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# Properties of intrinsic di-interstitials in GaAs

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## Abstract

Recent studies have shown evidence of self-interstitial aggregation in ion-implanted Si, resulting in nanoscopic damage structures. Similarly, self-interstitial atoms are expected to play an important role for defect clustering in ion-implanted GaAs. We report results on stable neutral di-interstitial complex configurations in GaAs composed of both As and Ga atoms addressed by first-principles total-energy calculations based on density-functional theory.

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

## 1. Introduction

Self-interstitials are commonly believed to be present in negligible concentrations in as-grown GaAs due to their high formation energies [1]. However, implanted materials can be far from thermodynamic equilibrium, and thus the presence of self-interstitials should be taken into account. Due to their mobility, self-interstitials can migrate and easily form larger aggregates. For example, extended  $\langle 311 \rangle$  defects are formed in Si via self-interstitial aggregation [2]. Nanoscale aggregates have also been observed in implanted GaAs through high-resolution transmission electron microscopy (HRTEM) [3–6], and thus reliable atomistic modelling is required for their proper interpretation. The electronic characterization of implanted GaAs should also take advantage of calculated electronic properties based on reliable atomistic models.

Recent studies have shown that the formation energy of the most stable As interstitial configuration (the As $\langle 110 \rangle$  dumbbell) is remarkably lower than was previously believed [7, 8]. The As $\langle 110 \rangle$  dumbbell has been found in the charge states of  $-1, 0, +1$  [7] and to be a negative  $U$  system [8].

In order to address the problem of intrinsic interstitial clustering by density-functional theory (DFT) methods, it is necessary to use 216-atom supercells to obtain converged results for both the geometrical properties and the formation energy. This was explicitly shown for the As di-interstitial and the ‘split antisite’ [8]. The use of the large supercell is necessary

to avoid the elastic interactions and the wavefunction overlap between the defect replicas [8]. The split interstitial complex, previously invoked to explain the donor band at 0.3 eV below the conduction band in low temperature (LT) grown GaAs, was shown not to support any Kohn–Sham one-electron state in the expected donor band [8, 9]. Moreover, the properties of the neutral As<sub>2</sub> di-interstitial complex have been calculated in a 218-atom supercell, showing that this structure is extremely stable, the binding energy being 2.35 eV in a fully relaxed supercell. In this paper we complete the scenario of stable, neutral di-interstitials in GaAs reporting calculations of di-interstitials also involving Ga atoms, i.e. the mixed and Ga<sub>2</sub> di-interstitials. The properties of these complexes (i-Ga<sub>2</sub>, i-As<sub>2</sub>, i-AsGa) will be discussed and compared with the As<sub>2</sub> di-interstitials. The purpose of the paper is to identify stable starting configurations for the nucleation of larger aggregates presumably present in ion-implanted GaAs.

## 2. Methods

We use the density-functional theory (DFT) within the local-density approximation (LDA) [10]. The calculations are performed using the self-consistent total-energy pseudopotential (PP) method. The Perdew–Zunger [11] parameterization of the Ceperley–Alder data [12] is used for the exchange–correlation energy. Norm-conserving Hamann PPs [13] in the Kleinman–Bylander form [14] have been used for both Ga and As atoms. The valence-electron wavefunctions are expanded in a plane-wave basis set up to a kinetic energy cutoff depending on the supercell size. Isolated Ga and As interstitials have been calculated in 64-atom supercells using the  $2 \times 2 \times 2$  Monkhorst–Pack (MP) [15]  $\mathbf{k}$ -point Brillouin zone sampling scheme and a 28 Ry energy cutoff. The di-interstitial configurations have been simulated in 218-atom supercells. Due to the computational workload, the sampling scheme of the Brillouin zone has been limited to the  $\Gamma$  point and the energy cutoff to 15 Ry. These choices ensure the convergence and the reliability of the obtained results. We use the LDA approximation also for unpaired spins because the energy differences with respect to spin-polarized calculations (LSDA) are expected to be small. The ground-state electron density for each atomic configuration has been obtained by the Williams–Soler algorithm [16]. The atomic configurations of the studied complexes have been fully relaxed using the BFGS algorithm [17].

