

## Hydrogen passivation of shallow acceptors and donors in *c*-Si: Comparisons and trends

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The equilibrium geometries and electronic structures of hydrogen-passivated acceptors (B, Al, and Ga) and donors (P and As) in crystalline silicon are calculated in two clusters:  $XHSi_7H_{18}$  and  $XHSi_{34}H_{36}$ , where  $X$  is the acceptor or donor. The results, obtained using the method of partial retention of diatomic differential overlap (PRDDO) and *ab initio* Hartree-Fock with various basis sets, show that all these complexes are metastable. In the case of passivated acceptors, the stable configuration corresponds to H close to the bond-centered site and the metastable one to H at the antibonding site of one of the Si atoms nearest to the acceptor. The configuration where H is antibonding to the acceptor is a saddle point of the energy. The effects of  $\langle 111 \rangle$  uniaxial stress on the position of the H passivator are qualitatively analyzed. In the case of donors, the lowest-energy site for H is at the antibonding site to one of the Si atoms nearest to the donor. The configurations where H is at the bond-centered site or is antibonding to the donor are nearly energetically equivalent. The similarities and differences between the various complexes are discussed.

### I. INTRODUCTION

Hydrogen is found in a variety of configurations in crystalline silicon. Neutral interstitial hydrogen (and its light isotope muonium<sup>1</sup>) is located at or close to the center of a relaxed Si—Si bond (stable) or the tetrahedral interstitial (*T*) site (metastable). Bond-centered hydrogen is now well documented theoretically<sup>2-6</sup> and experimentally<sup>7,8</sup> while the exact location of the metastable species still is the subject of some uncertainty,<sup>2-5,9-12</sup> although most authors agree that the barrier for diffusion is small. However, much of the current interest in interstitial H stems from its ability to passivate a number of electrically active defects, such as dangling bonds and various donors and acceptors (for a recent review, see Ref. 13). In particular, the passivation of shallow donors and acceptors in *c*-Si has been the subject of intense experimental and theoretical efforts in the past few years. The results of these investigations can be summarized as follows.

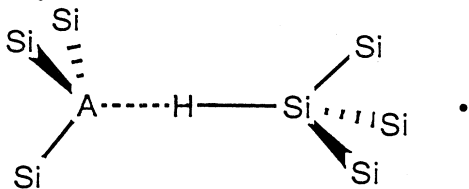
The first evidence of acceptor passivation in Si was obtained by Sah *et al.*<sup>14-16</sup> and the role of hydrogen was established by Pankove *et al.*<sup>17</sup> Up to 99% of the acceptors can be passivated.<sup>18-20</sup> The diffusing species responsible for the passivation is monoatomic hydrogen (or deuterium) as shown, e.g., by secondary-ion mass spectroscopy.<sup>21</sup> A sharp ir-absorption line around 1875  $\text{cm}^{-1}$  in B-doped silicon,<sup>22-25</sup> which shows an isotope shift when D replaces H, is interpreted as a Si—H stretching vibration perturbed by the presence of a nearby substitutional boron atom. A similar line at 2201  $\text{cm}^{-1}$  (predicted<sup>26</sup> by DeLeo and Fowler) was later observed<sup>27,28</sup> in Al-doped Si, and at 2171  $\text{cm}^{-1}$  in Ga-doped Si.<sup>28</sup> These lines narrow and shift towards higher frequencies upon cooling and sidebands appear.<sup>28</sup> These sidebands are more pronounced for passivated Al and Ga centers in Si than for

passivated B centers, and indicate the existence of a low-frequency excitation of the complexes. In addition, Raman-scattering experiments<sup>29</sup> show evidence of a new mode at 650  $\text{cm}^{-1}$  attributed to B-H pair formation. In H-passivated In-doped samples, Wichert *et al.*<sup>30</sup> observed two In-H complexes, the less abundant one having a higher quadrupole frequency.

Further microscopic information has been obtained from channeling and x-ray-diffraction experiments in passivated B-doped samples. Channeling<sup>31</sup> indicates that after passivation, B is displaced along the  $\langle 111 \rangle$  direction by  $0.22 \pm 0.04 \text{ \AA}$  from the substitutional site. The magnitude of this displacement is confirmed by estimates obtained from x-ray diffraction<sup>32</sup> (0.29  $\text{Å}$ ). Channeling experiments<sup>33</sup> in deuterium-passivated B-doped Si show that 87% of D is near a bond-centered (BC) site, but 0.2  $\text{Å}$  off the axis along a  $\langle 110 \rangle$  direction perpendicular to  $\langle 111 \rangle$ , and the remaining 13% near a *T* site. The off- $\langle 111 \rangle$ -axis location for H was recently confirmed by Raman-scattering experiments of passivated boron centers under uniaxial stress.<sup>34,35</sup> The absence of frequency splitting of the Si—H stretching vibration under  $\langle 111 \rangle$  stress, while splitting is observed for  $\langle 100 \rangle$ ,  $\langle 110 \rangle$ , and  $\langle 112 \rangle$  stresses, indicates that H is not on the trigonal axis. These experiments further show that the vibrations of B and H are decoupled, i.e., that there is no significant bonding between the two atoms. These results contrast with other recent measurements of vibrational absorption frequencies under uniaxial stress<sup>36</sup> for B-H and As-H centers. Hydrogen-passivated boron shows a large sensitivity to stress, interpreted as being due to the tendency of H to move off the trigonal axis. However, with no stress applied, the symmetry is found to be trigonal. The interpretation<sup>23</sup> of the early data assumed a threefold-coordinated acceptor (*A*) and the H interstitial saturating the fourth dangling bond. The pas-

sivation mechanism would involve the capture of a hole:  $A^- + h^+ + H^0 \rightarrow (AH)^0$ . However, it is now believed<sup>37-43(a)</sup> that the diffusing species is  $H^+$  rather than  $H^0$ , i.e.,  $H^0 + h^+ \rightarrow H^+$  followed by  $A^- + H^+ \rightarrow (AH)^0$ . This point is not yet fully resolved: Recent experiments<sup>43(b)</sup> indicate that  $H^0$  also participates in the passivation process, at least in the case of B-doped Si.

