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## Defect reaction network in C-doped GaAs: Numerical predictions

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# Defect reaction network in C-doped GaAs: Numerical predictions

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## Abstract

This Report characterizes the defect reaction network in carbon doped, *p*-type GaAs deduced from first principles density functional theory. The reaction network is deduced by following exothermic defect reactions starting with the initially mobile interstitial defects reacting with common displacement damage defects in C-doped GaAs until culminating in immobile reaction products. The defect reactions and reaction energies are tabulated, along with the properties of all the carbon-related defects in the reaction network. This Report serves to extend the results for intrinsic defects in: P.A. Schultz and O.A. von Lilienfeld, "Simple intrinsic defects in GaAs", *Modelling Simul. Mater. Sci Eng.*, Vol. **17**, 084007 (2009) and its numerical supplement in SAND 2012-2675, and the preliminary carbon defect network results in: P.A. Schultz, "First-principles defect chemistry for modeling irradiated GaAs and III-V semiconductors", *J. Rad. Effects, Res. and Eng.* Vol. **30**, p257 (2012).

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## NOMENCLATURE

CBE	conduction band edge
DFT	density functional theory
eV	electron Volt
FDSM	finite defect supercell model
GGA	generalized gradient approximation
LDA	local density approximation
LMCC	local moment countercharge
MSMSE	Modelling and Simulation in Materials Science and Engineering
n/x	not exist
PAS09	Article: P.A. Schultz and O.A. von Lilienfeld, MSMSE <b>17</b> , 084007 (2009).
PBE	Perdew/Burke/Ernzerhof, a “flavor” of GGA
PP	pseudopotential
SNL	Sandia National Laboratories
VBE	valence band edge

# 1. INTRODUCTION

The defect reaction network, the chain of reactions driven by species mobilized in primary displacement damage, is predicted and numerically characterized using first-principles density functional theory for irradiated carbon-doped,  $p$ -type gallium arsenide, GaAs. The reaction network is deduced from first principles: identifying the initial species mobilized during displacement damage, the arsenic and gallium interstitials, systematically investigating their reactions with dopants and immobile primary displacement damage defects and inserting into the network those reactions that are exothermic, and following this chain of reactions and potentially new mobile reaction products until culminating in immobile defects. The numerical predictions associated with this first-principles reaction network are presented in a series of numerical Tables containing parameters to populate defect physics packages needed for device simulations.

This Report focuses on carbon-containing defects. Results for density functional theory (DFT) calculations of properties of simple intrinsic defects in gallium arsenide have been published previously in “Simple intrinsic defects in GaAs”, P.A. Schultz and O.A. von Lilienfeld (2009), *Modelling and Simulation in Material Science and Engineering*, Vol. 17, Article # 084007 [1] (henceforth “PAS09”), and its supplement with numerical tables of intrinsic defect properties—charge transition defect level energies, formation energies, diffusion—published as a SAND Report [2]. Assessment of defect reaction network energies involving only intrinsic defects use values presented in these earlier works. The likely chain of defect reactions in carbon doped ( $p$ -type) and silicon doped ( $n$ -type) GaAs—the defect reaction networks—was presented previously [3], but properties of the defects in that network were not presented. This Report can be interpreted as a (partial, carbon-focused) numerical supplement to that work and as a numerical supplement to a paper yet to be published.

This Report focuses on first order reactions. Second order or greater (interstitial-interstitial, or interstitial-product) reactions are much less populous and unlikely to significantly affect electrical response of the bulk material, are therefore (mostly) neglected. Similarly, because  $p$ -type carbon doping will preferentially populate defects in their most positive charge states, emphasis is on careful characterization of defect evolution consistent with a Fermi level near the valence band edge (although all accessible charge states for each defect in the network are examined).

## 1.1. Computational methods

The details of the computational methods are the same as comprehensively described previously [1,2,3], and will only be summarized here.

