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Defect reaction network in Si-doped InP: Numerical predictions

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Defect reaction network in Si-doped InP: Numerical predictions

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Abstract

This Report characterizes the defects in the defect reaction network in silicon-doped, *n*-type InP 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 Si-doped InP until culminating in immobile reaction products. The defect reactions and reaction energies are tabulated, along with the properties of all the silicon-related defects in the reaction network. This Report serves to extend the results for intrinsic defects in SAND 2012-3313: “Simple intrinsic defects in InP: Numerical predictions” to include Si-containing simple defects likely to be present in a radiation-induced defect reaction sequence.

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CONTENTS

Defect reaction network in Si-doped inP: Numerical predictions	3
1. Introduction.....	7
1.1. Computational methods	7
1.2. Verification and validation	8
2. Results.....	9
2.1. Defect atomic structures	9
2.2. Defect charge transition energy levels.....	10
2.3. Defect formation energies.....	12
2.4. Silicon interstitial and migration.....	14
2.4.1. Silicon interstitial structural energies	14
2.4.2. Silicon interstitial diffusion	15
2.5. Defect network reaction energies.....	17
3. Conclusions.....	18
4. References.....	19

TABLES

Table 1. Ground state structure description for silicon reaction network defects.	9
Table 2. Defect levels for silicon reaction network defects, context = LDA.....	10
Table 3. Defect levels for silicon reaction network defects, context = PBE.	10
Table 4. Formation energies of silicon reaction network defects at VBE (in eV), context = LDA.	12
Table 5. Formation energies of silicon reaction network defects at VBE (in eV), context = PBE.	12
Table 6. Formation energies of silicon reaction network defects at CBE (in eV), context = LDA.	13
Table 7. Formation energies of silicon reaction network defects at CBE (in eV), context = PBE.	13
Table 8. Silicon interstitial ground state energies, in eV, context = LDA.....	14
Table 9. Silicon interstitial ground state energies, in eV, context = PBE.....	15
Table 10. Defect reaction energies, in eV.....	17

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
n/x	not exist
PBE	Perdew/Burke/Ernzerhof, a “flavor” of GGA
PP	pseudopotential
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 silicon-doped, *n*-type indium phosphide, InP. The reaction network is deduced from first principles: identifying the primary species likely mobilized during displacement damage, the phosphorus and indium 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 silicon-containing defects in InP. Numerical results for density functional theory (DFT) calculations of properties of simple intrinsic defects in indium phosphide have been presented in a previous SAND Report: 2012-3313, “Simple intrinsic defects in InP: Numerical predictions” [1]. That Report contains detailed tables of intrinsic defect properties—charge transition defect level energies, formation energies, diffusion—predicted with converged DFT. The current report presents the results of DFT calculations for the same defect properties, for silicon-containing defects. Assessment of defect reaction network energies involving only intrinsic defects use values presented in the earlier Report.

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, these reactions are therefore (mostly) neglected. Similarly, because *n*-type silicon doping will preferentially populate defects in their most negative charge states, emphasis is on careful characterization of defect evolution consistent with a Fermi level near the conduction 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], and will only be summarized here.

The DFT calculations are performed with the SEQQUEST code [2], using both the local density approximation (LDA) [3] and the Perdew-Burke-Ernzerhof (PBE) flavor of the generalized gradient approximation [4]. The comparison of LDA and PBE results is a partial assessment of the physical uncertainties within DFT functionals [5]. The pseudopotentials [6] (PP) for In and P are the same used for intrinsic defects calculations [1] and carefully verified. The close correspondence between the 3*d*-core and 3*d*-valence PP for the indium atom are evidence for a good transferability of the 3*d*-core PP for In. Calculations for silicon-containing InP defects are all done with 3*d*-core pseudopotentials (total valence charge $Z=3$) for the In atom, and not repeated with 3*d*-valence ($Z=13$) PP. We had determined that the PP construction for the In atom, the 3*d*-core vs. 3*d*-valence, had only modest effect on computed defect properties, the physical uncertainties in the DFT results being 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 In. The silicon PP in this

work are the same used and extensively validated in previous work for defects in bulk silicon [7] and silicon defects in GaAs [11,12]: generalized norm-conserving Hamann potentials [6], with a double-zeta plus polarization contracted-Gaussian basis set, as taken from the SEQQUEST library of optimized, transferable atomic potentials [2].

