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Migration barriers of neutral As di-interstitials in GaAs

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Abstract. The recent discovery of intrinsic di-interstitial stability against the isolated self-interstitial point defects in GaAs has evidenced the importance of such complexes in, for instance, irradiated GaAs. In this paper, we illustrate and discuss diffusion of such complexes in comparison with isolated self-interstitials. In particular, the diffusion barriers of neutral di-interstitials have been calculated in the framework of density functional theory, showing that, in addition to their being stable, di-interstitials can also diffuse rapidly through the lattice, similarly to isolated self-interstitials.

Contents

1. Introduction

Intrinsic interstitials in elemental and compound semiconductors have recently been considered for modelling the core structure of extrinsic extended defects in implanted and annealed semiconductors [1, 2]. In low-temperature grown gallium arsenide, the measured arsenic excess

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has been related to the formation of As interstitials [3] or, alternatively, to As antisites [4]. Moreover, intrinsic interstitials have been demonstrated to play a crucial role in the diffusion processes of p-type dopants in GaAs [5, 6]. However, differently from vacancy and antisite studies [7–10], pieces of experimental evidence for self-interstitials in III–V compound semiconductors are rare and indirect, being often inferred from diffusion experiments of dopant species [5, 6, 11, 12] or from the observation of extended defects [13–17]. Theoretical predictions of the intrinsic interstitials' main properties in GaAs have been attempted since the beginning of the 1990s in the framework of the density functional theory (DFT) with limited computational resources [18, 19]; then, this matter has recently been revised taking advantage of the enormous improvement in computational techniques and resources over the last 20 years [20–28]. The theoretical study of small complexes involving intrinsic interstitials in GaAs has evidenced that di-interstitials are stable against the components independently of their stoichiometric ratio [24, 28]. Moreover, it has been shown that, except for heavily doped GaAs, ground-state di-interstitial configurations are in the neutral charge state for a wide range of the electron chemical potential. Hence, in ion implanted semiconductors, for instance, it may happen that not all the Frenkel pairs recombine and self-interstitials, thanks to their high mobility, can migrate and form di-interstitial complexes. Recently, a semi-empirical tight-binding molecular dynamics scheme was employed to study the ground-state configurations of self-interstitial aggregates I_n with $n \geqslant 2$ showing that I_5 behave as a stable 'building block' of the core structure of extended defects in GaAs [1]; moreover, on the basis of the binding energy values calculated, it was demonstrated that both single interstitials I_1 and di-interstitials I_2 may participate in the aggregation processes favouring the coalescence of large aggregates. However, aggregation in large clusters may effectively take place only if I_1 and I_2 are able to migrate fast. While it is commonly recognized that isolated self-interstitials are quite mobile [5, 6, 11], no data are available concerning di-interstitials to the authors' knowledge. In this paper, we report and discuss the calculations of diffusion energy barriers encountered by As-based di-interstitials in GaAs.

2. Computational method

All the calculations have been performed in the framework of time-independent DFT with the spin-unpolarized local density approximation (LDA) for the exchange-correlation functional [29] that was revealed to be appropriate also for isolated interstitials [20, 24, 28]; the exchange-correlation energy and potential have been calculated with the Perdew–Zunger parametrization [30] of the Ceperley–Alder data [31]. The ionic potentials have been replaced by norm conserving Hamann-type pseudopotentials [32] in the Kleinman–Bylander form [33] for both Ga and As atoms. All the calculations have been performed using periodic boundary conditions and plane wave expansions of the electron wave functions and density. It is well known that convergence may be quite tricky for interstitials due to the possible artifacts that arise from the spurious elastic interaction and wavefunction overlap among the supercell replicas [20, 34]. As a consequence, sufficiently large cubic supercells have been employed, containing 218 (217) atoms, 216 GaAs lattice atoms and two (one) interstitials, which, as already shown in previous papers, guarantee the convergence by sampling the first Brillouin zone at the Γ point and by using an energy cutoff of 15 Ry for the wavefunctions [20, 24, 28]. This computational scheme is appropriate even in the case of heavily charged configurations [28, 35]. The ground-state electron density for each atomic configuration has been obtained by the

Williams–Soler algorithm [36], whereas the ground-state atomic configurations of the studied complexes have been fully relaxed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) scheme [37].

