Electronic and structural properties of germanium self-interstitials

M. Dionízio Moreira and R. H. Miwa
Faculdade de Física, Universidade Federal de Uberlândia, C.P. 593, CEP 38400-902, Uberlândia, MG, Brazil

P. Venezuela
Instituto de Física, Universidade Federal Fluminense, Campus da Praia Vermelha, Niterói, RJ, CEP 24210-340, Brazil
(Received 3 May 2004; published 29 September 2004)

The electronic and structural properties of self-interstitial and self-interstitial-related defects in Ge have been investigated by first-principles calculations. In accordance with previous works we find that the split [110] structure is the most stable energetically, among the self-interstitial defects in Ge. However, in disagreement with previous calculations, we find that the formation energy of the split [110] self-interstitial in Ge is larger than the formation energy of the same defect in Si. Our results differ from previous ones because our calculations are better converged with respect to Brillouin zone sampling. Concerning charged defects, we find that the $(+/0)$ ionization level of the split [110] self-interstitial in Ge is placed at 0.08 eV below the valence-band minimun (VBM), while the $(0/-)$ level is located at 0.37 eV above the VBM. Also, we find that a self-interstitial-related defect, called fourfold-coordinated defect, is stable in Ge with a formation energy of 2.82 eV.

DOI: 10.1103/PhysRevB.70.115215 PACS number(s): 71.15.Nc, 71.20.Nr, 71.55.−i

I. INTRODUCTION

Among the intrinsic point defects, the self-interstitials, vacancies, and Frenkel pairs are considered the most important ones. There are several ways to create intrinsic point defects in solid materials, during the growth process, by ion implantation, by plasma etching, and by electron irradiation. These point defects play an important role in the electrical properties, self-diffusion, and dopant diffusion processes in semiconductor materials. Since Si dominates the microelectronic industry, the electronic and structural properties of intrinsic defects in this material have attracted the majority of experimental as well as theoretical studies.

However, nowadays considerable interest exists also in the Si-Ge alloys because this material has been successfully applied in electronic and photonic devices. Indeed, there are numerous experimental and theoretical works addressing the electronic and structural properties of intrinsic defects in Si-Ge alloys. Griglione *et al.*[1] performed an experimental investigation of the Ge diffusion in $Si_{1-x}Ge_x/Si$ quantum wells; similarly Zangenberg *et al.*[2] studied the Ge diffusion in the $Si_{1-x}Ge_x$ alloys, as a function of the alloy concentration (x). From the theoretical point of view, vacancies and vacancy mediated Ge diffusion in Si-Ge alloys have been investigated by *ab initio* calculations.[3,4] And recently, we have performed an *ab initio* study on the formation of extended defects and their interaction with vacancies in Si-Ge alloys.[5] As expected, the physical properties of Si-Ge alloys mimic the properties of pure Si and pure Ge, in the Si-rich and Ge-rich limits, respectively. Thus, in order to understand the properties of intrinsic defects in Si-Ge, it is important to comprehend their properties in both materials, Si and Ge. However, differently from Si, there are quite a few experimental as well as theoretical works related to intrinsic defects in Ge.

Haesslein *et al.*[6] identified, by means of perturbed angular spectroscopy (PAC), two point defects produced by electron irradiation in Ge. They found that one of these defects, lying 0.20 eV above the valence-band maximum (VBM), was the monovacancy acceptor state. The other one, lying 0.04 eV below the conduction-band maximum (CBM), was initially tentatively assigned as a donor state for the self-interstitials (SI's). However, according to first-principles calculations,[7,8] the SI defect in Ge introduces an *acceptor* level near the CBM. This theoretical finding was the motivation for further PAC investigations,[9] in which it was shown that it is not possible, experimentally, to distinguish if the level introduced by the SI defect near the CBM is actually an acceptor or a donor state.