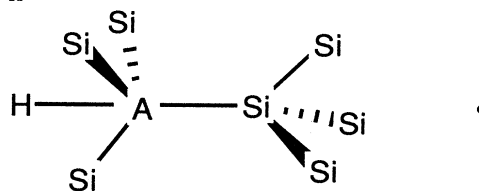
On the theoretical side, two configurations have been proposed for the passivation of shallow acceptors. In the first one,<sup>23,26,44</sup> after passivation, hydrogen is near the BC site and ties up the Si dangling bond, leaving the acceptor essentially threefold coordinated:



The geometries of DeLeo and Fowler<sup>26,44</sup> were calculated at the modified neglect of diatomic overlap (MNDO) level in the cluster  $AHSi_4H_{12}$  ( $A = B$  or  $Al$ ). In B-doped Si, the calculated Si—H bond length was 1.43 Å. The corresponding calculated vibrational frequency ( $1870\text{ cm}^{-1}$ ) is in excellent agreement with experiment. In the optimized geometry, the B atom is displaced off the substitutional site by 0.5 Å, i.e., about twice the experimentally estimated displacement.<sup>31,32</sup> In Al-doped Si, the predicted Si—H vibrational frequency ( $2220\text{ cm}^{-1}$ ) was later experimentally observed.<sup>27,28</sup> More recently, a similar model has been analyzed<sup>45</sup> in  $BHSi_7H_{18}$  at the *ab initio* Hartree-Fock (HF) level with a minimal basis set. This calculation finds no minimum (only a saddle point) for H at the boron antibonding (AB) site. At the BC site, the calculated Si—H (B—H) bond length is 1.46 Å (1.59 Å), and the Si—H bond is much stronger than the B—H bond. Finally, calculations of the potential-energy surface (PES) for hydrogen-passivated B-doped Si have been carried out by Chang and Chadi.<sup>46</sup> They used *ab initio* pseudopotentials in 8-atom/cell supercells. The absolute minimum of the energy is realized when H is close to the BC site with  $d_{Si-H} = 1.63\text{ Å}$ , and B is displaced by 0.47 Å from the substitutional site. The total energy drops by 0.01 eV for displacements of the H atom off the trigonal axis by 0.3 Å. The calculated frequency of the Si—H stretching vibration is  $1820\text{ cm}^{-1}$ , which fits very nicely the experimental value. They find two other minima of the energy for H at the AB site of B (+0.31 eV, with  $d_{B-H} = 1.47\text{ Å}$ ) and close to the T site of the nearest Si atom (+0.86 eV, with  $d_{Si-H} = 3.77\text{ Å}$ ). The former bond length is about 0.25 Å longer than would be expected for a B—H bond, and the latter position suggests no bonding character to the Si-H interaction. Finally, a recent<sup>47</sup> calculation predicts that the barrier for hydrogen motion between equivalent BC sites is of the order of 0.20 eV. Subsequent measurements<sup>48</sup> of reorientation kinetics show that this motion is thermally activated with an activation energy of 0.19 eV.

In the second model, proposed by Assali and Leite,<sup>49,50</sup> the stable site for H is at the AB site of the boron, with  $d_{B-H} = 1.8\text{ Å}$ :

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In the proposed configuration, B is fivefold coordinated and H forms a bond with each of the three nearest Si atoms and one with the boron. The latter would be responsible for the observed  $1875\text{-cm}^{-1}$  frequency. This calculation was performed using the Slater-Johnson multiple-scattering  $X\alpha$  method in a 25-Si-atom cluster and a spring model to calculate the frequencies. The same model was recently used<sup>51</sup> to predict vibrational frequencies for passivated Al and Ga centers as well. Despite the agreement between calculated and measured vibrational frequencies (to within  $1\text{ cm}^{-1}$ ), it will be shown below that the proposed geometry is unreasonable (this site for H was identified as a saddle point in a Comment to Ref. 49). Further, the equilibrium B—H bond length is of the order of 1.2 Å and the corresponding stretching frequency<sup>52</sup> is about  $2300\text{ cm}^{-1}$ . It is difficult to imagine how a B—H bond length of 1.8 Å could result in a frequency as high as  $1875\text{ cm}^{-1}$ . Baranowski and Tatkiewicz<sup>53</sup> suggested an AB position for the H atom in the case of B-doped Si, but a BC position for Al- and Ga-doped Si. In any case, the existence of several minima of the PES (with a metastable configuration for antibonding H) cannot be ruled out.<sup>32,33</sup>

The hydrogen passivation of donors in Si has been observed only recently<sup>54,55</sup> from combined resistivity and Hall effect measurements. New ir-absorption bands<sup>56</sup> showing isotope shifts upon substitution of D for H have been seen in passivated samples doped with P, As, and Sb. The two strongest lines (at about 809 and  $1560\text{ cm}^{-1}$ ) are virtually donor independent and suggest<sup>56</sup> that H is bound to a Si atom rather than to the donor itself, in a configuration having trigonal symmetry. The  $1560\text{-cm}^{-1}$  line is a Si—H longitudinal stretching vibration, and the  $809\text{-cm}^{-1}$  frequency is due to a doubly degenerate transverse wagging mode. The third band, of much smaller amplitude, is tentatively attributed to a donor-H bond. In P-doped samples, 52% of donor passivation is realized, and over 80% in As- and Sb-doped ones.<sup>56</sup> An empirical tight-binding calculation by Johnson *et al.*<sup>54</sup> predicted that the equilibrium configuration for the passivated complex corresponds to H antibonding to Si: P—Si—H. This would be lower by 0.41 eV than the H—P—Si conformation, which also results in passivation. The calculated Si—H (P—H) bond length is 1.61 Å (1.48 Å). The calculations of Chang and Chadi<sup>46</sup> qualitatively confirm these conclusions. The lowest-energy configuration corresponds to H at the Si AB site, with  $d_{Si-H} = 2.33\text{ Å}$ . The vibrational frequency associated with this unusually long Si—H bond is predicted to be around  $400\text{ cm}^{-1}$ . The observed stretching frequency ( $1560\text{ cm}^{-1}$ ) suggests a much stronger bonding. Two other equilibrium configurations are found<sup>46</sup> at the AB

site of P (+0.57 eV) and at the BC site (+1.13 eV, with  $d_{\text{Si-H}} = 1.75 \text{ \AA}$ ). The location of H at the Si AB site is confirmed<sup>36</sup> by uniaxial-stress studies of the vibrational absorption of H-passivated As centers in Si. The sensitivity to stress is much less pronounced than for hydrogen-passivated boron, and the degeneracy of the  $810\text{-cm}^{-1}$  wagging mode implies trigonal symmetry (this frequency splits under  $\langle 110 \rangle$  uniaxial stress).