The energy barriers for diffusion along various directions have been calculated at 0 K, i.e. without the entropic term; in particular, some of the principal lattice directions, such as [100], [110], [111] etc, have been taken into account as detailed in the next section. Moreover, due to the geometry and the symmetry properties of the various I_1 and I_2 configurations studied, the directions belonging to the $\langle 110 \rangle$ set that are equivalent in a perfect lattice are actually different for diffusion and therefore have been checked accordingly. It is known that the LDA approximation of the exchange-correlation functional results in an underestimation of the band gap; however, the properties here investigated depend only on the total energy that is much more robust in the LDA fashion. Concerning the migration barriers, indeed, the LDA approximation may either underestimate or overestimate the generalized gradient approximation (GGA) calculations, being sometimes closer to the experimental results [38, 39]. Recent migration barrier calculations of vacancies and interstitials in GaAs, performed using LDA, have shown similar results to the ones obtained with the Perdew, Burke and Ernzerhof (PBE), at least concerning interstitials [25, 40]. In any case the As migration barriers have been re-calculated as reference values, as the main aim of this paper is to compare the diffusion barriers of I_2 complexes to the isolated interstitial ones. The energy landscapes for diffusion have been sampled by moving the atoms of the complex along the chosen direction step by step: after each step, the structure has been fully relaxed, except for the moved atom that is constrained to relax in the plane orthogonal to the direction of motion. The criterion for convergence has been defined as $\Delta E \leqslant 10^{-6}$ eV of the total energy for four consecutive iterations. The step length has been chosen depending on the distance from the 'saddle point', being 0.14 Å close to it and 0.28 Å elsewhere. The adopted technique is based on the projected conjugate gradient (PCG) method proposed recently [41] and closely resembles the popular nudged elastic band method [42] used for the minimum energy path search; in the present case, instead, the adopted PCG method appears more appropriate because also larger barriers, i.e. the ones found for diffusion along various directions, were calculated. The same technique has recently been used to study the bi-stability properties of charged As di-interstitials in GaAs [28]. All the calculations have been performed with a private distribution of the code FINGER[2].

The binding energy calculations are based on the Zhang and Northrup formulation of the defects formation energy [44] and on the related experimental and theoretical data concerning the bulk phases involved [45–47]. We recall here that the formation energy of a given neutral defect in GaAs is

$$E_F = E_D - n_{Ga}\mu_{Ga} - n_{As}\mu_{As}, \tag{1}$$

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

$$E_F = E_D - \tfrac{1}{2}\mu_{GaAs}\left(n_{Ga} + n_{As}\right) - \tfrac{1}{2}\left(n_{Ga} - n_{As}\right)\left(\mu_{Ga}^b - \mu_{As}^b + \Delta\mu\right), \tag{2}$$

where μ_{Ga}^b and μ_{As}^b are the chemical potentials of the relevant bulk phases and

$$\Delta\mu = \left(\mu_{Ga} - \mu_{As}\right) - \left(\mu_{Ga}^b - \mu_{As}^b\right). \tag{3}$$

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[2] FINGER (FINnish General Electron Relaxator) is based on the techniques detailed in the paper by Laasonen *et al* [43] and was developed at Helsinki University of Technology, Espoo, Finland.
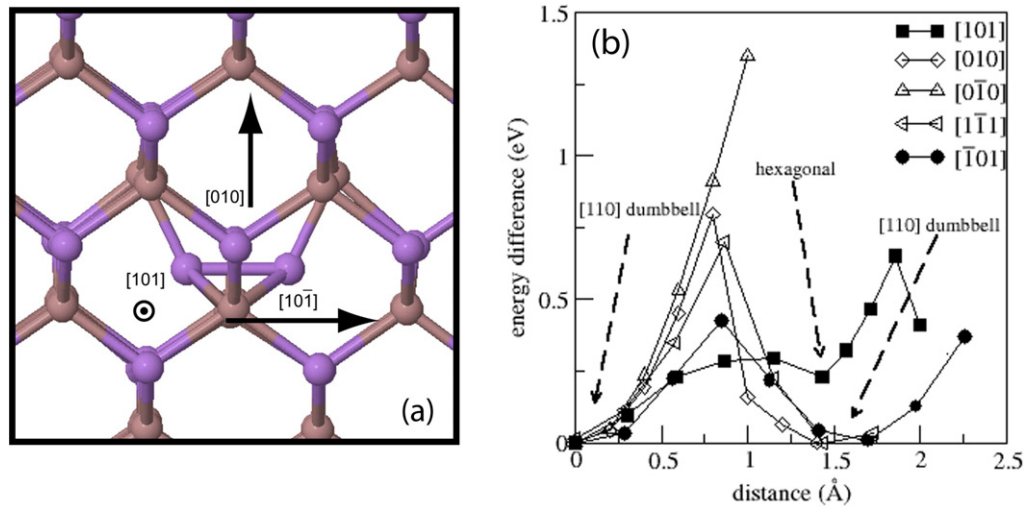
Figure 1. The As dumbbell self-interstitial diffusion. (a) Geometry and reference lattice directions; (b) landscape of the energy difference obtained by moving the As interstitial along some of the principal lattice directions; the total energy refers to that of the As dumbbell self-interstitial ground-state configuration.

