

**Carbon in  $\text{Si}_x\text{Ge}_{1-x}$ : An *ab initio* investigation**

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The electronic and structural properties of substitutional and interstitial C impurities in Si, Ge, and  $\text{Si}_x\text{Ge}_{1-x}$  alloy have been investigated based upon *ab initio* total-energy calculations. For pure materials, we find that the formation energy of substitutional C in Si is 0.81 eV lower than in Ge. For interstitial C, we find that the split(100) arrangement is energetically most favorable for both materials, Si and Ge. Similarly to substitutional C, the formation energy of interstitial C in Si is 0.74 eV lower than in Ge. By applying hydrostatic strain in the pure materials, we find an almost linear increase (decrease) of the formation energy for substitutional (interstitial) C with the lattice constant. In the  $\text{Si}_x\text{Ge}_{1-x}$  alloy, the C impurity properties were investigated for  $x = 0.50$  and  $0.85$ . We find that, for substitutional and interstitial C, the formation energies are lower for higher concentrations of Si at the nearest-neighbor sites of the impurity. Based on the calculated formation energies, we determined the equilibrium relative populations of Si and Ge atoms at the nearest-neighbor sites of C, as a function of the temperature and the alloy concentration.

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**I. INTRODUCTION**

Carbon is one of the most common impurities in semiconductors. This impurity is quite well understood in Si. However, in Ge and in  $\text{Si}_x\text{Ge}_{1-x}$ , a systematical *ab initio* theoretical investigation is still lacking. Carbon concentration in Si is typically in the range from  $10^{16}$  to  $10^{18}$   $\text{cm}^{-3}$ , and it is well established that the vast majority of the impurities are in the substitutional form ( $C_S$ ).

Even though the concentration of interstitial carbon ( $C_I$ ) in Si is much smaller than the concentration of  $C_S$ ,  $C_I$  is also important because C migrates in Si by interstitial sites. There is experimental evidence that the ground state of  $C_I$  in Si is a split(100) configuration.<sup>1</sup>

A better understanding of the properties of C in  $\text{Si}_x\text{Ge}_{1-x}$  is also important due to the interest in the ternary alloy  $\text{Si}_x\text{Ge}_{1-x-y}\text{C}_y$ . This material can be useful for the realization of semiconductors with band gaps ranging from 0.62 to 5.5 eV.<sup>2</sup> In addition, the strain of  $\text{Si}_x\text{Ge}_{1-x}$ , when it is grown pseudomorphically over Si substrates, could be compensated by the incorporation of a small concentration of C atoms.

Hoffmann *et al.*<sup>3</sup> have identified the  $C_S$  defect in Ge by a combination of infrared absorption spectroscopy, ion channeling, and cluster calculations. They implanted the impurities in single-crystalline Ge and were able to identify the local vibrational modes of the defect. Their theoretical calculations focused mainly on the vibrational properties of  $C_S$ . In particular, they did not report the impurity formation energy.

In  $\text{Si}_x\text{Ge}_{1-x}$ , the  $C_S$  impurity may have, in principle, five kinds of nearest-neighbor (NN) configurations:  $\text{Si}_4\text{Ge}_0$ ,  $\text{Si}_3\text{Ge}_1$ ,  $\text{Si}_2\text{Ge}_2$ ,  $\text{Si}_1\text{Ge}_3$ , and  $\text{Si}_0\text{Ge}_4$ . In other work by Hoffmann and collaborators,<sup>4</sup> the vibrational properties of  $C_S$

in the alloy were investigated by means of infrared absorption spectroscopy. They analyzed the intensities of the local vibrational modes showing a substantial preference for the  $\text{Si}_4\text{Ge}_0$  and  $\text{Si}_3\text{Ge}_1$  NN configurations. They also reported cluster calculations that reproduce correctly the vibrational experimental results. Furthermore, their calculations show that Si-C bonds is favored by 0.20 or 0.25 eV in comparison with Ge-C bonds.

As far as  $C_S$  in  $\text{Si}_x\text{Ge}_{1-x-y}\text{C}_y$  is concerned, Kanzawa *et al.*<sup>5</sup> have reported experimental results confirming that most of the  $C_S$  have  $\text{Si}_4\text{Ge}_0$  and  $\text{Si}_3\text{Ge}_1$  NN configurations.<sup>4</sup> Furthermore, they have shown that when the annealing temperature increases from 700 to 950 °C, the population of  $\text{Si}_3\text{Ge}_1$  NN configurations increases.