The formation energies of the different defect configurations are calculated using the well-known formulation of Zhang and Northrup [1]; the formation energy of one particular defect depends both on the Fermi level position and on the stoichiometry of the compound semiconductor. Thus for GaAs we have

$$E_F = E_{F0} + \mu_e Q - \frac{1}{2}(n_{\text{Ga}} - n_{\text{As}})\Delta\mu \quad (1)$$

where  $\mu_e$ ,  $Q$ ,  $n_{\text{Ga}}$ , and  $n_{\text{As}}$  are the electron chemical potential, the charge state of the defect, and the number of Ga and As atoms in the supercell;

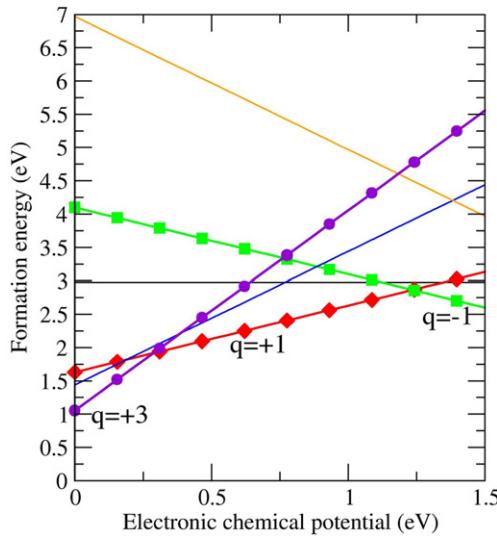
$$\Delta\mu = (\mu_{\text{Ga}} - \mu_{\text{As}}) - (\mu_{\text{Ga}_{\text{bulk}}} - \mu_{\text{As}_{\text{bulk}}}) \quad (2)$$

where  $\mu_{\text{Ga}}$ ,  $\mu_{\text{As}}$ ,  $\mu_{\text{Ga}_{\text{bulk}}}$ , and  $\mu_{\text{As}_{\text{bulk}}}$  are the Ga and As chemical potentials in the compound and in the bulk respectively;

$$E_{F0} = E_{SC} + \frac{1}{2}[(\mu_{\text{Ga}_{\text{bulk}}} - \mu_{\text{As}_{\text{bulk}}})(n_{\text{As}} - n_{\text{Ga}}) - \mu_{\text{GaAs}}(n_{\text{As}} + n_{\text{Ga}})] + QE_v \quad (3)$$

where  $E_{SC}$ ,  $\mu_{\text{GaAs}}$ , and  $E_v$  are the energy of the supercell containing the defect, the energy per As–Ga pair in bulk GaAs, and the energy of the valence band maximum. The stability of the studied di-interstitial configurations against the components is evaluated by calculating the binding energy of the complex; it is defined as

$$E_b^D = \sum_i E_f^i - E_f^D \quad (4)$$



**Figure 1.** The formation energies of the Ga tetrahedral configuration in various charge states (see the labels) as a function of electron chemical potential in stoichiometric GaAs. The monopole correction has been adopted to handle the spurious electrostatic interaction between the replicas of the charged defects.

where  $E_f^i$  and  $E_f^D$  are the formation energies of the  $i$ th isolated interstitial involved in the complex and of the di-interstitial respectively; the sum runs over all the isolated interstitials involved in the complex. The binding energy of the di-interstitial is, thus, the energy gain of the bonded structure with respect to the isolated components.

### 3. Results

The results for single As interstitials have been already reported in a recent paper [8] and thus we will not discuss them further. For isolated Ga self-interstitials we focus on the fully relaxed tetrahedral configuration which is the stablest for neutral Ga interstitials [8].