As previously [1], defect formation energies are quoted in the phosphorus-rich limit. The chemical potential of the phosphorus atom is set to the computed energy of the phosphorus in the elemental bulk $A7$ structure, and the chemical potential of the indium atom is set to be that required to make the formation energy of perfect InP equal to zero. The chemical potential of a silicon atom is arbitrary, all reactions considered in this Report are silicon number conserving. Here, it is set to the energy of one atom in the crystalline diamond structure of silicon.

The calculations of charged defects use the Finite Defect Supercell Model (FDSM) [7] to incorporate rigorous boundary conditions for the solution of the electrostatic potential in a charged supercell [8,9] and extrapolate the computed defect energies to the infinitely dilute limit. Results for silicon-related defects are presented for 216-site cubic supercells extrapolated to infinitely dilute limits. Cell-size convergence tests for intrinsic defects using results extrapolated from selected 64-site, 512-site, and 1000-site cubic supercells verify that results using 216-site supercell are numerically well converged [1], to less than the physical uncertainties embodied in the functional, satisfying a key criterion of verification and validation of subcontinuum-scale simulations [10]. The simulation contexts presented here correspond to the “LDA” and “PBE” simulation contexts defined in the Report for intrinsic defects in InP [1].

1.2. Verification and validation

The silicon-related defect level calculations all use SEQQUEST and the FDSM, the same methods used in DFT calculations of defects in silicon [7], intrinsic defects in GaAs [11,12], and for silicon-related defect chemistry in GaAs [13,14], 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 in bulk silicon [7] and GaAs [11]. This is the expected accuracy (uncertainties) of the methods for defect level calculations in InP, 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 InP [1] and GaAs [11,12].

2. RESULTS

The section contains the Tables that summarize the numerical results for DFT simulations of silicon-related defects and the radiation-induced defect reaction network in InP.

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 in III-V materials are likely to be the mobile species. 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 silicon substitutional (dopant) atoms. Reactions between mobile species, i.e., second order reactions, are mostly neglected. One of the reaction products in the reaction network for Si-doped InP is the silicon interstitial Si_i , and the current results indicate Si_i might also be a mobile specie, just as in GaAs [13,14]. Hence, its reactions with immobile defects are investigated, and the exothermic reaction products are added to the defect reaction network. The same set of defects analogous to the silicon chemistry in GaAs proved relevant in InP as well. No other reaction products are identified that are likely to be mobile.

2.1. Defect atomic structures

The following Tables summarize the ground state structures for the silicon-containing defects within the defect reaction network. The intrinsic defect structures have been presented previously [1,11] and the same nomenclature is used to describe silicon defect structures as used in the InP and GaAs intrinsic defects and illustrated for GaAs defects in Ref. 11.

Table 1. Ground state structure description for silicon reaction network defects.

