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# First-principles study of the diffusion mechanisms of the self-interstitial in germanium

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## Abstract

The self-interstitial in germanium can assume multiple configurations depending on the temperature and charge state. Here, we employ a first-principles density functional method to investigate the diffusion mechanisms of this defect. The energy barriers associated with the transformation between different structures are determined by the climbing nudged elastic band method, as a function of the charge state. The relation between the thermodynamic properties of the self-interstitial and the temperature evolution of electron radiation damage in germanium are discussed.

## 1. Introduction

The self-interstitial (I) and the vacancy (V), the primary intrinsic defects, are highly mobile and reactive, taking part in many defect reactions and mediating the diffusion of dopants and other impurities. In silicon, diffusing self-interstitials readily form complexes with O, B and H and other self-interstitials, some of them stable up to very high temperatures [1–5]. Many of these interstitial aggregates are electrically active acting as charge carrier traps and recombination centres, and their introduction in the active region of the devices has to be prevented. In germanium, the fate of the interstitials after irradiation or implantation and the reactions and complexes it is involved in are still not well understood. This basic knowledge is necessary to achieve the levels of doping and gettering efficiency required if germanium is to be viewed as an alternative material for CMOS technology.

Much of what is known today about the self-interstitial was obtained by monitoring the trapping of V and I at In probes by perturbed angular correlation spectroscopy (PACs) as a function of the temperature and doping [6]. Ge samples implanted with <sup>111</sup>In probes were submitted to 1.2 MeV electron irradiation at 77 K creating I–V pairs. Upon annealing,

two quadrupole interaction frequencies labelled  $\nu_{Q1}$  and  $\nu_{Q2}$ , corresponding to intrinsic defects trapped at the <sup>111</sup>In probes, appear in the PAC spectra. The first signal  $\nu_{Q1}$ , observed in p-type material upon annealing at 200 K, had already been produced in a previous study by the knock-on of <sup>111</sup>In atoms resultant from the neutrino-decay of <sup>111</sup>Sn atoms, and assigned to <sup>111</sup>In probes decorated with vacancies [7]. The  $\nu_{Q2}$  defect, observed only in the trapping experiment, was related to the other component of the Frenkel pair—the interstitial—trapped at the probe atom. The  $\nu_{Q2}$  defect was observed in moderately doped n- and p-Ge, but not in heavily doped material, above 220 K. As mobile radiation defects are expected to be trapped at the <sup>111</sup>In probes only if a long-range attractive interaction, usually Coulomb interaction, exists, the Fermi-level dependence of the trapping rate can simply be explained if the vacancy has an acceptor level at  $E_v + 0.2$  eV, and the self-interstitial has a donor level at  $E_c - 0.04$  eV. This is consistent with our recent calculation of a donor and double donor levels of the self-interstitial within about 0.2 eV from the conduction band [8]. Further, it suggests that in the conditions of the trapping experiment, V and I become mobile at 200 and 220 K, respectively.

However, in p-type germanium irradiated at 5 K with 1–2 MeV electrons, conductivity changes are already observed

at 100 K in the dark or at even at lower temperatures under light excitation [9–12]. As the vacancy is neutral in p-type Ge [13], these alterations have to be related to a transformation or migration of the self-interstitial.

Theoretical migration barriers ranging from 0.09 to 0.4 eV [14] were suggested for the neutral self-interstitial. However, we have recently shown that the potential energy surface for the self-interstitial in germanium is very dependent on the charge state, and therefore the migration energies are also expected to vary considerably [8, 15]. We thus find the need to go beyond [8] by describing the possible microscopic mechanisms for the motion of the self-interstitial in the three charge states, and discuss other transformations that may occur under ionizing conditions.

With this aim, we have carried out a first-principles study of the minimum energy migration paths in the three charge states  $I^0$ ,  $I^+$  and  $I^{++}$ . The details of the method used will be described in the next section. In section 3, we start by reviewing the equilibrium structures and the electrical activity of the defect. Then, we proceed to present a detailed study of the preferred diffusion paths and respective activation energies. Finally, in section 4 we review our conclusions and discuss how they link with experiment.

## 2. Method

We employ density functional pseudopotential calculations, carried out using the AIMPRO code [16]. A Padé parameterization of the exchange-correlation functional of Perdew–Wang was used together the dual space separable pseudopotentials of Hartwigsen, Goedecker and Hutter [17]. We included non-linear core-correction (NLCC) to account for the 3d semi-core electrons of Ge [18].

