

**{H,B}, {H,C}, and {H,Si} pairs in silicon and germanium**

Dj. M. Maric

*Swiss Scientific Computing Center, 6928 Manno, Switzerland*

P. F. Meier

*Physik-Institute, University of Zürich, 8057 Zürich, Switzerland*

S. K. Estreicher

*Department of Physics, Texas Tech University, Lubbock, Texas 79409-1051*

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The interactions between interstitial H and substitutional B, C, and Si in crystalline silicon and germanium are studied in molecular clusters at the *ab initio* Hartree-Fock level with large basis sets. The energetics, electronic structures, and relative stabilities of these pairs are determined. Our results show that the {H,B} pair is virtually identical in Si and Ge. Substitutional C is a strong trap for interstitial H in the two hosts. There are *two* trigonal, nearly energetically degenerate, and electrically active configurations of the electrically neutral {H,C} pair in each host. Substitutional Si in Ge is a weak trap for H. There are *four* configurations with trigonal symmetry of the {H,Si} pair in Ge within some 0.25 eV of each other. Two of these are electrically active with H covalently bound to the Si or to a Ge atom. The other two have H near tetrahedral interstitial sites. The {H,Si} pairs are much less stable than the {H,C} ones, and the reasons for this difference are discussed.

**I. INTRODUCTION**

The phenomenon of hydrogen passivation of electrically active centers in semiconductors has received a great deal of attention in the past ten years.<sup>1-3</sup> Experimental and theoretical studies have provided much insight, in particular regarding the passivation of shallow acceptors and donors in crystalline Si. These results are often the basis for the interpretation of experimental data in other hosts, such as compound semiconductors. Much less effort has been devoted to the study of hydrogen interactions in germanium. However, high-purity germanium was the first semiconductor in which hydrogen was observed to alter the electrical activity of impurities.<sup>4-8</sup> In Ge, hydrogen *activates* the normally inactive isovalent substitutional C and Si impurities, forming the  $A(H,C)$  and  $A(H,Si)$  shallow acceptors. Their existence was detected in ultrapure Ge with photothermal ionization spectroscopy (PTIS),<sup>5</sup> a technique sensitive to very low defect concentrations. The lowest concentrations of H and C or Si in Ge necessary to observe acceptor formation are of the order of  $10^{14}$  cm<sup>-3</sup>, but only a small fraction of the total number of C or Si impurities actually forms the acceptor complexes.

These experimental studies<sup>4-8</sup> have established that C or Si bind H, that the complexes are insensitive to applied stress, and that  $A(H,C)$  is stable up to 200 °C while  $A(H,Si)$  dissociates readily at room temperature. The interpretation of the early optical spectra was consistent with the H interstitial being located at a site with  $T_d$  symmetry, i.e., at the tetrahedral interstitial ( $T$ ) site. This led to a tunneling model<sup>7,9</sup> which explained some features of the data. The subsequent empirical calculations<sup>10,11</sup> of the electronic structures of these complexes did not in-

clude the evaluation of potential energy surfaces (PES's). More recent experiments<sup>12</sup> have shown that H is at a site with  $C_{3v}$  symmetry, implying that H is *bound* at either an antibonding (AB) or a bond-centered (BC) site very near C or Si.

A density-functional calculation<sup>13</sup> of the PES for various charge states of the {H,Si} pair in Ge has concluded that H is near the BC site in the 0 and +1 charge states, and AB to Si, 0.2 Å from the  $T$  site, in the -1 charge state. In each case, the calculated binding energies of H are very small, ranging from 0.02 to 0.05 eV. A recent study by us<sup>14</sup> has shown that the PES for the neutral {H,Si} pair in Ge has four local minima. In the lowest-energy configuration, hydrogen is AB to the Si atom. The BC configuration is some 0.25 eV higher in energy, higher in fact than two configurations where H is not bound.

This formation of the shallow  $A(H,C)$  acceptor has been observed in Ge only, although a neutral complex such as {H,C} could in principle be formed and be electrically active in Si as well. There is experimental evidence that H does form a pair with C, at least in *n*-type Si. The electrically charged {H,C}<sup>+</sup> pair<sup>15,16</sup> was found to have a deep donor level at  $E_c - 0.16$  eV.