Recently, it has been shown, by means of deep level transient spectroscopy,<sup>6-8</sup> that proton and electron irradiation generate  $C_I$  impurities in  $\text{Si}_x\text{Ge}_{1-x}$  ( $0.5 \leq x \leq 1.0$ ). However, to our knowledge, the local configuration of  $C_I$  in  $\text{Si}_x\text{Ge}_{1-x}$  and in Ge has not been determined.

In this paper, we present a theoretical investigation of the  $C_S$  and  $C_I$  impurities in Si, Ge, and  $\text{Si}_x\text{Ge}_{1-x}$ . In order to determine the energetically most favorable structure, for the  $C_S$  and  $C_I$  in the  $\text{Si}_x\text{Ge}_{1-x}$  alloy, we have considered a number of different atomic arrangements (or occupancies) for the Si and Ge atoms at the impurity nearest neighborhood. The formation energies of the  $C_S$  and  $C_I$  in the pure materials (Si and Ge), under hydrostatic strain, have been calculated aiming a better understanding of the strain and the chemical effects to the formation of these C impurities in the  $\text{Si}_x\text{Ge}_{1-x}$  alloy. Finally, our results for the  $C_I$  support the proposed Si-based migration path<sup>7</sup> for the C diffusion in the  $\text{Si}_x\text{Ge}_{1-x}$  alloy.

## II. THEORETICAL APPROACH

The *ab initio* total-energy calculations were performed in the framework of the density functional theory.<sup>9</sup> We have used the SIESTA code,<sup>10</sup> which performs fully self-consistent calculations solving the Kohn-Sham (KS) equations.<sup>11</sup> The KS orbitals are expanded using linear combinations of pseudoatomic orbitals.<sup>12</sup> In particular, we have used a double-zeta basis with polarization functions.<sup>13</sup> The calculations were done with the local-density approximation, using the Ceperley-Alder correlation<sup>14</sup> as parametrized by Perdew and Zunger.<sup>15</sup> The electron-ion interaction was treated by using norm conserving, *ab initio*, fully separable pseudopotentials.<sup>16</sup> A cutoff of 200 Ry for the grid integration was utilized to represent the charge density. Equilibrium atomic positions were determined by relaxation within a force convergence criteria of 50 meV/Å. We used supercells with 64 atoms and the Brillouin Zone was sampled by four Monkhorst-Pack<sup>17</sup>  $k$  points.

The formation energy of a neutral C atom in the host is given by

$$E_F = E_T - E_{host} + n\mu_i - \mu_C, \quad (1)$$

where  $E_T$  is the total energy of the supercell with the C impurity,  $E_{host}$  is the total energy of the defect-free supercell,  $\mu_C$  is carbon chemical potential, calculated as the energy per atom in diamond.  $n$  equals 1 for  $C_S$  and 0 for  $C_I$ , and for the case of  $C_S$ ,  $\mu_i$  is the chemical potential of the host atom that was replaced by the impurity.

We consider the  $\text{Si}_x\text{Ge}_{1-x}$  substitutional disorder explicitly by distributing the components of the alloy in the supercells as special quasirandom structures.<sup>18</sup> Details on the preparation of the supercells were given elsewhere.<sup>19</sup> In the alloy, the impurities may in principle sit in different vicinities ( $\sigma$ ). At the thermodynamical equilibrium, the relative population of the impurity in the  $\sigma$  vicinity is<sup>20</sup>

$$n^\sigma(x, T) = \frac{P^\sigma(x) \exp[-E_F^\sigma(x)/k_B T]}{\sum_\sigma P^\sigma(x) \exp[-E_F^\sigma(x)/k_B T]}, \quad (2)$$

where  $P^\sigma(x)$  is the configurational probability for the  $\sigma$  configuration to exist in the  $x$  concentration alloy,  $E_F^\sigma$  is the formation energy of the impurity at configuration  $\sigma$ , and  $T$  is the temperature.

## III. RESULTS AND DISCUSSIONS

### A. Substitutional and Interstitial C in Si and Ge

Here we present our results for  $C_S$  and  $C_I$  in Si and Ge. According to our calculations, the formation energies of  $C_S$  in Si and Ge are 1.69 and 2.50 eV, respectively. Hereafter, we call  $d_{SiC}$  and  $d_{GeC}$ , the Si-C and Ge-C bond lengths in bulk zinc-blende materials. In our calculations we have found  $d_{SiC} = 1.88$  Å and  $d_{GeC} = 1.95$  Å. For the calculations with the  $C_S$  impurities, the bond lengths between the impurity and its four NN atoms are about 7% larger than  $d_{SiC}$  and  $d_{GeC}$  for Si and Ge, respectively. Thus, for both hosts, the clusters formed by  $C_S$  and its NN atoms are under tensile strain.