The binding energy of a di-interstitial is the energy gain of the complex with respect to the isolated interstitials; thus, given the formation energy of the di-interstitial E_F, its binding energy is

$$E_b = \left(n_i^{Ga} E_F^{Ga_i} + n_i^{As} E_F^{As_i} \right) - E_F, \tag{4}$$

where n_i^{Ga}, n_i^{As} are respectively the numbers of Ga and As interstitials involved in the complex, and $E_F^{Ga_i}$, $E_F^{As_i}$ are the formation energies of the Ga and As isolated interstitials [44].

3. Results and discussion

We have preliminarily calculated the diffusion barriers of As self-interstitials whose ground-state configuration is the 'As [110] dumbbell', namely a dumbbell configuration at an As lattice site with the As–As site bond aligned along one direction of the ⟨110⟩ set [11, 18–20].

Thus, taking one As dumbbell along the [10$\bar{1}$] direction (see figure 1(a)), we have calculated its diffusion barriers along some of the principal lattice directions following the prescriptions detailed in the previous section. The results are shown in figure 1(b) where the total energy and the position of the As atom refer, respectively, to the same quantities measured in the case of a stable, fully relaxed As dumbbell. The lowest-energy path occurs by moving the As atom along the [101] direction, that is perpendicular to the dumbbell axis, and is characterized by an energy barrier of $\Delta E \approx 300$ meV between the dumbbell and the hexagonal configurations, the last one being 230 meV higher in energy. Moving the As atom further along [101], a tetrahedral configuration with four Ga neighbours is finally obtained. If the As atom moves along the dumbbell axis, a larger energy barrier of $\Delta E \approx 420$ meV is experienced between two adjacent ground-state dumbbell configurations, the saddle point consisting of a tetrahedral As self-interstitial. The barriers sampled as the As interstitial is moved along the [010] and [1$\bar{1}$1] directions are larger, being respectively $\Delta E \approx 700$ meV and $\Delta E \approx 800$ meV: when these
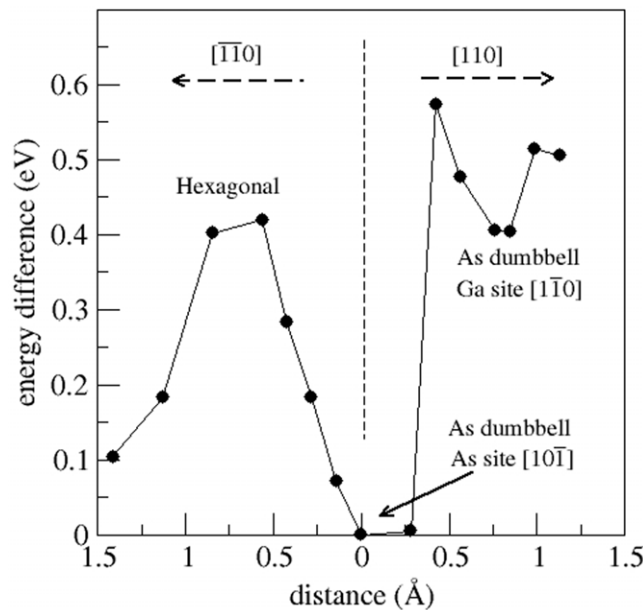
Figure 2. Total energy landscapes sampled along the [110] lattice direction for diffusion steps of the As interstitial; the total energy refers to that of the As dumbbell self-interstitial ground-state configuration.

barriers are exceeded, a $\langle 110 \rangle$ dumbbell configuration oriented differently is still present at the same lattice site. The [$10\bar{1}$] ground-state As dumbbell configuration may also move along another non-equivalent direction of the $\langle 110 \rangle$ set, namely the out of plane [110] one (or the [$\bar{1}\bar{1}0$] one) that forms an angle $\theta = 60^\circ$ with respect to the dumbbell axis. If the As atom moves along [$\bar{1}\bar{1}0$], a hexagonal configuration is encountered before forming another As dumbbell at a different As lattice site, while if it is moved along [110], the As atom approaches a Ga site forming there a dumbbell along [$1\bar{1}0$] that is 400 meV higher in energy (see figure 2).