The DFT calculations are performed with the SEQQUEST code [4], using both the local density approximation (LDA) [5] and the Perdew-Burke-Ernzerhof (PBE) flavor of the generalized gradient approximation [6]. The comparison of LDA and PBE results is a partial assessment of the physical uncertainties within DFT functionals [7]. The pseudopotentials (PP) for Ga and As are the same used for intrinsic defects calculations [1,2] and comprehensively verified [8]. Calculations for the carbon-containing GaAs defects are done with  $3d$ -core pseudopotentials (total valence charge  $Z=3$ ) for the Ga atom, and not repeated with  $3d$ -valence ( $Z=13$ ) PP. We had determined that the PP construction had only modest effect on computed defect properties, the physical uncertainties in the DFT results dominated by the difference between the physical

approximations of LDA and PBE [1]. If deemed necessary, the current calculations could be straightforwardly repeated using the more rigorous 3*d*-core PP for Ga. The carbon PP in this work are generalized norm-conserving Hamann potentials [9], with default settings, using the *l*=1 potential as the local potential, and a double-zeta plus polarization contracted-Gaussian basis set, from the SEQQUEST library of optimized, transferable atomic potentials.

Defect formation energies are quoted in the arsenic-rich limit. The chemical potential of the As is set to the computed energy of the As in the elemental bulk *A7* structure, that of Ga to be that required to make the formation energy of perfect GaAs equal to zero. The chemical potential of a carbon atom is arbitrary, all reactions considered in this Report are carbon number conserving. Here, it is set to the energy of one atom in the crystalline diamond structure.

The calculations of charged defects use the Finite Defect Supercell Model (FDSM) [10] to incorporate rigorous boundary conditions for the solution of the electrostatic potential in a charged supercell [11,12] and extrapolate the computed defect energies to the infinitely dilute limit. Results for carbon related defects are presented for 216-site cubic supercells extrapolated to infinitely dilute limits, with selected 64-site and 512-site cubic supercells to verify these results are converged, as demonstrated in PAS09. The simulation contexts presented here correspond to the “LDA” and “PBE” simulation contexts defined in the numerical supplement for intrinsic defects [2].

One difference in the current calculations from the previous Reports [1-3] in these simulation contexts must be noted. The real space grids used in the original simulation contexts for calculations of intrinsic defects proved inadequate to fully converge calculations with supercells containing carbon atoms. Rather than  $108^3$  grids used previously for the LDA and PBE simulation contexts, the new calculations here use  $144^3$  grids (the same grids that had been found necessary for the LDA3d and PBE3d contexts). Computed bulk properties and neutral defect formation energies are unaffected, to within 0.01 eV, with the finer grid. Mapping of computed ionization potentials to the valence band edge shifts (presented in Table 2 of PAS12) from 5.40 to 5.424 eV in the LDA context, and 5.15 to 5.172 eV in PBE, with the finer grid. With this adjustment, computed defect levels and formation energies of charged defects are also unaffected with the finer grid, to within 0.01 eV, the precision quoted in these reports.

## 1.2. Verification and validation

The carbon-related defect level calculations all use SEQQUEST and the FDSM, the same methods used in DFT calculations of defects in silicon, which yielded mean absolute errors of 0.1 eV and maximum absolute error of 0.2 eV for defect levels over a wide sampling of different defects [10]. This is the expected accuracy (uncertainties) of the methods for defect level calculations in GaAs, and is the limit (best possible) of the physical accuracy of the DFT approximations used in this analysis.

Using the same methods and models, the verification and validation of the PP and extrapolation model inherit directly from earlier results for intrinsic defects in GaAs [1,2]. Validation of the overall computational method for GaAs defects is also done previously, indicating accuracy of 0.1 to 0.2 eV for defect level calculations in GaAs [1,2], and is not repeated here.

## 2. RESULTS

This section contains the Tables that summarize the numerical results for DFT simulations of carbon-related defects and the radiation-induced defect reaction network in GaAs.

The process by which the reaction network is deduced is iterative. It starts with the defects species generated by displacement damage (vacancies and interstitials). Using DFT calculations, we had identified that the self-interstitials, and particularly the arsenic interstitial are mobile. Their reactions with all common immobile defects are investigated, and exothermic defect reactions are added to the reaction network. The “common” immobile defects are the vacancies and the divacancy, being primary displacement damage defects, and the carbon dopant (substitutional) atoms. Reactions between mobile species, i.e., second order reactions, are neglected. One of the reaction products in the reaction network is the carbon interstitial  $C_i$ , and the current results indicate  $C_i$  is also likely to be a mobile specie. Hence, its reactions with immobile defects are investigated, and the exothermic reaction products are added to the defect reaction network. No other reaction products are found that are likely to be mobile.

