PHYSICAL REVIEW B VOLUME 40, NUMBER 17 15 DECEMBER 1989-I

Hydrogen bonding and diffusion in crystalline silicon

K. J. Chang
Department of Physics, Korea Advanced Institute of Science and Technology, P.O. Box 150, Chongryang, Seoul 130-650, South Korea

D. J. Chadi
Xerox Corporation, Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, California 94304
(Received 3 August 1989)

The nature of hydrogen bonding and diffusion in crystalline Si was investigated using an *ab initio* self-consistent pseudopotential method. The relative energies of interstitial atomic hydrogen, diatomic hydrogen complexes, and shallow dopant-hydrogen complexes were examined. We present a mechanism for hydrogen diffusion which involves a new metastable diatomic complex with a much lower activation barrier for diffusion than molecular hydrogen. The effects on diffusion of diatomic-complex dissociation or its conversion to molecular hydrogen are discussed. The influence of temperature, hydrogen concentration, and dopant (n or p type) on hydrogen diffusion are examined. Metastable diatomic-complex formation is proposed to be highly likely at low temperatures and at high hydrogen concentrations, particularly in n-type Si. Diffusion through an ionized H^+ form is most likely to occur in p-type Si.

I. INTRODUCTION

Despite the fact that hydrogen is known to be diffusive in bulk crystalline Si, its diffusion mode is not well understood and the microscopic picture for the diffusion mechanism is still controversial.[1] Several experiments have shown that the diffusion coefficient in Si has a strong temperature, hydrogen-concentration, and dopant-impurity dependence.[1–9] Over thirty years ago, Van Wieringen and Warmoltz[2] measured the hydrogen permittivity over the temperature range of 970–1200 °C and their results have led to general agreement that diffusion occurs through an atomic mode at elevated temperatures. In a recent experiment, Seager and Anderson[10] have demonstrated that a rapidly diffusing species, most probably atomic hydrogen, exists in B-doped Si even at room temperature and at low hydrogen concentrations of 10^{14} cm^{-3}. This experiment has provided new insight into the role of hydrogen concentration on diffusion. At high hydrogen concentrations and in the temperature range of 27–600 °C, the measured diffusivities[11] of hydrogen were found to be about 3 orders of magnitude lower than that obtained from the high-temperature diffusivity data.[2]

Atomic hydrogen has been assumed to be the primary diffusion unit in Si because molecular hydrogen (H_2), although the most stable state of hydrogen, has a large diffusion barrier.[12–17] Recently, Johnson and Herring inferred a highly immobile species at moderate temperatures of ≤ 350 °C which they assigned to molecular hydrogen.[18,19] Because of the difference between the high- and low-temperature diffusivity data,[1,11] it is not yet clear whether diffusion at moderate temperatures occurs in the form of monatomic or molecular hydrogen, or possibly of some other complexes.

Hydrogen is observed to diffuse more rapidly in doped than in undoped Si. Furthermore, the efficiency of hydrogen diffusion is better in p-type than in n-type Si.[1–6] There is experimental evidence that hydrogen diffusion in p-type Si is strongly electric field dependent and proceeds by a positively charged species (H^+).[3,5] Negatively charged hydrogen (H^-), has been suggested to occur in both diffusion and in donor-hydrogen pair formation in n-type Si.[9,16,20,21] Neutral hydrogen (H^0) is expected to exist in both doped or undoped Si when the hydrogen concentration exceeds that of the dopant.

Transport measurements on resistance and Hall mobility have provided detailed information on hydrogen bonding with dopant impurities. At low temperatures, it is well known that atomic hydrogen passivates dopants by neutralizing their electrical activity, as evidenced by a decrease in the carrier concentration but an *increase* in the Hall mobility (resulting from a reduction in charged impurity scattering).[1,8,22–24] The passivated dopants are mostly reactivated by annealing above 150 °C in B-doped Si and above 120 °C in P-doped Si. The observation of hydrogen-associated vibrational frequencies indicates that hydrogen forms complexes with the impurities.[8,24–26] Hydrogen passivation was generally observed to be more effective in p-type than in n-type Si. A microscopic origin for the difference is provided by our recent calculations,[21] which show different structures and bonding energies for the B-H and P-H complexes.

In this paper we present a more detailed study of the results of our first-principles pseudopotential calculations[21,27] for the atomic and electronic structure of interstitial hydrogen in crystalline Si. We examine various configurations for interstitial hydrogen and dopant-hydrogen complexes in Si, and compare the energetics of diatomic versus monatomic hydrogen diffusion modes. The effects of dopant, hydrogen concentration, and tem-

 ©1989 The American Physical Society

perature on diffusion are also discussed.

The paper is organized as follows. The theoretical approach used in the calculations is briefly described in Sec. II. In Sec. III, we present the calculated binding energies of: (i) interstitial atomic hydrogen, (ii) various diatomic-hydrogen complexes, and (iii) dopant-hydrogen complexes. Hydrogen diffusion is discussed in Sec. IV and a summary of the main results is given in Sec. V.