Thus, most calculations on the passivation of boron agree that the minimum-energy configuration corresponds to H at (or near) the BC site. The various methods show that the boron moves off the substitutional site by about  $0.5 \text{ \AA}$ . However, the predicted Si—H bond lengths vary between  $1.43$  and  $1.63 \text{ \AA}$ . The disagreement is even more pronounced in the case of H at the AB site of the B atom: this site has been characterized both as a minimum<sup>46</sup> and a saddle point.<sup>45</sup> Only one calculation deals with the passivation of Al centers, but no details of the PES have been reported. As concerning donors, two calculations have been published in the case of P. They agree that H is at a Si AB site, but predict Si—H bond lengths of  $1.61 \text{ \AA}$  (Ref. 54) and  $2.33 \text{ \AA}$  (Ref. 46). Both papers report another minimum of the energy for H at the AB site of P.

In light of the above discussion, there is a clear need for the systematic study of these systems at a uniform theoretical level, using modern gradient-optimization techniques including Hessian update procedures.<sup>57</sup> The use of such procedures is highly desirable since they guarantee convergence only at true minima of the PES, and unambiguously distinguish between minima and saddle points. In the present contribution, we use such a method to characterize the stationary points of the PES, calculate the equilibrium geometries and electronic structures for several passivated acceptors (B, Al, Ga) and donors (P, As). In Sec. II we discuss how the calculations were done. The results are described in Sec. III, which includes a discussion of the effects of  $\langle 111 \rangle$  uniaxial stress on the position of H passivating an acceptor. The comparisons and trends are carried out in Sec. IV.

## II. DETAILS OF THE CALCULATIONS

We used the method of partial retention of diatomic differential overlap<sup>58,59</sup> (PRDDO) and the *ab initio* HF method with several basis sets. The PRDDO calculations were done in two clusters<sup>60</sup> to test the effects of cluster size<sup>61</sup> and allow the inclusion of second-nearest neighbor (NN) relaxations:  $X\text{HSi}_7\text{H}_{18}$  and  $X\text{HSi}_{34}\text{H}_{36}$ , where  $X$  stands for B, Al, Ga, P, or As. The former cluster contains two host-atom shells around the BC site, and the latter five host-atom shells around the substitutional site. *Ab initio* HF calculations could only be performed in the smaller of the two clusters. PRDDO is an all-electron, approximate *ab initio* HF method which contains no adjustable parameters. Equilibrium properties calculated with PRDDO have been extensively<sup>58,59,62,63</sup> tested against *ab initio* HF (minimal basis set), and against experiment for over 100 molecules and molecular ions. The method is particularly reliable for equilibrium geometries, even when transition-metal complexes are in-

cluded.<sup>64,65</sup> Typical errors for bond lengths, relative to experimental values, are of the order of  $0.02 \text{ \AA}$  for bonds between light elements, and about  $0.05 \text{ \AA}$  for bonds involving a heavier element, such as a transition metal. PRDDO has recently been applied to problems involving impurities in diamond<sup>61,66,67</sup> and silicon.<sup>3,60</sup> The method is much more computationally efficient than *ab initio* HF. It suffers from the well-known limitations inherent to all HF approaches, in particular, the lack of electron correlation, except for the antisymmetry of the wave function. Exchange, however, is fully included. The calculations have a tendency to overestimate potential-energy barriers<sup>3,66,67</sup> and vibrational frequencies. No predictions of vibrational frequencies will be attempted here, as the study of the systematic errors due to the PRDDO approximations in this regard have not yet been carried out. Furthermore, we caution the reader that vibrational frequencies are notoriously difficult to calculate by the quantum-chemical techniques typically employed for cluster calculations such as the ones considered here and in some of the previous works on these systems. For instance, *ab initio* calculations<sup>68</sup> on a series of 14 first- and second-row diatomic hydrides using very large basis sets (including a set of  $d$  orbitals on H and a set of  $f$  orbitals on the heavier atom), with corrections for electron correlation and anharmonic effects, yield an average error of  $14 \text{ cm}^{-1}$  for the stretching frequency. A more realistic approach (but still very difficult) for the large clusters considered here would be to calculate harmonic frequencies at the restricted HF level via analytic second derivatives. Such calculations are well known to produce force constants which are 15–20 % too high, particularly for bond stretches,<sup>69</sup> which results in errors of the order of  $100\text{--}200 \text{ cm}^{-1}$  for most  $X\text{--H}$  stretching frequencies. Similarly unreliable results are obtained at the MNDO level: A recent comparative study of MNDO and *ab initio* (6-31G\*) frequencies for eight simple organic molecules<sup>70</sup> yielded average calculated differences in vibrational frequencies of  $144 \text{ cm}^{-1}$  for 38 vibrational modes, with no systematic trends apparent (18 of the 38 MNDO frequencies were higher than the *ab initio* values, 20 were lower). Since the frequencies obtained with large basis sets *ab initio* HF calculations are systematically higher<sup>71</sup> than the experimental ones, by about 10%, this shows that some MNDO frequencies may be very close to the experimental values, while others may be far off. Finally, even with an *exact* PES, solutions of the vibrational Schrödinger equation for these complicated systems always involve approximations (e.g., a calculation of frequencies based only on the harmonic part of the potential function), which precludes accuracy at the  $\text{cm}^{-1}$  level.

