Self-Interstitial in Germanium

A. Carvalho,* R. Jones, and C. Janke
School of Physics, University of Exeter, Stocker Road, Exeter, EX4 4QL, United Kingdom

J. P. Goss and P. R. Briddon
School of Natural Sciences, University of Newcastle upon Tyne, Newcastle upon Tyne, NE1 7RU, United Kingdom

J. Coutinho
Department of Physics and 13N, University of Aveiro, 3810 Aveiro, Portugal

S. Öberg
Department of Mathematics, Luleå University of Technology, Luleå S-97187, Sweden
(Received 27 April 2007; published 26 October 2007)

Low-temperature radiation damage in n- and p-type Ge is strikingly different, reflecting the charge-dependent properties of vacancies and self-interstitials. We find, using density functional theory, that in Ge the interstitial is bistable, preferring a split configuration when neutral and an open cage configuration when positively charged. The split configuration is inert while the cage configuration acts as a double donor. We evaluate the migration energies of the defects and show that the theory is able to explain the principal results of low-temperature electron-irradiation experiments.

DOI: 10.1103/PhysRevLett.99.175502 PACS numbers: 61.82.Fk, 61.80.Az, 61.80.Ed, 61.80.Fe

Vacancies and self-interstitials are primary defects formed either thermally at high temperatures or by irradiation with particles or gamma rays, and which can compensate shallow donors and acceptors. They can be very mobile—the self-interstitial diffusing at 4 K in p-type Si—and are known to mediate the diffusion of dopants and participate in many defect complexes stable to high temperatures. These properties earn them a special and fundamental place in studies of defects and diffusion in any material.

Low-temperature irradiation of p-type silicon (p-Si) leads to the production of deep donor defects such as vacancies (V^{2+}) and BI^{+}, a complex of a self-interstitial (I) and boron, both of which compensate chemical acceptors [1]. The situation is very different in p-type germanium, where electron irradiation below 100 K leaves the carrier concentration *unaffected* [2,3]. It seems paradoxical that defects containing broken bonds should be electrically inert. In contrast with p-Ge, irradiation of n-Ge leads to the formation of Frenkel pairs stable up to 65 K. These are double acceptors [4] and readily understood in terms of charged vacancies [5] with a nearby neutral interstitial. Thus it seems that at 4 K, electron irradiation introduces interstitials in a neutral charge state both in n-Ge and p-Ge.

However, light excitation or annealing above 100 K of irradiated p-Ge reveals the presence of primary defects. Between 100 and 200 K, the free hole concentration decreases and a strange "two-state" defect is observed [6–8]. This defect, which seems to be an intrinsic donor [7,8], is a long-lived electron trap that can be cycled between two charge states, denoted "+" and "0", with a transition level around $E_c - 0.2$ eV [7,8]. The stable state in p-Ge is + but a burst of free electrons from ionizing radiation puts the defect into the 0 state. The latter state is correlated with the $S = 1/2$ P1 electron paramagnetic resonance (EPR) center and must therefore have an odd number of electrons [7]. Thus the true charge state of the 0 state cannot be neutral as has been assumed [8]. At about 200 K, the two-state donor defect disappears with an activation energy of 0.4 eV [8].

Density functional calculations showed that the neutral self-interstitial prefers a $\langle 110 \rangle$ split-interstitial configuration and has a high formation energy, even higher than that of the vacancy [9–11]. Here, we investigate the electrical activity and the diffusion energy of the various self-interstitial species. In contrast with previous studies [9–11], we considered the possibility of structural changes with charge state, which are known to occur in Si [12]. We show that bistability has important consequences for the mobility and electrical activity of the defect, and is necessary to explain low-temperature irradiation experiments on both n- and p-type Ge.

We employ density functional pseudopotential calculations, carried out using the AIMPRO code [13]. A Padé parameterization of the exchange-correlation functional of Perdew-Wang was used together the dual space separable pseudopotentials of Hartwigsen, Goedecker, and Hutter [14]. We included nonlinear core-correction (NLCC) to account for the $3d$ semicore electrons of Ge [15].