II. THEORETICAL METHOD

Our calculations are based on the *ab initio* total-energy pseudopotential method within the framework of the Hohenberg-Kohn-Sham local-density approximation (LDA).[29] The exchange and correlation functional is approximated by the Wigner interpolation formula.[30] Nonlocal pseudopotentials are generated using the scheme proposed by Hamman, Schlüter, and Chiang.[31] For the Si, B, and P atoms, the potentials were previously tested and found to be successful in predicting bulk structural and vibrational properties.[32–35]

For the H ionic pseudopotential, only the local *s* potential is important because the energies of the *p* and *d* orbitals are much higher than that of the *s* orbital. The exact $-1/r$ form of the potential was also tested as an alternative to the pseudopotential. The results show that energy differences are less than 10^{-4} eV for the two potentials. The accuracy of the H pseudopotential was further confirmed by calculating the bond distances of H_2 and silane (SiH_4) molecules, as previously reported.[21]

We performed total-energy calculations for interstitial monatomic hydrogen, molecular and other diatomic complexes in crystalline Si. The stable position for each charge state of H was determined by examining several interstitial positions as shown in Fig. 1. These include the bond-center (BC), antibonding (AB), tetrahedral (T_d), hexagonal (Hex), *C*, and *M* sites. The *M* point is located midway between two adjacent *C* sites where *C* labels the position at the center of the rhombus formed by the two neighboring Si—Si bonds. In the case of the diatomic complex, the energies were calculated at sites with high and low electronic charge densities as shown in Fig. 2.

The effects of dopants on the stability of various hydrogen interstitial positions were included by changing the position of the Fermi level in the gap. This procedure is valid when the hydrogen atoms are well separated from the impurity atoms. For H in the vicinity of substitutional dopants, the energies of the stable configurations of H-dopant complexes were determined for comparison with those for the separated H-dopant case.

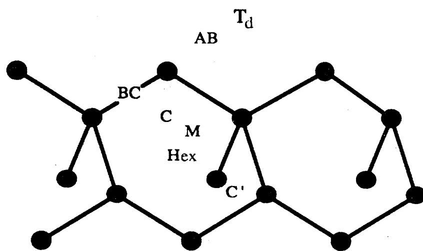


FIG. 1. The BC, AB, T_d, Hex, *C*, and *M* sites in the diamond lattice structure of Si are shown.

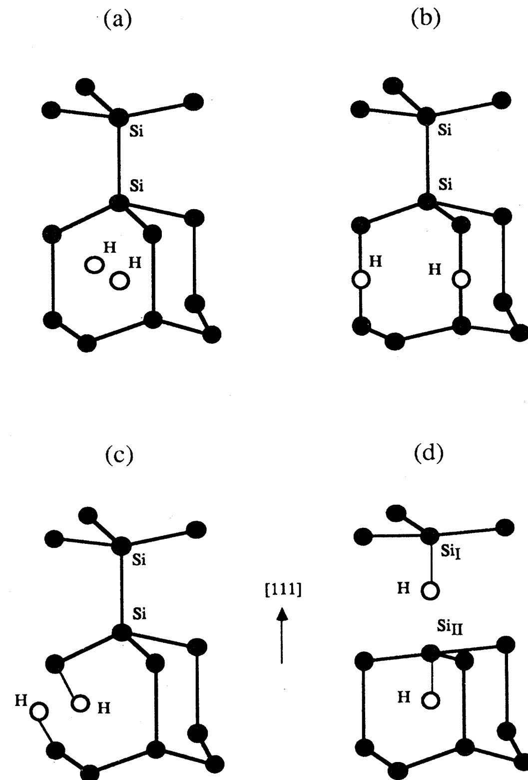


FIG. 2. Various diatomic hydrogen configurations are shown. The diatomic complex in (a) corresponds to an H_2 molecule at the T_d site. The hydrogen atoms are at the BC sites of neighboring Si—Si bonds parallel to the [111] axis in (b) while they occupy off-bond center sites in (c). The metastable H_2^* complex in (d) consists of the hydrogen atoms occupying the BC and T_d sites along the [111] axis.

For each geometry the total energy was calculated self-consistently in the momentum space representation.[36] Hellmann-Feynman forces[37] were calculated and the nearest neighbors of the interstitial H atoms were relaxed until the optimum atomic coordinates were established. The valence (pseudo-) wave functions were expanded in a plane-wave basis set with kinetic energy cutoffs of 11.5 and 10.0 Ry for eight-atom cubic and 18-atom $\sqrt{3}\times\sqrt{3}\times\sqrt{6}$ hexagonal supercells, respectively. These supercell geometries mimic systems where the defects are well separated.[38] Although the use of a larger sized supercell is desirable to minimize the uncertainty resulting from defect-defect interactions, we find that all essential information can be extracted from an eight-atom cell. For relative energy differences, we estimate the errors caused by the use of different-sized supercells to be about 0.1 eV. For diatomic hydrogen complexes, the larger 18-atom cell was used in the calculations because the relaxations of neighboring Si atoms were more spatially extended than for monatomic hydrogen. The summation over

the Brillouin zone was carried out using four and two special **k** points for the eight-atom and 18-atom supercells, respectively. These numbers correspond to 32 and 38 **k** points in a bulk crystalline Si lattice.

III. ENERGETICS OF VARIOUS CONFIGURATIONS OF HYDROGEN IN SI

A. Monatomic hydrogen

We consider first an interstitial hydrogen atom far apart from dopant impurities. The interaction between the dopant and H atoms can be considered to be negligible if their separation is larger than a cubic lattice constant of the eight-atom unit cell. This approximation is reasonable at hydrogen concentrations of $\leq 10^{20}$ cm^{-3} if the hydrogen atoms are assumed to be uniformly distributed.