Charge state	Si_{In}	Si_{P}	Si_i	$(\text{Si}_2)_{\text{In}}$	$(\text{PSi})_{\text{In}}$	Si_{Vv}
(2-)	-	-	-	C_2 twist-110 _{In}	-	$\text{C}_{1h} \text{V}_{\text{P}}\text{-Si}_{\text{In}}$ res-bond
(1-)	-	T_d	-	C_1 – twice-pucker 001 _{In}	-	$\text{C}_{1h} \text{V}_{\text{P}}\text{-Si}_{\text{In}}$ res-bond
(0)	$\{\text{T}_d\}^a$	$\{\text{T}_d\}^a$	C_{1h} split-00In _a pucker-Si	$\text{C}_{1h} \text{Si}_{\text{In}}\text{—}$ bridge-Si $[\text{T}_{i,\text{In}}]$	$\text{C}_{1h} \text{Si}_{\text{In}}\text{—}$ bridge-P $[\text{T}_{i,\text{P}}]$	$\text{C}_{1h} \text{V}_{\text{P}}\text{-Si}_{\text{In}}$ paired In-In
(1+)	T_d	-	C_{3v} Hex-site	$\text{C}_{2v} \text{Si}_{\text{In}}\text{—}$ Si $[\text{T}_{i,\text{P}}]$	$\text{C}_{1h} \text{Si}_{\text{In}}\text{—}$ bridge-P $[\text{T}_{i,\text{P}}]$	$\text{C}_{1h} \text{V}_{\text{P}}\text{-Si}_{\text{In}}$ paired In-In
(2+)	-	-	$\text{T}_{i,\text{P}}$ [Ida]	$\text{C}_{2v} \text{Si}_{\text{In}}\text{—}$ Si $[\text{T}_{i,\text{P}}]$	C_{1h} split-001 _{In} pucker-P	$\text{C}_{3v} \text{V}_{\text{P}}\text{-Si}_{\text{In}}$

(a) The DFT result is not a defect state, but the state is in reality likely a shallow donor (Si_{In}) or shallow acceptor (Si_{P}), and its level will be *assumed* to be at the respective band edge.

Two further, second-order defects were considered for this Report, the $(\text{InSi})_{\text{P}}$ and the $(\text{P}_2)_{\text{In}}$. The $(\text{InSi})_{\text{P}}$ takes charge states from (0) to (2+), all C_{3v} as a substitutional Si_{P} and nearby $\text{In}_i\{\text{T}_{i,\text{P}}\}$. The $(\text{P}_2)_{\text{In}}$ takes charge states from (1-) to (1+), all as a C_2 symmetry twisted split-110_{In}.

2.2. Defect charge transition energy levels

This section presents the defect charge transition levels of the silicon reaction network defects in InP, in eV, along with the neutral defect formation energies. The defect level predictions are the fundamental result of this Report, the later formation energies and reaction energies are all derived from these results. The quoted defect levels are thermodynamic values, without regard for whether a kinetic barrier might impede a structural rearrangement between the two atomic configurations of the two charge states. Table 2 presents the defect levels computed with in LDA context (all results extrapolated from 216-site cells to infinitely dilute bulk defects), and Table 3 presents the defect levels computed in the PBE context.

Table 2. Defect levels for silicon reaction network defects, context = LDA.

LDA Context	Neutral formation energy	Defect levels (eV), cf. VBE				
		(3+/2+)	(2+/1+)	(1+/0)	(0/1-)	(1-/2-)
$\text{Si}_{\text{In}}^{\text{x}}(0)/\text{Si}_{\text{In}}(+)$	2.24	-	-	3.11	-	-
Si_{In}	(0.55)	n/x	n/x	1.42^{CBE}	-	n/x
$\text{Si}_{\text{P}}(-)/\text{Si}_{\text{P}}^{\text{x}}(0)$	2.11	n/x	n/x	n/x	0.09	n/x
Si_{P}	(2.01)	n/x	n/x	n/x	0^{VBE}	n/x
Si_{i}	3.48	n/x	1.64	0.87	-	-
$(\text{Si}_2)_{\text{In}}$	3.29	1.10	0.34	1.23	0.81	n/x
$(\text{PSi})_{\text{In}}$	2.01	n/x	0.24	0.61	-	-
Si_{VV}	2.62	n/x	0.52	0.57	1.23	1.25
$(\text{InSi})_{\text{P}}$	3.94	n/x	0.74	0.98	-	-
$(\text{P}_2)_{\text{In}}$	2.60	-	-	1.40	1.42	-

Table 3. Defect levels for silicon reaction network defects, context = PBE.

