

## Properties of charged intrinsic di-interstitials in GaAs

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Stable intrinsic di-interstitials configurations in GaAs with different stoichiometric compositions are studied by first principles total-energy calculations. For each composition, fully relaxed stable and metastable structures have been obtained at different charge states to study the stability properties in different doping conditions and calculate the thermodynamic transition states, showing that the studied structures are stable against the isolated interstitials with large binding energies. The structural and electronic properties of the different configurations are also discussed in order to determine the relevant observables and to plan for possible future experiments aimed to detect them. In this context, we have focused particularly on different Ga di-interstitials configurations showing that the most stable one can be detected by means of state of the art deep level detection techniques, whereas more sophisticated experiments are required, involving symmetry and thermal activation processes, to detect As di-interstitials. Combining the different techniques in an sort of “differential diagnosis,” at least two of the three possible, stoichiometry dependent, di-interstitial configurations can be identified.

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### I. INTRODUCTION

The properties of intrinsic interstitials and their complexes are important mainly for ion implanted materials where, upon the annealing, these point defects can migrate and form stable aggregates affecting the electronic properties of the material. Thus, the study of intrinsic interstitials properties in GaAs by atomistic simulations has been first attempted in the beginning of the 1990s.<sup>1,2</sup> Moreover, due to the recent importance of these defects to understand the electrical properties of low-temperature grown As-rich GaAs and ion implanted samples, the main properties of intrinsic interstitials in GaAs have been recently revised by some authors,<sup>3-5</sup> taking advantage of the progress of the computational techniques and resources. In ion implanted GaAs, indeed, the collision cascades primed by the ions of the beam induce a large amount of Frenkel pairs (and thus of vacancies and interstitials) that are expected to recombine only partially upon the subsequent annealing; for low-temperature grown GaAs, As self-interstitials have been invoked to explain the measured As excess in the case of low temperature grown GaAs (Ref. 6) even though recent results seem to support the idea that the measured lattice dilation is due only to As antisites.<sup>7</sup> Moreover, it has been demonstrated that intrinsic self-interstitials mediate *p*-type dopants diffusion.<sup>8,9</sup>

The modeling of stable self-interstitial complexes in GaAs has been recently addressed by different authors using first principles total-energy calculations and tight binding molecular dynamics;<sup>4,5,10,11</sup> in particular, neutral di-interstitials have revealed large binding energies against the isolated self-interstitials, thus showing a strong tendency to form stable aggregates. Apart from some differences, basically belonging to the different approaches adopted, the main properties obtained with the two approaches agreed each other showing, besides similar geometry and binding energy, that As containing di-interstitials are characterized by larger binding energy than the Ga<sub>2</sub> complex.<sup>10,11</sup> Moreover, recent tight binding molecular dynamics simulations<sup>12</sup> evidenced

that complexes containing up to three interstitials (*I*<sub>3</sub> complexes) are stable against the components supporting the idea of further aggregation processes to form nanostructured defects similarly to the case of implanted and annealed Si.<sup>13-15</sup> This idea is also supported experimentally by high resolution transmission electron microscopy analyses<sup>16,17</sup> that evidenced postannealing residual nanosized defects probably originated by self-interstitial migration and clustering. However, small self-interstitial complexes such as *I*<sub>2</sub> and *I*<sub>3</sub> have not been directly observed so far.

In the previous papers, the electronic properties of neutral di-interstitials were analyzed in the frame of the adopted approaches looking at the relevant one-electron states, namely, the eigenenergy of the tight binding Hamiltonian and the Kohn-Sham states. However, it is known that Kohn-Sham eigenstates cannot be considered as true electron levels in the gap, while the electronic structure obtained in the frame of tight binding molecular dynamics is affected by the lack of accuracy inherent into the adopted scheme.

In this paper, we complete the scenario on intrinsic *I*<sub>2</sub> in GaAs calculating, in the frame of the density functional theory (DFT),<sup>18</sup> the properties of charged configurations and the thermodynamic transition states for the all the stable configurations with different stoichiometric compositions, namely, the As<sub>2</sub>, the Ga<sub>2</sub>, and the As<sub>1</sub>Ga<sub>1</sub> di-interstitials. Due to the lack of clear experimental data on di-interstitials in GaAs, this paper is also aimed to give support to future experiments that could be planned to detect such complexes.