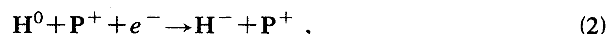
The H-related energy level is found to be significantly dependent on interstitial position. At a BC site, hydrogen breaks the nearest-neighbor Si—Si bond and forms a new three-center Si—H—Si bond. The Si-Si distance is stretched to approximately 3.2 Å which is 30% larger than a normal bond length. In this configuration, the occupied bonding state arising from the H s and Si sp^3 orbitals lies deep in the valence band while the singly occupied antibonding gap state is near the conduction-band minimum when the H atom is in a neutral charge state. The electronic charge density for H^0 is found to be piled up in the antibonding regions. The charge distribution associated with an H^+ ion at the BC site is not, therefore, the same as that of a bare proton but that of a positively charged state of the Si—H—Si complex.

Since the antibonding state is derived primarily from the conduction bands, its energy level position is expected to be underestimated with respect to the valence-band maximum. This is similar to the case for semiconductor band gaps and results from well-known limitations of the local-density approach.[29] A correction to the underestimation of the gap will affect, therefore, the total energies for H^0 and H^- where the antibonding levels are occupied whereas the energy of H^+ will not change. Table I shows the calculated binding energies for H^+, H^0, and H^- at their most stable positions relative to H^0 in vacuum. These energies are plotted in Fig. 3 as a function of the Fermi-level position. In p-type Si, monatomic hydrogen is most stable in a positively charged state at the BC position. In this case, compensation by a free hole (h) occurs by the exothermic reaction

$$H^0+B^-+h \rightarrow H^+ + B^- . \quad (1)$$

This result is consistent with the hydrogen deep-donor model previously suggested.[5,12,13]

For H at the T_d site, the electronic level is mostly related to the Hs orbital because the bonding with the neighboring Si atoms is weak. The T_d position is in a region of nearly empty charge density and the H potential at this site is screened less effectively by the electronic charge density of neighboring Si atoms. Therefore, the H-related energy level is lower than that for H at the BC site, lying near the valence-band maximum. In n-type materials, the negatively charged state of H is found to be most stable at the T_d site,[21,39] thus the H atom behaves as an acceptor, inducing the reaction



$$H^0+P^+ + e^- \rightarrow H^- + P^+ , \quad (2)$$

where e^- denotes a free electron. Because the charge density of H at the T_d site is approximately atomiclike,[21] its wave function is not conduction-band derived. The correction to the band-gap narrowing resulting from the LDA calculations should not be significant, therefore, for

TABLE I. The energies for various interstitial configurations of atomic hydrogen, diatomic hydrogen complex, and dopant-hydrogen complexes in p- and n-type Si are calculated and compared. The energies are in units of eV per H atom *except* for H_2 and H_2^* where the energies are in eV *per diatomic complex*. The energy of a free H atom in free space is taken as the zero of energy.

Interstitial H	p-type Si	n-type Si
$H^-(T_d)$	−0.4	−1.54
$H^0(T_d)$	−1.1	−1.1
H^+(BC)	−1.85	−0.71
H_2^*	−3.4	−3.4
H_2	−3.8	−3.8
B-H	−2.5	
P-H		−2.0

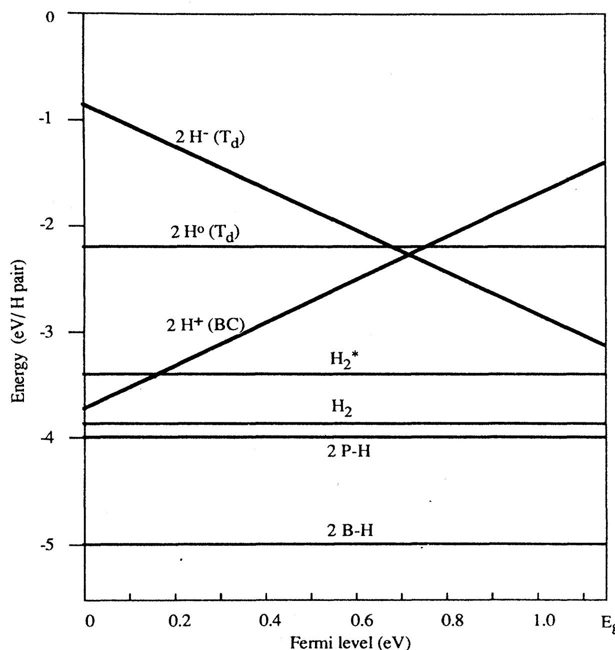


FIG. 3. Energies of interstitial H^+, H^0, and H^- atoms at their stable positions are plotted as a function of the Fermi level E_F and they are compared with those for H_2^*, H_2, B-H, and P-H complexes. Energies are in units of eV per *two* H atoms. For p- and n-type Si the Fermi level has the values $E_F=0$ and $E_F=E_g$, respectively, where E_g is the band gap.

either a negatively charged or a neutral H atom at this site.

For neutral H, several different interstitial positions have been suggested as being stable. These include the M (Ref. 14), T_d (Ref. 40), and BC (Refs. 15–17) sites. The calculations of Corbett *et al.* for the M site show it to be a metastable configuration only when the surrounding Si "cage" atoms are kept in fixed positions.[14] Relaxation of these atoms leads to the prediction of a BC site for H.[15] Our calculations show that the T_d site is more stable than the BC site. This stable position is expected because as discussed earlier the H-related electronic level at the T_d site is lower than that for H at the BC site. Moreover, the stability of the T_d site over the BC site is likely to be enhanced by a band-gap correction which will adversely affect the BC site in the LDA calculations. For H^0, the calculated binding energy of 1.1 eV, which is obtained by comparing the energy of H^0 in Si with that in free space, is in good agreement with the value of 1.0 eV derived from the experimental data.[9] Our results for the stable positions of H^+ and H^- are consistent with other recent calculations;[16,17] however, our identification of the interstitial site for H^0 does not agree with the results of some calculations.[14–17] When second-order Löwdin perturbation theory is used (Ref. 17) the BC site is found to be more stable. The disagreement between the two results, therefore, may be due to the use of different matrix diagonalization schemes and convergence criteria, and to the relatively small energy difference (≤ 0.25 eV) between the two configurations for H^0.