PBE Context	Neutral formation energy	Defect levels (eV), cf. VBE				
		(3+/2+)	(2+/1+)	(1+/0)	(0/1-)	(1-/2-)
$\text{Si}_{\text{In}}^{\text{x}}(0)/\text{Si}_{\text{In}}(+)$	2.14	-	-	3.19	-	-
Si_{In}	(0.37)	n/x	n/x	1.42^{CBE}	-	n/x
$\text{Si}_{\text{P}}(-)/\text{Si}_{\text{P}}^{\text{x}}(0)$	2.35	-	-	-	-0.02	-
Si_{P}	(2.33)	n/x	n/x	n/x	0^{VBE}	n/x
Si_{i}	3.53	n/x	1.69	0.94	-	-
$(\text{Si}_2)_{\text{In}}$	3.13	1.07	0.39	1.28	0.87	n/x
$(\text{PSi})_{\text{In}}$	1.80	n/x	0.34	0.70	-	-
Si_{VV}	2.53	n/x	0.73	0.62	1.32	1.33
$(\text{InSi})_{\text{P}}$	4.18	n/x	0.78	0.99	-	-
$(\text{P}_2)_{\text{In}}$	2.16	-	-	1.36	1.48	-

The first entry for Si_{In} (Si_{P}) in Table 2-3 is the explicit DFT calculated defect level using the site-shifted neutral reference, and the second entry is for the full prediction derived for the on-site dopant defect. Silicon is a shallow n -type dopant in InP, sitting in the indium substitutional site, Si_{In} . Being a shallow donor, Si_{In} has a $(1+/0)$ transition near the valence band edge. However, the DFT calculation buries this state deep in the conduction band and the $\text{Si}_{\text{In}}[0]$ (and its compensating partner $\text{Si}_{\text{P}}[0]$) is not a clean defect state, reflecting a DFT difficulty has treating shallow effective-mass-like states. To evaluate a formation energy for $\text{Si}_{\text{In}}[1+]$ ($\text{Si}_{\text{In}}[1-]$), a clean neutral defect state is needed. A neutral reference state is obtained by exchanging the silicon and a neighboring indium, to create a $\text{P}_{\text{In}}\text{-Si}_{\text{P}}$ [$\text{In}_{\text{P}}\text{-Si}_{\text{In}}$] pair defect, designated as $\text{Si}_{\text{In}}^{\text{x}}(0)$ [$\text{Si}_{\text{P}}^{\text{x}}(0)$], which does have a clean defect state with neutral charge. With this neutral defect and the charge transition energy, the formation energy of $\text{Si}_{\text{In}}[1+]$ (and $\text{Si}_{\text{P}}[1-]$) is obtained directly from the DFT calculations, without assumptions regarding the location of the (computationally inaccessible) shallow on-site transition. The formation energy of the charged substitutional is obtained by reference to the site-switched $\text{Si}_{\text{In}}^{\text{x}}(0)$ [$\text{Si}_{\text{P}}^{\text{x}}(0)$], and then the *neutral* simple substitutional formation energy of Si_{In} [Si_{P}] is obtained by assuming that the level lies at the band edge, *assuming* a band gap of 1.42 eV (the experimental band gap).

The computed levels in the LDA and PBE contexts are very similar, all within 0.2 eV of one another, and mostly within 0.1 eV. 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 defect levels listed in these tables only quote those charge states that are thermodynamically accessible. For example, clean defect states for the $(\text{PSi})_{\text{In}}$ and Si_{i} can be found for $[1-]$ and $[2-]$ charge states and a DX (offset-Si) configuration for Si_{In} , is a clean defect state as a $[1-]$ charge, but none of these is thermodynamically stable, they will spontaneously emit electrons to form the neutral defects. Alternatively stated, the electronic levels are above the CB 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 presented in Table 2-3 in the previous section. As for all the results presented in this Report, the defect formation energies in the following Tables are presented in the phosphorus-rich limit. For consistency with the intrinsic defect results [1], the formation energies of the charged defects are presented with a Fermi level set to be at the VBE. The Tables present the formation energies of the silicon reaction network defects, segregated by simulation context. Only thermodynamically accessible charge states are listed.

Table 4. Formation energies of silicon reaction network defects at VBE (in eV), context = LDA.