### II. COMPUTATIONAL METHODS

As mentioned, we use the DFT approach in the frame of the local-density approximation (LDA).<sup>18</sup> The calculations are performed using the self-consistent total-energy pseudo-potential (PP) method. The Perdew-Zunger parametrization<sup>19</sup> of the Ceperley-Alder data<sup>20</sup> is used for the exchange-correlation energy. Norm-conserving Hamann PPs (Ref. 21) in the Kleinman-Bylander form<sup>22</sup> have been used for both Ga

and As atoms. We have used periodic boundary conditions and thus both the electron wave functions and density have been expanded in plane waves. It is well known that interstitial configurations are quite tricky for the convergence because the artifacts, arising mainly from the spurious elastic interaction and wave function overlap among the neighboring replicas of the simulation cell, tend to affect dramatically the simulation results.<sup>3,23</sup> Thus, in order to ensure the convergence, sufficiently large supercells must be used; indeed, for neutral di-interstitial, it has been shown that a good convergence can be obtained using cubic supercells containing 218 atoms, 216 GaAs lattice atoms, and two interstitials.<sup>3,10</sup> Moreover, due to the workload of this computational scheme, the first Brillouin zone sampling has been limited to the  $\Gamma$  point and the energy cutoff to 15 Ry. These choices have been demonstrated to ensure the convergence and the reliability of the obtained results for neutral di-interstitials<sup>3,10</sup> and are expected to give reliable results for charged states too, even in the case of heavily charged configurations.<sup>24</sup>

We use the LDA approximation also for unpaired spins because the energy difference with respect to spin-polarized calculations (local-spin-density approximation) has revealed to be small for intrinsic interstitials. The ground-state electron density for each atomic configuration has been obtained by the Williams-Soler algorithm,<sup>25</sup> whereas the atomic configurations of the studied complexes have been fully relaxed using the BFGS (Broyden-Fletcher-Goldfarb-Shanno) scheme.<sup>26</sup> All the calculations have been performed using a private distribution of the code FINGER. The well known formulation of Zhang and Northrup<sup>27</sup> has been used for the calculation of the formation energy that depends on the doping level of the material (through the electron chemical potential) and on the chemical composition of the investigated system. The formation energy  $\Omega$  of a neutral defect in GaAs is

$$\Omega = E_D - n_{\text{Ga}}\mu_{\text{Ga}} - n_{\text{As}}\mu_{\text{As}}, \quad (1)$$

where  $E_D$  is the total energy of the defect supercell containing  $n_{\text{Ga}}$  Ga and  $n_{\text{As}}$  As atoms and  $\mu_{\text{Ga}}$  and  $\mu_{\text{As}}$  are the Ga and As chemical potentials, respectively. Reminding that  $\mu_{\text{GaAs}} = \mu_{\text{Ga}} + \mu_{\text{As}}$ , Eq. (1) can be rewritten as

$$\Omega = E_D - \frac{1}{2}\mu_{\text{GaAs}}(n_{\text{Ga}} + n_{\text{As}}) - \frac{1}{2}(n_{\text{Ga}} - n_{\text{As}})(\mu_{\text{Ga}}^b - \mu_{\text{As}}^b + \Delta\mu), \quad (2)$$

where  $\mu_{\text{Ga}}^b$  and  $\mu_{\text{As}}^b$  are the chemical potentials of the relevant bulk phases and

$$\Delta\mu = (\mu_{\text{Ga}} - \mu_{\text{As}}) - (\mu_{\text{Ga}}^b - \mu_{\text{As}}^b). \quad (3)$$

The range where  $\Delta\mu$  may vary is defined by the constraint on the Ga/As chemical potentials that must be lower than the relevant bulk phase chemical potentials in order to avoid precipitation. Thus,

$$-\Delta H_f \leq \Delta\mu \leq \Delta H_f, \quad (4)$$

where  $\Delta H_f = \mu_{\text{GaAs}} - (\mu_{\text{Ga}}^b + \mu_{\text{As}}^b)$  is the heat of formation of bulk GaAs, which is experimentally known [ $\Delta H_f = 0.74$  eV

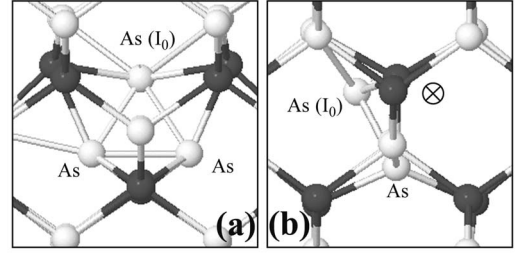


FIG. 1.  $\text{As}_2$  di-interstitial ground state configuration for the neutral complex as viewed along (a) the  $[110]$  and (b) the  $[1\bar{1}0]$  directions evidencing the  $C_{1h}$  symmetry: the symbol  $\otimes$  indicates the mirror site that  $I_0$  can occupy to form the equivalent  $\text{As}_2$  structure.

