Numerical characterization of the Ga interstitial self-diffusion mechanisms in GaAs

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Recent diffusion experiments by Bracht and Brotzmann [H. Bracht and S. Brotzmann, Phys. Rev. B 71, 115216 (2005)] show that the dominant charge states for Ga\(_I\) diffusion in GaAs should be 0 and +1 with surprisingly high enthalpy barriers of 5.45 ± 0.12 and 5.80 ± 0.32 eV, respectively. Using the activation-relaxation technique, coupled with the \textit{ab initio} code SIESTA, we identify possible migration pathways and barriers for these two charge states. In the +1 charge state, we observe two different migration paths between tetrahedral sites surrounded by Ga atoms (tetra\(_{[Ga-Ga]}\)), implicating either a tetrahedral interstitial surrounded by As atoms (tetra\(_{[Ga-As]}\)) or a \langle 111\rangle-oriented split configuration, with total barriers of 1.4 and 1.3 eV, respectively. Including formation energy, the enthalpy barriers that we find are lower than the experimentally derived values. We analyze the possible causes and the significance of this discrepancy and offer a partial explanation based on the correction method used for finite-size effects. © 2008 American Institute of Physics.

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I. INTRODUCTION

Gallium self-interstitials in GaAs (Ga\(_I\)) are known to play an important role in the diffusion of common acceptor dopants such as Be and Zn, which is mediated both by vacancies through a dissociative mechanism, and by Ga\(_I\) through a “kick-out” mechanism.\(^{1-8}\) Whereas the diffusion of vacancies in GaAs has been thoroughly studied, however, the diffusion of Ga\(_I\) has only been studied experimentally as part of inquiries into dopant (mostly Be and Zn) migration.

One of these recent studies, by Bracht and Brotzmann,\(^{1}\) establishes the dominant charge states for Ga\(_I\) involved in Zn diffusion in GaAs to be 0 and +1, by fitting a charge-dependent kick-out model to diffusion profiles obtained by themselves as well as previously published profiles from Bosker \textit{et al.}\(^{2}\) This experiment solves the inconsistency observed in previously published works which report that the +2 and +3 charge states are dominant while failing to observe the electrical compensation that should have resulted from such charge states. In the same study, Bracht and Brotzmann also establish that the activation enthalpies for these 0 and +1 charged Ga\(_I\) should be 5.45 ± 0.12 and 5.80 ± 0.32 eV, respectively. The charge state results are in agreement with a recently published \textit{ab initio} study of the relaxed Ga\(_I\) configurations in GaAs by Malouin \textit{et al.}\(^{9}\) Using density functional theory (DFT) calculations in the local density approximation (LDA) with a local atomic orbital basis set as implemented in the SIESTA\(^{10}\) package, they determined that the dominant charge state of Ga self-interstitials is +1 for all relaxed configurations (see Table II in Malouin \textit{et al.},\(^{9}\)) while the tetrahedral configuration with Ga neighbors (tetra\(_{[Ga-Ga]}\)) and with As neighbors (tetra\(_{[Ga-As]}\)) should be, respectively, the first and second most likely defect configurations. But, their numerical work, as well as that of previous authors, has focused only on the structure and charge state of the relaxation configurations, however, and there has not been, to our knowledge, any numerical studies into the actual mechanisms by which Ga\(_I\) diffusion occurs in GaAs.

In this work, we attempt to partially fill this gap by studying Ga\(_I\) diffusion in GaAs using \textit{ab initio} calculations and the activation-relaxation technique (ART nouveau).\(^{11,12}\) Starting from the three most energetically favorable defect configurations obtained by Malouin \textit{et al.},\(^{9}\) all of which are found in the +1 charge state, we establish through an extensive search possible migration pathways for defects, without the need for a guess trajectory. Similar calculations are performed in the neutral charge state for two defect configurations obtained from the same source, in order to compare calculated migration barriers with the experimental data available for both neutral and +1 charge states.

II. METHODOLOGY

A. Starting configurations

As a starting point for our migration pathway calculations in the +1 charge state, we use the tetra\(_{[Ga-Ga]}\), tetra\(_{[Ga-As]}\), and 111-split\(_{[Ga-As]}\) configurations, as obtained by Malouin \textit{et al.}\(^{9}\) (see Figs. 1 and 2 in the corresponding reference). Only the tetrahedral configurations, identified as the most energetically favorable, are studied in the neutral state as the (111)-split interstitial is metastable in the neutral state and relaxes to a (110)-split with a formation energy of 4.24 eV, 0.8 eV higher than for tetra\(_{[Ga-Ga]}\). These structures were obtained from relaxation calculations performed on eight different 216+1 atom systems under periodic boundary conditions (PBC), using DFT in the local density approximation (LDA) with a numerical atomic orbital basis as imple-
mented in the SIESTA (Ref. 10) package. We use the double-
zeta polarized basis set (DZP) for both atomic species with a
$2 \times 2 \times 2$ Monkhorst-Pack (MP) (Ref. 13) mesh sampling.
Each configuration is relaxed until are all forces fall below
0.002 eV/Å. To correct for the PBC-induced errors in for-
mation energies, the Makov and Payne\textsuperscript{14,15} approximate cor-
rection scheme is also used.