This last case deserves further consideration: from this complex, indeed, either As or Ga diffusion may occur from the original Ga lattice site: in the first case, As migration along [110] results in the formation of a ground-state As [101] dumbbell at the adjacent As lattice site from which the As interstitial can diffuse further, as already detailed previously; in the second case, instead, a different energy landscape is sampled for Ga diffusion along the two orthogonal [101] and [$10\bar{1}$] directions, as shown in figure 3(a); the large energy barrier measured seems to suggest that the substitution reaction $As_i + Ga \rightarrow As_{Ga} + Ga_i$ is unlikely; however, a low reaction energy path can be found if the structure obtained at the fifth diffusion step along [101] is fully relaxed: from the relaxed configuration, indeed, diffusion can proceed further along the [$10\bar{1}$] orthogonal direction, resulting in a low-energy 'zigzag' diffusion path for Ga (see figure 3(b) and the relevant diffusion barrier reported in table 1), showing that As antisites may form easily as a consequence of As diffusion in GaAs via the substitution reaction $As_i + Ga \rightarrow As_{Ga} + Ga_i$.

Concerning the di-interstitials, we have first examined the diffusion properties of the stoichiometric As_1Ga_1 complex. Its ground-state configuration has recently been studied by both total energy *ab initio* calculations and tight binding [24, 26, 28], and is characterized by an isosceles triangular structure in the (101) plane (with a C_{2v} point group symmetry) made of two interstitials and one As atom sharing one As lattice site and with the As–As bond aligned
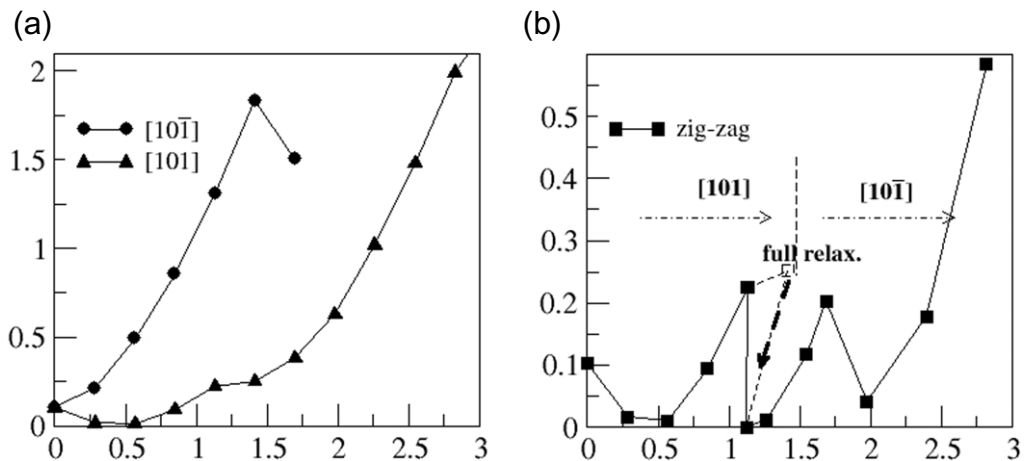
(a)

(b)

Figure 3. (a) Energy differences sampled in a substitution reaction at the Ga site $As_i + Ga \rightarrow As_{Ga} + Ga_i$ along two directions of the $\langle 110 \rangle$ set; (b) the same energy differences obtained in a zigzag diffusion with one intermediate step fully relaxed (see the text).

Table 1. Lowest-energy barriers for diffusion along the relevant lattice directions of the I_1 and I_2 configurations studied. In the last column are reported the meta-stable configurations obtained as soon as the barriers are exceeded.