In the present paper the focus will be on employing PRDDO in the areas where it is the most reliable, in particular, the calculation of equilibrium structures. These calculations are complemented by the use of *ab initio* HF with various basis sets as often as computationally feasible. At first, we used PRDDO in the smaller of the two clusters ( $X\text{HSi}_7\text{H}_{18}$ ,  $X = \text{B, Al, Ga, P, or As}$ ) with gradient-based geometry-optimization routines, including Hessian procedures,<sup>57</sup> to find the positions of  $X$ , H, and the nearest Si which minimize the total energy in the

various possible conformations for the passivator: BC, AB to Si, and AB to X. These calculations include all nine geometrical degrees of freedom for X, H, and Si. As shown below, the results of these optimizations indicate that in the BC configuration, H always is slightly off the trigonal axis. This displacement is by no means very pronounced and the energy gain relative to the on-axis position is of the order of a few hundredths of an eV. The bond lengths, electronic structures, charge distributions, and other microscopic properties, are virtually identical in both situations. However, the point-group symmetry reduces from  $C_{3v}$  to  $C_1$ . For all practical purposes, keeping H on the trigonal axis yields equivalent results. Therefore, the geometry optimizations in larger clusters were performed assuming that H is on the  $\langle 111 \rangle$  axis. In  $XHSi_{34}H_{36}$  we optimized X, H, and Si, and the other three NN's to X and to Si these atoms, denoted by  $Si_{NN}(X)$  and  $Si_{NN}(Si)$ , were displaced parallel to the trigonal axis as well as relative to the substitutional site initially occupied by X or Si. No symmetry-lowering displacements of these atoms were considered. As will be demonstrated below, these second-NN relaxations lower the energy by a few tenths of an eV, but do not significantly modify any of the conclusions that can be drawn from the smaller cluster results. This indicates a strong localization of the interactions within the complex, justifies the use of clusters for this problem, and is consistent with earlier calculations dealing with bond-centered H.<sup>3,60,67</sup>

Higher-level calculations were then performed on  $XHSi_7H_{18}$  with the *ab initio* HF method using the standard<sup>72</sup> STO-3G basis set, and a 6-31 split-valence<sup>73</sup> (SV) basis set on the three atoms of interest (X, H, and Si) (STO denotes Slater-type orbital; G denotes Gaussian orbital). In the case of Ga and As, we used 3G expansions of the single- $\xi$  atomic orbital exponents of Clementi and Roetti<sup>74</sup> for the core 1s, 2s, 2p, 3s, and 3p orbitals, and 2G expansions of their double- $\xi$  atomic exponents for the 3d orbitals. In order to obtain molecular exponents for the valence (4s, 4p) orbitals, we have scaled their atomic double- $\xi$  exponents by minimizing the total energy relative to the scaling factor in  $GaH_3$  and  $AsH_3$  in their experimental equilibrium structures.<sup>75</sup> The optimized or-

bital exponents for the PRDDO calculations involving Ga and As are close to the *ab initio* ones, although not identical since PRDDO uses Slater orbitals, while *ab initio* HF techniques use linear combinations of Gaussians. In the case of P, we added a set of d orbitals on P (at the PRDDO level) as well as on the nearest Si atom (at the *ab initio* level). Since the inclusion of polarization functions on an atom with five valence electrons generally stabilizes fivefold coordination, this is of particular interest for the configuration where H is antibonding to P.

### III. RESULTS

#### A. Passivation of acceptors

##### 1. Boron

Table I shows the equilibrium geometries calculated in various clusters with various methods. The symmetry is assumed to be trigonal, and only the lowest-energy configuration is shown (H close to the BC site). The PRDDO results for  $BHSi_{34}H_{36}$  include the second-NN relaxations discussed in the preceding section. Using the gradient-based PRDDO geometry optimizations described above for  $BHSi_7H_{18}$ , we find that the absolute minimum corresponds to H located 0.022 Å off the trigonal axis, with  $\Delta E = -0.014$  eV relative to H on the axis. This displacement and energy difference are very small, and absolute numbers should be used with caution. What is clear is that H is quite free to move in the plane perpendicular to the BC site. Our calculations agree with other published results<sup>26,45,46</sup> that B is displaced off its substitutional site by about 0.5 Å. This contrasts with the smaller displacement (about 0.25 Å) estimated experimentally.<sup>31,32</sup> The nearest Si, however, is displaced from its substitutional site by only about half the displacement of the boron.

The second-NN relaxations around the BC configuration followed by readjustments of B, H, and Si lower the total energy by 0.31 eV, but otherwise have little impact on the calculated properties of the complex: For example, the B—H degree of bonding<sup>76</sup> is 0.18 without and 0.20 with second-NN relaxations. The “degree of bond-

TABLE I. Calculated equilibrium geometries in various clusters using various methods (see text). The results were obtained by chain optimizing the positions of B, H, Si, and of the group Si—H assuming trigonal symmetry. The results for  $BHSi_{34}H_{36}$  include second-NN relaxations. The displacements of B and Si relative to their respective substitutional sites are positive if the atoms are moving away from the BC site. (a) Ref. 26; (b) Ref. 45; (c) Ref. 46. Note that Ref. 46 predicts that the H passivator is off the trigonal axis by 0.3 Å, and that this displacement lowers the total energy by 0.01 eV relative to the on-axis site.

Distance (Å)	PRDDO		<i>Ab initio</i> HF		Other calculations		
	$BHSi_7H_{18}$	$BHSi_{34}H_{36}$	STO-3G	SV	(a)	(b)	(c)
$d_{B-H}$	1.679	1.661	1.511	1.484	1.68	1.59	
$d_{B-Si_{NN}(B)}$	2.235	2.201	2.235	2.239			
$d_{Si-H}$	1.438	1.442	1.470	1.484	1.43	1.46	1.63
$d_{Si-Si_{NN}(Si)}$	2.278	2.284	2.312	2.308			
$d_{B-subst}$	0.504	0.491	0.500	0.472	0.50	large	0.47
$d_{Si-subst}$	0.262	0.261	0.130	0.144	0.27	small	

ing" measures the covalent character of the bond between two atoms: its value is 0.00 for a purely ionic bond, 1.00 for a purely covalent two-electron bond, etc. The  $B-Si_{NN}(B)$  and  $Si-Si_{NN}(Si)$  bond lengths readjust very little as each of the displaced Si atoms itself moves against three covalent bonds.