In addition, Ehrhart and Zillgen[10] verified a high concentration of Frenkel pairs, also created by electron irradiation in Ge. Fazzio *et al.*[11] performed an *ab initio* investigation of the electronic and structural properties of vacancies in Ge. While, recently, Janotti *et al.*[12] and Silva *et al.*[7,8] investigated, using *ab initio* calculations, the SI's in Ge. They considered, for the SI's, the structural models which had been previously proposed for Si.[13] Similarly to Si, the split [110] structure in Ge has the lowest formation energy. However, Silva *et al.*[8] indicated that the formation energy of SI's for Ge is "much smaller than for Si." As far as ionization levels are concerned, they calculated[7,8] a donor state at 0.07 eV above the VBM, and an acceptor state at VBM+0.31 eV (already mentioned in the last paragraph).

Recently, a new structural arrangement, which is energetically stable, has been proposed for SI in Si,[14] it has been called the "displaced hexagonal." Also, a self-interstitial-related defect, called fourfold-coordinated defect (FFCD),[14–16] has been proposed recently. The FFCD is formed by a single vacancy and a SI, where the defect exhibits a perfect fourfold coordination. Total energy results indicate that the FFCD has a small formation energy in Si. However, the FFCD has not been identified experimentally. Furthermore, to our knowledge, there are no *ab initio* investigation of the FFCD and the displaced hexagonal intrinsic point defects in Ge. It is worth to point out that the FFCD

 ©2004 The American Physical Society

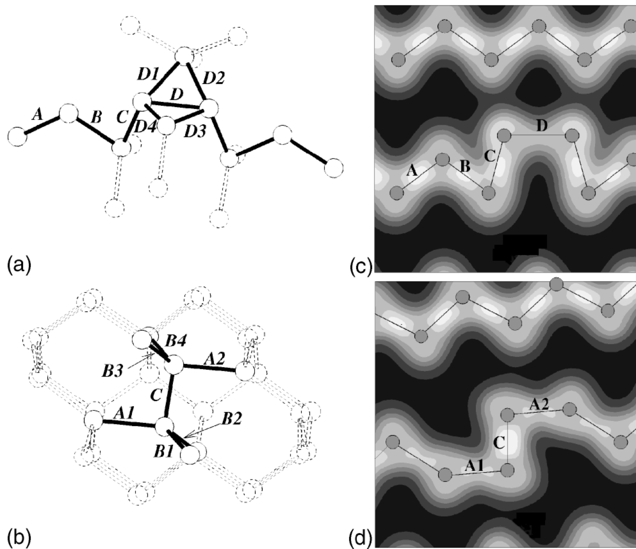

FIG. 1. Structural models and the total charge densities for the self-interstitial defects in Ge, (a), (c) split [110], and (b), (d) FFCD.

cannot be considered just as a kind of self-interstitial defect, since the number of atoms is conserved in the FFCD, and the SI defect involves an excess of one atom.[15]

In this article, we report a *first-principles* investigation of the SI defect in Ge. We have considered the split [110], hexagonal, tetrahedral, and the displaced hexagonal models. We also investigated the FFCD defect in Ge. The equilibrium geometries of the FFCD and the split [110] structures have been detailed. For the split [110] model, we have calculated the position of the (+/0) and (0/−) ionization levels, and compared them with experimental results.[6,9]

II. THEORETICAL APPROACH

The calculations were performed in the framework of the density functional theory,[17] within the local density approximation, by using the Ceperley-Alder correlation[18] as parametrized by Perdew and Zunger.[19] The electron-ion interaction was treated by using norm-conserving pseudopotentials.[20] The wave functions were expanded in a plane wave basis with an energy cutoff (E_{CUT}) up to 16 Ry. The Brillouin zone (BZ) was mapped by using up to 14 special k points.[21] To simulate the self-interstitial defects, we used periodic supercells of 64 and 128 atoms. To obtain the equilibrium geometry, the atoms were relaxed within a force convergence criterion of 25 meV/Å.