Starting configuration	Lattice direction	ΔE (meV)	Final configuration
As_1 dumbbell	[101]	300	Hexagonal (unstable)
Ga_1 substitution reaction	$[101] \rightarrow [\bar{1}01]$	225	As antisite + Ga_1 tetrahedral
As_1Ga_1	$[\bar{1}01]$	290	Figure 5(b)
As_2	$[101]/[\bar{1}01]$	550	Figures 6(f)/(h)

along, for example, the $[10\bar{1}]$ direction. In figure 4 are reported the energy landscapes sampled as either one of the two As or Ga atoms of the complex are moved along the principal lattice directions. Low migration barriers of $\Delta E \approx 290$ and $\Delta E \approx 360$ meV are measured if As moves along $[\bar{1}01]$ and [101], respectively. In the first case, as the As atoms moves, the As–As bond is stretched and the Ga interstitial is dragged in the same direction so that the As_1Ga_1 complex migrates almost rigidly (with a barrier even smaller than that measured for As dumbbells) jumping from an As row to an adjacent Ga row where the di-interstitial geometry is reversed (see figure 5(b)). If the As atom is moved in the opposite direction (i.e. $[10\bar{1}]$), the diffusion pattern observed is almost the same but as the As–As bond is compressed, a larger energy barrier of about 500 meV is measured before getting again the As_1Ga_1 ground-state configuration. In the second case, the As atom moving along [101] still experiences, at least initially, a small energy barrier (but larger than the previous case) because, after the first few steps, a new meta-stable configuration, unknown before, is obtained that consists of one As and one Ga self-interstitial placed at adjacent tetrahedral sites and interacting with each other (see figure 5(c)) and is about 340 meV larger in energy than the ground state.

The As_1Ga_1 di-interstitial may also diffuse via Ga and the migration energies sampled in this case are shown in figure 4; while migration is inhibited along [010], it is favoured
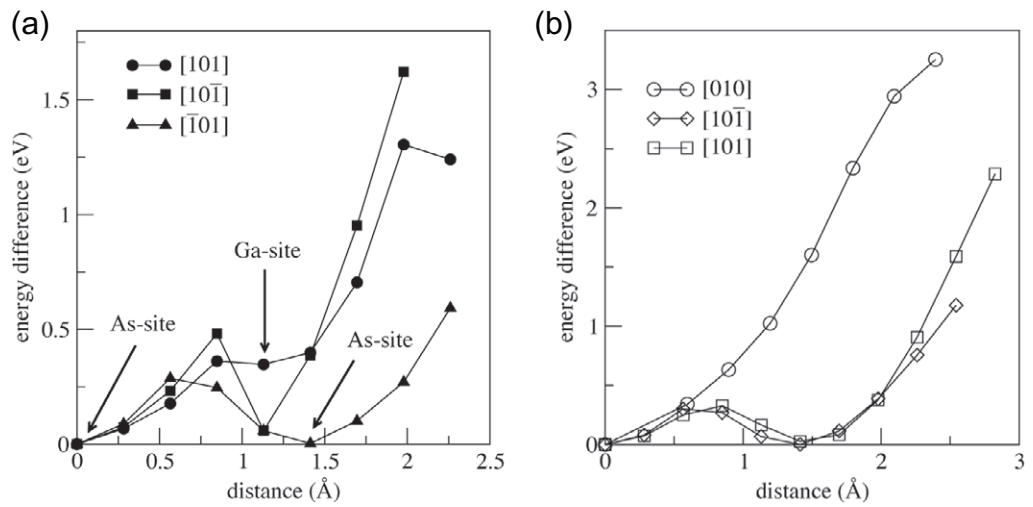
Figure 4. Energy differences sampled along different lattice directions for diffusion steps of the As interstitial (a) or the Ga interstitial (b) involved in the stoichiometric di-interstitial complex As_1Ga_1. The total energy refers to that of the As_1Ga_1 ground-state configuration.
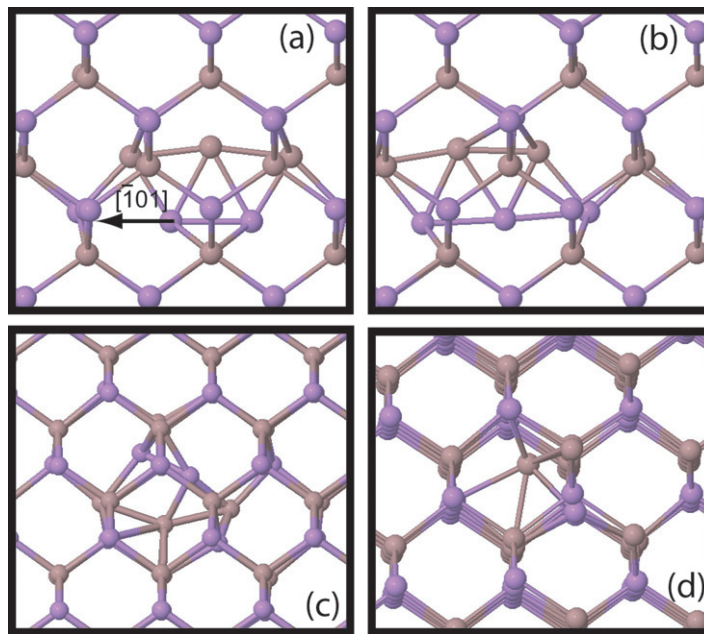