B. Choice of system size and basis set

We use a 216+1 atom system size in all calculations in
order to achieve compatibility with previous simulation,\textsuperscript{9} as
well as to ensure reduced interaction between defects and
their PBC counterparts during migration pathway calcula-
tions. Total energy calculations, which serve to determine
energy barriers, are performed using a DZP basis set\textsuperscript{16,17} and
a $3 \times 3 \times 3$ MP mesh sampling (shifted by 0.5, 0.5, 0.5) to
achieve satisfactory accuracy with modern computer facili-
ties. The lattice constant used with this basis is obtained by
allowing a 216-atom bulk GaAs system to relax until all
forces are below 0.001 eV/Å, with variable cell volume. Its
value is 5.605 Å, close to the 5.65 Å experimental value.

For migration pathway calculations, which require a
large number of force evaluations, a single-zeta polarized
basis set with $1 \times 1 \times 1$ MP mesh sampling (shifted by 0.5,
0.5, 0.5) is used in order to reduce calculation times. The
lattice constant obtained for this basis set, and the one used
in all migration pathway calculations, is 5.633 Å. As dis-
cussed below, the full DZP basis set is used for a final relax-
ation at the identified saddle point, in order to compare with
the energy at the local minima.

C. Pathway calculations

Migration pathway calculations are performed using
ART nouveau\textsuperscript{11,18} to sample the ($3N$-dimensional) configurational
space. Starting from a local minimum, the local sym-
metry around each atom first is broken by slightly displacing
every atom in a random direction of real space, allowing for
a faster determination of the transient configuration. The
impurity and its near neighbors are then pushed in a random
direction of its configurational space; this step ensures that
all events that take place involve the impurity, to limit com-
putational efforts. This random direction is followed until the
lowest eigenvalue of the Hessian becomes negative. At this
point, the system is moved along the eigenvector associated
with this negative eigenvalue, while the energy is minimized
in the perpendicular directions. A transition state is consid-
ered reached when the total force falls below a given thresh-
old. The configuration is then given a small “nudge” to get
past the saddle point and relaxed into a new minimum using a
standard conjugate gradient method. In this work, forces
and energy calculations are handled by SIESTA.

The preliminary saddle point convergence threshold is set
to a total force of 2.00 eV/Å. Once a pathway is estab-
lished, its saddle point is further refined with a threshold of
0.50 eV/Å to reduce the error in its total energy.

All saddle point energies and new minima are then op-
tered reached when the total force falls below a given thresh-
old. The configuration is then given a small “nudge” to get
past the saddle point and relaxed into a new minimum using a
standard conjugate gradient method. In this work, forces
and energy calculations are handled by SIESTA.

All saddle point energies and new minima are then op-
timized using a full DZP basis and $3 \times 3 \times 3$ MP basis set as
discussed in Sec. II B, with all distances scaled to the appro-

D. Error evaluation

The error on the energy barriers combines the effect of
$k$-point convergence, choice of the system size, and saddle
point convergence. The error due to system size was evalu-
ated in similar work done on the diffusion of Ga in Si,\textsuperscript{19}
where we estimated the energies to be converged to less than
0.1 eV using a 216-atom system with regard to a larger,
512-atom system. The effect of $k$-point convergence is evalu-
ated by comparing total energy calculations done on some of
our “GaAs + defect” systems with $2 \times 2 \times 2$ and $3 \times 3 \times 3$
MP mesh sampling (both shifted by 0.5, 0.5, 0.5). Total en-
ergies are found to be converged to roughly 0.01 eV, leading
to a total error due to the first two effects of about 0.1 eV.

In order to quantify the effect of the saddle point con-
vergence criterion (which determines how precisely the
saddle point is found), we compare the total energy of a
saddle point converged to a force criterion of 0.5 eV/Å to
that of the same saddle point further refined to 0.35 eV/Å,
using the reduced basis and mesh sampling. We obtain an
energy difference of 0.04 eV. As further refinement is not
expected to improve convergence by more than a few hun-
dredths of an electron volt, our conservative estimate of the
precision of the energy barriers, based on all three effects
listed, is of 0.2 eV at most.