Recent muon-spin-resonance measurements have shown the existence of both normal and abnormal muonium occupying T_d and BC sites, respectively.[41,42] Only one experimental group has reported detecting an ESR signal from H in Si.[43] Kiefl and Estle have recently shown[43] that the muon-spin-resonance parameters obtained from their experiments are consistent with those determined by Gorelkinskii *et al.*[43] from an analysis of ESR data. The ESR signals have been attributed to neutral H in a BC site. The results of our calculations in Fig. 3 indicate that atomic hydrogen behaves as a negative-U ($U_{\text{effective}} \simeq -0.05$ eV) center. As the Fermi level increases, the stable charge state of H changes from positive to negative while the neutral charged state remains unstable. This result is also consistent with other calculations.[17] However, it should be noted that in a small region of energy near midgap the existence of stable neutral H cannot be excluded within the accuracy of our calculations because of the small value of U.

B. Diatomic hydrogen complex

Hydrogen clusters in Si may be generalized by H_n where $n \geq 2$ denotes the number of hydrogens in the cluster.[18] Because H is a monovalent atom, the most favorable configuration in clusters is the H_2 molecule in which a direct bond between the 1s orbitals lowers the energy. Although clusters with $n > 2$ are not ruled out, the lowest energy per H is not expected to be lower than that in an H_2 molecule. Recent findings of H-induced microdefects in P-doped Si represent an example of giant-sized clusters,[44] however, the atomic structure and energetics of formation of these clusters are not as yet resolved. In the following we focus on diatomic complexes for simplicity.

The hydrogen molecule is an electronically inactive species which is not easily accessible to experimental tests. The existence of the hydrogen molecule was demonstrated in voids of amorphous Si (Ref. 45) and in B-doped crystalline Si.[18,19] However, experimental determinations of the bond length and interstitial position of H_2 in crystalline Si are not yet available. We find the T_d site [see Fig. 2(a)] to be the most stable position for H_2, consistent with other theoretical results.[14–17] Our calculated bond distance of about 0.85 Å is close to that of the hydrogen molecule in vacuum. The binding energy is calculated to be about 3.8 eV for molecular orientations along either the [111] or the [001] axes. The H_2 molecule in Si is calculated to be about 1.6 eV more stable than two dissociated interstitial neutral atomic hydrogens.

We have considered other diatomic-complex configurations shown in Fig. 2. For the complex in Fig. 2(b), the hydrogen atoms are at neighboring BC sites aligned along the same crystalline direction. The elongation of Si—H—Si bonds shown in Fig. 2(b) was suggested to be the source of H-induced platelets observed in n-type materials.[44] In the second complex shown in Fig. 2(c) the two hydrogen atoms occupy split-off sites of a BC position. We find the energies of these configurations to be 1.8–2.2 eV higher than that of an H_2 molecule.

The other class of diatomic complexes we have examined are those in which the two hydrogen atoms occupy low and high charge-density sites. The low-density sites are positioned along the channel going through the T_d and Hex sites while the high density channel crosses the BC and C sites. Such a diatomic complex is found to be most stable when the two hydrogen atoms occupy a BC and a neighboring T_d site aligned along the [111] axis as shown in Fig. 2(d). In the following we refer to this complex by H_2^*. A complex similar to H_2^* has also been recently suggested as a result of theoretical studies on H in diamond clusters.[46] The results of our calculations show that each H atom in the H_2^* complex is strongly bonded to its adjacent Si atom causing large relaxations at these atoms. The bond-centered hydrogen in Fig. 2(d) pushes the Si_I atom by 0.24 Å towards the antibonding region while the Si_{II} atom bonded to the tetrahedrally positioned H atom moves away from its ideal position by 0.79 Å towards the interstitial site, ending up approximately in the plane of its three neighboring Si atoms. The relaxations have C_{3v} symmetry and change the hybridizations of the Si—Si bonding orbitals on the Si_I and Si_{II} atoms from sp^3 to sp^2. Although these rehybridizations are usually unstable in Si, a reduction in energy resulting from the bonding of the two interstitial hydrogens with the Si_I and Si_{II} atoms is sufficient to stabilize the geometry of H_2^*. The H_2^* complex is found to be metastable with respect to molecular hydrogen formation at the T_d site (see Fig. 3). In diamond, however, it was shown that the H_2 molecule dissociates into a diatomic complex similar to our H_2^* since the sp^2 hybridization in C is more stable than in

Si.[46] We note that if the combination of each Si-H pair in H_2^* is considered to be approximately equivalent to that of an As atom, the bond-breaking configuration for H_2^* is similar to that for the metastable As-antisite defect[47] (or the *DX* center[48]) in GaAs.