Figure 5. Diffusion pattern of the As_1Ga_1 complex obtained by moving the top As atom along the $[\bar{1}01]$ direction ((a) and (b)); in (c) and (d) are depicted the meta-stable configurations obtained, respectively, after diffusion steps of either the As (c) or the Ga (d) atoms along the [101] lattice direction.

along the $[10\bar{1}]$ and [101] directions where small diffusion barriers of $\Delta E \approx 300\,\text{meV}$ and $\Delta E \approx 320\,\text{meV}$ have been measured, respectively. Anyway, despite the similarity of the barriers encountered, the phenomena occurring in these two cases are quite different; in the first case,

the moving Ga atom drags the As atoms in the same direction and diffusion proceeds as in the previous analogous case where As atoms were moved; in the second case, in contrast, a meta-stable configuration is obtained with the Ga interstitial located at a tetrahedral site close to the As dumbbell that remains at the original As site (see figure 5(d)); this configuration is just $\Delta E \approx 30\,\mathrm{meV}$ larger in energy than the As_1Ga_1 ground state (as a consequence its binding energy is $E_b = 2.21\,\mathrm{eV}$, only 30 meV smaller than the ground state one [24, 28]) and can be obtained also in the context of a 'capture' process when a diffusing Ga atom approaches an As dumbbell or vice versa. As a consequence, the meta-stable configuration found is an intermediate state in the capture/release processes occurring when As_1Ga_1 either forms or dissolves. Hence, the rate-limiting barrier for the As_1Ga_1 formation is the one between the present intermediate configuration and the one involving two well-separated As and Ga interstitials, being thus nearly equal to the diffusion barriers of the isolated interstitials. Ultimately, it turns out that the diffusion of isolated As or Ga interstitials and the formation of As_1Ga_1 complexes are concurrent phenomena occurring, with quite similar energy barriers, wherever As and Ga interstitials are both present.

Recent *ab initio* total energy calculations have predicted As_2 as the most stable di-interstitial in GaAs [24, 28]; its ground-state configuration is made of three As atoms (two interstitials and one lattice atom) that share one As lattice site forming a bi-stable triangular structure with C_{1h} symmetry, two As atoms being aligned in a dumbbell fashion along one of the $\langle 110 \rangle$ directions. As shown in figures 6(a) and (b), As_2 can diffuse by moving either the top 'As' atom (labelled as $As_{(1)}$) or one of the two As atoms of the dumbbell (labelled as $As_{(2)}$) and the energy landscapes obtained are reported in figure 7. Concerning $As_{(1)}$, the barrier measured for the direction $[10\bar{1}]$ is $\Delta E \approx 820\,\mathrm{meV}$ (see figure 7(a)), i.e. 120 meV larger than the energy barrier between the two equivalent ground-state configurations along the [101] bi-stability pattern [28]. At the saddle point, a distorted As_2 configuration is formed at an adjacent Ga lattice (see figure 6(c)) that, as the barrier is exceeded by moving two steps further, results in the formation of a 'reversed' As_2 ground-state configuration at the nearest As lattice with the As dumbbell aligned along [101] (see figure 6(d)). In contrast, as $As_{(1)}$ is moved along the [101] direction, no diffusion occurs but, rather, a dissociation/capture phenomenon involving two As dumbbells with a capture radius of about 1.6–1.8 Å: beyond this distance, indeed, two, almost independent, As dumbells at adjacent As sites appear as also testified by a total energy increase with respect to the ground-state di-interstitial nearly equal to the As_2 binding energy ($E_b = 2.35\,\mathrm{eV}$ [20, 24, 28]) (see figure 7(a)). The same energy curve, moreover, shows that the 'activation' energy of the capture phenomenon, i.e. the energy barrier that an As dumbbell must overcome to get into the capture radius of another one, is $\Delta E \approx 190\,\mathrm{meV}$ and thus is even about 100 meV smaller than the As dumbbell diffusion barrier; therefore it can be stated that the aggregation process is rate limited by the As dumbbell diffusion barrier of 300 meV.