TABLE I. Formation energy, in eV, of  $C_I$  in Si and Ge, for several configurations.

	Si	Ge
Tetrahedral	6.02	5.88
Hexagonal	4.93	5.49
Split(110)	4.15	→ (100)
Split(100)	4.02	4.76

As far as the electronic structure of  $C_S$  is concerned, these isoelectronic impurities do not introduce any defect level in the band gaps, as expected.

We have also investigated the  $C_I$  in Si and in Ge. First, it is important to determine which interstitial configurations are the most stable for these hosts. For  $C_I$  in Si, there is experimental evidence<sup>1</sup> that the split(100) is the most stable configuration. However, to our knowledge, there are no experiments or *ab initio* calculations concerning the configuration of  $C_I$  in Ge and in  $\text{Si}_x\text{Ge}_{1-x}$ . We have determined the formation energy of  $C_I$  in the tetrahedral, hexagonal, split(110), and split(100) configurations. The values are shown in Table I, where it can be seen that, for both hosts, the split(100) is the most stable configuration. The split(110) in Ge is peculiar because this configuration is not stable. When the C atom is placed at the split(110) site in Ge, it relaxes to the split(100) site following a barrierless path.

Hereafter, when we refer to the  $C_I$  impurity we will be considering only the split(100) configuration, which is shown in Fig. 1. In this configuration the C atom is bonded to three host atoms which are labeled as 1, 2, and 3 in the figure. There are two inequivalent bonds between the impurity and its NN atoms. According to our calculations, the bond lengths between the impurity and the host atom labeled as 3 in the figure are about 7% smaller than  $d_{SiC}$  and  $d_{GeC}$  for Si and Ge, respectively. And the bond lengths between the impurity and the host atoms labeled as 1 and 2 in the figure are about 3% smaller than  $d_{SiC}$  and  $d_{GeC}$  for Si and Ge, respectively. Thus, the clusters formed by the  $C_I$  and its three NN atoms are under compressive strain.

The  $C_I$  formation energies are 2.33 and 2.26 eV larger than the  $C_S$  formation energies, in Si and Ge, respectively.

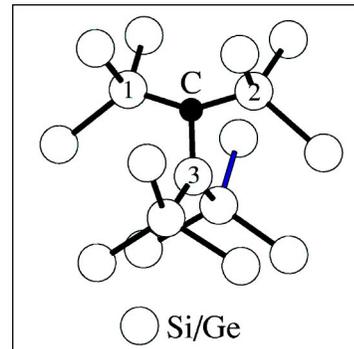


FIG. 1. Atomic arrangement for the split(100) interstitial C in  $\text{Si}_x\text{Ge}_{1-x}$ .

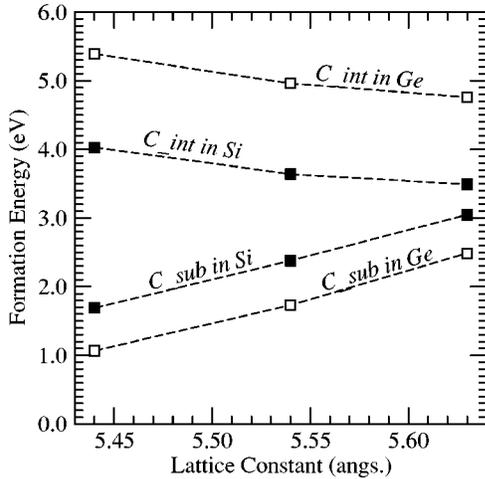


FIG. 2. Formation energy for substitutional and interstitial C in Si and in Ge, as a function of the lattice parameter.

Consequently, for both hosts and under equilibrium conditions, the vast majority of C impurities will occupy substitutional sites.

The  $C_I$  impurities introduce two defect levels into the gaps of the hosts. For the neutral impurities the lowest of these levels are occupied by two electrons and the other ones are empty. In Si, these levels lie at 0.10 and 0.50 eV above the valence-band maximum (VBM) and in Ge at 0.03 and 0.22 eV above the VBM.