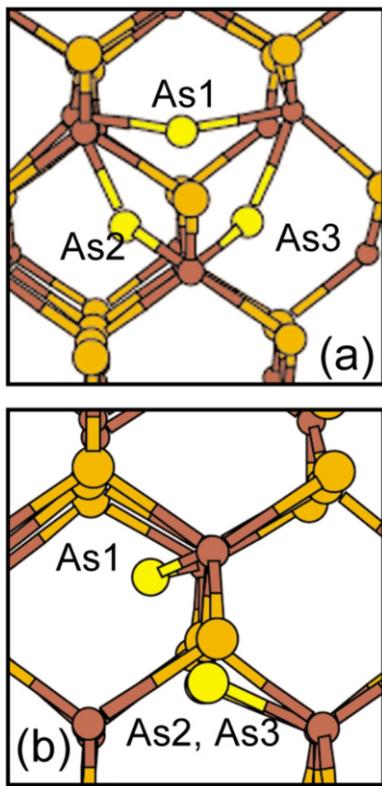
In figure 1 the formation energy for different charge states of a tetrahedral  $\text{Ga}_i$  is reported as a function of the electron chemical potential for stoichiometric GaAs ( $\Delta\mu = 0$ ). The results show that the stable charge states are +3, +1, and -1, and the ionization levels (+3|+1) and (+1|-1) are located at 0.29 and 1.23 eV above the valence band maximum, respectively.

The results for di-interstitials will be next reported in two subsections dealing with structural and energetic properties and electronic properties, respectively.

#### 3.1. Structure and energetics

Before discussing di-interstitials containing Ga, we briefly summarize the properties obtained for  $\text{As}_2$  di-interstitials, extensively studied in [8].

**3.1.1.  $\text{As}_2$  di-interstitial.** The geometry is shown in figure 2. It is composed, essentially, of one  $\langle 110 \rangle$  dumbbell, slightly off the site normally occupied by an isolated  $\text{As}\langle 110 \rangle$  dumbbell, and one extra As atom. The formation energy for stoichiometric GaAs ( $\Delta\mu = 0$ ) is 5.8 eV, while the binding energy of the complex is 2.35 eV. The symmetry point group is  $\text{C}_{1h}$ , where



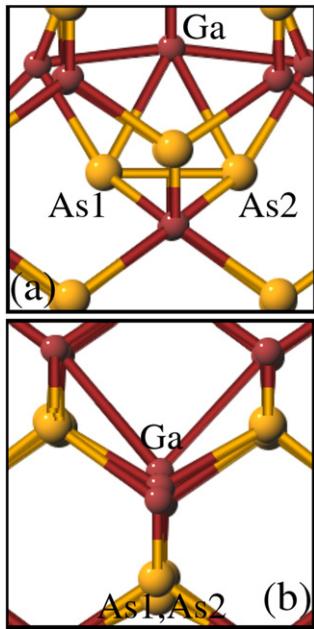
**Figure 2.** The  $\text{As}_2$  di-interstitial configuration viewed along two perpendicular  $\langle 110 \rangle$  directions (a) and (b).

the mirror plane contains the extra As atom added to the pre-existing dumbbell. The three As atoms are bonded each other and are fourfold and fivefold coordinated.

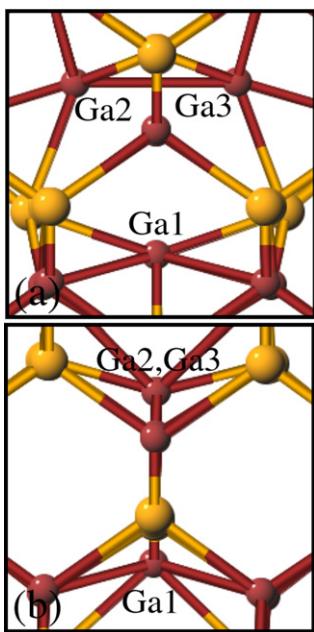
**3.1.2.  $\text{AsGa}$  di-interstitial.** The complex examined has been obtained taking as the starting structure one  $\text{As}\langle 110 \rangle$  dumbbell and one Ga in the closest tetrahedral site. The resulting structure, after atomic relaxation, is shown in figure 3. The formation and binding energies are, respectively, 4.8 and 2.24 eV, which indicates that the formation of such a complex is relatively easy. The point group of this complex is close to  $\text{C}_{2v}$  with a deviation of  $\sim 0.5\%$  in the atomic distances, the mirror planes being two orthogonal  $(110)$  planes. Actually, the  $(110)$  plane containing the two interstitials deviates more from the mirror symmetry than the orthogonal one. Thus the symmetry is, in some sense, closer to  $\text{C}_{1h}$  than  $\text{C}_{2v}$ .