As mentioned before, As_2 may also diffuse via $As_{(2)}$. The total energy values sampled in this case are shown in figure 7(b), evidencing that, except for the $[10\bar{1}]$ direction, the migration barriers measured are much wider than those found so far, extending over a larger distance between 2.5 and 3.0 Å. Moreover, the barrier heights measured, $\Delta E \approx 550\,\mathrm{meV}$, are smaller than those encountered by $As_{(1)}$ but still 250 meV larger than the As dumbbell diffusion barrier. The widest barrier of approximately 3.0 Å is obtained by moving the $As_{(2)}$ atom along the [101] direction where the energy plateau corresponds to a set of very similar transition configurations depicted in figure 6(e) and made of two As interstitials at close tetrahedral sites along two orthogonal $\langle 110 \rangle$ channels; once the plateau is overtaken, another As_2 ground-state
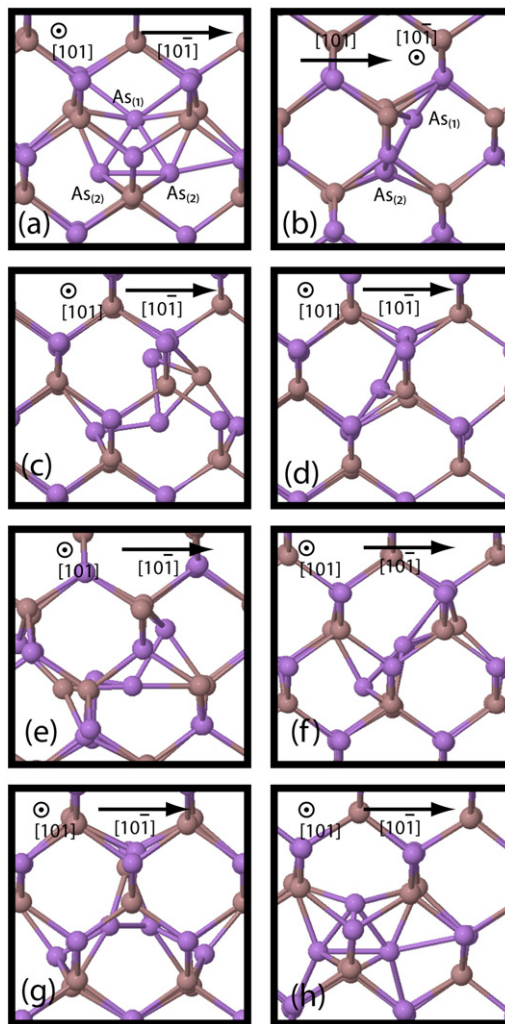
Figure 6. Configurations obtained for diffusion of the As_2 di-interstitial complex. As_2 di-interstitial ground-state configuration ((a) and (b)); the transition (c) and final (d) configurations obtained by moving the 'top' As atom along the $[10\bar{1}]$ direction; the transition (e) and final (f) configurations obtained as one of the $As_{(2)}$ atoms moves along the $[101]$ direction; the transition (g) and final (h) configurations obtained as one of the $As_{(2)}$ atoms moves along the $[\bar{1}01]$ direction.

configuration forms at an adjacent As lattice site and, consequently, As_2 migrates through the GaAs lattice (see figure 6(f)). A similar phenomenon occurs when the $As_{(2)}$ atom moves along $[\bar{1}01]$ but in this case the plateau is shorter (about 1 Å) and the saddle point configuration consists of two As interstitials and one Ga lattice atom occupying close tetrahedral sites in the vicinity of a Ga lattice site (see figure 6(g)). The migration energies obtained by moving $As_{(2)}$ are very close because both the saddle configurations are made of two As interstitials at close tetrahedral sites.