We have also investigated how the formation energies of  $C_S$  and  $C_I$  in Si and in Ge vary with the lattice parameter, i.e., under hydrostatic strain. It was done for the lattice parameters of Si,  $\text{Si}_{0.5}\text{Ge}_{0.5}$ , and Ge, which in our calculations are: 5.44, 5.54, and 5.63 Å, respectively. The results for  $C_S$  and  $C_I$  are shown in Fig. 2. For both hosts, we find that the formation energy of  $C_S$  ( $C_I$ ) increases (decreases) almost linearly with the lattice parameter. These results can be explained by elastic energy arguments. When a C atom occupies a substitutional site, a  $X_4\text{C}$  ( $X=\text{Si}$  or  $\text{Ge}$ ) cluster is formed. We have seen in the beginning of this section that this cluster is under tensile strain. Thus, increasing the lattice parameter, the tensile strain also increases as well as the  $C_S$  formation energy. On the other hand, for  $C_I$ , the  $X_3\text{C}$  clusters are under compressive strain, which is relieved with the increase of the lattice parameter, and as a consequence the  $C_I$  formation energy decreases for larger lattice parameters.

### B. Substitutional C in $\text{Si}_x\text{Ge}_{1-x}$

We have investigated the properties of  $C_S$  in  $\text{Si}_x\text{Ge}_{1-x}$  for two concentrations:  $x=0.50$  and  $x=0.85$ . To determine the properties of this impurity we have used three different models in which the NN configurations were  $\text{Si}_4\text{Ge}_0$ ,  $\text{Si}_2\text{Ge}_2$ , and  $\text{Si}_0\text{Ge}_4$ . In Fig. 3 we show the formation energies as a function of the number of Ge atoms at the NN sites. The empty and the filled squares represent the impurities in the alloys with  $x=0.50$  and  $x=0.85$ , respectively. The diamonds represent the formation energies of  $C_S$  in Si and in Ge, for comparison.

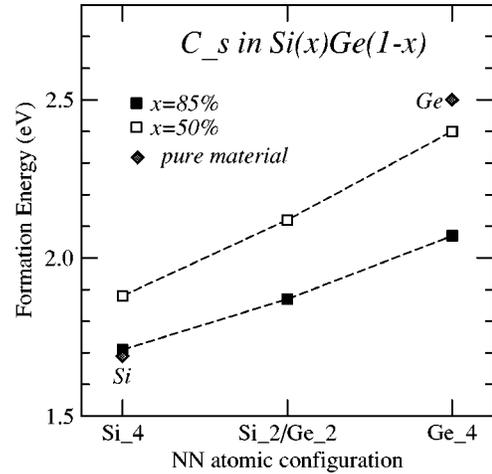


FIG. 3. Formation energy for substitutional C in  $\text{Si}_x\text{Ge}_{1-x}$  for different atomic configurations at the NN sites.

Similarly to what was found for  $C_S$  in Si and in Ge, the clusters formed by the  $C_S$  and its four NN atoms, for all configurations studied in the alloy, are under tensile strain. The bond lengths between the impurity and the NN atoms are larger than  $d_{\text{SiC}}$  and  $d_{\text{GeC}}$  for Si-C and Ge-C bonds, respectively. This is the reason why the formation energies are larger for the alloy with the smallest Si concentration ( $x=0.50$ ).

For both concentrations, the formation energy of  $C_S$  increases when the number of Ge-C bonds increases. The formation energies increase 0.12 and 0.09 eV per Ge-C bond for  $x=0.50$  and  $x=0.85$ , respectively. In previous cluster calculations<sup>4</sup> an increase of about 0.2 eV per Ge-C bond was found.

We have also made several calculations with the NN configurations shown in Fig. 3, but with different second neighborhood (SN) configurations. When one SN atom is changed from Si to Ge, or vice versa, the formation energy changes typically by only 10 meV. Thus, we conclude that the formation energy of  $C_S$  depends mainly on the NN configurations and on the lattice parameter of the alloy.

From the formation energies shown in Fig. 3, we can calculate the equilibrium relative population of each NN configuration using Eq. (2). The relative population, for typical annealing temperatures,<sup>4,5</sup> are shown in Table II. At  $T=550^\circ\text{C}$ , our results are in agreement with the experiments from Hoffmann *et al.*,<sup>4</sup> because there is a clear preference for

TABLE II. Relative Population of the different NN configurations, for  $C_S$  in  $\text{Si}_x\text{Ge}_{1-x}$  (Ref. 21).