III. RESULTS AND DISCUSSION

A. Migration paths

Starting from the tetrahedral Ga-Ga configuration, we find a mi-
gration pathway toward a tetrahedral Ga-As configuration, through a
hexagonal interstitial (Ga$_{het}$) saddle point (see Fig. 1). The
calculated energy barriers for the neutral defect are 1.3 eV in
the forward direction, and 0.9 eV in the reverse direction.
Corresponding barriers in the +1 charged system are almost
identical, with 1.4 and 1.1 eV in the forward and reversed
directions, respectively, accounting for the energy between
of the split defect allows for more than one equally probable configuration of the +1 tetrahedral configurations. As the configuration is thus expected to rapidly disappear to the benefit of a comparable total barrier of 1.4 eV, making it only slightly less likely than the reverse mechanism, with the same barrier energies.

Starting from the +1 charged 111-split[Ga-As] configuration, we find a migration path where the Ga moves toward a tetra[Ga-Ga] configuration, as the As atom returns to its lattice site (see Fig. 2), leading to an energy gain of 0.9 eV with respect to the split configuration. The calculated energy barrier is 0.4 eV in the forward direction, and 1.3 eV in the reverse direction.

The relatively low barrier for this latter event indicates that it should be rather frequent, and the 111-split[Ga-As] configuration is thus expected to rapidly disappear to the benefit of the +1 tetrahedral configurations. As the (111) orientation of the split defect allows for more than one equally probable tetra[Ga-Ga] site for the Ga in the complex to migrate to, we can envision a Ga migration path between positively charged tetra[Ga-Ga] configurations through an intermediary 111-split[Ga-As], with an overall barrier of 1.3 eV. A similar, two-step migration path through a tetra[Ga-As] would have a comparable total barrier of 1.4 eV, making it only slightly less likely. The calculated barriers are summarized in Table I.

B. Activation enthalpies

Activation enthalpies are calculated as the sum of a defect’s formation energy and energy barrier for its migration,

$$H_A = E_f + \Delta E.$$  

where $E_f$ and $\Delta E$ are the formation energy and the energy difference between the final and initial state. We use the formation energies obtained by Malouin et al., and the barriers obtained in Sec. III A. The estimated errors on $E_f$, along with those on $\Delta E$, lead to an overall estimated precision of 0.3 eV for $H_A$. In the +1 charged case, formation energies and thus activation enthalpies depend on the doping conditions through the Fermi level $\mu_F$. In order to allow comparison with the experimental values of Bracht and Brodzianka,1 we evaluate $H_A$ at intrinsic doping conditions, i.e., $\mu_F$ at midgap (0.76 eV above the valence band maximum). In the +1 charge state, we obtain $H_A=4.6 \pm 0.3$ and $H_A=4.5 \pm 0.3$ eV for the tetra[Ga-Ga]→tetra[Ga-As] and 111-split[Ga-As]→tetra[Ga-Ga] migration paths, respectively. In the neutral state, we obtain $H_A=4.7 \pm 0.3$ eV for the first path.

These values differ from the 5.45±0.12 and 5.80±0.32 eV found experimentally for neutral and +1 charged defects, respectively. The discrepancy is higher (nearly doubly so) in the positively charged system. It seems unlikely that these differences are due to the calculation of the barriers, as the formation energies used in the calculation of $H_A$ would imply barriers of 2 eV and higher to match Bracht and Brodzianka’s data. Such a value would certainly be much higher than what should be expected for interstitial migration. We must therefore look somewhere else for an explanation.

It is more likely that these discrepancies are due to errors in the evaluation of the defects’ formation energies. For example, Uberuaga et al. found that the activation energy of a diffusing vacancy in Ge was underestimated by more than 0.5 eV using the local-density approximation instead of a Hartree-Fock exchange term.20 This correction is not universal; however, LDA gives reasonably good results for a number of semiconductors (see, for example, Refs. 12 and references therein). Charge corrections could also be important. In the case of the +1 charged defect, it has been shown21 that the method of Makov and Payne, used by Malouin et al. to correct for the PBC-induced errors, is unreliable, and can itself lead to errors of a few tenths of an electron volt when compared to the more accurate method of finite-size scaling.22 To evaluate the effect of this method, we use finite-size scaling, as outlined in a previous paper,19 to extrapolate the formation energy of the tetra[Ga-Ga] at infinite supercell size, thus correcting for finite-size errors. The fitted curve is shown in Fig. 3. We obtain a 0.3 eV increase in formation energy with respect to the results of Malouin et al., leading to an enthalpy barrier of about $H_A=4.9 \pm 0.3$ and $H_A=4.9 \pm 0.3$ eV for the tetra[Ga-Ga]→tetra[Ga-As] and 111-split[Ga-As]→tetra[Ga-Ga] migration paths, respectively. This result is coherent with the higher observed discrepancy in the case of the charged defect. However, this partial explanation is not sufficient to completely account for the observed discrepancy, leaving a difference on the order of about 0.5 eV for each defect, taking the estimated error into account.