In addition to the activation of C and Si, hydrogen also passivates electrically active centers such as shallow dopants. In perfect Si, the lowest-energy site for H<sup>0</sup> is the BC site (H\*) with a metastable state at or near the  $T$  site (H<sub>T</sub>).<sup>17,18</sup> In the BC configuration, the odd electron does not participate in the bonding but is in a nonbonding orbital primarily localized on the two nearest neighbors (NN's) to the proton. Thus, H\* is easily ionized and forms<sup>18</sup> H<sup>+</sup> which is also at the BC site. The existence of H<sup>+</sup> and its role in speeding up acceptor passivation in Si are now generally accepted.<sup>19</sup>

Nearly 100% of substitutional single acceptors in Si are easily passivated by H at room temperature. This is probably due to the long-range Coulomb attraction between  $H^+$  and  $B^-$ , resulting in the formation of the  $\{H,B\}^0$  complex. In Ge, the passivation of B by H is very difficult to achieve.<sup>20</sup> *A priori*, this could be due to differences in the microscopic structure or the stability of the  $\{H,B\}$  pair, or to a large difference in the capture radius of H by B. Recent muon spin rotation<sup>21</sup> and thermal effusion<sup>22</sup> data suggest that  $H^+$  is less abundant in Ge than in Si.

In the present work we report calculations of the energetics, electronic structures, and relative stabilities of the neutral  $\{H,B\}$ ,  $\{H,C\}$ , and  $\{H,Si\}$  pairs in Si and Ge. For each pair, we studied all the possible configurations with trigonal symmetry. In the case of the shallow  $A(H,C)$  and  $A(H,Si)$  acceptors in Ge, we also optimized the geometries in the negative ( $-1$ ) charge state. Section II contains a discussion of the method, and the results for the  $\{H,B\}$ ,  $\{H,C\}$ , and  $\{H,Si\}$  pairs in Si and Ge are given in Secs. III, IV, and V, respectively. A discussion of the results and of the key factors influencing the stability of H-related pairs in Si and Ge is in Sec. VI.

## II. THEORETICAL BACKGROUND

All the results presented below were obtained at the *ab initio* Hartree-Fock (HF) level with split-valence basis sets and polarization functions on selected atoms: The H has two  $s$  and a set of  $p$  orbitals, while the C and Si atoms located on the relevant trigonal axis have one orbital per core orbital, two orbitals per valence orbital, and one set of  $d$ 's. In the case of Si, all electron calculations were performed. For Ge, model pseudopotentials<sup>23</sup> were used for the core orbitals, each valence orbital was described by two orbitals, and an extra set of  $d$  functions was added. The Ge core pseudopotentials include the necessary relativistic corrections. In selected cases, we also optimized the geometries with minimal basis sets in order to study the influence of basis-set size. These effects are included in the discussions of the results wherever appropriate.

The geometries of all the configurations studied were optimized using gradient-based techniques in order to obtain the best possible equilibrium geometries. This approach guarantees convergence toward true minima of the PES. The host crystals were represented by two clusters:  $HXY_7H_{18}$  and  $HXY_{13}H_{24}$ , where H is hydrogen, X is substitutional B, C, or Si, and Y is the host atom (Si or Ge). The hydrogen saturators (18 for the first cluster and 24 for the second one) are used to tie up the host atom dangling bonds at the surface of the clusters. These saturators are located at energy-optimized Si-H or Ge-H bond lengths (1.4878 Å for Si and 1.5347 Å for Ge). These surface conditions have been extensively studied<sup>24</sup> and are known to minimize the influence of the surface of the cluster on the calculated properties of localized defects.

The  $HXY_7H_{18}$  cluster contains two host atom shells around the BC site and the  $HXY_{13}H_{24}$  cluster contains both the BC and the  $T$  sites, each with two complete host atoms shells around them. The use of larger clus-

ters at this level of theory is computationally prohibitive at the present time. However, a number of computational studies<sup>1-3</sup> of hydrogen-impurity pairs in Si have shown that the equilibrium geometries, relative stabilities, and electronic structures, are quite well described in such clusters or in supercells of comparable size. The calculated equilibrium bond lengths between host atoms in the cluster with no impurity are 2.3854 Å in Si and 2.4827 Å in Ge, i.e., some 0.03 Å longer than the experimental values for crystalline Si (2.3512) and Ge (2.4508).