A C44G\* contracted basis set of Cartesian Gaussian orbitals (CGOs) [19] was optimized for bulk germanium [20]. The basis consisted of 2, 6 and 5 s, p and d-type atom-centred Gaussian orbitals, in a total of 13 functions per atom.

The germanium crystal was modelled by large hydrogen-passivated clusters ( $\text{Ge}_{329}\text{H}_{172}$ ) generated using the experimental lattice constant of Ge ( $a_0 = 5.657 \text{ \AA}$ ), and centred on a lattice site [21]. The defects were placed at the centre of the clusters, which were then relaxed maintaining the outer Ge–H units locked in their initial positions. To confirm the independence of the results on the boundary conditions,  $\text{Ge}_{181}\text{H}_{116}$  atom-centred cluster and a  $\text{Ge}_{329}\text{H}_{172}$  cluster centred on the tetrahedral interstitial site were employed [8]. All results presented here were calculated in the  $\text{Ge}_{329}\text{H}_{172}$  cluster unless otherwise stated.

The equilibrium structures, which correspond to local minima of the potential energy surface, were relaxed using the conjugate gradient algorithm [16], without imposing a restriction on the configurational symmetry, as described in [8]. Donor and acceptor levels for these structures were calculated using the semi-empirical marker method, which consists of comparing the electron affinities or ionization energies of the defects with the equivalent quantities calculated for well known defects (the markers) [19]. As marker we have used substitutional S and its experimental levels were taken

**Table 1.** Calculated energies (eV) of germanium self-interstitials in the  $\langle 110 \rangle$  split-interstitial, puckered hexagonal and tetrahedral configurations. Letters indicate the final position that an unstable initial configuration relaxes to.

Initial configuration	0	+	++
D	0.00	0.08 ( $D_d$ )	T
H	0.50	0.00 ( $H_d$ )	T
T	H	$H_d$	0.00

from [22]. The difference between calculated  $E(0/+)$  energies if  $\text{Au}_s$  or  $\text{S}_s$  are chosen as markers is just 0.01 eV.

The diffusion and reorientation barriers were calculated by using the climbing nudged elastic band method (NEB) [23]. The starting point of the diffusion calculation is the initial and final equilibrium structures,  $\mathbf{R}_A \equiv \mathbf{R}_1$  and  $\mathbf{R}_B \equiv \mathbf{R}_N$ . The first chain of intermediate structures  $\mathbf{R}_i$  with  $i = 2, \dots, N - 1$ , named images, is generated by linear extrapolation of the initial and final structures. Each pair of successive images is coupled by a virtual elastic band, and the atoms of each image are moved until the forces vanish. The images are allowed to move maximizing the energy along the direction of the band (climb) after three iterations of the regular NEB method. A set of five images ( $N = 5$ ) was used in the present calculations. In the cases when a high-symmetry saddle point is found, relaxation under symmetry restriction was subsequently used to verify its energy.

To avoid rounding errors, we quote energies with two decimal digits. However, the real accuracy of the calculated values when compared to experimental values is typically lower, due to the theoretical approximations employed.

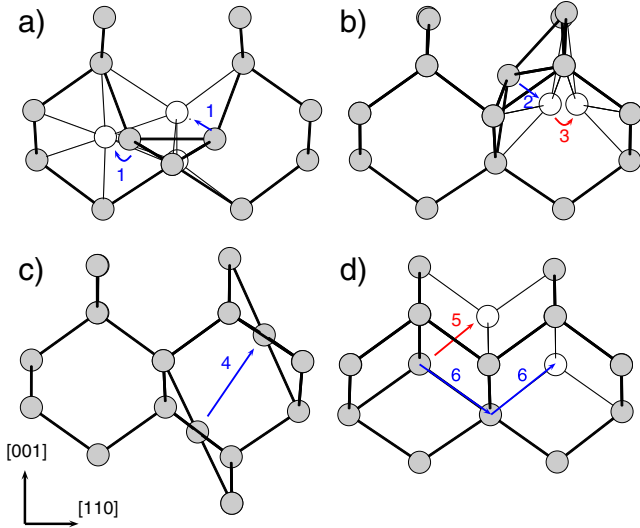
## 3. Results

### 3.1. Equilibrium structures and electrical levels

The high-symmetry configurations of the self-interstitial which will be discussed here are the  $I_T$  configuration, where the self-interstitial is at the tetrahedral interstitial (T) site, the  $I_H$  configuration, where the interstitial is at the puckered hexagonal (H) interstitial site, and the  $\langle 110 \rangle$  split-interstitial (or ‘dumbbell’) structure ( $I_D$ ) where the split-interstitial unit is centred at the lattice site. Depending on the charge state, these are minimum, maximum or saddle points of the energy surface [8].