Charge state	Si _{ln}	Si _p	Si _i	(Si ₂) _{ln}	(PSi) _{ln}	Si _{vv}	(lnSi) _p	(P ₂) _{ln}
(2-)	-	-	-	-	-	5.11	-	-
(1-)	-	2.01	-	4.10	-	3.86	-	4.02
(0)	(0.55) ^a	(2.01) ^a	3.48	3.29	2.01	2.62	3.94	2.60
(1+)	-0.87	-	2.61	2.05	1.40	2.05	2.97	1.20
(2+)	-	-	0.98	1.72	1.16	1.53	2.23	-
(3+)	-	-	-	0.62	-	-	-	-

a) For T_d on-site Si_{ln}[0] and Si_p[0], assuming a shallow level exactly at the respective band edges, and assuming a band gap of 1.42 eV (the experimental band gap).

Table 5. Formation energies of silicon reaction network defects at VBE (in eV), context = PBE.

Charge state	Si _{ln}	Si _p	Si _i	(Si ₂) _{ln}	(PSi) _{ln}	Si _{vv}	(lnSi) _p	(P ₂) _{ln}
(2-)	-	-	-	-	-	5.19	-	-
(1-)	-	2.33	-	4.00	-	3.85	-	3.64
(0)	(0.37) ^a	(2.33) ^a	3.53	3.13	1.80	2.53	4.18	2.16
(1+)	-1.05	-	2.60	1.85	1.10	1.91	3.19	0.80
(2+)	-	-	0.90	1.47	0.76	1.18	2.40	-
(3+)	-	-	-	0.39	-	-	-	-

a) For T_d on-site Si_{ln}[0] and Si_p[0], assuming a shallow level exactly at the respective band edges, and assuming a band gap of 1.42 eV (the experimental band gap).

The formation energies for the CBE Fermi level consistent with the *n*-type character of Si doping in InP is trivially obtained by simple arithmetic using a band gap energy. Tables 6-7 present the equivalent results to Tables 4-5, arithmetically re-referenced to have the Fermi level at the CBE, appropriate to *n*-type InP given by Si doping, assuming a band gap of 1.42 eV.

**Table 6. Formation energies of silicon reaction network defects at CBE (in eV),
context = LDA.**

Charge state	Si _{ln}	Si _p	Si _i	(Si ₂) _{ln}	(PSi) _{ln}	Si _{vv}	(lnSi) _p	(P ₂) _{ln}
(2-)	-	-	-	-	-	2.27	-	-
(1-)	-	0.59	-	2.68	-	2.44	-	2.60
(0)	(0.55)^a	(2.01)^a	3.48	3.29	2.01	2.62	3.94	2.60
(1+)	0.55	-	4.03	3.47	2.82	3.47	4.39	2.62
(2+)	-	-	3.82	4.56	4.00	4.37	5.07	-
(3+)	-	-	-	4.88	-	-	-	-

a) For T_d on-site Si_{ln}[0] and Si_p[0], assuming a shallow level exactly at the respective band edges, and assuming a band gap of 1.42 eV (the experimental band gap).

**Table 7. Formation energies of silicon reaction network defects at CBE (in eV),
context = PBE.**

Charge state	Si _{ln}	Si _p	Si _i	(Si ₂) _{ln}	(PSi) _{ln}	Si _{vv}	(lnSi) _p	(P ₂) _{ln}
(2-)	-	-	-	-	-	2.35	-	-
(1-)	-	0.91	-	2.58	-	2.43	-	2.22
(0)	(0.37)^a	(2.33)^a	3.53	3.13	1.80	2.53	4.18	2.17
(1+)	0.37	-	4.02	3.27	2.52	3.33	4.61	2.22
(2+)	-	-	3.75	4.31	3.60	4.02	5.24	-
(3+)	-	-	-	4.65	-	-	-	-

a) For T_d on-site Si_{ln}[0] and Si_p[0], assuming a shallow level exactly at the respective band edges, and assuming a band gap of 1.42 eV (the experimental band gap).