The germanium crystal was modeled by large hydrogen-passivated clusters. The surface germanium atoms and their hydrogen terminators were kept fixed, and all the other atoms were allowed to move during structural optimizations. Donor and acceptor levels were calculated using the semiempirical marker method, which consists of com-

TABLE I. Calculated relative energies (eV) of germanium self-interstitials in the ⟨110⟩ split-interstitial (D), hexagonal (H) and tetrahedral (T) configurations. Letters indicate the final structure upon relaxation of an unstable initial configuration. Previous *ab initio* supercell calculations found the T and H configurations to be 0.90 (0.29) eV and 0.65 (0.44) eV higher in energy than the D, as reported in Ref. [9] (Ref. [10]).

Cluster		This work				
	Charge	2−	−	0	+	2+
$Ge_{329}H_{172}$	D	0.00	0.00	0.00	0.08	T
	H	1.02	0.73	0.50	0.00	T
	T	1.30	1.10	H	H	0.00
$Ge_{338}H_{184}$	D	0.00	0.00	0.00	0.11	T
	H	0.89	0.66	0.48	0.00	T
	T	1.18	1.07	H	H	0.00

paring the electron affinities or ionization energies of the defects with the equivalent quantities calculated for well-known defects (the markers) [16]. Experimental levels for the markers were taken from Refs. [17,18]. Diffusion energies were obtained using the climbing nudged elastic band (NEB) method [19].

To confirm the independence of the results with the boundary conditions, we used clusters of different sizes and shapes for comparison. Two of them were octahedral, centered on a lattice site, but differed in size, having $Ge_{181}H_{116}$ and $Ge_{329}H_{172}$ compositions. Relative energies of different configurations were found to differ less than 0.1 eV between both clusters, and the donor levels were found to be converged within 0.05 eV using substitutional Au or S as marker, or 0.15 eV using Te as marker. We also used a cluster centered on the tetrahedral interstitial site, with composition $Ge_{338}H_{184}$, and obtained the same relative energies within 0.1 eV.

We studied the structure of self-interstitials in the charge states ranging from double negative (2−) to double positive (2+). A variety of configurations was considered for each of the charge states, including the high symmetry hexagonal (H) and tetrahedral (T) interstitial sites and several distortions of those, and the configurations obtained by replacing a lattice atom by two germanium atoms split along the ⟨110⟩, ⟨100⟩, ⟨111⟩ or ⟨311⟩ directions. The symmetry was not restricted during the structural optimizations, and small perturbations were deliberately introduced in the atomic positions to test the stability of the final structures.

We find that the neutral interstitial (I^0) has the lowest energy in the form of a ⟨110⟩ split-interstitial or dumbbell (Table I) in agreement with previous calculations [9–11]. There is a large energy difference of 0.5 eV separating this structure from I^0 occupying an hexagonal site (Fig. 1). The ⟨110⟩ dumbbell (D) interstitial has neither a donor nor acceptor level lying in the gap (Table II). This is always the case when using either Te, S, Au, or VO as markers. The long range migration energy of this defect is also close to 0.5 eV (Table III).

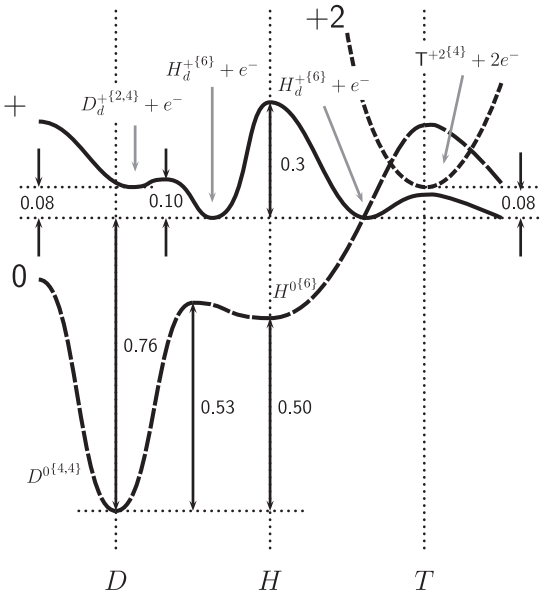

FIG. 1. Configuration-coordinate diagram for the self-interstitial. All energies shown are in eV and were calculated in the $Ge_{329}H_{172}$ cluster, using S as marker. Coordination numbers of the interstitial atom(s) are given in superscript, brackted. Ge-Ge bonds within 10% of the bulk bond length were considered.

In the positive charge state, this configuration is metastable and the interstitial prefers to be in an open cage, where it possesses a donor level. The lowest energy form of I^+ is a ⟨111⟩ distorted hexagonal (H_d) interstitial, favorable by only 0.08 eV relative to the D configuration (Table I). The long range migration energy of the positive H_d interstitial is 0.3 eV (Table III).