## III. THE $\{H,B\}$ PAIR

Hydrogen passivation of shallow acceptors in Si has been extensively studied in recent years.<sup>1-3</sup> As discussed in the Introduction, H easily passivates virtually all the substitutional B atoms in Si, while only a small fraction (at best) of them is passivated in Ge. Further, when formed, the  $\{H,B\}$  pairs are less stable in Ge than in Si: All are completely dissociated<sup>25</sup> around 100 °C in Ge, but survive up to some 180 °C in Si. In order to determine the origin of these differences, we calculated the equilibrium structure of the neutral  $\{H,B\}$  pair in both hosts. We also determined the geometries and energies of the metastable states, and considered several additional points on the PES for H in the vicinity of B. These calculations were done with closed-shell restricted Hartree-Fock (RHF) wave functions, except for H distant from B (two-spin system) where unrestricted wave functions were used (see below).

The lowest-energy configurations of the  $\{H,B\}$  pair in Si and Ge are shown in Fig. 1. In both hosts, H is near the BC site, strongly bound to the host atom and only weakly overlapping with the B atom. Within the constraints of  $C_{3v}$  symmetry, we found two other local minima of the PES. Their energies relative to the stable configuration (Fig. 1) are given in Table I. A detailed comparison between Si and Ge of the amount of displacement of each atom in all three configurations shows very small differences. For example, in the BC configuration, Si moves by 0.162 Å away from the perfect substitutional site, while Ge moves by 0.159 Å. There is also little difference in the details of the electronic structures, as can be seen, e.g., in the bonding indices shown in Fig. 1.

In order to further compare the PES's for H near sub-

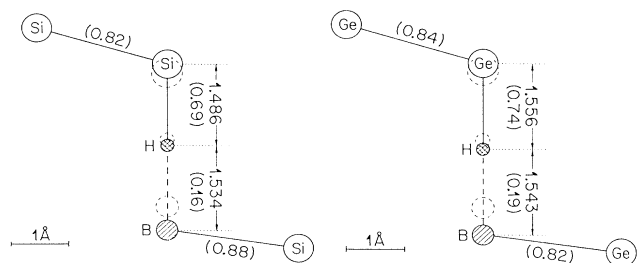


FIG. 1. Equilibrium configuration of the  $\{H,B\}$  pair in Si and Ge. The bond lengths (in Å) and bond indices (in parentheses) are shown. The dashed circles show the location of the perfect lattice sites.

TABLE I. Relative energies of the various configuration of the {H,B} pair in Si and Ge.

Configuration	Energy (eV)	
	In Si	In Ge
Si-H···B	0.00	0.00
Si···B-H	1.47	1.51
H-Si···B	1.83	1.75

stitutional B in Si and Ge, we calculated two other configurations: H at the BC site between two host atoms near B, and H at several  $T$  sites, again near B. For these calculations, we used unrestricted wave functions in both the singlet and the triplet states. The purpose of these calculations was to check whether substantial differences in the PES exist. Were it the case, we would have pursued the matter using two open-shells ROHF (restricted open-shell) wave functions. However, the numbers we obtained were very close to each other, and the PES for H near B in Ge is only slightly more flat than in Si. This difference is far too small to explain the difference in the formation rates of the {H,B} pairs.

Thus, once formed, the {H,B} pairs in Si and Ge are very similar. The stable and metastable structures are nearly identical (Fig. 1), and are separated by very similar amounts of energy. The PES is somewhat flatter in Ge than in Si, which is consistent with the debonding of the pair occurring at a lower temperature in Ge than in Si. However, the difference is much too small to explain why shallow acceptors are so easy to passivate in Si and so hard to passivate in Ge.