(Ref. 28)] and the lowest (highest) value corresponds to Ga (As) rich conditions.

All the terms on the right side of Eq. (2) can be calculated in the frame of the *ab initio* DFT scheme and thus the bulk Ga and As chemical potentials are needed for the formation energy calculation.<sup>29,30</sup>

In the case of charged configurations, the formation energy  $E_F$  depends also on the electron chemical potential  $\mu_e$  as follows:

$$E_F = \Omega + Q(\mu_e + E_V), \quad (5)$$

where  $Q$  is the charge state and  $E_V$  is the energy of the valence band maximum (VBM). The three different di-interstitials stoichiometric configurations, i.e., the  $\text{As}_2$ , the  $\text{Ga}_2$ , and the mixed di-interstitials have been investigated in all the charge states ranging from 3- to 3+. The Makov-Payne correction<sup>31</sup> has been applied to the electrostatic energy of the charged configuration for the adopted finite cubic supercell.

The binding energy is the energy gain of the complex with respect to the isolated interstitials,

$$E_b = (n_i^{\text{Ga}} E_F^{\text{Ga}_i} + n_i^{\text{As}} E_F^{\text{As}_i}) - E_F, \quad (6)$$

where  $n_i^{\text{Ga}}$  and  $n_i^{\text{As}}$  are, respectively, the numbers of Ga and As interstitials involved in the complex,  $E_F^{\text{Ga}_i}$  and  $E_F^{\text{As}_i}$  are the formation energies of the Ga and As isolated interstitials, and  $E_F$  is the formation energy of the complex.<sup>27</sup>

### III. RESULTS

#### A. $\text{As}_2$ di-interstitial

The ground state of the neutral  $\text{As}_2$  complex lies in the (111) habit plane and is characterized by  $C_{1h}$  symmetry as reported in Fig. 1. Figure 2 reports the formation energies of the different  $\text{As}_2$  charged states depending on the electron chemical potential for GaAs far from the As or Ga rich conditions ( $\Delta\mu=0$ ). It emerges that the stable charge states are 2+, 0, 1-, and 2- depending on the GaAs doping conditions. We found three thermodynamic transition states: one donor state (2+/0) at  $\mu_e \approx 0.1$  eV and two acceptor states, namely, (0/1-) at  $\mu_e \approx 1.11$  eV and (1-/2-) at  $\mu_e \approx 1.25$  eV. It is important to note that, concerning the donor states,  $\text{As}_2$  behaves as a “negative- $U$  system”<sup>32,33</sup> because the singly posi-

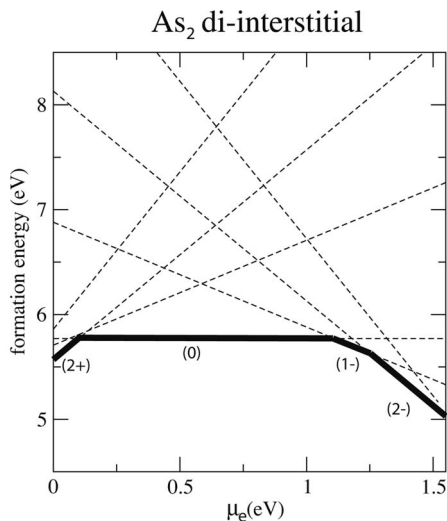


FIG. 2. Formation energy and thermodynamic transition states of the  $As_2$  complex.

tive charge state is metastable against the neutral and the doubly positive charge states and this is accomplished through a symmetry change: indeed, the doubly positive charge configuration undergoes through a structural distortion causing a marked deviation from the  $C_{1h}$  point group ( $\approx 25\%$ ). The symmetry breaking of the 2+ charge state with respect to the neutral configuration arises from the emptying of the topmost Kohn-Sham eigenstate that contributes to one of the As-As bonding involved in the complex. Moreover, the habit plane of the doubly charged  $As_2$  complex moves away from (111) toward (211) so that the structure appears distorted with respect the  $C_{1h}$  symmetry. Similar to the neutral configuration, the negatively charged stable configurations belong to the  $C_{1h}$  within the error inherent the present LDA calculation.