2.4. Silicon interstitial and migration

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

2.4.1. Silicon interstitial structural energies

The following Tables present the relative energies of different structures of the silicon 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 Si_i . Of note, and not too surprising, the In site, replacing the larger atom, is more accommodating of more substitutional atoms than the P site. There is, overall, compared to their GaAs analogs, a greater propensity for ejecting interstitial atoms from an in-network covalently bound configuration to leave an on-site atom and a non-bonded interstitial. The relatively flat potential energy surface, on the In and P sites, within 1 eV, indicates a likelihood for thermal diffusion.

Table 8. Silicon interstitial ground state energies, in eV, context = LDA

Structure	Context	Energy relative to ground state structure		
		$\text{Si}_i(0)$	$\text{Si}_i(1+)$	$\text{Si}_i(2+)$
C_{1h} split-001 _{In} pucker-Si (“p-Si”)	LDA	0.17	—> H	-
C_{2v} split-001 _{In}	LDA	1.33	0.81	1.54
C_{1h} split-110 _{In}	LDA	0.35	0.30	—> H- $\text{T}_{i,\text{In}}$
C_{3v} split-111 _{In}	LDA	0.66	0.40	0.79
C_{1h} split-111 _{In} bent In-bridge (to $\text{T}_{i,\text{P}}$)	LDA	0.53	0.33	—> C_{3v}
C_{1h} split-111 _{In} bent In-bridge (to $\text{T}_{i,\text{In}}$)	LDA	0.17	—> H	-
C_{1h} split-001 _P (p-P)	LDA	0	0.31	—> $\text{Si}_\text{P}+\text{P}_i$
C_{2v} split-001 _P	LDA	0.57	0.59	1.80
C_{1h} split-110 _P	LDA	0.36	—> $\text{T}_{i,\text{P}}$	—> $\text{T}_{i,\text{P}}$
C_{1h} bent P-bridge (to $\text{T}_{i,\text{In}}$)	LDA	0.89	—> C_{2v} -001 _P	-
C_{3v} H-site interstitial	LDA	0.23	0	1.21
T_d $\text{T}_{i,\text{P}}$ -site	LDA	CB	CB	0
T_d $\text{T}_{i,\text{In}}$ -site	LDA	1.10	0.48	0.76
C_{3v} H- $\text{T}_{i,\text{In}}$ -site	LDA	H	H	0.66

Table 9. Silicon interstitial ground state energies, in eV, context = PBE

Structure	Context	Energy relative to ground state structure		
		Si _i (0)	Si _i (1+)	Si _i (2+)
C _{1h} split-001 _{In} pucker-Si (“p-Si”)	PBE	n/a	—> H	-
C _{2v} split-001 _{In}	PBE	1.08	0.65	1.33
C _{1h} split-110 _{In}	PBE	0.32	0.29	—> H-T _{i,In}
C _{3v} split-111 _{In}	PBE	0.43	0.25	0.74
C _{1h} split-111 _{In} bent In-bridge (to T _{i,p})	PBE	0.51	0.31	-
C _{1h} split-111 _{In} bent In-bridge (to T _{i,In})	PBE	0.05	—> T _{i,In}	-
C _{1h} split-001 _P (p-P)	PBE	0	0.34	—> Si _P +P _i
C _{2v} split-001 _P	PBE	0.45	0.48	—> P _P +Si _i (T _{i,In})
C _{1h} split-110 _P	PBE	0.27	—> T _{i,P}	—> T _{i,P}
C _{1h} bent P-bridge (to T _{i,In})	PBE	0.75	—> C _{2v} -001 _P	-
C _{3v} H-site interstitial	PBE	0.19	0	1.19 (T.S.)
T _d T _{i,P} -site	PBE	CB	CB	0
T _d T _{i,In} -site	PBE	CB	CB	0.87
C _{3v} H-T _{i,In} -site	PBE	CB	CB	0.69

The LDA and PBE structural landscapes for the silicon interstitial are similar to each other. The PBE results tend to have more states that rise into the conduction band rather than remain defect states, but the ground state structures are mostly unaffected. The silicon interstitial strongly favors in-network sites when neutral, and favors non-bonding interstitial sites when positively charged, dissociating into an on-site atom (P or Si) and a nearby interstitial.