NN	$x=0.50$		$x=0.85$	
	$T=550^\circ$	$T=950^\circ$	$T=550^\circ$	$T=950^\circ$
$\text{Si}_4\text{Ge}_0$	0.51	0.33	0.80	0.73
$\text{Si}_3\text{Ge}_1$	0.38	0.43	0.18	0.24
$\text{Si}_2\text{Ge}_2$	0.10	0.20	0.02	0.03
$\text{Si}_1\text{Ge}_3$	0.01	0.04	0.00	0.00
$\text{Si}_0\text{Ge}_4$	0.00	0.00	0.00	0.00

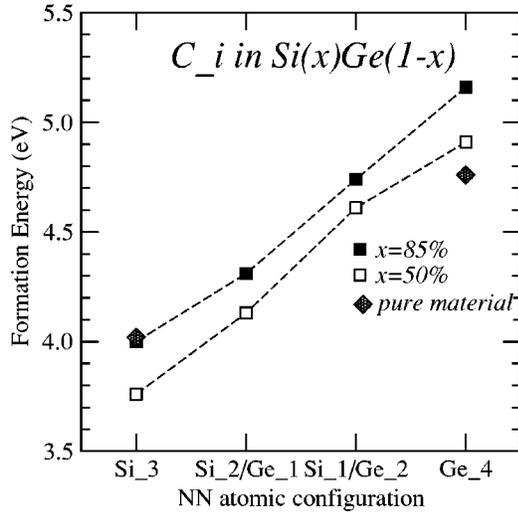


FIG. 4. Formation energy for interstitial C in  $\text{Si}_x\text{Ge}_{1-x}$  for different atomic configurations at the NN sites.

NN configurations with four and three Si atoms. In addition, when the temperature is increased to  $950^\circ\text{C}$ , we verify that the population of  $\text{Si}_3\text{Ge}_1$  NN configurations increases, supporting the experimental findings by Kanzawa *et al.*<sup>5</sup>

### C. Interstitial C in $\text{Si}_x\text{Ge}_{1-x}$

In Sec. III A, we have shown that in the pure materials, Si and Ge, the most stable configuration of  $C_I$  is the split(100). Thus, it is reasonable to assume that in the alloy the split(100) will also be the most stable configuration for  $C_I$ . Thus, for all calculations in this section, we have considered only the split(100) geometry for the  $C_I$ .

The properties of  $C_I$  in  $\text{Si}_x\text{Ge}_{1-x}$  were also investigated for two concentrations  $x=0.50$  and  $x=0.85$ . To determine the properties of this impurity we have used four different NN configurations:  $\text{Si}_3\text{Ge}_0$ ,  $\text{Si}_2\text{Ge}_1$ ,  $\text{Si}_1\text{Ge}_2$ , and  $\text{Si}_0\text{Ge}_3$ . In Fig. 4 we show the formation energies as a function of the number of Ge atoms as NN. For both concentrations, the formation energy of  $C_I$  increases about 0.38 eV per bond, when the number of Ge-C bonds increases.

Similarly to what was found for  $C_I$  in Si and in Ge, the clusters formed by the  $C_I$  and its three NN atoms, for all configurations studied in the alloy, are under compressive strain. Since the bond lengths between the impurity and the NN atoms are smaller than  $d_{\text{SiC}}$  and  $d_{\text{GeC}}$  for Si-C and Ge-C bonds, respectively. This explains why the formation energies of  $C_I$  for the alloy with the largest Si concentration ( $x=0.85$ ) are larger.

So, in general, for all cases shown here, the  $C_S$  ( $C_I$ ) impurities are in tensile (compressive) strain environments. This explains why the energy cost to change a Si-C bond by a Ge-C bond is about 0.1 eV for  $C_S$  and about 0.4 eV for  $C_I$ . For  $C_S$  impurities, there is a competition between chemical energy, which always favors the Si-C bonds, and strain energy that favors the bond with larger length in a tensile strain environment. On the other hand, for  $C_I$  impurities, the Si-C bonds are favored by both mechanisms, related to chemical and strain energies.

TABLE III. Relative Population of the different NN configurations, for  $C_I$  in  $\text{Si}_x\text{Ge}_{1-x}$ .