The length of the As-As bond lying along the  $[1\bar{1}0]$  direction does not differ much between the different stable charged configurations, being approximately 2.53/2.54 Å.

The formation energy plot must be shifted rigidly by  $\Delta H \approx 1$  eV (that is the theoretical value we have obtained with the chosen parameters) toward lower (higher) energy values in As (Ga) rich conditions. This shift, anyway, does not affect the obtained values of the thermodynamic transitions states but only the absolute value of the formation and binding energy that, for neutral  $As_2$ , results  $E_b = 2.35$  eV.<sup>10</sup>

### B. $As_1Ga_1$ di-interstitial

The stable mixed di-interstitial is  $C_{2v}$  symmetric and is located at an As site in analogy with the  $As_2$  case (see Fig. 3).

If one looks at the (110) habit plane, the Ga interstitial is located above the As dumbbell, in the upper channel along the  $[1\bar{1}0]$  direction so that the triangle appears to be centred at the As lattice row. The formation energy of the mixed di-interstitial for the investigated charge states is reported in Fig. 4 for stoichiometric GaAs ( $\Delta\mu = 0$ ). Equation (2) shows

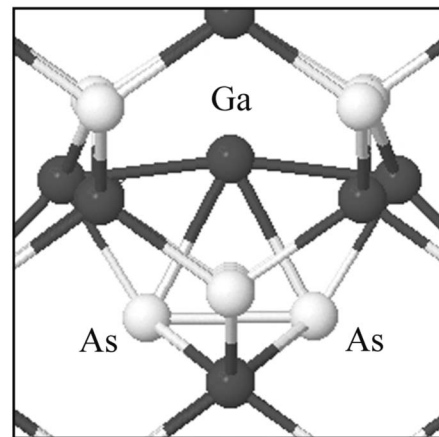


FIG. 3.  $As_1Ga_1$  di-interstitial ground-state configuration viewed along the  $[110]$  direction.

that in the present case, the formation energy plot does not change for different thermodynamic conditions because the term containing  $\Delta\mu$  is proportional to  $n_{Ga} - n_{As} = 0$ . The thermodynamic transition states are  $(1+/0)$ ,  $(0/1-)$ , and  $(1-/2-)$  at, respectively,  $\mu_e = 0.07$  eV,  $\mu_e = 1.1$  eV, and  $\mu_e = 1.23$  eV above the VBM. The stable charged configurations, namely, 1+, 1-, and 2-, keep the same  $C_{2v}$  symmetry as the neutral configuration within the error bar of the present calculation and thus the thermodynamic transition states do not depend on the symmetry properties of the stable configurations. The geometrical parameters that characterize the different stable charged configurations are basically the lengths of the As-As dumbbell and of the As-Ga bonds belonging to the complex: the length of the As dumbbell is the same for the negatively charged and neutral states (about 2.53 Å), while it is shorter ( $\approx 3\%$ ) for the singly positive charge state. The As-Ga bond lengths of the neutral and sin-

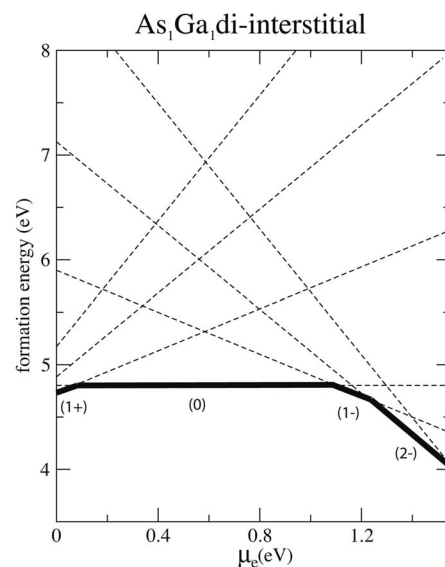


FIG. 4. Formation energy and thermodynamic transition states of the  $As_1Ga_1$  di-interstitial complex.