III. RESULTS AND DISCUSSIONS

In order to find out the energetically most stable structure for the neutral Ge SI defect, we have initially examined three different atomic arrangements, viz., split [110] [shown in Fig. 1(a)], tetrahedral, and hexagonal. Our calculated formation energies, summarized in Table I, indicate that the split [110] model is the energetically most favorable. This result is in accordance with previous theoretical works.[7,8,12] Similar results have been verified for SI defects in Si, namely the split [110] configuration also exhibits the lowest formation energy.[13,14]

It is important to note that, if we consider only the Γ point for the BZ integration, the formation energy of the split [110] structure in Ge is lower than the same defect structure in Si.[7,8,12] Using a supercell with 128 atoms, E_{CUT}=12 Ry, and the Γ point for the BZ integration, we obtained a formation energy of 2.34 eV for the split [110] defect in Si, which is 0.43 eV higher than the formation energy of the same defect in Ge. On the other hand, improving the BZ sampling, by increasing the number of special k points (up to fourteen), we find that the formation energy of the Ge SI defect is higher than the formation energy of the Si SI defect. For instance, the formation energy of the split [110] arrangement in Ge is 3.55 eV (128 atoms, 4 special k points, and E_{CUT}=12 Ry, see Table I); meanwhile for Si (using the same calculation procedure) we find a formation energy of 3.49 eV. Thus we can state that, in contrast with previous theoretical investigations,[7,8,12] the formation energy of the SI defects in Ge is higher than the same defects in Si. Such disagreement is due to an inappropriate BZ sampling by using only the Γ point.

Recently, Al-Mushadani and Needs[14] performed a very comprehensive theoretical study addressing the intrinsic point defects in Si. They find a displaced hexagonal structure, where the interstitial Si atom moves outward from the hexagonal site by 0.48 Å, which is 0.03 eV lower in energy with respect to the (perfect) hexagonal configuration. Using a supercell with 128 atoms, E_{CUT}=12 Ry, and four special k points for the BZ integration, we also obtained the displaced hexagonal arrangement in Si. We find a formation energy 0.02 eV lower than the hexagonal configuration, and the interstitial Si atom is displaced by 0.29 Å from the hexagonal ring toward the tetrahedral site. However, we do not find any

TABLE I. Formation energies (in eV) of the self-interstitial defects in Ge, as a function of the number of atoms in the supercell, number of special k points, and energy cutoff.

Atoms/supercell	128	128	128	64	64
BZ sampling	$1k(\Gamma)$	$4k$	$4k$	$14k$	$14k$
E_{CUT}	12 Ry	12 Ry	16 Ry	12 Ry	16 Ry
Split [110]	1.91	3.55	3.55	3.58	3.54
Tetrahedral	2.29	3.85	3.84	3.85	3.84
Hexagonal	2.49	3.99	3.99	3.99	4.00

TABLE II. Equilibrium geometry of the FFCD in Ge. The bonds Ai, Bi, and C are shown in Fig. 1(b). The calculations were perfomed using a supercell with 128 atoms and $E_{\mathrm{CUT}}=16$ Ry. The bond lengths are in Å.

$A1-A2$	$B1-B4$	C
2.57	2.41	2.27

energetically stable position, for the Ge SI atom, between the tetrahedral and hexagonal sites. That is, the displaced hexagonal structure is not expected to occur in Ge.

The FFCD, shown in Fig. 1(b), has been proposed as an energetically stable structure in Si.[14–16,22] This point defect, formed by an self-interstitial-vacancy pair, has a relatively small formation energy. Al-Mushadani and Needs obtained a formation energy of 2.80 eV for the FFCD, in agreement with previous calculations by Goedecker *et al.*,[16] who obtained 2.34 eV. We have also calculated the FFCD in Si, and we obtained a formation energy of 2.73 eV. More importantly, we find that the FFCD is also stable in Ge, with a formation energy of 2.82 eV. The equilibrium geometry of the FFCD in Ge is summarized in Fig. 1(b) and Table II. The C Ge-Ge bond is compressed by 5% compared with the bond length of the Ge bulk (2.39 Å), while the $A1$ and $A2$ bonds are stretched by 8%. Furthermore, the calculated total charge density, depicted in Fig. 1(d), indicates an increase (reduction) of the eletronic concentration along the C ($A1$ and $A2$) bond(s).