The degrees of bonding within the complex are shown in Fig. 1(b). Even though this information is somewhat qualitative, it is useful when comparing the various bonds: the hydrogen passivator forms some 20% of a single bond with the boron, and about 75% with the nearest Si. This accounts for almost all of the electron density associated with H and calculations of the overlap population between H and other atoms in the lattice clearly confirms this. Thus, H is primarily bound to a Si atom which is fourfold coordinated. Both B and this Si form almost perfect single bonds with their NN.

The metastable site for H, which also leads to passivation, corresponds to H at the AB site of one of the Si

nearest to B. With B, H, and Si optimized along the trigonal axis, the energy is about 1.64 eV above the BC configuration. The exact number slightly varies with cluster size and basis set. In this configuration, B moves off the substitutional site by 0.55 Å, forms almost perfect single bonds with the three  $Si_{NN}(B)$  (the degree of bonding is 0.96) but no bond at all (0.005) with the fourth Si. The latter is fourfold coordinated [to the three  $Si_{NN}(Si)$  and to H] in a conformation similar to an open umbrella<sup>77</sup> with  $Si-H$  being the handle. The  $H-Si-Si_{NN}(Si)$  angle is very close to 90°.

Finally, calculations with H at the AB site of the boron atom show that this is a saddle point of the PES, about 3.5 eV above the BC configuration (also see the Comment, Ref. 49). This energy difference is large enough to firmly rule out this site as a possible candidate for passivation.

## 2. Aluminum

Our calculations show that the stable configuration of passivated Al is very similar to that of passivated B. Table II gives the various bond lengths in the equilibrium configuration. The absolute minimum of the total energy occurs for H slightly off the  $\langle 111 \rangle$  axis (0.047 Å), with  $\Delta E = -0.011$  eV relative to the on-axis position. As was the case for B, these numbers are small, and indicate a very flat potential for H around the BC site. The displacement of Al and Si with respect to their perfect substitutional positions are about 0.4 Å (Al) and 0.3 Å (Si), i.e., the acceptor is displaced more than the host atom, but the difference is less than in the case of boron. No significant change in the microscopic structure of the defect results from second-NN relaxations, which lower the energy by 0.30 eV. The degrees of bonding are shown in Fig. 1(c).

The metastable site corresponds to H at the AB site to Si, and is 2.01 eV above the BC configuration. The  $H-Si-Si_{NN}(Si)$  angle is very close to 90° and the Al-Si degree of bonding is very small (0.013). The configuration in which H is AB to Al is a saddle point of the energy, some 4.8 eV above the BC site.

## 3. Gallium

The situation for Ga is very similar to that described above for B and Al. The geometry is described in Table III, and the absolute minimum is realized for H off the trigonal axis by 0.091 Å, with  $\Delta E = -0.002$  eV. The displacement of Ga from the substitutional site still is slightly larger than the displacement of Si, but less than for Al. Second-NN relaxations lower the energy only by 0.18 eV. Figure 1(d) shows the degrees of bonding. The metastable site (H at the AB site of Si) is 2.27 eV above the BC site, and the saddle point corresponding to H at the AB site of Ga is 3.23 eV above the BC site.

## 4. Effects of uniaxial stress

We investigated the effects of  $\langle 111 \rangle$  uniaxial stress on the position of bond-centered H passivating an acceptor A ( $A = B, Al, \text{ or } Ga$ ) in the following manner. Assum-

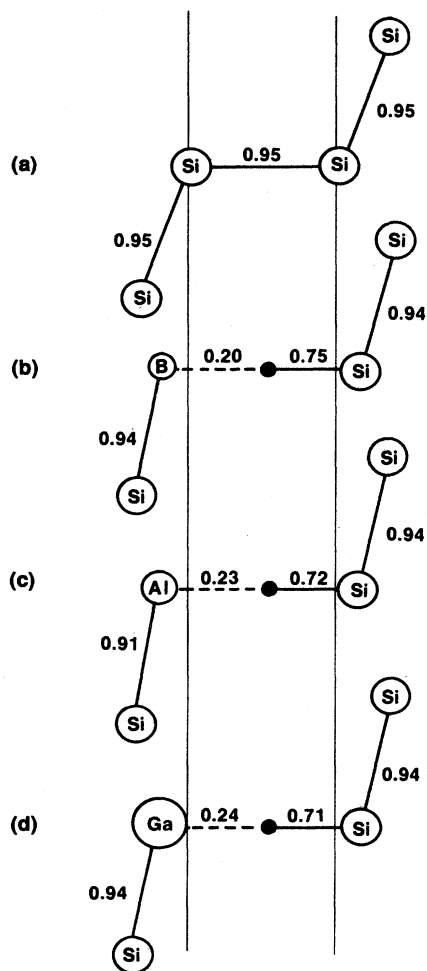


FIG. 1. Degrees of bonding (Ref. 76) in the lowest-energy configuration for (b) H-passivated B, (c) Al, and (d) Ga in *c*-Si. The H atom is the solid circle. The vertical lines are a guide to the eye, indicating the location of the perfect substitutional sites. The undisturbed lattice (a) is shown for comparison.

TABLE II. Calculated equilibrium geometries in various clusters using various methods (see text). The results were obtained by chain optimizing the positions of Al, H, Si, and of the group Si—H assuming trigonal symmetry. The results for AlHSi<sub>34</sub>H<sub>36</sub> include second-NN relaxations. The displacements of Al and Si relative to their respective substitutional sites are positive if the atoms are moving away from the BC site. Calculation (a) refers to numbers obtained from Fig. 2 in Ref. 26.