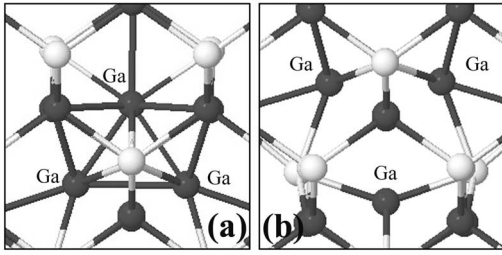


FIG. 5. Equilibrium atomic configurations for (a) type I and (b) type II Ga di-interstitials viewed along the  $[110]$  direction.

gly negative configurations are nearly the same ( $\approx 2.68 \text{ \AA}$ ), while are larger ( $\approx 1.6\%$ ) for the singly positive configuration and shorter ( $\approx 0.5\%$ ) for the doubly negative charge state. The binding energy for the neutral configurations is  $E_b = 2.24 \text{ eV}$ .<sup>10</sup>

### C. Ga<sub>2</sub> di-interstitial

Due to the fact that the mixed and the As<sub>2</sub> stable complexes are located at an As lattice site, we have first studied the structure involving one Ga lattice atom and two Ga interstitials forming a triangle that is centred at an As lattice row. The structure obtained after the relaxation is reported in Fig. 5(a): the Ga isosceles triangle lies in the  $(110)$  plane in between two As lattice atoms whose distance is slightly enlarged.

The other structure (type II Ga<sub>2</sub>) is obtained from two interstitials: one Ga(110) dumbbell at the Ga site and one Ga interstitial located at the closest tetrahedral site. The resulting structure is shown in Fig. 5(b): it is basically made of three Ga atoms (one lattice atom and two interstitials) sharing the Ga site that was formerly occupied by the Ga lattice atom.

Both of the above structures are  $C_{2v}$  symmetric within the error bar of the present DFT-LDA scheme. The formation energy plot for the two structures are shown in Fig. 6 and

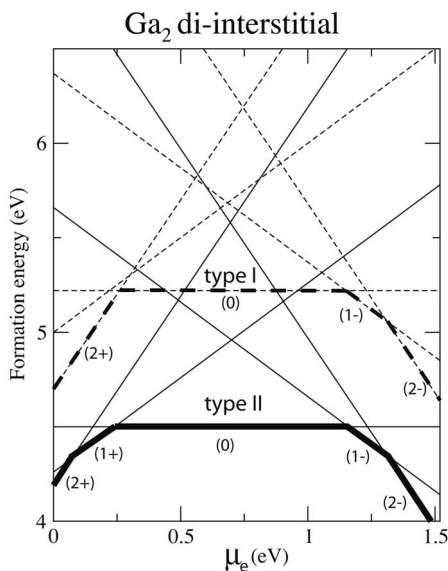


FIG. 6. Formation energy and thermodynamic transition states of type I and type II Ga<sub>2</sub> complexes.

evidence that the type II Ga<sub>2</sub> complex is the stable configuration, while the type I Ga<sub>2</sub> complex is metastable. The type I Ga<sub>2</sub> complex has one deep donor transition ( $2+/0$ ) at  $0.26 \text{ eV}$  and two deep acceptor transitions ( $1-/0$ ) and ( $2-/1-$ ) at  $1.15$  and  $1.3 \text{ eV}$ , respectively. The stable type II Ga<sub>2</sub> complex has four deep traps: two donors ( $2+/1+$ ) and ( $1+/0$ ) at  $0.06$  and  $0.24 \text{ eV}$ , respectively, and two deep acceptors ( $0/1-$ ) and ( $1-/2-$ ) at  $1.16$  and  $1.31 \text{ eV}$ , respectively. It is worth to note that the two Ga<sub>2</sub> complexes have the same acceptor levels and thus the two complexes can be distinguished only by looking at the donor levels; indeed, in the first case, we have a negative- $U$  system<sup>32-34</sup> at  $0.26 \text{ eV}$ , while in the second case we have, besides a deep donor with similar energy ( $0.24 \text{ eV}$ ), another donor level that is very close to the valence band maximum. The negative- $U$  system of type I Ga<sub>2</sub> is accomplished because the neutral charge state undergo a structural transition to an isosceles triangle from the nearly equilateral triangle we have in the case of the doubly positive charge state. Similar to the As<sub>2</sub> case, the thermodynamic transition states are unaffected by the growth condition (As rich or Ga rich conditions) because the curves shown in Fig. 6 shift rigidly toward larger or smaller formation energy values for As rich and Ga rich conditions. The binding energy for the neutral state of the stable type II Ga<sub>2</sub> complex is  $E_b = 1.46 \text{ eV}$ .<sup>10</sup>

### D. As<sub>2</sub> barrier

Among the different  $I_2$  complexes reported here, the As<sub>2</sub> di-interstitial is the only one showing the  $C_{1h}$  symmetry similar to the  $I_2$  complex in Si.<sup>15</sup> This is related to the existence of a specular ground state configuration that is obtained if the As interstitial (marked as  $I_0$  in Fig. 1) occupies the opposite site along the  $[110]$  direction [marked in Fig. 1(b)] with respect to the  $(\bar{1}\bar{1}0)$  plane containing the As dumbbell. The two equivalent specular ground-state configurations are separated by an energy barrier that can be also considered as a diffusion-reaction energy barrier of an isolated interstitial moving along the  $[110]$  channel close to a ground state As dumbbell interstitial.