Having stabilished that the split [110] model corresponds to the most probable structure for the self-interstitial defects in Ge, we summarize its equilibrium geometry in Fig. 1(a) and Table III. We have considered two different calculation procedures, viz., (a) $E_{\mathrm{CUT}}=12$ Ry and the Γ point for the BZ integration, and (b) $E_{\mathrm{CUT}}=16$ Ry and four special k points for the BZ integration. Using the calculation procedure (a), we find: (i) The equilibrium bond length of the Ge dimer, aligned along the [110] direction [D in Fig. 1(a)], is equal to 2.54 Å, corresponding to a bond stretch of 6% compared with the bond length of the Ge bulk. (ii) The bond lengths $D1-D4$ (neighboring the Ge dimer) are all identical, and also with the same value as the Ge-dimer bond length (D). (iii) A, B, and C Ge-Ge bonds are slightly compressed/stretched within a range of 0.02 Å, compared with the Ge-Ge bond length in the perfect crystal. These results compare very well with those obtained by Silva *et al.*[8] On the other hand, using the calculation procedure (b), we obtained a different picture for the equilibrium geometry: (i) The Ge dimer

TABLE III. Equilibrium geometry of the neutral Ge self-interstitial defect in the split [110] configuration, as a function of the number of special k points (N_k). The bonds $A-Di$ are shown in Fig. 1(a). The calculations were performed using a supercell with 128 atoms and $E_{\mathrm{CUT}}=16$ Ry. The bond lengths are in Å.

N_k	A	B	C	D	$D1-D4$
1(Γ)	2.39	2.43	2.38	2.54	2.54
4	2.35	2.41	2.37	2.51	2.55

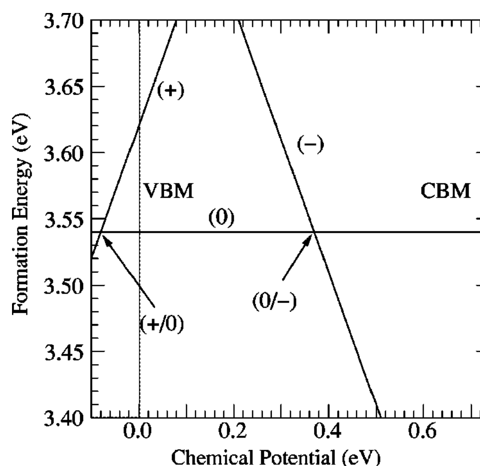

FIG. 2. Formation energies of the split [110] self-interstitial defect in Ge, as a function of the electronic chemical potential. The arrows indicate the (−/0) and (0/+) ionization energies.

is stretched by 5% (2.51 Å), while (ii) the neighboring Ge-Ge bond lengths ($D1-D4$) are equal to 2.55 Å. (iii) The Ge-Ge bond length A (B) is compressed (stretched) by 0.04 Å (0.04 Å), compared with the bond length of the Ge bulk. Identical results were obtained for $E_{\mathrm{CUT}}=12$ Ry.

Figure 1(c) depicts the total charge density along the Ge dimer of the split [110] structure. The Ge dimer exhibits a covalent character, with a slightly reduced charge density along the Ge-Ge bond, which is attributed to the increase of the Ge-Ge dimer bond length.

Concerning the properties of charged defects, we calculated the ionization energies of the Ge SI defect. The formation energies, considering three charge states (q):−1, 0, and +1, were calculated using the procedure described in Ref. 23. We find that the average potentials, $\bar{V}_D$ and $\bar{V}_H$ [see Eq. (8) of Ref. 23], are aligned within an energy range of 0.02 eV in the bulklike region of the defect-containing supercell. Figure 2 ilustrates our calculated formation energies. The ionization levels, with respect to the Ge bulk VBM, correspond to the electronic chemical potential where the formation energies of two different charge states become equal.[23] We find that the (+/0) level is placed at 0.08 eV below the VBM, i.e., resonant in the valence band of bulk Ge, and the (0/−) ionization level is located at 0.37 eV above the VBM. Meanwhile, Silva *et al.*[8] find the (+/0) level near the VBM (VBM+0.07 eV), and the (0/−) level 0.31 eV above the VBM. Recent experimental investigations[6,9] verified a level, for the SI defect in Ge, lying 0.04 eV below the CBM of Ge. However, the experiments were not able to distinguish if this level is an acceptor or a donor state. Thus, our calculations, in accordance with Silva *et al.*,[8] indicate that the experimentally verified ionization level at 0.04 eV below the CBM is indeed an acceptor state.