### 2.1. Defect atomic structures

The following Tables summarize the ground state structures for the carbon-containing defects within the defect reaction network. The intrinsic defect structures have been presented previously [1,2] and the same nomenclature is used to describe carbon defect structures as used in the intrinsic defects and illustrated in PAS09.

**Table 1. Ground state structure description for carbon reaction network defects.**

Charge state	$C_{As}$	$C_{As}$	$C_i$	$(C_2)_{As}$	$(GaC)_{As}$	$C_{Vv}$
(4-)	-	-	-	-	-	$C_{3v} V_{Ga} C_{As}$
(3-)	-	-	-	-	-	$C_{3v} V_{Ga} C_{As}$
(2-)	-	-	$C_{1h}$ split-001 <sub>As</sub> puckered-As	-	-	$C_{3v} V_{Ga} C_{As}$
(1-)	$T_d$	$T_d$	$C_{1h}$ split-001 <sub>As</sub> puckered-As	$D_2$ split-001 <sub>As</sub> twisted	$C_{3v}$ split 111 <sub>As</sub> ( $\sim C_{As}$ -Ga-Ga <sub>i</sub> )	$C_{3v} V_{Ga} C_{As}$
(0)	$\{T_d\}^{(a)}$	$T_d$	$C_{1h}$ split-001 <sub>As</sub> puckered-As	$D_2$ split-001 <sub>As</sub> twisted	$C_{3v} C_{As}$ -Ga[ $T_{i,As}$ ]	$C_{1h} V_{As} As_{Ga} C_{As}$
(1+)	-	$T_d$	$C_{2v}$ split-001 <sub>Ga</sub>	$D_{2d}$ split-001 <sub>As</sub>	$C_{3v} C_{As}$ -Ga[ $T_{i,As}$ ]	(b)
(2+)	-	-	$C_{2v}$ split-001 <sub>Ga</sub>	-	-	(b)

(a) The DFT result is not a defect state, but the state is in reality likely a shallow acceptor.

(b)  $C_{Vv}$  has defect structures from [1+] to [4+], but all thermodynamically unstable to the site-shifted  $C_{Vv}[0]$

**Table 2. Ground state structure description for selected second-order defects.**

<b>Charge state</b>	<b>(AsC)<sub>Ga</sub></b>	<b>(As<sub>2</sub>)<sub>Ga</sub></b>
<b>(4-)</b>	-	-
<b>(3-)</b>	-	-
<b>(2-)</b>	-	-
<b>(1-)</b>	-	C <sub>1h</sub> split-001 <sub>Ga</sub> pucker-As
<b>(0)</b>	C <sub>1h</sub> split-001 <sub>Ga</sub> pucker-As	C <sub>2</sub> split-110 <sub>Ga</sub> twisted
<b>(1+)</b>	C <sub>1h</sub> split-001 <sub>Ga</sub> pucker-As	C <sub>2</sub> split-110 <sub>Ga</sub> twisted
<b>(2+)</b>	C <sub>1h</sub> split-001 <sub>Ga</sub> pucker-As	-

- (a) Only the results for high-symmetry C<sub>3v</sub> di-antisite structures are presented. The symmetry-reducing distortions (to C<sub>1h</sub>) give negligible energy lowering.
- (b) The C<sub>2</sub> twisted form of the split-110<sub>As</sub> had not been discovered at the time PAS09 was published. The lowering from the C<sub>2v</sub> split-110<sub>As</sub> is negligible (<0.01 eV) for the 3d-core LDA contexts, but is 0.05 for the LDA-3d and PBE and 0.10 for PBE-3d context, and therefore merits updating.

## 2.2. Defect charge transition energy levels

This section presents the defect charge transition levels of the carbon reaction network defects in GaAs, in eV, along with neutral formation energies. The defect level calculations are the fundamental result of this Report, the later formation energies and reaction energies are all derived from these results. The defect levels are thermodynamic values, differences in energies between global ground state structures of two charge states, without regard for whether a kinetic barrier might impede a structural rearrangement between the two atomic configurations.