These results lead us to conclude that the explanation lies in a large difference in the *capture radius* of hydrogen by boron in the two hosts. In Si, the passivation results mainly from the reaction  $B^- + H^+ \rightarrow \{H,B\}^0$ , which is characterized by a long-ranged Coulomb attraction between the two charged species. There is now convincing experimental evidence<sup>19</sup> that at room temperature in Si, hydrogen spends much of its time in the +1 charge state. However, the stable site for H in Ge may well be the  $T$  site, implying that  $H^0$  dominates.<sup>26</sup> Then, passivation can only be accomplished via a reaction such as  $B^- + H^0 + h^+ \rightarrow \{H,B\}^0$ , where  $h^+$  is a hole. This has a much smaller, non-Coulombic, capture radius, and H has to stumble almost “accidentally” upon B for passivation to occur. Further, the presence in the subsurface layer of a large concentration of rapidly diffusing  $H^0$  species at  $T$  sites—a condition realized in plasma treatments—favors the formation of  $H_2$  molecules, thus hindering<sup>22</sup> the penetration of atomic hydrogen into the bulk.

#### IV. THE {H,C} PAIR

Substitutional C is a common impurity in Si and Ge crystals, especially those grown from a melt. In Ge, interstitial H forms an electrically active complex with C, the shallow  $A(H,C)$  acceptor.<sup>4,5</sup> This complex has  $C_{3v}$  symmetry<sup>12</sup> and is stable up to 200 °C.

We found two nearly energetically degenerate configurations for the neutral {H,C} pair in Si and in Ge (Fig. 2). The lowest-energy one corresponds to H near the BC site, bound primarily to a host atom. The unpaired electron resides almost entirely in a nonbonding orbital on the C atom, which is nearly  $sp^2$  hybridized. We compared this configuration to the one with C at the perfect substitutional site and H far outside the clusters. One *gains* 1.42 eV (in the case of Si) and 1.83 eV (in the case of Ge) by forming the {H,C} pair with H near the BC site. By comparison, at the same level of theory, it *costs* 1.44 eV (for Si) and 1.20 eV (for Ge) to form the BC structures Si-H-Si and Ge-H-Ge, starting with H far outside a cluster, without substitutional C. These numbers show that substitutional C is a strong trap for interstitial H in both hosts.

The metastable configuration of the {H,C} pair, also shown in Fig. 2, corresponds to H antibonding to C, which is now fourfold coordinated: Three  $sp^2$  hybrids

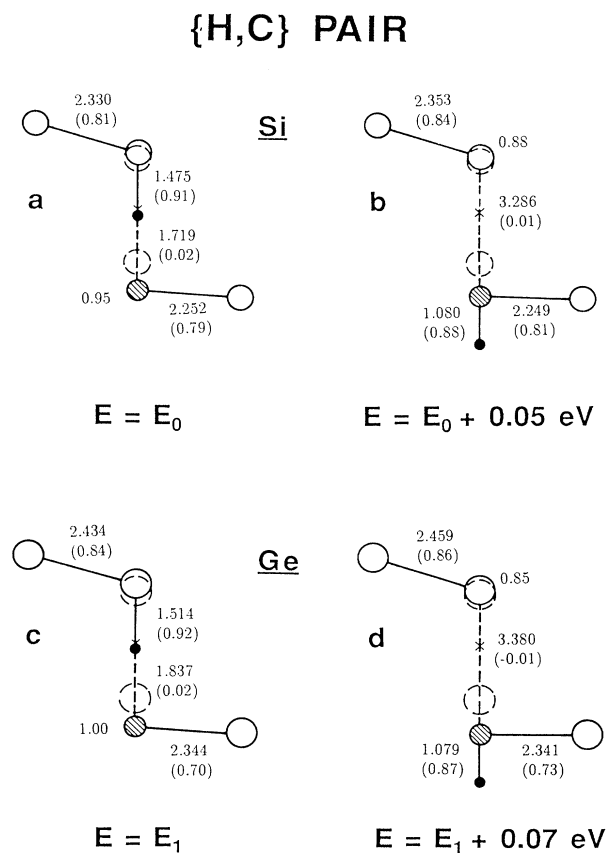


FIG. 2. The {H,C} pair has two nearly energetically degenerate configurations in Si [(a) and (b)] and in Ge [(c) and (d)]. The stable one has H near the BC site attached to a host atom, with the odd electron in a nonbonding orbital on C, and the metastable one has H antibonding to C and bound to it, with the odd electron on a threefold-coordinated host atom. The bond lengths (in Å), bond indices (in parentheses), and relative energies are shown. The atomic spin population shows the location of the unpaired electron. All of these configurations should be electrically active.

with three host atoms and H attached to the remaining  $2p_z$  orbital. The host atom near C along the  $\langle 111 \rangle$  axis remains very near its ideal substitutional site and carries most of the odd electron, again in a nonbonding orbital.