The equilibrium structures found by relaxation and their relative energies are shown in table 1. The  $\langle 110 \rangle$  split-interstitial is the lowest energy configuration for the neutral interstitial, as found by previous studies [24–26]. However, when positively charged, this structure becomes unstable upon relaxation on the  $\langle 110 \rangle$  plane, ending up in a  $C_{1h}$  atomic arrangement 0.16 eV lower in energy than  $I_D$ , which we label  $D_d$ .

The position of the energy minimum along the  $\langle 111 \rangle$  between the T and H sites is also charge state dependent. It is at the H interstitial site when the interstitial is neutral ( $I_H^0$ ), at the T interstitial site when double positive ( $I_T^{+2}$ ), and in a  $C_{3v}$  configuration, displaced 0.76  $\text{\AA}$  from the H site, when single



**Figure 1.** Structural transformations involved in the migration of the self-interstitial (a) reconfiguration of the neutral defect (step 1) from a dumbbell structure to the nearest H site; (b) reorientation of  $I_{H_d}^+$ , through the undistorted H site (step 2), and reorientation inside the cage (step 3); (c)  $\langle 111 \rangle$  migration of  $I_H$  (step 4) through the T site and (d) migration of  $I_T^{+2}$  along the  $\langle 111 \rangle$  chain (step 5) or by knock-on (step 6).

(This figure is in colour only in the electronic version)

positively charged ( $I_{H_d}^+$ ) [8]. Some other split-interstitial structures such as a  $\langle 100 \rangle$  split-interstitial, were also found to be local energy minima, but they are too high in energy to be relevant. For  $I_T^{+2}$ , though, we found no energy minimum other than the T site.

The  $\langle 110 \rangle$  dumbbell interstitial is electrically inactive. The  $(0/+)$  donor level is found to be at  $E_c - 0.84$  eV, or about 0.1 eV below the valence band, in agreement with previous calculations [24]. However, in disagreement with [24], we found that the acceptor level of  $I_D$  lies in the conduction band. This discrepancy may be due to a difficulty in the interpretation of defect levels calculated in [24] using the formation energy method which lie between the calculated and experimental positions of the conduction band [19].

The caged interstitial (at H, T or  $H_d$  depending on its charge) is a double donor, with  $E(+/+2) = E_c - 0.08$  eV and  $E(0/+) = E_c - 0.24$  eV. This is close to the level measured by the PACs experiments at  $E_c - 0.04$  eV [6]. Self-interstitial levels close to the conduction band were also reported by conductivity experiments in n-type Ge ( $\sim E_c - 0.07$  eV) and p-type Ge ( $\sim E_c - 0.1$  eV) which may be related to the self-interstitial [27, 10]. No acceptor level was found for any of the defects investigated. The typical uncertainty of calculated electrical levels due to the underlining approximations is about 0.1 eV [8].

Hence, there are three charge states in which the self-interstitial can migrate: neutral, positive and double positive, and the potential energy surface has different minima and saddle points for each of them.

**Table 2.** Lowest activation energies ( $W$ ) in eV for the single-barrier transformations of the self-interstitial. Primes (') indicate the same defect in different positions (figure 1).

Transformation	Charge	$W$
$D \xrightarrow{\text{step 1}} H$	0	0.53
$D_d \xrightarrow{\text{step 1}} H_d$	+	0.10
$H_d \xrightarrow{\text{step 2}} H'_d$	+	0.29
$H_d \xrightarrow{\text{step 3}} H'_d$	+	0.06
$H \xrightarrow{\text{step 4}} H'$	0	0.50
$T \xrightarrow{\text{step 5}} T'$	+2	1.23
$T \xrightarrow{\text{step 6}} T'$	+2	1.47

**Table 3.** Lowest calculated migration energies (eV) and respective diffusion paths of the self-interstitial. When more than one atomic transformation is involved,  $W_{\text{mig}}$  is taken to be the dominant energy barrier. Primes (') indicate the same defect in different positions (figure 1).