This energy barrier has been calculated by moving the  $I_0$  As interstitial along the  $[110]$  channel step by step, each of them being  $0.14 \text{ \AA}$  close to the saddle point and  $0.28 \text{ \AA}$  far from it. After moving  $I_0$  one step along the channel, the structure has been optimized with the constraint that  $I_0$  is allowed to relax only in the  $(110)$  plane, while all the other atoms can move freely. We have thus found the ground-state structure for each intermediate diffusion step consisting of a distorted As<sub>2</sub> complex with the  $I_0$  As atom belonging to each of the  $(110)$  planes we have ideally located along the diffusion path. The formation energy plot along the  $[110]$  diffusion channel evidenced the existence of an energy barrier for each of the As<sub>2</sub> charge configurations that resulted stable at different doping conditions (namely, the  $2-$ ,  $1-$ ,  $0$ , and  $2+$  charge states).

Moreover, we have calculated the energy barrier also for the singly positive charge state to study the behavior of the negative- $U$  system when  $I_0$  is moved along the  $[110]$  diffusion path. The calculated diffusion barriers are reported in

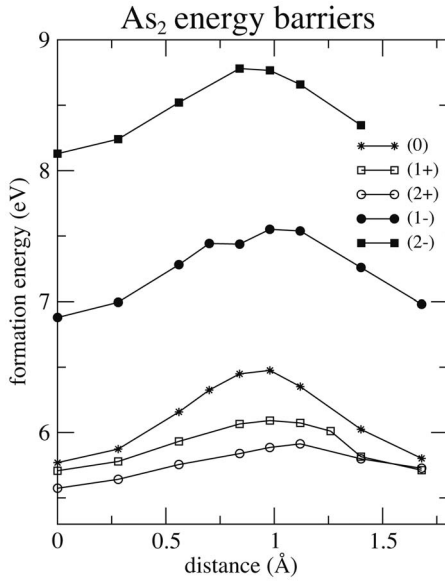


FIG. 7. Formation energy barriers for different charge states of the  $\text{As}_2$  complex calculated for  $\mu_e=0$ . The barriers are meant concerning the  $I_0$  atom moving along the  $(110)$  direction (see the text).

Fig. 7 for the case of  $\mu_e=0$  eV. For each diffusion step, the formation energy difference between the neutral and the negatively charged states is roughly the same indicating that the acceptor states are nearly unaffected by the diffusion process; on the contrary, the energy and the charge of the donor states depend very much on the localization along the diffusion path due to the different energy changes of the neutral and the positive charge states.

As shown in Fig. 7, the neutral and the negative charge states have similar barriers at the saddle point  $0.65 \text{ eV} \leq E_d \leq 0.7 \text{ eV}$ . On the contrary, the positively charged configurations experience an energy barrier that is much lower than the one for neutral  $\text{As}_2$ : indeed, we have found  $E_d=0.3 \text{ eV}$  for the singly positive charge state and  $E_d \approx 0.34 \text{ eV}$  for the doubly positive charge state. The thermodynamic transition states at the saddle point for the neutral  $\text{As}_2$  (approximately  $1 \text{ \AA}$  away from the ground state position along the  $[110]$  channel) reveal two donor states ( $2+/1+$ ) and ( $1+/0$ ) at  $\mu_e \approx 0.2$  and  $\mu_e \approx 0.4 \text{ eV}$ , respectively while, as already mentioned, the acceptor transitions are very similar to the ones found for the ground state configurations. The different energy barriers found for the neutral and the positively charged configurations imply that the negative- $U$  behavior involving these configurations should be suppressed at certain point of the  $[110]$  diffusion path.