The first configuration (H near the BC site) is stabilized by having the unpaired electron in a nonbonding orbital on the most electronegative atom (C), while the second configuration (H antibonding to C) is stabilized by the formation of a C–H bond, which is stronger than the Si–H or the Ge–H bond. That these two very different configurations are within a few hundredths of an electron volt from each other is probably coincidental, and we see no reason why a similar set of circumstances should occur for other complexes, such as {H,Si} in Ge (see below). However, our results imply that both configurations should be realized with nearly the same probability. They are both electrically active.

Note that the {H,C}<sup>0</sup> pairs could either trap an extra electron and form {H,C}<sup>-</sup> or lose the odd electron and become {H,C}<sup>+</sup>. We have no direct way of calculating the relative energy of these species, and their formation probability depends, among other factors, on the position of the Fermi level. A change in the charge state may well result in a change in the ground-state configuration of the complex, as is documented,<sup>27</sup> e.g., in the case of the {H,P} pair in Si.

Because of the large lattice relaxation around the defect, of the presence of an unpaired electron, and of a threefold-coordinated C or Si (or Ge) atom, both {H,C}<sup>0</sup> pairs are likely to trap a second hydrogen interstitial and form {H,H,C}. The result, starting with any one of the two configurations, is the same: One H near the BC site bound to a host atom, the second AB to C and bound to it ( $X-H \cdots C-H$ , with  $X=Si$  or Ge). This configuration, very reminiscent of the  $H_2^*$  complex proposed<sup>28</sup> for hydrogen dimers in Si, should be electrically (but not optically) inactive. Theoretical investigations of {H,H,C} are under way.

We also investigated the configuration where H is AB to a host atom, and found it to be substantially higher in energy: 0.94 eV in the case of Si, and 1.63 eV in the case of Ge. The unbound configurations (H at the  $T$  site near C or near a host atom at perfect substitutional sites) are even higher in energy. Finally, in the negative ( $-1$ , spin singlet) charge state, the configurations shown in Figs. 2(b) and 2(d) are the most stabilized by the capture of an additional electron and become the lowest-energy states. However, the configurations in Figs. 2(a) and 2(c) are only 0.05 eV (in the case of Si) and 0.19 eV (in the case of Ge) higher in energy. Thus, both conformations remain very close in energy and should coexist in both charge states.

## V. THE {H,Si} PAIR

The situation is quantitatively very different for the neutral {H,Si} pair than for the {H,C} in Ge for three reasons. First, the Si–H bond is *weaker* than the C–H bond, and therefore the gain in energy resulting from the capture of H is smaller. Second, the odd electron is *not*

as stable in a nonbonding orbital on Si or Ge as it is on C. Third, the Si–Ge bond length for substitutional Si in Ge is *very close* to the Si–Ge one in molecules. This was not the case for C (see Sec. VI).

Our calculations show that four configurations are very close in energy. They are shown in Fig. 3. The most stable one, 3(a), has H antibonding to Si, bound to it, with the unpaired electron mostly localized on the Ge atom. Then are two configurations [3(b) and 3(c)] with the Si and all the host atoms very near their perfect substitutional site and H in a nonbonded configuration at either one of the two  $T$  sites along a trigonal Ge–Si axis. These two configurations do not result in activation. Finally, the BC configuration 3(d) is 0.27 eV above the ground state. The energy is +0.64 eV when H is AB to Ge (not shown). Note that our results conflict with a density-functional calculation of the same complex: Denteneer, Van de Walle, and Pantelides<sup>13</sup> found our configuration 3(d) to be the stable one and they do not discuss metastable states.