Charge	Suggested mechanism	$W_{\text{mig}}$
0	$D \xrightarrow{\text{step 1}} H \xrightarrow{\text{step 1}} D'$	0.53
+	$H_d \xrightarrow{\text{step 2}} H'_d \xrightarrow{\text{step 3}} H''_d$	0.29
+2	$I_T^{+2} + e^- \rightarrow I_H^+ \xrightarrow{\text{step 2}} I_H^{+'}$	$[E^{(+2/+)} - E_F] + 0.29$

### 3.2. Diffusion paths

Long-range migration paths can be decomposed into single-barrier jumps between the energy minimum points. These elementary steps comprise transformations between different interstitial structures (figure 1(a)), defect re-orientations (figure 1(b)) and jumps between equivalent configurations (figures 1(c) and (d)).

The low-energy migration paths and the energy barriers associated with each of these steps were found by applying the nudged elastic band algorithm as described in section 2.

**3.2.1. Migration of neutral  $I$ .** The neutral self-interstitial is stable at the D site, but also at the H site where it is only 0.50 eV higher in energy (table 1).  $I_T$  is a saddle point, 1.00 eV higher in energy than at  $I_D$ .

The activation energy required to transform  $I_D$  into  $I_H$ , as depicted in figure 1(a), was found to be 0.53 eV only (table 2). This makes the succession of reconfigurations  $D \xrightarrow{\text{step 1}} H \xrightarrow{\text{step 1}} D'$  a preferred diffusion path. From a H site, there are six equivalent neighbouring lattice atoms which  $I_H$  can move to and form a dumbbell with, and each  $I_D$  can jump with equal probability into one of four H sites in two distinct interstitial cages. Migration along the  $\langle 111 \rangle$  (figure 1(c)) is very unlikely, since it involves a passage through the highly unstable T site.

We thus estimate the dominant barrier for the long-range diffusion of the neutral self-interstitial to be  $\sim 0.5$  eV (table 3).

**3.2.2. Migration of  $I_H^+$ .** The ground state structure of the positive interstitial is  $I_{H_d}^+$ , in which it occupies an intermediate position between the T and H sites.

Long-range migration has to produce a net displacement to a distinct T–H–T cage. This can be accomplished via a succession of the re-orientations 2 and 3 shown in figure 1(b).

$H_d \xrightarrow{\text{step 3}} H'_d$  is a reorientation inside the interstitial cage, in the neighbourhood of the T site, and requires very little energy. The dominant energy for the long-range diffusion is given by step 2, a jump over the 0.3 eV energy barrier centred at the undistorted H site.

An alternative migration path would involve a transformation  $H_d^+ \xrightarrow{\text{step 1}} D_d^+$  and reverse. The calculated energy barrier for this transformation is of the order of only 0.1 eV, but as the (+/0) level of  $I_D$  is below the valence band, the respective transition rate will probably be negligible under non-ionising conditions.

We thus found a migration energy of 0.3 eV for  $I^+$ , providing that the defect remains enough time in this charge state. This issue will be further explored in section 4.

**3.2.3. Migration of  $I_T^{+2}$ .** The double positive interstitial is stable only in the T interstitial site, and unlike for  $I^+$ , its potential energy surface is very steep. The preferred migration energy is a zig-zag motion along the  $\langle 111 \rangle$  (step 5), as represented in figure 1(d). The energy at the saddle point, the H site, is 1.23 eV higher than at T.

A knock-on mechanism, through a split  $\langle 110 \rangle$  interstitial-like configuration (path 6 depicted in figure 1(d)) would be even less probable, with an activation energy of 1.47 eV.

Depending on the lifetime of the  $I_H^+$  charge state, the trapping of an electron from the conduction band by a double positively charged interstitial followed by the fast migration of  $I_H^+$  becomes the dominant over the pure thermal diffusion of  $I_T^{+2}$ . This process may be faster even in p-Ge, since there are reports of donors which act as long-lived electron traps close to the conduction band in p-type Ge below 200 K [10, 11].