Distance (Å)	PRDDO		<i>Ab initio</i> HF		Other calculation (a)
	AlHSi <sub>7</sub> H <sub>18</sub>	AlHSi <sub>34</sub> H <sub>36</sub>	STO-3G	SV	
$d_{\text{Al-H}}$	1.677	1.692	1.590	1.611	1.77
$d_{\text{Al-Si}_{\text{NN}}(\text{Al})}$	2.245	2.307	2.256	2.253	
$d_{\text{Si-H}}$	1.423	1.423	1.415	1.421	1.42
$d_{\text{Si-Si}_{\text{NN}}(\text{Si})}$	2.266	2.285	2.272	2.270	
$d_{\text{Al-subst}}$	0.431	0.453	0.368	0.383	0.62
$d_{\text{Si-subst}}$	0.317	0.310	0.286	0.297	0.19

ing that such a stress results in a shorter *A*-Si separation, we brought back the two atoms towards their perfect substitutional positions by a fraction of the zero-stress displacement: thus, "0%" means zero stress, and *A* and Si in the configuration shown in Tables I–III. On the other hand, "100%" means that *A* and Si occupy their perfect substitutional sites. For each percent of stress applied, the position of H was optimized. Figure 2 shows the net increase in energy and the optimized *A*—H—Si angle  $\alpha$ . It is surprising that even significant contractions cost very little energy, and that the variations of  $\alpha$  with applied stress are all but linear. For small stress, H changes its relative bonding to *A* and Si, but remains essentially on the axis. At a value of the stress of about 22% (in the case of Ga) or 30% (in the case of Al), the H atom suddenly moves off the axis. In the case of B, the passivator always remains rather close to the axis. With applied stress, the *A*—H (and *A*—Si) degree of bonding monotonically (almost linearly) increases at the expense of the Si—H degree of bonding. This change is not negligible. For example, in the case of B, between 0% and 40%, the B—H degree of bonding increases from 0.18 to 0.36, while the Si—H one decreases from 0.78 to 0.63. As stress increases, the Si—H bond length remains very close to 1.44 Å (it increases from 1.438 to 1.444 Å), while B—H decreases from 1.68 to 1.37 Å. Very similar results are obtained for Al and Ga. Clearly, the effects of uniaxi-

al  $\langle 111 \rangle$  stress cannot be interpreted in terms of Si—H interactions alone, because the H-acceptor coupling considerably increases with stress.

## B. Passivation of donors

### 1. Phosphorus

The lowest-energy configuration corresponds to H at the AB site one of the Si atoms nearest to P. The equilibrium geometry is summarized in Table IV. In contrast to the displacements realized in the case of acceptors, the donor moves off the substitutional site much less than the Si atom. The latter is displaced as far as the plane of the three Si<sub>NN</sub>(Si) atoms (this plane corresponds to a displacement of 0.784 Å). The degrees of bonding are shown in Fig. 3(b): The Si atom forms a single covalent bond with its three Si NN and with H, but virtually zero covalent bond with the donor. The five valence electrons of P form a lone pair and three covalent bonds with the three Si<sub>NN</sub>(P). Second-NN relaxations lower the energy by an additional 0.26 eV, but do not otherwise change much of the electronic structure.

We performed polarized basis set calculations by including valence *d* electrons on P (with PRDDO) and on the nearest Si (at the *ab initio* level). After reoptimizing

TABLE III. Calculated equilibrium geometries in various clusters using various methods (see text). The results were obtained by chain optimizing the positions of Ga, H, Si, and of the group Si—H assuming trigonal symmetry. The results for GaHSi<sub>34</sub>H<sub>36</sub> include second-NN relaxations. The displacements of Ga and Si relative to their respective substitutional sites are positive if the atoms are moving away from the BC site. The split-valence basis set used is described in the text.

Distance (Å)	PRDDO		<i>Ab initio</i> HF	
	GaHSi <sub>7</sub> H <sub>18</sub>	GaHSi <sub>34</sub> H <sub>36</sub>	STO-3G	SV
$d_{\text{Ga-H}}$	1.688	1.717	1.595	1.603
$d_{\text{Ga-Si}_{\text{NN}}(\text{Ga})}$	2.246	2.291	2.249	2.248
$d_{\text{Si-H}}$	1.423	1.441	1.439	1.437
$d_{\text{Si-Si}_{\text{NN}}(\text{Si})}$	2.267	2.269	2.275	2.275
$d_{\text{Ga-subst}}$	0.428	0.468	0.407	0.412
$d_{\text{Si-subst}}$	0.312	0.338	0.276	0.276

the geometry, we find that the lowest-energy configuration (described above) remains essentially unchanged: In the case of a nearly trigonal configuration for P such as the one realized here, the P-Si interactions are dominated by the  $sp^2$  hybridization, and the participation of valence  $d$  orbitals is not very important.

We also optimized the geometry in the configurations

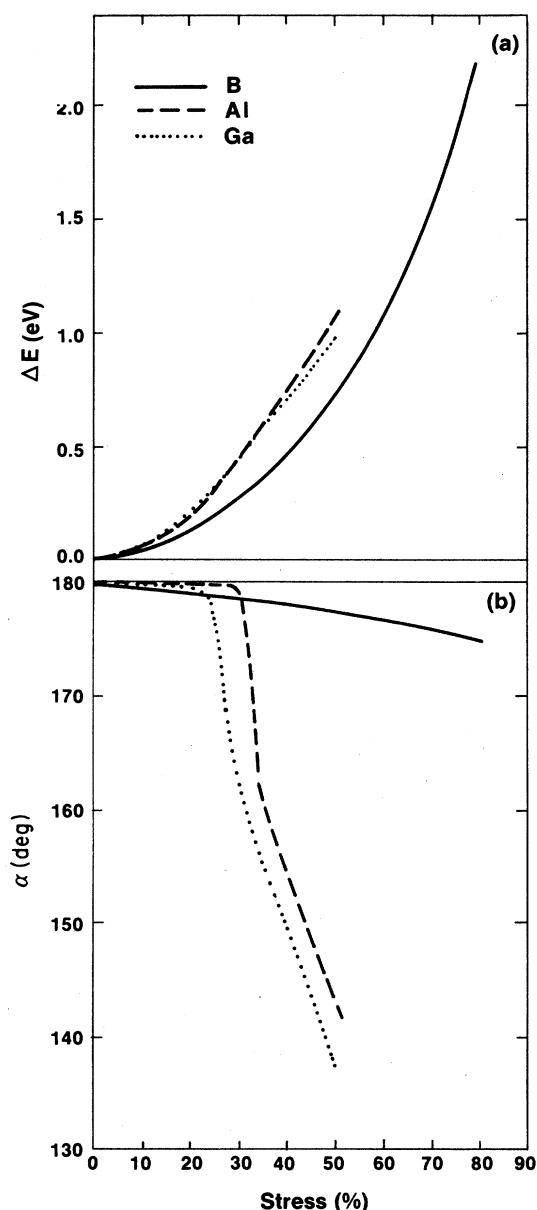


FIG. 2. Uniaxial  $\langle 111 \rangle$  stress is simulated by moving the acceptor ( $A$ ) and the Si atom toward their respective substitutional sites by a fraction of their initial displacement: 0% corresponds to zero stress (fully relaxed configurations), and 100% to  $A$  and Si at the perfect substitutional sites. (a) shows the increase in energy after optimization of the coordinates of H for a given stress, and (b) shows the optimized  $A$ -H-Si angle  $\alpha$ . The solid line corresponds to B, the dashed line to Al, and the dotted line to Ga.