**Table 3. Defect levels for carbon reaction network defects: LDA context**

LDA Context	Neutral formation energy	Defect levels (eV), cf. VBE						
		(3+/2+)	(2+/1+)	(1+/0)	(0/1-)	(1-/2-)	(2-/3-)	(3-/4-)
$C_{As}$	(5.28) <sup>(a)</sup>	n/x	n/x	n/x	(-2.33) <sup>(a)</sup>	n/x	n/x	n/x
$C_{Ga}$	4.12	n/x	n/x	1.10	1.26	n/x	n/x	n/x
$C_i$	5.00	n/x	0.32	0.53	1.03	1.23	n/x	n/x
$(C_2)_{As}$	4.85	n/x	n/x	0.97	1.18	n/x	n/x	n/x
$(GaC)_{As}$	4.76	n/x	0.45	-0.10	n/x	n/x	n/x	n/x
$C_{VV}$	5.13	-	-	-	1.07	0.74	0.91	1.32
$(AsC)_{Ga}$	4.68	-	0.21	0.53	-	-	n/x	n/x
$(As_2)_{Ga}$	3.42	n/x	-	1.21	1.05	-	-	n/x

(a) The on-site  $C_{As}(0)$  is not a clean defect state in a DFT calculation, despite being a shallow acceptor state. The energy quoted for  $C_{As}[0]$  is for the site-switched  $Ga_{As}-C_{Ga}$  pair, and the (0/1-) transition energy between this site-switched form and the  $C_{As}(1-)$ .

**Table 4. Defect levels for carbon reaction network defects: PBE context**

PBE Context	Neutral formation energy	Defect levels (eV), cf. VBE						
		(3+/2+)	(2+/1+)	(1+/0)	(0/1-)	(1-/2-)	(2-/3-)	(3-/4-)
$C_{As}$	(5.24) <sup>(a)</sup>	n/x	n/x	n/x	(-2.19) <sup>(a)</sup>	n/x	n/x	n/x
$C_{Ga}$	3.97	n/x	n/x	1.06	1.20	n/x	n/x	n/x
$C_i$	4.71	n/x	0.42	0.60	1.10	1.46	n/x	n/x
$(C_2)_{As}$	4.41	n/x	n/x	1.12	1.26	n/x	n/x	n/x
$(GaC)_{As}$	4.78	n/x	0.51	0.01	n/x	n/x	n/x	n/x
$C_{VV}$	4.97	-	-	-	1.16	0.63	0.93	1.35
$(AsC)_{Ga}$	4.42	-	0.29	0.62	-	-	n/x	n/x
$(As_2)_{Ga}$	3.19	n/x	-	1.25	1.21	-	-	n/x

(a) The on-site  $C_{As}(0)$  is not a clean defect state in a DFT calculation, despite being a shallow acceptor state. The energy quoted for  $C_{As}[0]$  is for the site-switched  $Ga_{As}-C_{Ga}$  pair, and the (0/1-) transition energy between this site-switched form and the  $C_{As}(1-)$ .

Carbon is a shallow  $p$ -type dopant in GaAs, sitting in the arsenic substitutional site,  $C_{As}$ . Being a shallow acceptor, it has a (1-/0) transition near the valence band edge. However, the DFT calculation buries this state deep in the valence band and the  $C_{As}[0]$  is not a clean defect state. To evaluate a formation energy for  $C_{As}[1-]$ , a clean neutral defect state is needed. A neutral reference state is obtained by swapping the carbon and a neighboring gallium, a defect which is a clean defect state with neutral charge. With this and the charge transition energy, the formation energy of the  $C_{As}[1-]$  can be obtained directly from the DFT calculations, without assumptions regarding the location of the (computationally inaccessible) shallow on-site transition.

The computed levels in the LDA and PBE contexts are very similar, mostly within 0.1 eV of one another. The exception with the largest deviation is the  $C_i(2-/1-)$  transition, with an LDA energy of 1.23 above the VB edge and the PBE energy 0.23 eV higher. This similarity is despite differences in defect formation energies that are typically 0.2 eV or more, and is, first, evidence, that electronic transition levels are benefitting from a cancellation of errors and, second, consistent with and evidence for a physical uncertainty in defect levels of 0.1-0.2 eV.