Moreover, noting that the formation energy values for the curves plotted in Fig. 7 refer to the case  $\mu_e=0$ , it comes out that for different values of the electron chemical potential, the curves concerning the charged states must be shifted rigidly to smaller or larger values and thus could cross each other. This means that the diffusion of the  $I_0$  As atom is enhanced for  $p$ -type doping conditions with  $\mu_e \leq 0.4 \text{ eV}$ : as the diffusion process proceeds, indeed, the charge reaction

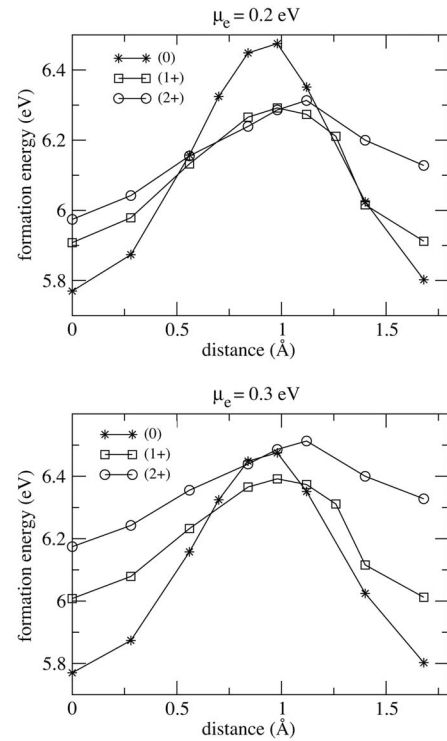


FIG. 8. Charge reaction enhanced diffusion of  $I_0$  for the  $\text{As}_2$  configuration (see the text) in  $p$ -type GaAs with different doping levels: (top)  $\mu_e=0.2 \text{ eV}$  and (bottom)  $\mu_e=0.3 \text{ eV}$ .

$\text{As}_2^0 \Rightarrow \text{As}_2^+ + e$  is favored by atomic relaxation and thus the diffusion barrier is reduced. This is accomplished by the fact that the negative- $U$  behavior of the neutral and the positive charged states is clearly found only at the ground-state position for  $I_0$  and practically disappears just after the first diffusion step along the  $[110]$  direction. This is evidenced in Fig. 8 where it is reported the formation energy barriers for the neutral and the positive charged states with two different values of the electron chemical potential, namely,  $\mu_e = 0.2 \text{ eV}$  and  $\mu_e = 0.3 \text{ eV}$ .

#### IV. DISCUSSION AND CONCLUSIONS

From the above described data, it emerges that the type II  $\text{Ga}_2$  di-interstitial is the one with the lowest formation energy and thus with the highest concentration in as-grown stoichiometric GaAs. However, if we deal with irradiated GaAs, where self-interstitials are introduced by the collision cascades, the binding energy is the quantity one should look at to evaluate the stability and the concentration of di-interstitials. As already mentioned in the text, previous total energy calculations<sup>10</sup> have demonstrated that neutral  $I_2$  complexes have quite large binding energies, particularly when As interstitials are involved. Therefore, in irradiated GaAs, it is most likely that  $I_2$  centers are present and eventually aggregate in larger complexes and, in this sense, the  $\text{As}_2$  seems to be favored due to its largest energy gain versus the isolated interstitials.

TABLE I. Thermodynamic transitions for the ground-state configurations of  $I_2$  complexes in GaAs.

Di-interstitial	Donor states		Acceptor states	
As <sub>2</sub>	(0/2+)		(0/1-)	(1-/2-)
	$E_v+0.1$ eV		$E_v+1.11$ eV	$E_v+1.25$ eV
As <sub>1</sub> Ga <sub>1</sub>	(0/1+)		(0/1-)	(1-/2-)
	$E_v+0.07$ eV		$E_v+1.1$ eV	$E_v+1.23$ eV
Ga <sub>2</sub>	(1+/2+)	(0/1+)	(0/1-)	(1-/2-)
	$E_v+0.06$ eV	$E_v+0.34$ eV	$E_v+1.16$ eV	$E_v+1.31$ eV

In spite of the data indicating the role played by self-interstitials in diffusion processes,<sup>8,9</sup> there is still no conclusive experimental result showing the existence of intrinsic interstitials in stable configurations. However, they are expected to be highly mobile and thus it has been thought that the reason why they are invisible is related to the formation of stable complexes in which they are involved. Recent results<sup>3,10,11</sup> suggest that  $I_2$  complexes could be considered good candidates to explain the invisibility of self interstitials due to the large binding energy involved in these complexes, certainly larger than the one obtained for the complexes involving also antisites that are commonly invoked as responsible for the invisibility of self-interstitials.