Thus, there is little incentive (0.08 eV) for H to form an electrically active center with substitutional Si in Ge. When it does, the resulting configuration is much less stable than the {H,C} pair, in agreement with experimental observations. Note that it *costs* 0.53 eV to bring

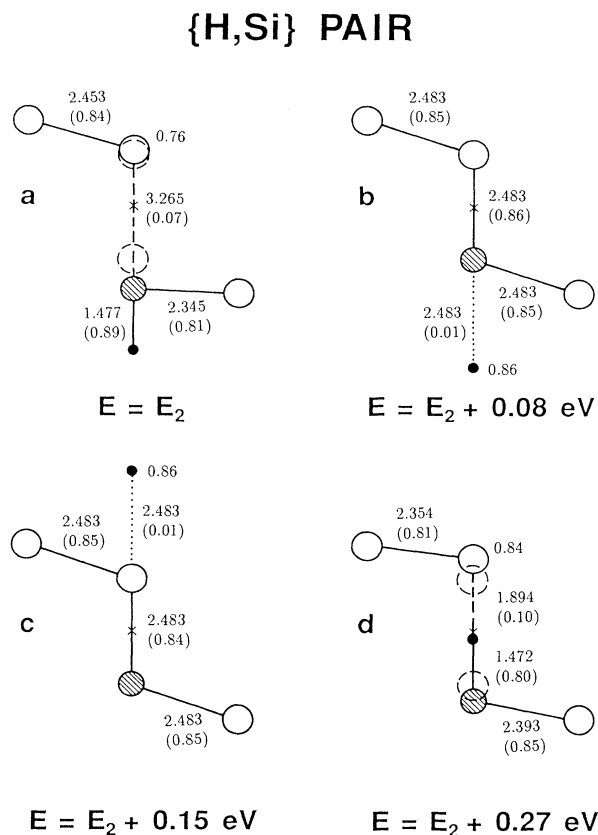


FIG. 3. The {H,Si} pair in Ge has four configurations very close in energy. The lowest-energy (a) and the highest-energy (d) ones are electrically active, but the intermediate configurations [(b) and (c)] are not. The notation is the same as the one used for Fig. 2.

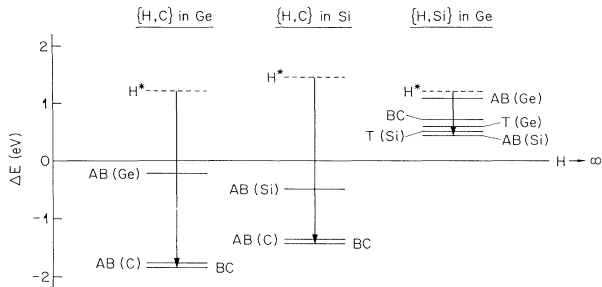


FIG. 4. Energies of the various configurations of the  $\{H,C\}$  and  $\{H,Si\}$  pairs in Si and Ge relative to the BC configuration in the perfect lattice, denoted  $H^*$ . The zero of the energy corresponds to the cluster containing the substitutional impurity at an unrelaxed site and atomic H far outside. The configurations are AB( $X$ ) for H antibonding to atom  $X$ , BC for H near the bond-centered site, and  $T(X)$  for H at or near the  $T$  site located near atom  $X$  along the trigonal axis. The lowest-energy configurations are shown in Figs. 2 and 3.

H from far outside the Ge cluster (containing substitutional Si) and put it in the lowest-energy configuration [Fig. 4(a)]. By comparison, at the same theoretical level, one *gains* 1.83 eV by forming the analogous  $\{H,C\}$  pair (see above), while it costs even more energy (1.44 eV) to form the usual BC interstitial ( $H^*$ ) center in perfect Si, which is the analogous of the  $\{H,Si\}$  pair in Si.

In the negative ( $-1$ , spin singlet) charge state, it is the configuration shown in Fig. 3(a) which is the most stabilized by the presence of the additional electron, and all the other configurations end up several tenths of an electron volt higher in energy. Thus, only one configuration survives the capture of an electron.