The levels listed in these tables only quote those charge states that are thermodynamically accessible. For example, clean defect states for the  $C_{Vv}$  can be found for all positive charge states ranging down to  $[4+]$ , but none of these is thermodynamically stable, all will spontaneously emit holes to form the  $C_{Vv}[0]$ . Alternatively stated, the electronic levels are below the VB edge, as a consequence of the structural rearrangements that occur.

### 2.3. Defect formation energies

The ground state defect formation energies, as a function of charge state are trivially obtained by simple arithmetic from the neutral formation energies and the computed defect charge transition energy levels in the previous section. As for all the results presented in this Report, the defect formation energies in these Tables are presented in the arsenic-rich limit. The formation energies of the charged defects are presented with the Fermi level at the VBE. The Tables present the formation energies of the carbon reaction network defects, segregated by simulation context. Only thermodynamically accessible charge states are listed.

**Table 5. Formation energies of carbon reaction network defects at VBE (in eV), context = LDA.**

Charge state	$C_{As}$	$C_{Ga}$	$C_i$	$(C_2)_{As}$	$(GaC)_{As}$	$C_{Vv}$	$(AsC)_{Ga}$	$(As_2)_{Ga}$
(4-)	-	-	-	-	-	9.17	-	-
(3-)	-	-	-	-	-	7.85	-	-
(2-)	-	-	7.26	-	-	6.94	-	-
(1-)	2.95	5.38	6.03	6.03	-	6.20	-	4.47
(0)	<b>(2.95)<sup>(a)</sup></b>	<b>4.12</b>	<b>5.00</b>	<b>4.85</b>	<b>4.76</b>	<b>5.13</b>	<b>4.68</b>	<b>3.42</b>
(1+)	-	3.02	4.47	3.88	4.85	-	4.15	2.20
(2+)	-	-	4.15	-	4.40	-	3.94	-

(a) For a  $T_d$  on-site  $C_{As}[0]$ , assuming a shallow acceptor level is exactly at the VB edge. Note difference from the neutral formation energy reported in Table 1 defect level calculations.

**Table 6. Formation energies of carbon reaction network defects at VBE (in eV), context = PBE.**

Charge state	$C_{As}$	$C_{Ga}$	$C_i$	$(C_2)_{As}$	$(GaC)_{As}$	$C_{Vv}$	$(AsC)_{Ga}$	$(As_2)_{Ga}$
(4-)	-	-	-	-	-	9.05	-	-
(3-)	-	-	-	-	-	7.70	-	-
(2-)	-	-	7.27	-	-	6.76	-	-
(1-)	3.06	5.16	5.80	5.67	-	6.13	-	4.41
(0)	<b>(3.06)<sup>(a)</sup></b>	<b>3.97</b>	<b>4.71</b>	<b>4.41</b>	<b>4.78</b>	<b>4.97</b>	<b>4.42</b>	<b>3.19</b>
(1+)	-	2.91	4.11	3.29	4.78	-	3.80	1.95
(2+)	-	-	3.69	-	4.26	-	3.52	-

(a) For a  $T_d$  on-site  $C_{As}[0]$ , assuming a shallow acceptor level is exactly at the VB edge. Note difference from the neutral formation energy reported in Table 1 defect level calculations.

## 2.4. Carbon interstitial and migration

In the evolution of the defect reaction network, as the mobile As and Ga interstitials react with the immobile fixed defects, the carbon interstitial is the only defect that shows the prospect to be also mobile, and therefore must be considered in extending the defect reaction network.

### 2.4.1. Carbon interstitial structural energies

The following Table presents the relative energies of different structures of the carbon interstitial relative to the ground state structure for that charge state. This is not a comprehensive listing of possible structures considered, but does survey all the potentially important structures for  $C_i$ .