In the double positive charge (I^{2+}), only the T interstitial is stable and its migration energy is 1.2 eV. The (+/2+) level is calculated to be at about $E_c - 0.2$ eV. Thus, the self-interstitial can exist in three different charge states: 0, +, and 2 + , and in each of them the defect has a different atomic arrangement.

Previous studies of the electrical activity of the interstitial concentrated on the dumbbell form only [9–11]. The earliest work [9] found a deep donor level at $E_v + 0.07$ eV and an acceptor level at $E_v + 0.1$ eV, while subsequent work [10] found that the donor level lies 0.08 eV below E_v

TABLE II. Calculated self-interstitial levels (eV), obtained in $Ge_{329}H_{172}$ clusters. Donor levels calculated using Au_s as reference are a better estimate for defect levels close to E_v, while the Te_s marker gives better estimates of the defect levels close to E_c. The calculated difference of ionization energies of Au_s and Te_s is 0.70 eV, to be compared with 0.60 eV from experimental data.

Marker	(−/0)	(0/+)	(+/2+)
Configuration	$D \rightarrow D$	$D \rightarrow H$	$H \rightarrow T$
Au_s	$\sim E_v + 1$	$E_v - 0.03$	⋯
S_s	⋯	$E_c - 0.76$	$E_c - 0.08$
Te_s	⋯	$E_c - 0.87$	$E_c - 0.20$

TABLE III. Calculated activation energies (eV) for the dominant annealing mechanisms for the isolated I and V. Experimental values previously assigned to those defects [20–22] and to the two-state defect [7,8] are also shown for comparison.

Defect	Mechanism	W_{calc}	W_{expt}
$I_D \rightarrow I_H$	Transformation	0.5	
I^0	Migration	0.5	
I^+	Migration	0.3	0.1–0.6[a]
I^{2+}	Migration (through H site)	1.2	
V^0	Migration	0.7[b]	0.52[c]
V^-	Migration	0.5[b]	0.42[c]
V^{2-}	Migration	0.3[b]	0.1–0.2[d]

[a]Refs. [7,8,20]
[b]Ref. [23]
[c]Ref. [22]
[d]Refs. [21]

and the acceptor level at $E_v + 0.37$ eV. No results for the cage sited interstitials were reported. A difficulty in the assignment of the acceptor level is the position of the conduction band edge in the calculation which typically lies between E_v and $E_v + 0.4$ eV, and is very dependent on the calculation approach, in particular, the pseudopotentials used. To circumvent this difficulty, we have used the marker method to compare the ionization energy and electron affinity of the interstitial with those of standard donors and acceptors. We found that the dumbbell form is neutral, having neither a donor or acceptor level in the gap.

One important consequence of the bistability of the defect is that at high temperature, i.e., when the interstitial has enough thermal energy to overcome the barrier (>0.5 eV) between the neutral D and H forms (Fig. 1), the self-interstitial becomes a negative-U defect. This means that I^+ will not be thermodynamically stable, since the reaction $2I_H^+ \rightarrow I_D^0 + I_T^{2+}$ is exothermic. Consequently, for Fermi levels above the $(0/2+)$ occupancy level, which is close to midgap, the defect will be neutral, and double positive charged otherwise. However, at low temperatures there is no transformation between the caged and split-interstitial forms and the defect exists in the three charge states.

Similar modeling of the vacancy in germanium found it to possess single and double acceptor levels close to $E_v + 0.2$ eV [5], in agreement with experiment [20]. Its migration barrier is charge dependent, varying between 0.3 eV for V^{2-} and 0.7 eV for V^0 [23]. Of relevance for the present Letter is to note the absence of a donor level, in contrast with Si, and the rapid diffusivity of V^{2-}.

We now use the theoretical properties of I and V to understand the evolution of radiation damage at low temperature.