where H is near the BC site, and at the AB site of the P atom. The results are basis set dependent, particularly for H antibonding to P: the fivefold coordination of the group-V atom is considerably stabilized by the inclusion of valence  $d$  orbitals in the basis set. Without  $d$  orbitals, at the PRDDO level, the BC configuration is metastable with  $\Delta E_1 = 1.10$  eV relative to that with H at the Si AB site, and the phosphorus AB site is a saddle point of the energy with  $\Delta E_2 = 5.20$  eV above the lowest-energy configuration. However, with a set of  $d$  orbitals on the P atom, after reoptimizing the geometry, we get (with PRDDO)  $\Delta E_1 = 0.93$  eV and  $\Delta E_2 = 0.98$  eV. Further, if we also add  $d$  orbitals on the Si atom located on the relevant  $\langle 111 \rangle$  axis,  $\Delta E_1 = 1.33$  eV and  $\Delta E_2 = 0.92$  eV (after geometry optimization, with *ab initio* HF). It is likely that further increases in the basis set size will change  $\Delta E_1$  and  $\Delta E_2$  only by very small amounts. In any case, the lowest-energy configuration (H at the Si AB site) remains almost 1 eV below any other. As will be discussed in Sec. IV, there is no comparable basis-set dependence in the case of passivated acceptors.

## 2. Arsenic

Without  $d$  orbitals in the valence shell ( $4d$ ), the PRDDO and *ab initio* results are very similar to those obtained in the case of P without  $d$  orbitals. The lowest-energy configuration is described in Table V and the degrees of bonding are shown in Fig. 3(c). The BC configuration is 1.3 eV higher, and the AB to As configuration for H is a saddle point of the energy, some 4.5 eV above the Si AB one. Geometry optimizations with polarized basis set involving As bound several Si atoms are very demanding in computer time and disk space. However, since covalent bonds involving As are generally weaker than those involving P, the stabilization resulting from the inclusion of valence  $d$  orbitals on As and the neighboring Si atoms should be less than in the case of P. In view of the large energy differences obtained with PRDDO and *ab initio* HF calculations (with minimal and expanded basis sets), we therefore predict that the stable site corresponds most probably to H at the Si AB site, and that the other two sites are metastable.

## IV. DISCUSSION

### A. Passivation of acceptors

The lowest-energy configuration for hydrogen-passivated B, Al, and Ga centers in  $c$ -Si corresponds to H near the BC site. The absolute minimum of the energy corresponds to H slightly off the trigonal axis (0.022 Å in the case of B, 0.047 Å for Al, and 0.091 Å for Ga). The energy difference relative to the on-axis position is very small ( $-0.014$ ,  $-0.011$ , and  $-0.002$  eV, respectively), indicating that the PES is quite flat in the plane orthogonal to the trigonal axis. The acceptor moves off its substitutional site more than the Si-atom does. The largest displacement occurs in the case of boron, and is calculated to be almost twice the experimentally estimated<sup>31,32</sup> value.

TABLE IV. Calculated equilibrium geometries in various clusters using various methods (see text). The results were obtained by chain optimizing the positions of P, H, Si, and of the group Si—H assuming trigonal symmetry. The results for  $\text{PHSi}_{34}\text{H}_{36}$  include second-NN relaxations. The displacements of P and Si relative to their respective substitutional sites are positive if the atoms are moving away from the BC site. According to our calculations, Si is displaced beyond the plane of the three  $\text{Si}_{\text{NN}}(\text{Si})$  if no second-NN relaxations are allowed. (a) Ref. 46; (b) Ref. 54.

Distance (Å)	PRDDO		<i>Ab initio</i> HF		Other calculations	
	$\text{PHSi}_7\text{H}_{18}$	$\text{PHSi}_{34}\text{H}_{36}$	STO-3G	SV	(a)	(b)
$d_{\text{P-Si}}$	3.347	3.278	3.204	3.161		
$d_{\text{P-Si}_{\text{NN}}(\text{P})}$	2.299	2.325	2.345	2.342		
$d_{\text{Si-H}}$	1.396	1.396	1.470	1.531	2.33	1.61
$d_{\text{Si-Si}_{\text{NN}}(\text{Si})}$	2.217	2.249	2.218	2.217		
$d_{\text{P-subst}}$	0.177	0.187	0.020	0.030	0.05	
$d_{\text{Si-subst}}$	0.819	0.739	0.832	0.780	0.09	

This results from PRDDO as well as *ab initio* HF calculations (with minimal and split-valence basis sets), and is consistent with other published results.<sup>26,44,46</sup>

With zero applied stress, our calculations show that the large variation of covalent radii between B and Ga is not sufficient to force the H passivator significantly off

the trigonal axis. In fact, the calculations which mimic the effects of uniaxial stress indicate that H still has quite a bit of room on this axis. The effects of uniaxial stress is not only to push H off the  $\langle 111 \rangle$  axis, but also to strengthen the acceptor-H bond at the expense of the Si—H bond.

When H is near the BC site, the Si atom is almost tetrahedrally coordinated, and the acceptor is nearly trigonal planar. The latter is reminiscent of the geometry of the free molecule<sup>78</sup> (e.g., borane  $\text{BH}_3$ ). In this configuration, there is a vacant *p* orbital on the axis perpendicular to the trigonally coordinated group-III atom. In the present case, this axis is, of course, the  $\langle 111 \rangle$  axis, and this vacant *p* orbital interacts with the Si—H bond: In chemical jargon, the situation is analogous to a “donor-acceptor pair,” the “donor” being the Si—H bond itself.