Another possible source of error, which applies to both studied charge states, arises from the fact that the formation energy calculations on which our $H_A$ calculations are based do not take into account possible thermal/entropic effects on these formation energies and the ionization levels. It has indeed been shown23,24 that the inclusion of thermal and en-

![FIG. 2. (Color online) Migration pathway for the 111-split(Ga-As) configuration, where the Ga moves toward a tetra(Ga-Ga) configuration and the As returns to its lattice site. Red (dark gray) and green (light gray) circles indicate the migrating Ga and As atom, respectively. In the last state, the As has moved on the lattice site and is hidden behind the As atom in the front row.](image-url)

<table>
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<th>Charge state</th>
<th>Barrier</th>
<th>Asymmetry</th>
<th>Barrier</th>
<th>Asymmetry</th>
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<td>1.4</td>
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<tr>
<td>111-split(Ga-As)→tetra(Ga-Ga)</td>
<td>–</td>
<td>–</td>
<td>0.4</td>
<td>–0.9</td>
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TABLE I. Energy barriers and asymmetry for different diffusion mechanisms and charge states, in electron volts. The asymmetry is computed as the energy difference between the final and initial state. Hyphens (–) in the neutral column indicate calculations not performed, as the split configuration is oriented in the (110) direction for this charge state.
tropic terms in the calculation of formation free energies can lead to thermal variations of these formation energies and, in the case of GaAs vacancies, to a reversal of the most energetically favorable state as the temperature is varied. Since experiments are performed at 620 °C and above, entropic and thermal effects could be important. However, these corrections, which are typically less than 1 eV for the relevant temperatures, actually tend to lower the formation energies, so it seems unlikely that they could explain the observed discrepancy.

This in turn puts into question the accuracy of the experimental values used in our comparison. Indeed, the model employed by Bracht and Brotzmann is a complex one, requiring certain assumptions that can lead to errors. Notably, it is assumed that the only two diffusion mechanisms implying self-interstitials occur for neutral or +1 charged Ga\(_{\text{I}}\). The authors justify this choice by the absence of observed dopant deactivation, which would occur if the diffusion was mediated by +2 and +3 charged Ga\(_{\text{I}}\) as supposed by previous authors’ models. It is perhaps an oversimplification to assume that because no generalized deactivation occurs, no +2 and +3 charged Ga\(_{\text{I}}\) are involved whatsoever, especially considering the comparable agreement obtained by preceding authors such as Bosker et al., between experimental data and a model that uses only +2 and +3 charged self-interstitials, neglecting the possible participation of neutral and +1 charge states. Moreover, as mentioned in the previous paragraph, it is possible that the favored charge state changes with the system temperature, once again putting into question the validity of a model limited to two charge states for all temperatures. Finally, it is assumed in the Bracht and Brotzmann’s model that Ga\(_{\text{I}}\) diffusion is limited to the Ga sublattice, and that there is therefore no interference between Ga and As diffusion. Our own results show the implication in Ga\(_{\text{I}}\) diffusion of the 111-split\([\text{Ga-As}]\) defect (in which a Ga and As atom share an As lattice site), which contradicts this hypothesis.

IV. CONCLUSION

We have obtained, by \textit{ab initio} calculations based on ART nouveau, migration paths for neutral and +1 charged Ga self-interstitials in GaAs, based on previously published relaxed configurations. Our results indicate that a positively charged Ga self-interstitial can migrate between two tetra[\(\text{Ga-Ga}\)] configurations by going through either a tetra[\(\text{Ga-As}\)] or 111-split[\(\text{Ga-As}\)] transient configuration. The total barriers for these events are similar: 1.4 and 1.3 eV, respectively. Only the first of these paths has been observed in the neutral charge states, with a 1.3 eV energy barrier. Activation enthalpy calculations based on these barriers and previous calculations of the formation energies are found to be in disagreement with the available experimental values. These discrepancies are partially explained by the use of LDA as well as by the method employed to correct for size effects in the charged system; however, this explanation is insufficient and does not apply to the neutral system. The remaining difference is unlikely to be explained by thermal and entropic effects on the formation energy—which were not calculated for this system—since these tend to decrease the activation energy. Errors on the formation energy, finally, do not seem to be sufficiently large to explain fully the observed discrepancy. We suspect that it is also partly due to the model used to analyze the experimental data. This model uses certain questionable assumptions and approximations, notably the restriction of Ga\(_{\text{I}}\) to the Ga sublattice, which our own results contradict. Further work, including calculations of the thermal and entropic effects as well as comparison with an upgraded model for experimental data analysis that takes our migration pathway results into account, would be needed to clarify the situation.

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19 K. Levasseur-Smith and N. Mousseau (unpublished).