rangle$ split-interstitials in next nearest neighbour sites. It is found to be particularly stable due to the remarkable fact that all atoms are fully coordinated with bond-lengths and angles close to that of bulk Ge. In Si this centre has been attributed [2] to the B3 EPR centre and a donor level at $E_v + 0.29\,\text{eV}$. It is likely that I_4 has a donor level close to the valence band top in Ge.

CONCLUSIONS

It is confirmed that the $\langle 110\rangle$-oriented split-interstitial is the ground state structure for the single self-interstitial in the neutral charge state. For the 1+ and 2+ charge states the tetrahedral interstitial was found to be the lowest in energy, which has potential implications for enhanced interstitial migration under ionising conditions. For I_2, three models very similar to each other in geometry were also found very low in energy. Additional to the Kim and Coomer models, two new models which have C_2 symmetry were suggested. It is probable that reorientation between different structures has a low energy barrier. Empty levels in the band-gap for I_2 and I_3 suggest the possibility that they are detectable via absorption or luminescence processes. The lowest energy I_4 configuration is the same as predicted for Si. I_1 is predicted to have a double donor level close to the conduction band in the T_d configuration, but the $\langle 110\rangle$ split-interstitial is electrical inert. All interstitial aggregates we have studied appear to have donor levels close to the valence band top, which could have implications for p-type material.

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