It should be pointed out that the diatomic complexes considered here are ESR inactive and these results are consistent with the experimental failure to detect any ESR signal from H in Si. In both the molecular and metastable H_2^* complexes, the electrons of the H atoms are paired with their energies lying in the valence bands. The diatomic complex shown in Fig. 2(b), would lead to an ESR signal if it were not an unstable configuration. If atomic hydrogen were stable in undoped Si, a strong ESR signal would be expected since it would then occur in large numbers in the neutral and spin active state. This is because the negative-U reaction

$$H^0 + H^0 \rightarrow H^+ + H^- \qquad (3)$$

is weakly (0.05 eV) exothermic; therefore a temperature-dependent ESR signal would be expected. However, such an effect has not been experimentally observed.

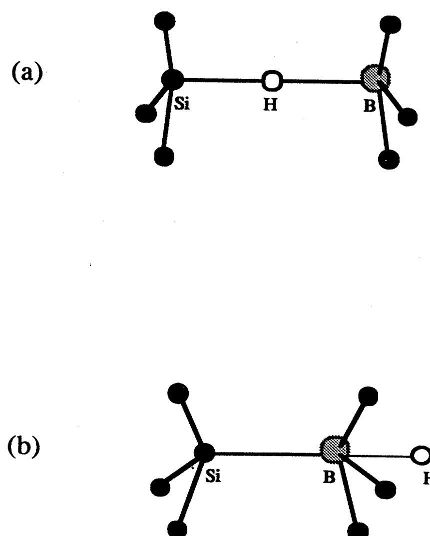


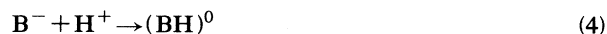
FIG. 4. The (a) BC and (b) AB positions of an interstitial H atom interacting with a substitutional B atom are shown.

C. Dopant-hydrogen complexes

It is well known that hydrogen exposed to doped Si passivates group-III acceptors as well as group-V donors by neutralizing their electrical activities.[22,23,25] In these cases, the carrier concentration decreases whereas the Hall mobility increases as a result of the reduction in the density of charged scattering centers. The electrical activity is usually recovered, however, upon annealing above 150 °C.

A suggestive model for hydrogen passivation is that a defect-hydrogen complex is created, making the defects electronically inactive. As the temperature increases, the defect-hydrogen complex dissociates and this leads to electrical reactivation. The idea of complex formation in hydrogen passivation has been supported by many experimental results, e.g., the detection of H-associated vibrational frequencies,[25,49,50] the position of interstitial deuterium from ion-channeling experiments,[51,52] the disappearance of acceptor-bound excitons,[53] and the increase of the Hall mobility[24] after hydrogenation in *p*-type Si. Similar experiments such as the detection of H-associated vibrational frequencies[54] and an increase of the Hall mobility[9] with hydrogenation have also been reported in *n*-type Si.

In B-doped Si, two atomic models for the B-H complex have been proposed: the bond-center-site model in Fig. 4(a) by Pankove *et al.*[23] and DeLeo and Fowler[55] and the antibonding-site geometry in Fig. 4(b) by Assali and Leite.[56] In our recent calculations,[21] the BC model for the interstitial H atom was found to be most stable in the vicinity of a substitutional B impurity, consistent with the previous theoretical results. For a stable B-H complex, the binding energy is calculated to be 2.5 eV (see Fig. 3) with the use of an 18-atom unit cell. This energy is consistent with that obtained from the smaller eight-atom unit cell.[21] Because the binding energy for the B-H complex is larger than that of an interstitial H^+ resulting from the reaction in Eq. (1), in which H^+ is far from a B^- acceptor, the neutral B-H pair formation is energetically more favorable than compensation. Dopant neutralization proceeds, therefore, by complex formation:



$$B^- + H^+ \rightarrow (BH)^0 \qquad (4)$$

and the reaction is calculated to be exothermic by 0.65 eV.

We compare the binding energy of a B-H complex with those for diatomic complexes in Table I. In B-doped Si, the B-H pair is 0.6 eV and 0.8 eV per H atom more stable than for H_2 and H_2^* complexes, respectively. However, $2H^+$ is more stable than H_2^* and its energy is close to that of H_2. The B-H complex formation process is likely to occur during hydrogen diffusion at moderate temperatures. If the hydrogen concentration exceeds the B concentration, the excess hydrogen atoms would be either in the form of neutral atoms or diatomic complexes. However, if the B-H complex dissociates as the temperature increases, the formation of H^+ or H_2 will be more favorable than H_2^* because the energy of $2H^+$ is lower than H_2^*.

The linear Si-H-B chain shown in Fig. 4(a) is found to be easily bent by moving the H atom off axis along the $[1\bar{1}0]$ and $[11\bar{2}]$ directions normal to the [111] Si—B bond axis. For displacements as large as 0.3 Å, the energy is lowered by less than 0.01 eV. Recent experiments by Stavola *et al.*[25,57] and by Herrero and Stutzman[58] indicate that the H atom may be stable off the Si-B axis. The energy varies slowly with the H motion perpendicular to the Si—B bond, and the small activation energy of 0.15 eV is found from one BC site to another in the B-H complex. The maximum energy in this motion occurs at an intermediate *C* site. This result is in good agreement with recent experimental[59] and theoretical results.[60]