One of the key questions is which of the two defects, I or V, first becomes mobile. Indirect evidence of vacancy motion at low temperatures has been obtained by infrared absorption studies on high-resistivity oxygen-doped Ge. Following electron irradiation at 25 K and an anneal between 60 and 80 K, the growth of two oxygen related local vibrational modes at 719 and 736 cm^{-1}, attributed to a metastable precursor of the VO defect (VO^*), is observed [21]. In high-resistivity material, we expect the presence of I^{2+} and V^{2-}. The calculated migration barriers of I^{2+} and V^{2-} (Table III) suggest that V^{2-} becomes mobile before I^{2+}. Moreover, detailed calculations of the vibrational modes of $(VO^*)^-$ and $(VO^*)^{2-}$ support the assignment of the above bands [24], thus confirming the view that a fraction of the vacancies, in the V^{2-} state, migrates at 60–80 K, leaving isolated interstitials.

In p-Ge, we suppose irradiation at cryogenic temperatures creates neutral I^0 and V^0 defects. According to our calculations, the neutral interstitial forms a dumbbell configuration, which like V, does not possess a donor level. This immediately explains why compensation of chemical acceptors at low temperatures does not occur [2,8]. A barrier of about 0.5 eV prevents I^0 from switching sites to form the more stable caged sited ionized defects. We suggest that this only takes place in the 100–150 K region. The interstitial then can lose up to two electrons to become I_T^{2+}. This transformation occurs in a time scale of minutes [8]. Injecting electrons into the conduction band leads to the conversion of I_T^{2+} into I^+ and I^0. It is I^+ and I^{2+} which are to be identified with the 0 and + states of the two-state donor defect which is observed in this temperature region: in the 0 state, I^+ is the P1 $S = 1/2$ EPR center [7], which must contain an odd number of electrons and excludes an identification with neutral I. The two-state donor defect cannot be a vacancy as the latter acts only as an acceptor.

Investigations of the variation of the densities of P1 and free holes with temperature [7,8] place the $(+/2+)$ level of the two-state donor defect about 0.1 or 0.2 eV below E_c in agreement with the calculations for the interstitial at the cage site (Table II). This assignment is also consistent with the measured capture cross sections for electrons of 10^{-15} cm^2, and $<10^{-27}$ cm^2 for holes of the 0 state (I^+) [6].

The reorientation barrier among the four H_d sites surrounding a T-site is of 0.06 eV only, and it is possible that I^+ is able to tunnel assuming an effective T_d symmetry. Other effects not taken into account by our calculations, such as spin-orbit coupling, may account for a further distortion and justify the observed C_{2v} symmetry of the P1 EPR center [7].

The loss of I^{2+} around 200 K, with a 0.4 eV barrier, is not due to the migration of I^{2+} but probably to a movement of V^0 followed by I-V annihilation. In fact, perturbed angular correlated spectroscopy (PAC) experiments [20] in p-Ge find that V^0 is mobile at this temperature. However, long range migration of I^+, with a barrier around 0.3 eV, cannot be excluded. Any surviving damage must be due to the complexes of I^{2+} and V^0 with impurities or multivacancy defects.

The evolution of radiation damage is very different in n-Ge. Immediately after low-temperature irradiation (4 K),

close by V^0-I^0 Frenkel pairs are present and firstly trap a single electron [4]. Secondly, a further electron can be trapped to form V^{2+}-I^0 at ~20 K. The Frenkel pairs are thus double acceptors [4]. We expect the pair to be stable up to about 65 K, as indeed observed, when V^{2-} becomes mobile. A small fraction of V and I survive the 65 K stage and the next recovery stage is around 200–300 K [6,25].

Two deep level transient spectroscopy (DLTS) centers labeled M2 and M3, created by low-temperature irradiation and disappearing at 200 K, have also been attributed to interstitials [26]. The measured have levels are $E_c - 0.05$ and $E_c - 0.12$ eV, respectively, consistent with the calculated double donor properties of the caged interstitial.

The barriers for long range migration of the cage interstitials are dependent on charge state. I^+ is the most mobile, diffusing through H sites with a barrier of 0.3 eV. PAC experiments show that I^+ or I^{2+}, but not I^0, migrate around 220 K, and are trapped at In^- probes in moderately doped n- and p-Ge, and place the transition level 40 meV below E_c [20]. This could be either the $(+/2+)$ or $(0/+)$ level of the caged interstitial within the accuracy of our calculation. The migration energy was estimated to be 0.5–0.6 eV [20].