NN	$x=0.50$		$x=0.85$	
	$T=550^\circ$	$T=950^\circ$	$T=550^\circ$	$T=950^\circ$
$\text{Si}_3\text{Ge}_0$	0.98	0.92	0.99	0.97
$\text{Si}_2\text{Ge}_1$	0.02	0.08	0.01	0.03
$\text{Si}_1\text{Ge}_2$	0.00	0.00	0.00	0.00
$\text{Si}_0\text{Ge}_3$	0.00	0.00	0.00	0.00

For the case where there are two Ge atoms and one Si atom in the NN sites of  $C_I$ , we calculated the formation energy for two different configurations with the Si atom placed in the sites 2 and 3 of Fig. 1. The energy difference between these configurations is only 40 meV, so they can be considered equivalent. We also examined the importance of the Si/Ge concentration at the NN sites considering Si $\leftrightarrow$ Ge exchanges at these sites. We find total-energy variations of less than 20 meV.

In Table III the equilibrium relative population of each NN configuration of the  $C_I$  impurity is shown. From Table III we conclude that almost every  $C_I$  impurity has three Si atoms at the NN sites, for both concentrations, even for temperatures as large as  $950^\circ\text{C}$ . This result is important for the understanding of C diffusion in  $\text{Si}_x\text{Ge}_{1-x}$ , because the diffusion of this impurity proceeds by interstitial sites. Recent C diffusion experiments in  $\text{Si}_x\text{Ge}_{1-x}$  (Refs. 6–8) indicate that the rate of C diffusion reduces with the increase of the Ge concentration. The authors of Refs. 6–8 proposed two different models to explain their experimental findings,<sup>7</sup> viz: (i) “the  $C_I$  defects migrate via a Si-based migration path.” (ii) with the increase of Ge concentration “the Si- $C_I$  pairs converts to Ge- $C_I$  which might be less mobile.” In their next work, they excluded the diffusion model based on Ge- $C_I$  pairs.<sup>8</sup> They claimed that the formation of  $C_I$  pairing with Ge atoms is not expected to occur since the infrared results for the  $C_S$  impurities in  $\text{Si}_x\text{Ge}_{1-x}$ , with  $x \geq 0.50$ , indicate a preference for configurations with the substitutional C bonded with four Si atoms.<sup>4</sup> First, the results shown in Table III support the exclusion of the model (ii). However, such a conclusion cannot be reached based on the  $C_S$  results. Since our results for  $C_S$ , as well as the experimental findings by Kanzawa and co-workers,<sup>5</sup> indicate an increase of  $\text{Si}_3\text{Ge}_1$  NN configurations when temperature is increased, see Table II. On the other hand, the proposed model (i) seems to be very reasonable. Our total-energy results indicate a dominant formation of  $C_I$  bonded to three Si atoms, as shown in Table III, which support the C diffusion along the Si-rich paths.

## IV. CONCLUSION

In summary, we have investigated the properties of substitutional and interstitial C in Si, Ge, and  $\text{Si}_x\text{Ge}_{1-x}$  by means of *ab initio* total-energy calculations.

The formation energies of  $C_S$  in Si and Ge are 1.69 and 2.50 eV, respectively. For both hosts, the formation energies of  $C_S$  increase with lattice parameters. In Si and in Ge the

split(100) configuration is the energetically most stable for  $C_I$ . Our results indicate formation energies in Si and Ge of 4.02 and 4.76 eV, respectively. In contrast to what we found for the  $C_S$ , for both hosts the formation energies of  $C_I$  decrease with lattice parameters.

In the alloy, we investigated the properties of the impurities for concentrations of  $x=0.50$  and  $x=0.85$ . The formation energies of  $C_S$  and  $C_I$  are minimized when there are only Si atoms at the nearest neighborhood of the impurities. For other configurations in the vicinity of the impurities, the formation energies increase by about 0.1 and 0.4 eV per Ge-C bond added, for  $C_S$  and  $C_I$ , respectively. Finally, we have

calculated the relative equilibrium populations of the different configurations at the vicinity of the impurities, for temperatures between 550 and 950 °C. We find that for  $C_S$ , most of the impurities have four or three Si atoms at their nearest neighborhood. While for  $C_I$ , most of the impurities have almost exclusively Si atoms at their nearest neighborhood.

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<sup>21</sup>For the  $\text{Si}_3\text{Ge}_1$  ( $\text{Si}_1\text{Ge}_3$ ) NN configuration we considered the formation energy as being the mean value between  $\text{Si}_4\text{Ge}_0$  ( $\text{Si}_0\text{Ge}_4$ ) and  $\text{Si}_2\text{Ge}_2$  NN configurations.