Our calculated single-particle energy levels, for the neutral split [110] structure in Ge, reveal that the highest occupied state (HOMO) is placed at 0.04 eV above the VBM. Figure 3(a) shows that the HOMO spreads out along the Ge-Ge bonds, with a strong valence band character. On the other hand, at 0.20 eV below the VBM, namely resonant

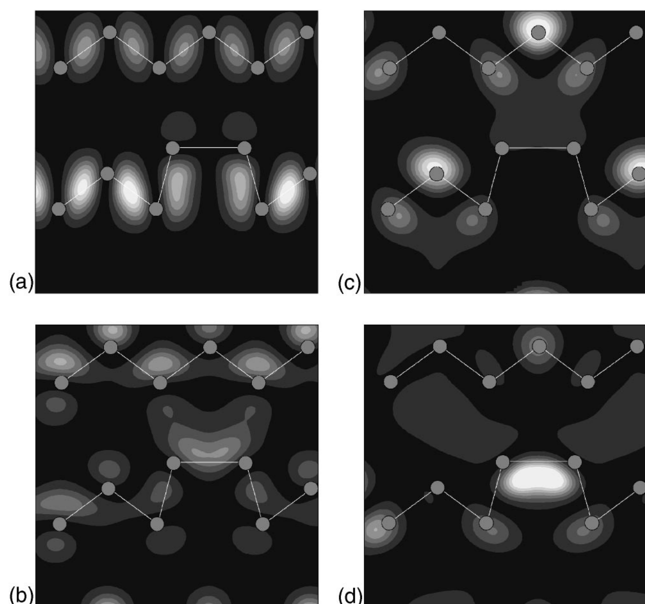

FIG. 3. (a) Highest occupied electronic state at 0.04 eV above the VBM, (b) occupied electronic state at 0.20 eV below the VBM, (c) lowest unoccupied electronic state at 0.18 eV from VBM, and (d) unoccupied electronic state at 0.24 eV from VBM.

with the Ge valence band, we find a σ-like bonding state along the SI defect, as shown in Fig. 3(b). Similar electronic distribution has been obtained by Silva *et al.* [see Fig. 3(a) of Ref. 8]. At 0.18 eV from the VBM, we find the lowest unoccupied state (LUMO). The electronic distribution of the LUMO is depicted in Fig. 3(c). It is interesting to note that the LUMO is localized on the Ge atoms neighboring the split [110] SI defect. In contrast, at 0.24 eV from VBM, we find an unoccupied state localized along the Ge-Ge bond of the SI defect, cf Fig. 3(d).

IV. CONCLUSIONS

In summary, using first-principles calculations, we have examined the energetic stability, equilibrium geometry, and the electronic structure of SI defects and SI-related defects in Ge. We find that the split [110] SI structure is energetically more stable than the tetrahedral and hexagonal models by 0.29 eV and 0.44 eV, respectively. The energetic preference of the split [110] model has also been verified for SI defects in Si. However, in contrast with previous theoretical works,[8] we find that the SI defect formation energy in Ge is higher compared with the same defects in Si. In Ref. 8 the formation energies of 3.20 and 2.29 eV have been reported for SI defects in Si and Ge, respectively, while here we find 3.49 and 3.55 eV for the same defects. Our results differ from previous ones because our calculations are better converged with respect to BZ sampling. It is worth to point out that an accurate determination of intrinsic defects formation energies in Si and Ge is important for understanding SiGe alloy properties, for instance, self-diffusion and diffusion of impurities.