The Ga atom in the complex is fourfold coordinated, while the As atoms in the dumbbell are both fivefold coordinated. The tetrahedron whose centre is the As lattice site shared by two As atoms and one Ga atom dilates by about 40% with respect to the volume of the perfect lattice tetrahedron, i.e. slightly more than the lattice dilation induced by the As di-interstitial; thus one isolated extra Ga–As molecule induces 40% local lattice dilation.

**3.1.3.  $\text{Ga}_2$  di-interstitial.** The starting configuration of the  $\text{Ga}_2$  di-interstitial consisted of three Ga atoms (two interstitials plus one lattice Ga atom) forming an equilateral triangle around one Ga site. This structure was fully relaxed and the obtained ground state configuration is

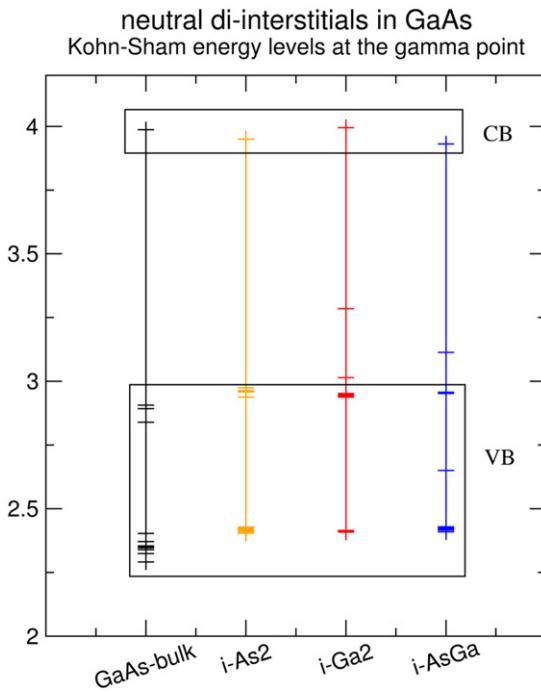


**Figure 3.** The mixed di-interstitial configuration viewed along two perpendicular  $\langle 110 \rangle$  directions (a) and (b).



**Figure 4.** The Ga<sub>2</sub> di-interstitial configuration viewed along two perpendicular  $\langle 110 \rangle$  directions (a) and (b).

shown in figure 4. The stable structure consists of three Ga atoms sharing one Ga lattice site. Two of the Ga atoms form a  $\langle 110 \rangle$  dumbbell while the third is very close to the tetrahedral



**Figure 5.** Kohn–Sham one-electron energy levels in the gap for the three intrinsic di-interstitials configurations, compared to the electronic structure of bulk GaAs.

site. As one can see, the coordination number of each Ga atom sharing the Ga lattice site is three, while each As atom bonded to one of the three Ga atoms is fivefold coordinated (the distance between the two Ga atoms forming the dumbbell is 22% longer than the As–Ga bond). The formation energy of the resulting structure is 4.5 eV, just 0.5 eV higher than for the isolated As(110) dumbbell [8]. The binding energy of this structure is 1.46 with respect to the most stable configuration, i.e. the tetrahedral one. This structure can also be considered as resulting from one Ga(110) dumbbell and one Ga tetrahedral. Using this as the reference, the binding energy would be  $E_b = E_{\text{Ga,dumb}}^f + E_{\text{Ga,tetra}}^f - E_{\text{Ga}_2}^2 = 2$  eV, still lower than the binding energy of the As<sub>2</sub> di-interstitial. The symmetry of the structure is C<sub>2v</sub> with a deviation of about 0.034% based on the distances and the angles. The mirror planes are two (110) planes: the one containing the three Ga atoms that share the Ga site and the one orthogonal to the Ga(110) dumbbell. The volume of the tetrahedron whose centre is the Ga site shared by the three Ga atoms and whose vertices are the four As atoms is increased by 28% over the volume of the tetrahedron in bulk GaAs.