In P-doped Si, using a semiempirical tight-binding method, Johnson *et al.*[9] proposed a structural model for the donor-H complex in which the H atom is located at the antibonding site of a Si atom bonded to substitutional P. Our previous *ab initio* pseudopotential calculations[21] showed similar results, i.e., that the energy for H is minimum near a T_d site of a Si atom adjacent to the substitutional P as shown in Fig. 5. A recent uniaxial stress study by Bergman *et al.*[61] has provided further support for the antibonding model for the donor-H complex. However, detailed information on the exact atomic position is not yet available. Using a larger 18-atom cell, we have calculated a binding energy of 2.0 eV for a P-H pair, which is consistent with our previous results.[21] Although negatively charged H coming from the reaction in Eq. (2) is the most stable form of atomic H in n-type Si as shown in Fig. 3, it is unstable with respect to P-H complex formation, since the reaction

$$P^+ + H^- \rightarrow (HP)^0 \quad (5)$$

is exothermic by 0.45 eV.[39]

In contrast to p-type Si, the dopant-H complex in n-type Si competes with the formation of H_2 and H_2^*. The *binding energy* for the P-H complex is found to be larger by only 0.1 and 0.3 eV per H atom as compared to H_2 and H_2^* (see Table I). Therefore, the H atom binds less strongly to the substitutional P atom than to the B atom. If the P-H complexes dissociate either into interstitial H^- atoms or into an H_2 molecule, the dissociation energy of a P-H pair is smaller than that of a B-H complex. This result provides an explanation for why donor passivation is either not observed[7,8] or is less effective than acceptor passivation.[6,9]

IV. HYDROGEN DIFFUSION IN Si

In this section, we discuss the hydrogen-diffusion mode and its dependence on temperature, hydrogen concentration, and type of dopant. At very high temperatures of around 1000 °C, it has been accepted that hydrogen diffuses mostly in atomic form and is highly mobile with diffusion coefficients of 10^{-3}–10^{-4} cm^2/sec.[2] Similar diffusivities at $T > 1000$ °C were also calculated in a recent molecular dynamics study for H^+ diffusion in Si.[62] Moreover, there is evidence for the existence of the atomic diffusion mode even at room temperature in B-doped Si with very low hydrogen concentrations of 10^{14} cm^{-3}.[10]

Within the hydrogen deep-donor model,[5,12,13] hydrogen diffuses as a positively charged unit. The existence of H^+ has been supported by the observations of the electric-field dependent diffusion at moderate temperatures only in p-type Si.[3,4,18,19] However, the measured diffusivity was shown to be reduced by several orders of magnitude as compared to the high-temperature diffusivity data,[7] and the activation energy of $E_a \approx 0.85$ eV is higher than the value of $E_a \approx 0.45$ eV measured[7] at elevated temperatures. Furthermore, since the measured activation energy at moderate temperatures is much higher than the recently calculated values of 0.1–0.3 eV for the H^+ and H^- species,[16,17] the atomic diffusion mode by itself cannot be fitted to the data at these temperatures. A molecular hydrogen-diffusion mode cannot explain the diffusivity data either because molecular hydrogen has a large binding energy and a high diffusion barrier of 2–3 eV.[1,16] An upper limit for the diffusion coefficient of H_2 was suggested to be 10^{-14} cm^2/sec at 350 °C.[18,19] To explain the reduced diffusivity at moderate temperatures, it has been speculated that hydrogen diffuses by being trapped and detrapped via the formation and dissociation of molecular and defect-hydrogen complexes. However, a quantitative description has not been successfully obtained when molecular formation is taken into account.[12]

Here we discuss a new diffusion mode which involves diatomic complexes. A brief description of diatomic complex diffusion was given in Ref. 27. We choose diatomic complex configurations as in Fig. 2(d) in which the hydrogen atoms occupy regions of high and low electronic charge densities. The other diatomic complexes in Fig. 2 are not likely during hydrogen diffusion because H_2 is highly immobile by itself and the energies of the complexes in Figs. 2(b) and 2(c) are very high. The high-density channel labeled as path I in Fig. 6 is defined by BC(1), C(1), BC(2), C(2), BC(3), C(3), BC(4), etc., and has large relaxations of neighboring Si atoms. Such a diffusion path actually crosses the points close to the C sites and the hydrogen behaves as a donor becoming positively charged. Therefore, path I is almost identical to the one previously suggested for atomic H^+.[17] On the other hand, the negatively charged species moves along the low-density channel labeled as path II, which crosses $T_d(1)$, Hex(1), $T_d(1)'$, Hex(2), $T_d(2)$, etc., because of the negative-U behavior for H in the presence of H^+ at any location of path I. One exceptional case is the configuration H_2^* shown in Fig. 2(d) in which both the associated H atoms become neutral. This is caused by a large relaxation of the Si_{II} atom towards H^- and by a resulting charge transfer from Si_{II} to the H^+ ion bonded to the Si_I atom. A regeneration of charged diffusing species occurs if the linear geometry of H_2^* is no longer maintained. When the H atom initially occupying a BC site moves to the neighboring C site then following path I, the ionized Si_{II} atom relaxes back to its original position and forms a normal Si—Si bond, thereby making the H atom go into a positively charged state.

For the diatomic complex diffusion, it is generally necessary to consider the motions of the two hydrogen atoms simultaneously. However, in order to reduce the

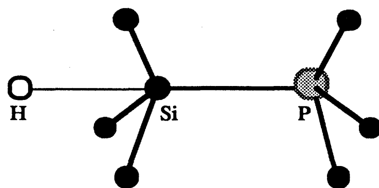


FIG. 5. The stable position of an interstitial H atom interacting with a substitutional P atom is shown.