The metastable configuration corresponds to the H at the AB site of a Si atom nearest to the acceptor. The difference in energy  $\Delta E$  between stable and metastable configurations increases as one goes down the Periodic Table:  $\Delta E = 1.62, 2.01, \text{ and } 2.27$  eV for B, Al, and Ga. The large value of  $\Delta E$  is mainly due to two factors. First, the Si atom—even though fourfold coordinated—is at the center of a highly distorted tetrahedron in a conformation very similar to that shown in Fig. 3(b). The amount of energy associated with this distortion can be estimated by comparing the tetrahedral and trigonal configurations of, e.g.,  $\text{H-Si-(SiH}_3)_3$ . At the PRDDO level, the configuration in which Si is exactly trigonal [with H as in Fig. 3(b)] is higher by 1.69 eV than the tetrahedral one. Even though the two situations are not identical, it appears that this distortion accounts for most of the  $\Delta E$  discussed above. Second, the vacant *p* orbital of the acceptor on the  $\langle 111 \rangle$  axis does not overlap as is the case when H is at the BC site: the acceptor-Si degree of bonding on this axis is very close to zero (0.005, 0.013, and 0.015 for B—Si, Al—Si, and Ga—Si, respectively).

The AB site to the acceptor always is a saddle point of the energy (it is a minimum only along the  $\langle 111 \rangle$  direction). Even though many examples of fivefold-coordinated group-III atom can be found in the chemical literature<sup>77</sup> (e.g., in boron chemistry), the cases where only four electron pairs are present are characterized by

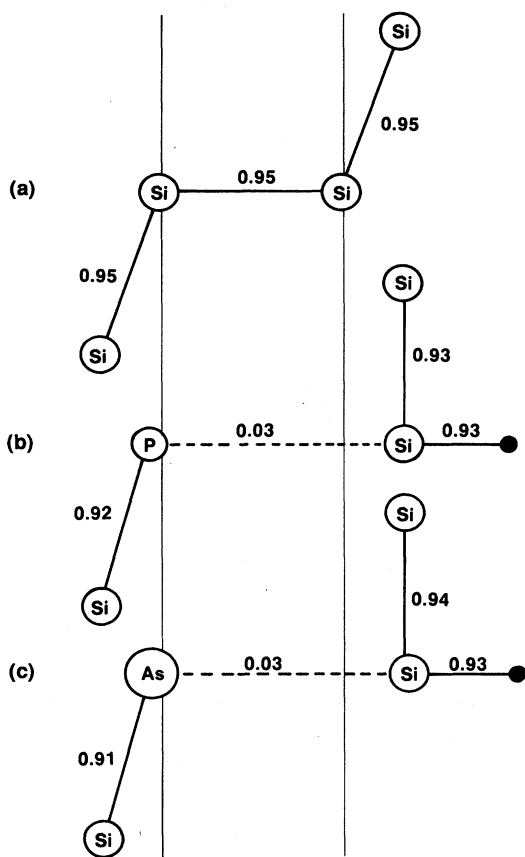


FIG. 3. Degrees of bonding (Ref. 76) in the lowest-energy configuration for (b) H-passivated P and (c) As in *c*-Si. The H atom is the solid circle. The vertical lines are a guide to the eye and show the location of the perfect substitutional positions. (a) is the unperturbed lattice.



TABLE V. Calculated equilibrium geometries in various clusters using various methods (see text). The results were obtained by chain optimizing the positions of As, H, Si, and of the group Si—H assuming trigonal symmetry. The results for AsHSi<sub>34</sub>H<sub>36</sub> include second-NN relaxations. The displacements of As and Si relative to their respective substitutional sites are positive if the atoms are moving away from the BC site. The Si atom is displaced slightly beyond the plane of the three Si<sub>NN</sub>(Si). The split-valence basis set used is described in the text.

Distance (Å)	PRDDO		<i>Ab initio</i> HF	
	AsHSi <sub>7</sub> H <sub>18</sub>	AsHSi <sub>34</sub> H <sub>36</sub>	STO-3G	SV
$d_{\text{As-Si}}$	3.266	3.312	3.142	3.078
$d_{\text{As-Si}_{\text{NN}}(\text{As})}$	2.319	2.363	2.353	2.369
$d_{\text{Si-H}}$	1.404	1.390	1.460	1.529
$d_{\text{Si-Si}_{\text{NN}}(\text{Si})}$	2.217	2.244	2.217	2.217
$d_{\text{As-subst}}$	0.105	0.177	-0.003	-0.050
$d_{\text{Si-subst}}$	0.809	0.783	0.793	0.776

much more electron delocalization than is the case here. Further, the inclusion of valence  $d$  orbitals on B or Al does not stabilize the acceptor AB site for H as it does in the case of donors. For example, without  $d$  orbitals, the AB to Si and to Al sites for H are 2.13 and 4.83 eV above the BC site, respectively. The addition of a set of  $d$  orbitals on Al changes these numbers to 2.51 and 4.61 eV, after geometry optimization. In the case of boron, the change is much smaller.

### B. Passivation of donors

The lowest-energy configuration for H-passivated P and As centers corresponds to H at the AB site of one of the Si atoms nearest to the donor. This result confirms earlier predictions.<sup>46,54</sup> In this configuration, the donor moves very little from its substitutional site. Two of its five valence electrons form a lone pair, and the donor is threefold coordinated with the three Si<sub>NN</sub>(P) or Si<sub>NN</sub>(As). There is nearly zero overlap between the donor and the fourth Si atom. The latter is considerably displaced off the substitutional site, typically unto the plane of the three Si<sub>NN</sub>(Si). It is fourfold coordinated, and forms a covalent single bond with the H passivator. The qualitative features of this configuration are the same

with PRDDO and *ab initio* HF and are basis set independent (minimal, expanded, and polarized basis sets were used).

Without valence  $d$  orbitals in the basis set, the metastable configuration corresponds to BC hydrogen, while the donor AB site for H is a saddle point of the energy. However, the presence of valence  $d$  orbitals stabilizes the fivefold coordination of the donor. The metastable site corresponds to H antibonding to the donor, which is about 1 eV above the stable site. This result qualitatively agrees with previous calculations.<sup>46,54</sup>

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