**Table 7. Carbon interstitial ground state energies, in eV, relative to ground state**

Structure	Context	Charge state				
		$C_i(2-)$	$C_i(1-)$	$C_i(0)$	$C_i(1+)$	$C_i(2+)$
split-001 <sub>Ga</sub> puckered-C $C_{1h}$	LDA	n/x	n/x	0.15	—> $C_{2v}$	—> $C_{2v}$
	PBE	n/x	n/x	0.17	—> $C_{2v}$	—> $C_{2v}$
split-001 <sub>Ga</sub> $C_{2v}$	LDA	n/x	n/x	0.22	<b>0</b>	<b>0</b>
	PBE	n/x	n/x	0.25	<b>0</b>	<b>0</b>
split-110 <sub>Ga</sub> $C_{1h}$	LDA	n/x	n/x	1.10	0.98	0.57
	PBE	n/x	n/x	1.27	1.09	0.63
split-001 <sub>As</sub> puckered-C $C_{1h}$	LDA	0.24	0.01	<b>0</b>	0.15	—> $C_{2v}$
	PBE	<b>0</b>	<b>0</b>	<b>0</b>	0.12	—> $C_{2v}$
split-001 <sub>As</sub> $C_{2v}$	LDA	0.49	0.28	0.26	0.17	0.22
	PBE	0.24	0.25	0.24	0.14	0.19
split-110 <sub>As</sub> $C_{1h}$	LDA	<b>0</b>	<b>0</b>	0.24	0.53	0.75
	PBE	+0.00	0.15	0.33	0.61	—> BC
“BC” bond-center $C_{3v}$	LDA	n/x	1.47	1.13	0.76	0.54
	PBE	n/x	n/x	1.01	0.59	0.33
H-site interstitial $C_{3v}$	LDA	-	-	1.02	1.17	1.11
	PBE	-	-	1.08	1.19	1.10
$T_{i,As}$ -site interstitial $T_d$	LDA	-	-	2.06	1.56	1.11
	PBE	-	-	1.99	1.53	1.11
$T_{i,Ga}$ -site interstitial $T_d$	LDA	-	-	1.94	1.94	1.92
	PBE	-	-	2.04	1.99	2.00

### 2.4.2. Carbon interstitial diffusion

Unlike for the arsenic interstitial [1], there is no apparent path that enables athermal migration [13] of the  $C_i$  via a Bourgoin-Corbett mechanism [14]. The capture of a carrier does not lead to a switch in site for the carbon for any of its stable structures, at most leading to slight intra-site reorientation. This does not preclude recombination enhancement to diffusion. The capture of a carrier by the interstitial could possibly deposit part of its excess energy in local vibrational modes which could aid in overcoming the barrier to inter-site diffusion, but the DFT results predict that diffusion of carbon is not driven by the cyclical capture of carriers alone.

The  $C_i$  strongly favors in-network sites, it dislikes the non-bonding interstitial sites. Otherwise, the energy landscape of the  $C_i$  is notably flat, with multiple competitive structures within 1 eV at each charge state, both on-site (either As or Ga site) reorientation, and between the two sites. This is particularly true for the positive charge states that are most strongly populated in  $p$ -type (carbon-doped) GaAs, indicating  $C_i$  has the potential to be (thermally) mobile, and therefore the possible diffusion of a  $C_i$  must be considered in developing a defect reaction network.

**Table 8. Diffusion barriers for the carbon interstitial, in eV.**

Pathway:	Hop between split-As and split-Ga site			Reorientation on split-As site		
	$C_i(0)$	$C_i(1+)$	$C_i(2+)$	$C_i(0)$	$C_i(1+)$	$C_i(2+)$
<b>Context</b>						
<b>LDA</b>	0.48	0.69	0.85	0.24	0.53	0.57
<b>PBE</b>	0.51	0.74	0.82	0.33	0.59	0.41

Table 8 indicates predicted barrier energies for  $C_i$ , relative to the ground state structure in each charge state. As shown in the Table, the ground state 2+ interstitial faces a  $\sim 0.8$  eV barrier in hopping between a split-As site and split-Ga site. This barrier decreases as the  $C_i$  captures additional electrons, to  $\sim 0.7$  eV for the 1+ charge state and to a readily surmountable (at operating temperatures) 0.5 eV for the neutral defect. The close agreement between the PBE and LDA results for activation energies for diffusion increase the confidence in the predictions of the diffusion activation barriers. The usual 0.1-0.2 eV physical uncertainties in these DFT predictions likely need to be increased to account for an unknown DFT error in saddle points.

The pathways are straightforward, along a (p-As)100<sub>As</sub> to (p-C)001<sub>Ga</sub> path, which (except for the PBE 2+) is lower than the planar 001—001 pathway. Diffusion of the carbon progresses by hopping from split-Ga to split-As, and then on to another split-Ga, hopping from site to site.