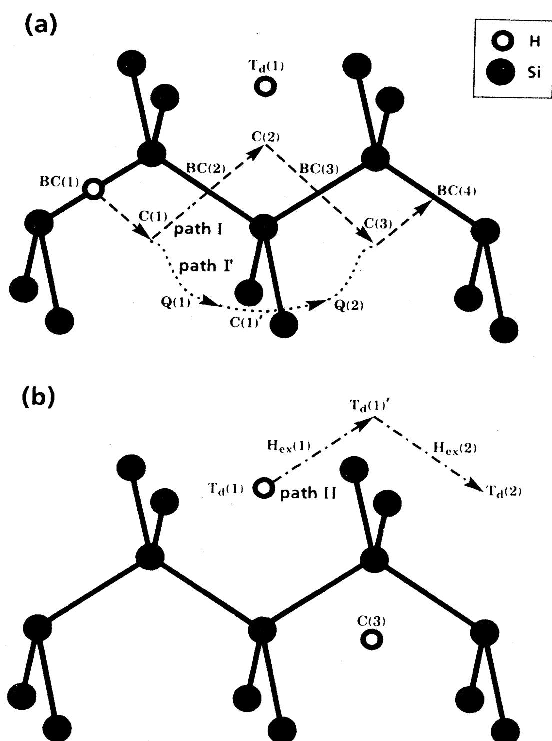


FIG. 6. Possible diffusion paths are marked by arrows for (a) the H^+ and (b) H^- species. Relaxation effects are neglected. Paths I, I′, and II are drawn by dashed, dotted, and dotted-dashed lines, respectively.

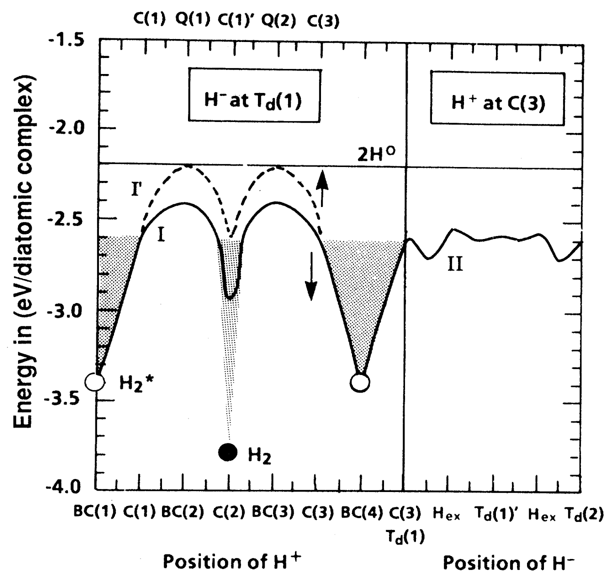


FIG. 7. Calculated energies of the diatomic complex are plotted for the diffusion paths I, I′, and II shown in Fig. 6. The energies for H_2 and H_2^* are marked by open and solid circles. Shaded areas represent self-trapping regions induced by H_2 or H_2^* formation.

computational effort, we examine here the motion of one H atom of the complex at a time keeping the position of its counterpart fixed. In Fig. 7, we show the variation of the binding energies for the H^+ and H^- diffusions along paths I and II, respectively. With the metastable H_2^* complex as the starting configuration for the diffusion, the first step is to consider the migration of the H^+ ion at the BC(1) site. Since this atom has to overcome a 0.8-eV energy barrier, which is the largest barrier for the diffusion of the complex, to migrate to the neighboring $C(1)$ site, the hydrogen atoms of the complex should be "self-trapped" by H_2^* formation prior to the start of diffusion. Following the $C(1)$ site, there are two possible diffusion paths for H^+ labeled I and I′ where the path I′ is connected by $C(1)$, $Q(1)$, $C(1)'$, $Q(2)$, $C(3)$, etc., and the C' site lies on the plane perpendicular to a (110) plane with the same symmetry as C (see Fig. 1). The $Q(1)$ and $Q(2)$ sites are in antibonding regions of BC(3) and BC(2), respectively, and these points are separated by 0.25 Å from the neighboring T_d sites. The diffusion path I′ is more or less parallel to the zig-zag chain of Si—Si bonds.

For H^+ diffusion from the $C(1)$ to the $C(3)$ site, the migration paths I and I′ are symmetric about the intermediate $C(2)$ and $C(1)'$ positions, respectively, as shown in Fig. 7. We find that the maximum energies occur at the BC(2) and BC(3) sites along path I while path I′ has energy maxima at the $Q(1)$ and $Q(2)$ sites. Since the energy barrier of path I is lower by 0.2 eV than that of path I′, hydrogen is likely to diffuse along the low-energy channel. On the other hand, the maximum energies along path I′ are similar to those for two isolated neutral hydrogen ($2H^0$), therefore, the diffusing diatomic complex is likely to dissociate into atomic hydrogens at the peak positions.

Each diffusion path for the H^+ species is found to have a local minimum energy at the corresponding intermediate C site. However, the energy at the $C(2)$ site on path I is lower by 0.3 eV than that at the $C(1)'$ position, which is similar to those at the $C(1)$ and $C(3)$ positions. At the $C(2)$ site, however, there is a high probability that the diatomic complex can transform into molecular hydrogen because of the proximity of the two H atoms in the complex. The nuclear separation between the H^+ and H^- ions occupying the $C(2)$ and $T_d(1)$ positions is about 1.5 Å, respectively. The H_2 molecule is easily formed by displacing the complex 0.54 Å along the [001] direction and by reducing the separation between H^+ and H^- to 0.85 Å. Molecular formation at the empty $T_d(1)$ site further increases the binding energy of the diatomic complex by 0.9 eV as shown in Fig. 7. Since the energy of an H_2 molecule is lower by 0.4 eV than for H_2^*, molecular formation provides an even deeper trap for the diatomic complex diffusion.