However, in spite of these theoretical results strongly supporting the existence of  $I_2$  complexes in GaAs and their tendency to aggregate further, they have not been experimentally detected so far as already mentioned in Sec. I. This is also due to the lack of good predictions on the properties of  $I_2$  complexes that could eventually drive the interpretation of experimental data. Thus, the main property one should investigate is the possible existence of trap levels eventually related to  $I_2$  complexes and, to this aim, we have first of all calculated the thermodynamic transition states of di-interstitials. The above reported results concerning the  $I_2$  related traps are summarized in Table I. The main characters that emerge from these data are that both acceptor and donor traps are quite deep in the gap that makes difficult their detection by state of the art methods such as deep level transient spectroscopy (DLTS), photoinduced current transient spectroscopy (PICTS), or similar techniques.

The calculated formation energy plots evidence also that  $I_2$  complexes are most likely neutral both in  $p$ -type and  $n$ -type irradiated GaAs and, as a consequence, they result also invisible by electron paramagnetic resonance (EPR) because all of them have paired electrons in the neutral state. However, in principle, it should be possible to distinguish at least the Ga<sub>2</sub> di-interstitial from the other two complexes due to the (0/1+) donor state at  $E_v+0.34$  eV; on the contrary, the other traps are characterized by quite similar energy values independently on the stoichiometry of the  $I_2$  complex (see, for example, the acceptor states of the different complexes). In particular, it is worth to evidence that among the cited difficulties, the standard experimental techniques seem

unfit to detect the double donor at  $E_v+0.1$  eV that is the As<sub>2</sub> peculiar fingerprint due to the fact that this donor trap energy is extremely deep and very similar to the donor trap of the As<sub>1</sub>Ga<sub>1</sub> complex.

Intrinsic interstitials and di-interstitials have been ignored for long time due to their low concentration in as grown materials (related to their high formation energy) and to the lack of experimental evidences concerning them. However, the present results show that  $I_2$  formation in implanted GaAs (for instance) is strongly supported by the calculated binding energy data. Moreover, we have also demonstrated that the traditional deep trap experimental techniques, such as PICTS and DLTS, are suitable to detect the Ga<sub>2</sub> complex only, thanks to the well evidenced deep donor trap at  $E_v+0.34$  eV, whereas both the As<sub>2</sub> and the Ga<sub>1</sub>As<sub>1</sub> complexes seem invisible in the context of the trap detection techniques. Actually, it must be evidenced that even the Ga<sub>2</sub> complex is difficult to be accessed in the usual temperature range of DLTS or PICTS due to the deepness of the trap level found and thus, maybe, photoconduction spectroscopy should be more convenient. However, using the symmetry properties of the As<sub>2</sub> di-interstitial, it is shown that experiments can be planned to identify and distinguish it from the other two complexes and particularly from the As<sub>1</sub>Ga<sub>1</sub> mixed di-interstitial. Indeed, differently from the other  $I_2$  complexes that are  $C_{2v}$ , the As<sub>2</sub> complex, belongs to the  $C_{1h}$  point group and thus is characterized by one mirror plane only; therefore, for the As<sub>2</sub> complex, there are two equivalent ground state configurations that are separated by an energy barrier at the  $C_{2v}$  saddle point along the [110] channel. The transition between the two equivalent configurations is therefore thermally activated with an activation barrier depending on the charge state and the doping conditions. Thus, due to the thermal activation, we can expect that part of the As<sub>2</sub> point defects fluctuate between the two equivalent  $C_{1h}$  configurations appearing, in the average, as  $C_{2v}$ . If one takes into account this phenomenon, the energy barriers calculated for the neutral and the positive charge states, together with the formation energy plot versus the electron chemical potential, give us another possible observable that could be investigated to evidence the presence of As<sub>2</sub> in  $p$ -type GaAs. From Fig. 8, indeed, it comes out that in  $p$ -type GaAs, for instance, with  $\mu_e=0.2$  eV, the As<sub>2</sub> symmetry should change from  $C_{1h}$  to  $C_{2v}$  with an activation energy of about 0.52 eV; this is accomplished by a “charge reaction”  $As_2^0 \Rightarrow As_2^+ + e$  that arises

with an activation energy of 0.32 eV. Therefore, in these conditions ( $p$ -type GaAs with  $\mu_e=0.2$  eV), temperature dependent EPR should be able to detect  $\text{As}_2^+$  with a thermal activation energy of 0.52 eV and common values of the pho-

ton energy and the magnetic field, while trap detection techniques should be able to evidence the donor level at  $E_T \approx E_v + 0.32$  eV if are used experimental techniques suitable to access very deep electron traps.

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