The on-site reorientation barrier, between different directions—(001) to (100), for example—for the split-As interstitial is less than the hopping barrier, assuring that the split-As orientation is randomized as the  $C_i$  diffuses, removing any direction bias to diffusion. Again, the close correspondence of the LDA and PBE results, shown in the above Table, increases the confidence in these predictions. The DFT reorientation barriers for the split-Ga sites are much higher, and inconsequential for carbon migration. Therefore, the activation energy for carbon interstitial migration is fully represented by the simple barrier to inter-site diffusion tabulated in Table 8.

## 2.5. Defect network reaction energies

Using the defect formation energies tabulated above for the carbon-related defects, and the defect formation energies previously tabulated for intrinsic defects [2], it is straightforward to compute the defect reaction energies of possible reactions in the defect reaction network for C-doped GaAs. All reactions of the three potentially mobile species, the arsenic and gallium self-interstitials and the carbon interstitials, with the common immobile defects, the vacancies and dopants are considered. Selected second order reactions, e.g.,  $As_i + As_{Ga} \rightarrow (As_2)_{Ga}$  (second order noting that  $As_{Ga}$  itself is a product of a mobile  $As_i$  and an immobile  $v_{Ga}$ ), are also included. The results for charge conserving reaction are presented in the following table.

**Table 9. Defect reaction energies, in eV.**

Charge conserving defect reaction						Reaction energy <sup>(a)</sup>	
Reactant defects				Product defect		Simulation context	
Mobile specie	charge	Immobile target	charge	Defect	charge	LDA	PBE
$As_i$	0	$v_{Ga}$	0	$As_{Ga}$	0	-4.77	-4.84
$As_i$	0	$v_{As}$	0	0	0	-7.13	-6.90
$As_i$	0	$vv$	0	$v_{Ga}$	0	-5.08	-4.40
$As_i$	0	$As_{Ga}$	0	$(As_2)_{Ga}$	0	-1.66	-1.54
$As_i$	+1	$Ga_{As}$	0	$Ga_i$	+1	-3.58	-3.41
$As_i$	+1	$C_{As}$	-1	$C_i$	0	-0.60	-0.74
$As_i$	-1	$C_{Ga}$	+1	$(AsC)_{Ga}$	0	-2.76	-2.83
$Ga_i$	+1	$v_{Ga}$	-1	0	0	-5.43	-5.32
$Ga_i$	+1	$v_{As}$	-1	$Ga_{As}$	0	-3.19	-3.09
$Ga_i$	+1	$vv$	0	$v_{As}$	+1	-3.81	-3.39
$Ga_i$	+1	$As_{Ga}$	0	$As_i$	+1	-1.11	-1.06
$Ga_i$	+1	$C_{As}$	-1	$(GaC)_{As}$	0	-0.45	-0.46
$C_i$	0	$v_{Ga}$	+1	$C_{Ga}$	+1	-4.33	-3.85
$C_i$	0	$v_{As}$	-1	$C_{As}$	-1	-6.17	-5.76
$C_i$	0	$vv$	0	$C_{vv}$	0	-4.06	-3.33
$C_i$	0	$As_{Ga}$	0	$(AsC)_{Ga}$	0	-1.82	-1.56
$C_i$	0	$Ga_{As}$	0	$(GaC)_{As}$	0	-3.43	-3.13
$C_i$	0	$C_{As}$	-1	$(C_2)_{As}$	-1	-1.92	-2.10

(a) A negative energy denotes exothermic (downhill) reaction.

### 3. CONCLUSIONS

The defect reaction network for *p*-type carbon doped gallium arsenide is developed, beginning with the interstitials mobilized in displacement damage, following the reactions with the immobile displacement damage defects and the dopant atoms, and culminating in immobile reaction products. The defect reaction energies computed with DFT are presented for each reaction in the network, and the computed properties needed to describe each defect in the network—stable charge states, energy levels, formation energies—are tabulated. Both LDA and PBE results are presented. The results are only presented using “large-core”  $Z=3$  Ga pseudopotentials. The calculations could be straightforwardly repeated with the small-core  $Z=13$  Ga pseudopotentials.

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