2.4.2. Silicon interstitial diffusion

The Si interstitial favors in-network bonds in the neutral charge state that will dominate *n*-type InP. A comprehensive assessment of diffusion for the neutral defect, computation of continuous pathways and explicit migration barriers, is likely impractical using a semilocal functional, because of extensive regions, particularly the non-network configurations, where the defect state crosses into the conduction band. However, thermal migration might be facile, with many configurations on the In site and the P site having energies within 1 eV of the ground state.

Unlike for the arsenic interstitial in GaAs [13], there is not an identified path that could mediate athermal diffusion [15] of the silicon interstitial via a Bourgoin-Corbett mechanism [16], in either the LDA or PBE context simulations. With the bistability with charge state—different metastable configurations having different relative stabilities with a change in charge state—however, one can anticipate that recombination-enhanced diffusion will contribute significantly to the diffusion of the Si interstitial. There is a possibility of athermal diffusion, an extreme limit of recombination-enhanced diffusion where there is no thermal barrier, as the Si interstitial changes from an in-network neutral defect to non-network ionized interstitial defect. Recombination-enhanced diffusion by this mechanism would likely be enabled in non-equilibrium radiation-damaged regions of InP.

2.5. Defect network reaction energies

Using the defect formation energies tabulated above for the silicon-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 Si-doped InP. All reactions of the three potentially mobile species, the phosphorus and indium self-interstitials and the silicon interstitials, with the common immobile defects, the vacancies and substitutional dopant, are considered. The results for charge conserving reaction among intrinsic defects and also silicon-containing reactions are presented in the following Table, with a sampling of second-order defect reactions.

Table 10. Defect reaction energies, in eV.

Charge conserving defect reaction						Reaction energy ^(a)	
Reactant defects				Product defect		Simulation context	
Mobile specie	charge	Immobile target	charge	Defect	charge	LDA	PBE
P _i	0	v _{In}	0	P _{In}	0	-4.17	-4.15
P _i	0	v _P	0	0	0	-5.79	-5.66
P _i	0	v _V	0	v _{In}	0	-4.45	-3.93
P _i	0	In _P	0	In _i	0	-1.82	-1.86
P _i	0	P _{In}	0	(P ₂) _{In}	0	-2.47	-2.44
In _i	0	v _{In}	0	0	0	-7.11	-7.02
In _i	0	v _P	0	In _P	0	-3.98	-3.80
In _i	0	v _V	0	v _P	0	-5.76	-5.29
In _i	0	P _{In}	0	P _i	0	-2.94	-2.93
In _i	0	Si _P	0	(InSi) _P	0	-0.33	-0.55
P _i	-1	Si _{In}	+1	(PSi) _{In}	0	-1.29	-1.15
In _i	-1	Si _{In}	+1	Si _i	0	-1.08	-0.90
Si _i	0	v _{In}	+1	Si _{In}	+1	-6.15	-6.23
Si _i	0	v _P	-1	Si _P	-1	-4.93	-4.77
Si _i	0	v _V	0	Si _{v_V}	0	-5.19	-4.80
Si _i	0	P _{In}	0	(PSi) _{In}	0	-3.32	-3.39
Si _i	0	Si _{In}	+1	(Si ₂) _{In}	+1	-0.55	-0.63
Si _i	0	In _P	0	(InSi) _P	0	-2.35	-2.48

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

Note that the direction of the charge-conserving reactions does not necessarily align with direction of the thermodynamic reaction. In particular, a reaction that is uphill(downhill) in charge-conserving form, might be downhill(uphill) thermodynamically for a Fermi level at the CB edge, i.e., allowing for the capture of carriers appropriate to that Fermi level.

3. CONCLUSIONS

The defect reaction network for *n*-type silicon-doped indium phosphide 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 the 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” $Z=3$ In pseudopotentials. The calculations could be straightforwardly repeated with the small-core $Z=13$ In pseudopotentials.

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