## VI. DISCUSSION

We have calculated all the possible structures compatible with trigonal symmetry for the  $\{H,B\}$ ,  $\{H,C\}$ , and  $\{H,Si\}$  pairs in Si and Ge. The electronic structures have been obtained for the stable and metastable configurations in the 0 charge state for  $\{H,B\}$  and in the 0 and  $-1$  charge states for the other two pairs. The results can be summarized as follows.

(i)  $\{H,B\}$  pair: The equilibrium structure of the hydrogen-passivated B acceptor is virtually the same in Si and Ge. The PES for H is only a little more flat in Ge, which is consistent with the observed lower reactivation temperature.<sup>27</sup> Differences in the efficiency of acceptor passivation are not related to the details of the  $\{H,B\}$  pair, but most probably to differences in the capture radii of hydrogen by boron in Si and Ge, and/or to the formation of  $H_2$  molecules near the surface of Ge upon plasma exposure, thus preventing atomic H from penetrating the sample.

(ii)  $\{H,C\}$  pair: Substitutional C is a strong trap for H in both Si and Ge. The formation of the  $\{H,C\}$  pair is preferred over the formation of  $H^*$  in the perfect crystal by 2.8 eV in the case of Si, and 3.0 eV in the case of Ge.

TABLE II. Bond-length “mismatch” (see text) for isovalent substitutional impurities in Si and Ge. The ideal bond length is the one realized at equilibrium in molecules or radicals. The bond length realized for the substitutional impurity corresponds to the host-host bond length (lattice relaxation around the isolated substitutional impurity is neglected here). The mismatch in the case of C is very large, illustrating how much energy is to be gained from relaxations upon the capture of interstitial H.

Bond	Bond length (Å)		Mismatch (%)
	Optimal	In the crystal	
C–Ge	1.94	2.45	26
C–Si	1.85	2.35	27
Si–Ge	2.40	2.45	2
Si–Si	2.35	2.35	0
Ge–Ge	2.35	2.45	0

This will be further discussed below (iv). Two configurations of the  $\{H,C\}^0$  pair coexist in each host. Both are electrically active and should be traps for a second hydrogen interstitial.

(iii)  $\{H,Si\}$  pair: Substitutional Si is a weak trap for H in Ge. There are four configurations for the  $\{H,Si\}^0$  pair within 0.27 eV of each other. The lowest- and highest-energy ones have H bound to the Si atom, and these configurations should be electrically active. The two intermediate configurations have an atomlike H near a  $T$  site, and should be electrically inactive. It is possible that the bound  $\{H,Si\}^0$  pairs could trap a second H, but the resulting gain in energy should be much less than in the case of the  $\{H,C\}^0$  pair.

(iv) Stability of  $\{H,C\}$  vs  $\{H,Si\}$ : Isovalent substitutional impurities such as C or Si in Si and Ge are normally not electrically active because all their valence electrons play well-defined roles in the covalent bonding. All the bonding orbitals are doubly occupied and lie rather low in energy while the antibonding ones are empty and lie rather high in energy. However, even though the host lattice relaxes to accommodate for the presence of the substitutional impurity, the bond length of the four bonds may be quite different from the optimal bond length realized in molecules or radicals.

This bond-length “mismatch” is much larger in the case of substitutional C than Si. Table II shows the optimal bond length (for the molecule) and the bond length actually realized (without lattice relaxation) for substitutional C and Si in Si and Ge. The huge bond-length mismatch in the case of C (more than 25%) is the main reason for the large amount of energy gained from the capture of interstitial H: this capture allows the C atom to shorten three of its four bonds at a substantial gain in energy. On the other hand, the bond-length mismatch in the case of substitutional Si in Ge is very small, and there is much less energy to be gained from the formation of the  $\{H,Si\}$  pair. In the case of the perfect lattice (i.e., substitutional Si in Si or substitutional Ge in Ge), the bond-length mismatch is zero and it costs energy to insert H at the BC site.

The energy gain resulting from the formation of the various complexes discussed above is shown in Fig. 4. The zero of the energy corresponds to atomic H far outside the cluster containing the substitutional impurity. The gain resulting from the formation of the {H,C} and {H,Si} pairs in Si and Ge relative to H\* is shown by arrows.

#### ACKNOWLEDGMENTS

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