**3.2.4. Ionisation-enhanced diffusion.** We have seen that the potential energy transverse for the caged self-interstitial ( $I_H/I_T$ ) between T and H sites varies with charge state, so that the saddle point for  $I^0$  is an equilibrium position for  $I^{+2}$  and vice-versa. Hence, in addition to the thermal migration processes described, it is possible that under ionizing conditions the migration of self-interstitials through the interstitial cages is enhanced by the Bourgoin mechanism and/or energy release mechanism [28]. A possible Bourgoin migration mechanism for the self-interstitial can be conceived as follows: The equilibrium position for  $I^{+2}$  is the T site, but if it traps two electrons, the  $I_T^0$  structure is no longer stable. The double electron capture is then followed by a spontaneous relaxation to one of the two neighbouring H sites. Then, a subsequent trapping of two holes would leave the self-interstitial in the  $I_H^{+2}$  state forcing a relaxation to one of the neighbouring T sites. This provides a possible process for a thermal migration in the presence of excess free carriers, as during irradiation or under other source of excitation, similar to what has been suggested to happen in p-Si [28], which may be in the origin of the radiation annealing and light-induced annealing at cryogenic temperatures reported in n-type and p-type Ge [29–31, 27].

## 4. Discussion and conclusions

We start by discussing the consequences of the  $D \rightarrow H$  transformation for the electrical activity of the defect. Since the  $I_D$  form is electrically inactive, but the caged ( $I_H/I_T$ ) interstitial is a double donor with a level close to the conduction band, once the defect has enough thermal energy to overcome the  $\sim 0.5$  eV energy barrier, we expect it to display negative- $U$  behaviour. The (0/+) level, associated with the  $I_D^0 \rightarrow I_H^+ + e^-$  transformation, is found in our calculations to be close below the valence band maximum ( $E_v - 0.02$  eV), and well below the  $I_{H \rightarrow T}^{(+/+2)}$  level at  $E_c - 0.1$  eV. This implies that, at high temperatures, the most mobile species  $I^+$  is thermodynamically unstable, since the reaction  $2I_H^+ \rightarrow I_D^0 + I_T^{++}$  is exothermic.

We found that the most mobile self-interstitial species is  $I_{H_d}^+$ , which diffuses with an activation energy of about 0.3 eV. However, migration of the self-interstitial in this charge state is only possible if, in average,  $I^+$  remains positively charged enough time to undertake one migration step or equivalently, if the lifetime of  $I_H^+$  is larger than the average time taken by the  $H_d \xrightarrow{\text{step 2}} H'_d \xrightarrow{\text{step 3}} H''_d$  process.

The neutral self-interstitial is also highly mobile, undertaking long-range migration via a succession of transformations between  $I_D$  and  $I_H$ , with a dominant energy barrier of  $\sim 0.5$  eV.

The double positive interstitial, however, was only found to be stable at the T site and needs to overcome a minimum barrier of about 1.2 eV to move through the minimum energy path passing at the H site. In this case, we propose that, depending on the Fermi energy and on the attempt frequencies associated with the electron capture and atomic motion, trapping an electron from the conduction band and moving as  $I^+$  may be a more efficient diffusion process for  $I^{+2}$ . The energy required for this combined mechanism, under the adiabatic approximation, can be estimated as  $E(+2/+) - E_F + 0.29$  eV.

PACs trapping experiments determined a migration energy of 0.5–0.6 eV for the self-interstitial in p-type germanium [7]. As the Fermi level crosses the  $E_c - 0.04$  eV level (calculated to be at  $\sim E_c - 0.2$  eV), some of the neutral self-interstitials, most of them in the dumbbell form, first become positively charged ( $I_H^+$ ) then double positively charged ( $I_T^{+2}$ ), and start their migration towards the negatively charged probes. Thus, the measured activation energy is larger than the calculated migration barrier for the most mobile species  $I_H^+$  of 0.3 eV since, in p-type Ge, additional energy is necessary to activate the release of a hole by  $I^{+2}$ . A lower activation energy for the motion of the  $I^+$  species is consistent with the fact that, in p-type Ge irradiated at 5 K, conductivity changes are already observed from 100 K in the dark [9–11]. We have suggested previously that this may be triggered by the motion of the positively charged self-interstitial [8].

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