### 3.2. Electronic structures

Let us now focus on the electronic properties of the studied complexes. In figure 5 the Kohn–Sham levels of As<sub>2</sub>, Ga<sub>2</sub> and mixed di-interstitials are compared against each other and those of perfect GaAs. As discussed in [8], the As<sub>2</sub> di-interstitial does not support any localized state in the gap, the extra levels associated with the interstitials being resonant in the valence band. The extra ten electrons of the di-interstitial mainly contribute to the bonding of the As atoms sharing the As site. Figure 6 shows the highest occupied state which, even though not fully localized, mainly contributes to As–As and As–Ga bonding at the di-interstitial.

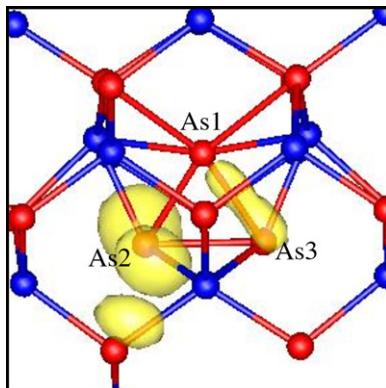


Figure 6. Iso-density plot of the highest occupied state in  $\text{As}_2$  di-interstitial.

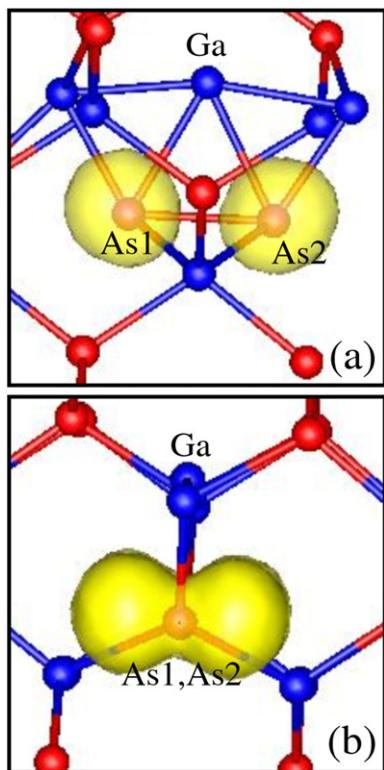
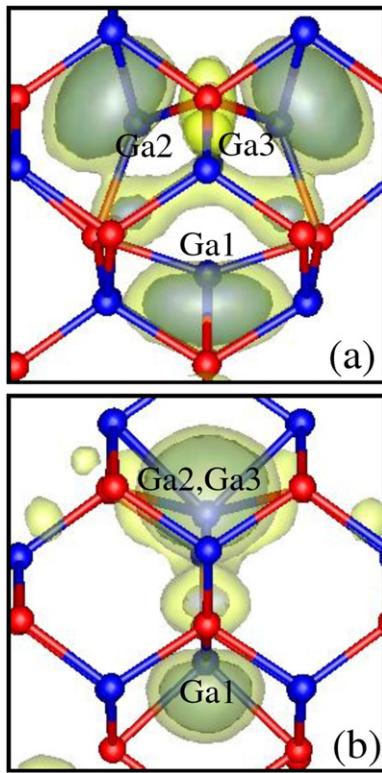


Figure 7. Iso-density plot of the highest occupied state in mixed di-interstitial.

The AsGa di-interstitial supports one localized level in the gap 150 meV above the valence band maximum. This corresponds to one spin degenerate state well localized around the complex; in particular this state is p-type and is located at the As atoms forming the dumbbell, as shown in figure 7.

Finally let us focus our attention on the complex made by two Ga interstitials. The electronic structure is characterized by two occupied one-electron states in the gap at about 60



**Figure 8.** Iso-density plots (higher (a) and lower (b) isodensity values) of the highest occupied state in  $\text{Ga}_2$  di-interstitial.