In the end, the As_2 migration patterns examined have evidenced dissociation phenomena that involve large energy barriers, capture processes with low activation barriers (similar to
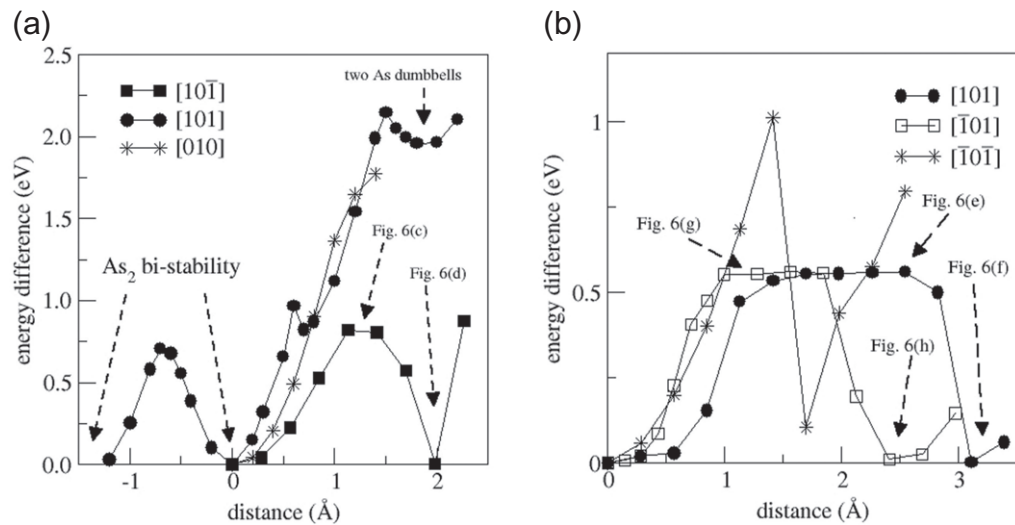
Figure 7. Total energy differences sampled by moving along some of the principal lattice directions either the $As_{(1)}$ atom (a) or one of the $As_{(2)}$ atoms (b) belonging to the As_2 di-interstitial complex. The total energy refers to that of the As_2 ground-state configuration (see figures 6(a) and (b)).

the As interstitial diffusion barriers) and diffusion processes; in this last case, the minimum energy barrier measured is 550 meV, which is more than 50% larger than the As dumbbell diffusion barrier. These results indicate that the diffusion of isolated As dumbbells and the formation of As_2 di-interstitial complexes are concurrent phenomena with the same rate and that neutral As_2 complexes, once formed, diffuse more slowly; hence the scenario here drawn entails rapid diffusion of As self-interstitials that may interact and easily form stable, slowly migrating di-interstitials.

4. Conclusions

The recent finding that I_1 and I_2 are both important for the growth of extrinsic defects in GaAs was based on the binding energy properties of the ground-state configurations of I_n complexes. However, because any aggregation process involving I_2 can actually take place only if these complexes are able to migrate rapidly through the lattice, the migration paths and the capture/release processes of neutral I_1 and I_2 complexes involving As interstitials have been studied by *ab initio* calculations. Concerning I_1, a low-energy path has been found for the substitution reaction $As_i + Ga \rightarrow As_{Ga} + Ga_i$, corroborating the idea that diffusing As interstitials may easily produce As antisites.

Regarding I_2, the sampling of the energy landscape obtained indicates that the migration barrier of the stoichiometric As_1Ga_1 di-interstitial is as low as the As dumbbell diffusion barrier. Therefore, the stoichiometric di-interstitials, which form easily where interstitials are present, being favoured energetically over the components, participate significantly in the diffusion processes of interstitial-derived species. The situation for As_2 is more complex: diffusion still occurs but the barriers involved are almost twice those found for I_1. However, when the 'top' As atom moves along the As_2 bi-stability direction path, a capture/release process takes place,

forming or dissolving the As_2 complex. In particular, the capture process is characterized by an activation energy barrier that is quite close to the diffusion energy barrier of As self-interstitials; therefore the diffusion of I_1 and the formation of As_2 complexes are concurrent phenomena but, as soon as pure As di-interstitials are formed, their diffusion proceeds with larger energy barriers than those calculated for the As self-interstitials and the As_1Ga_1 di-interstitial. We can summarize this scenario suggesting that stoichiometric I_2 favours diffusion while As di-interstitials may induce clustering more easily.

Acknowledgments

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