The self-interstitial-related FFCD, previously verified in Si, is also energetically stable in Ge. On the other hand, based upon our total energy results, the displaced hexagonal structure (also an energetically stable SI defect Si) is not expected to occur in Ge.

The calculated ionization energies, for the split [110] structure, indicate that the $(+/0)$ level is resonant within the valence band (0.08 eV below the VBM), and the $(0/-)$ ionization level lies 0.37 eV above the VBM. These results, in accordance with Silva *et al.*,[8] indicate that the experimentally verified[6,9] ionization level at 0.04 eV below the CBM is indeed an acceptor state. From our calculated single particle energy levels, we find that the HOMO exhibits a strong valence band character, and at 0.2 eV below the VBM we find a σ-like bonding state along the Ge-Ge bond of the SI defect. Similarly, we verified an unoccupied state at 0.24 eV above the VBM strongly localized along the Ge-Ge bond of the SI defect.

ACKNOWLEDGMENTS

This work received financial support from the Brazilian agencies CAPES, CNPq, and FAPEMIG, and computer time from CENAPAD-SP.

[1] Michelle Griglione, Timothy J. Anderson, Yaser M. Haddara, Mark E. Law, Kevin S. Jones, and Alex van der Bogaad, J. Phys.: Condens. Matter **88**, 1366 (2000).

[2] N. R. Zangenberg, J. Lundsgaard Hansen, J. Fage-Pedersen, and A. Nylandsted Larsen, Phys. Rev. Lett. **87**, 125901 (2001).

[3] G. M. Dalpian, P. Venezuela, Antônio J.R. da Silva, and A. Fazzio, Appl. Phys. Lett. **81**, 3383 (2002).

[4] P. Venezuela, G. M. Dalpian, Antônio J.R. da Silva, and A. Fazzio, Phys. Rev. B **65**, 193306 (2002).

[5] R. H. Miwa, P. Venezuela, and A. Fazzio, Phys. Rev. B **67**, 205317 (2003).

[6] Helmut Haesslein, Rainer Sielemann, and Christian Zistl, Phys. Rev. Lett. **80**, 2626 (1998).

[7] Antônio J.R. da Silva, R. Baierle, R. Mota, and A. Fazzio, Physica B **302-303**, 364 (2001).

[8] Antônio J.R. da Silva, A. Janotti, A. Fazzio, R. Baierle, and R. Motta, Phys. Rev. B **62**, 9903 (2000).

[9] R. Sielemann, H. Haesslein, and Ch. Zistl, Physica B **302-303**, 101 (2001).

[10] P. Ehrhart and H. Zillgen, J. Phys.: Condens. Matter **85**, 3503 (1999).

[11] A. Fazzio, A. Janotti, Antônio J.R. da Silva, and R. Mota, Phys. Rev. B **61**, R2401 (2000).

[12] A. Janotti, R. Baierle, Antônio J.R. da Silva, R. Mota, and A. Fazzio, Physica B **273-274**, 575 (1999).

[13] R. J. Needs, J. Phys.: Condens. Matter **11**, 10437 (1999), and references therein.

[14] O. K. Al-Mushadani and R. J. Needs, Phys. Rev. B **68**, 235205

(2003), and references therein.
[15] F. Cargnoni, C. Gatti, and L. Colombo, Phys. Rev. B **57**, 170 (1998).
[16] S. Goedecker, T. Deutsch, and L. Billard, Phys. Rev. Lett. **88**, 235501 (2002).
[17] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
[18] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[19] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[20] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982); X. Gonze, R. Stumpf, and M. Scheffler, Phys. Rev. B **44**, 8503 (1991).
[21] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[22] M. Tang, L. Colombo, J. Zhu, and T. D. de la Rubia, Phys. Rev. B **55**, 14 279 (1997).
[23] T. Mattila and Alex Zunger, Phys. Rev. B **58**, 1367 (1998), and references therein.