In summary, we have shown that the interstitial in Ge is bistable having an electrically inert dumbbell configuration, but behaving as a double donor when at a cage site. The defect does not possess an acceptor level. Thus, the defect exists in the 0, + and 2+ charge states, but assuming different structures in each of them. Based on the charge-dependent properties of I and V, it is possible to understand many characteristics of electron-irradiation damage and how they depend on the Fermi level. We find that V^{2-}-I^0 Frenkel pairs are the double acceptors present in irradiated n-Ge, and suggest an interstitial model for the two-state donor defect observed in p-Ge. The kinetics of the first stage in recovery in n-Ge and oxygen rich undoped Ge, and possibly p-Ge, are controlled by vacancy migration. The metastable I^+ at a distorted cage site is the most mobile interstitial species, migrating at about 200 K [20,26]. The dumbbell self-interstitial is electrically inactive and this may explain the absence of induced donors in p-type Ge at low temperatures immediately after irradiation.

The authors thank Professor D. W. Palmer and Professor V. V. Emtsev for their comments and criticism. The FCT and INTAS are acknowledged for financial support.

*carvalho@excc.ex.ac.uk

[1] G. D. Watkins, Mater. Sci. Semicond. Process. **3**, 227 (2000).
[2] J. E. Whitehouse, Phys. Rev. **143**, 520 (1966).
[3] V. Emtsev, Mater. Sci. Semicond. Process. **9**, 580 (2006).
[4] T. A Calcott and J. W. Mackay, Phys. Rev. **161**, 698 (1967).
[5] J. Coutinho, R. Jones, V. J. B. Torres, M. Barroso, S. Öberg, and P. R. Briddon, J. Phys. Condens. Matter **17**, L521 (2005).
[6] W. L. Brown, W. M. Augustyniak, and T. R. Waite, J. Appl. Phys. **30**, 1258 (1959).
[7] D. L. Trueblood, Phys. Rev. **161**, 828 (1967).
[8] T. M. Flanagan and E. E. Klontz, Phys. Rev. **167**, 789 (1968).
[9] A. J. R. da Silva, A. Janotti, A. Fazzio, R. J. Baierle, and R. Mota, Phys. Rev. B **62**, 9903 (2000).
[10] M. D. Moreira, R. H. Miwa, and P. Venezuela, Phys. Rev. B **70**, 115215 (2004).
[11] J. Vanhellemont, P. Śpiewak, and K. Sueoka, J. Appl. Phys. **101**, 036103 (2007).
[12] R. Car, P. J. Kelly, A. Oshiyama, and S. T. Pantelides, Phys. Rev. Lett. **52**, 1814 (1984).
[13] P. R. Briddon and R. Jones, Phys. Status Solidi B **217**, 131 (2000).
[14] C. Hartwigsen, S. Goedecker, and J. Hutter, Phys. Rev. B **58**, 3641 (1998).
[15] S. G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B **26**, 1738 (1982).
[16] J. P. Goss, M. J. Shaw, and P. R. Briddon, Top. Appl. Phys. **104**, 69 (2006).
[17] E. Simoen and C. Claeys, *Germanium-based Technologies: From Materials to Devices* (Elsevier, London, 2007).
[18] H. G. Grimmeiss, L. Montelius, and K. Larsson, Phys. Rev. B **37**, 6916 (1988).
[19] G. Henkelman and H. Jónsson, J. Chem. Phys. **113**, 9978 (2000).
[20] H. Haesslein, R. Sielemann, and C. Zistl, Phys. Rev. Lett. **80**, 2626 (1998); R. Sielemann, Nucl. Instrum. Methods Phys. Res., Sect. B **146**, 329 (1998); Physica (Amsterdam) **308B**, 529 (2001).
[21] R. E. Whan, Appl. Phys. Lett. **6**, 221 (1965); Phys. Rev. **140**, A690 (1965).
[22] V. V. Emtsev, T. V. Mashovets, and V. V. Mikhnovich, Fiz. Tekh. Poluprovodn. **26**, 20 (1992) [Sov. Phys. Semicond. **26**, 12 (1992)].
[23] H. M. Pinto, J. Coutinho, V. J. B. Torres, S. Öberg, and P. R. Briddon, Mater. Sci. Semicond. Process. **9**, 498 (2006).
[24] A. Carvalho, R. Jones, J. Coutinho, V. J. B. Torres, and P. R. Briddon (unpublished).
[25] J. Zizine, in *Radiation Effects in Semiconductors*, edited by F. L. Vook (Plenum Press, New York, 1968).
[26] J. C. Bourgoin, P. M. Mooney, and F. Poulin, Conf. Ser. Inst. Phys. **59**, 33 (1981).