**Table 1.** Summary of calculated results for di-interstitial complexes.

	i-As <sub>2</sub>	i-AsGa	i-Ga <sub>2</sub>
Formation energy (eV)	5.8	4.8	4.5
Binding energy (eV)	2.35	2.24	1.46 (2.0)
Symmetry	$\text{C}_{1h}$	$\text{C}_{2v}$	$\text{C}_{2v}$
KS localized states	No	1	2
Local lattice dilation (%)	38	40	28

and 330 meV above the valence band maximum, respectively. The electron density distribution corresponding to the highest energy occupied state is quite complex, as shown in figure 8, where two electron density isosurfaces are shown. The higher electron density iso-surface (darker in figure 8) shows three lobes located near the three Ga atoms sharing the Ga lattice site. The lower isosurface (lighter in figure 8) shows that the electron density is also shared between the four As atoms bonded to the three Ga atoms so that the lobes are directed from the empty Ga sublattice site to the four As neighbours with a tetrahedral-like symmetry.

#### 4. Discussion

For a comprehensive discussion on the properties of the structures represented in the previous section let us summarize in table 1 the main results obtained.

All of the studied complexes show high values of binding energy, indicating that the interstitial aggregates are readily formed from migrating isolated interstitials. The highest energy gains arise in the case of As interstitials being involved in the complex and thus, particularly, in the case of the As di-interstitial.

On the other hand, the absolute values of the formation energy are higher when As interstitials are involved. When intrinsic interstitials are created (by ion bombardment, for instance) the clustering is energetically favoured particularly for As interstitials. In contrast, in as-grown GaAs, where the concentration of any point defect depends strictly on its formation energy, it is clear that the  $\text{Ga}_2$  di-interstitial is favoured over the other two complexes due to its relatively low formation energy, just 0.5 eV higher than the isolated As dumbbell formation energy. This complex is, however, less stable over the isolated interstitials than the  $\text{As}_2$  di-interstitials due to its lower binding energy. The mixed and Ga di-interstitials have similar structures with the same symmetry, while the ground state configuration of the i- $\text{As}_2$  is characterized by a lower degree of symmetry. The  $\text{Ga}_2$  di-interstitial is better accommodated in the host lattice than the others, as testified by the lower local distortion induced in the lattice. The electronic structures of the studied configurations show that the neutral di-interstitial containing Ga atoms have localized one-electron levels in the gap, while the  $\text{As}_2$  neutral di-interstitial does not induce gap states. This means that DLTS (deep level transient spectroscopy) or CTS (current transient spectroscopy) could presumably detect Ga containing neutral di-interstitials but not  $\text{As}_2$  neutral di-interstitials. The electrons occupying localized energy levels are paired, which excludes the detection of neutral di-interstitials by spin-resonance techniques such as EPR. Of course, this is not true for charged di-interstitials that are planned to be investigated in the near future in order to give a complete insight into di-interstitial properties. The simulation of charged configurations is also required to calculate the thermodynamic ionization levels that are far more robust than the one-electron levels in order to evaluate the electronic properties of the investigated structures. However, the one-electron levels can be still considered good indicators for the electronic properties of neutral di-interstitials, at least for a first insight into the problem.

## 5. Summary

We have investigated the building blocks of interstitial aggregates in GaAs, in order to address the problem of characterization of nano-aggregates in implanted GaAs. We have completed the approach of [8] simulating also Ga-containing neutral di-interstitials. The binding energy calculations show that As-containing di-interstitials are more stable than those containing Ga. This hierarchy is reversed in as-grown GaAs where, due to the lower formation energy of isolated Ga interstitials and  $\text{Ga}_2$  di-interstitials, the latter complex is more likely to form. Moreover, all the studied structures are not detectable by EPR: indeed, the neutral intrinsic di-interstitial in GaAs do not have any paramagnetic character because all the electrons are paired. Ga-containing di-interstitials in the neutral charge state should be detectable by DLTS and CTS because these complexes induce localized levels in the gap.

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