To consider the next diffusion step of the H^- atom, the H^+ ion, after becoming either detrapped from an H_2 molecule at the $T_d(1)$ site, or if it has avoided molecular formation, after having migrated along path I′, is assumed to remain fixed at the $C(3)$ position. Since the $C(1)$ and $C(3)$ sites are symmetric with respect to the $T_d(1)$ posi-

tion, their energies are the same. The H^- species is not expected to migrate to the neighboring $C(2)$ and then to the BC(3) site because the diatomic complex formed during this diffusion is similar to that in Fig. 2(c), and thus has a high diffusion barrier. The most probable migration route of H^- is along path II going through the tetrahedral and hexagonal sites. The H^- diffusion path is similar to path I′ for H^+; however, the total-energy variation along path II is only 0.15 eV, which is much smaller than that for H^+ diffusion. As compared to paths I and I′, the maximum energy barrier is found to be lower by 0.2–0.4 eV, respectively. Moreover, there are no traps along path II, therefore H^- should be more diffusive than the H^+ unit of the diatomic complex.

In our diatomic complex diffusion mode, the hydrogen atoms migrate via a zig-zag motion in which the H^+ and H^- ions repeat paths I (or I′) and II, respectively. As compared to the neutral atomic H in its most stable position, the energies of the complex are generally lower as shown in Fig. 7 because of the interactions between the H atoms in the complex. The interactions between H^+ and H^- are significant along paths I and II because their atomic separations of 0.85–2.5 Å are smaller. Along path I′, however, the interactions becomes weak, particularly at the maximum energy positions $Q(1)$ and $Q(2)$ which are separated by about 4.5 Å from the $T_d(1)$ site, resulting in the likely dissociation of the complex. The calculated activation energy for the diffusion of a diatomic complex is about 0.5 eV when the hydrogen atoms bypass traps. In the case of trapping, the formation of H_2^* and H_2 complexes increases the activation energy by 0.5 and 0.9 eV, respectively. Therefore, the activation energy for diatomic complex diffusion is higher and its diffusivity is lower than that for atomic hydrogen.[2] However, its activation energy is lower than that for H_2 diffusion.

We now discuss the influence of temperature, hydrogen concentration, and dopant on hydrogen diffusion. At very high temperatures, the atomic diffusion mode is highly likely because diatomic hydrogen complexes as well as the dopant-hydrogen pairs tend to dissociate. If the atomic diffusion mode dominates, the diffusing unit consists of atomic H^+ in p-type Si and H^- in n-type Si at high hydrogen concentrations as discussed earlier. Since the probability at diatomic complex formation increases with the density of H atoms, the possibility of atomic hydrogen diffusion at very low hydrogen concentrations cannot be excluded. Indeed, this suggestion is consistent with the observation of a rapidly diffusing unit at room temperatures in B-doped Si with a low H concentration.[10] However, in n-type Si, because the metastable H_2^* complex is more stable than H^- (see Fig. 3), the diatomic diffusion modes is more likely to occur than the atomic one. This result is in good agreement with the recent observation that diffusion in n-type Si involves more than just an atomic hydrogen species, and some type of hydrogen complex was inferred.[19] Our results further suggest that if the atomic diffusion mode would exist in n-type Si, the hydrogen concentration has to be extremely low as in Ref. 10.

At moderate temperatures, the diffusing hydrogens can be trapped via the formation of dopant-hydrogen pairs or H_2 and H_2^* units as shown in Fig. 3. The formation of H_2^* complexes is more likely in n-type Si where molecular formation is energetically favorable and the energy barrier of 1.0 eV from H_2^* to H_2 is not too high. The smaller 2 eV binding energy per H for a P-H pair [as compared to the 2.5 eV (per H) energy for a B-H pair in p-type Si] is not appreciably larger than the H_2 formation energy of 1.8 eV per H in n-type Si and H_2 formation competes, therefore, with dopant-H pair formation. Moreover, the formation of an H_2^* complex can occur via the pairing of charged hydrogen atoms resulting from compensation by free carriers through the following reactions:

$$H^0+H^+ \rightarrow H_2^* + h \quad (6)$$

and

$$H^+ + H^+ \rightarrow H_2^* + 2h \quad (7)$$

in p-type Si, and

$$H^0 + H^- \rightarrow H_2^* + e^- \quad (8)$$

and

$$H^- + H^- \rightarrow H_2^* + 2e^- \quad (9)$$

in n-type Si. Here, the reaction involving two neutral hydrogen atoms is not considered because its energetics is independent of the type of dopant. From Fig. 3, only the reactions (8) and (9) are exothermic, thereby H_2^* formation is more likely to occur in n- than in p-type Si. These results lead to the conclusion that the diatomic diffusion mode is more probable in n-type Si, and provide an explanation for the lower probability of atomic hydrogen diffusion in n- than in p-type Si. In addition, since the diatomic complex has a higher activation energy and can be easily trapped by H_2 and H_2^* formation, its diffusivity in n-type Si is expected to be much lower than atomic hydrogen in p-type Si. In p-type Si, the diffusion mode is suggested to be atomic when either the B-H and H_2 complexes dissociate (at high temperatures, for example), or when the B and H concentrations are low enough to result in fewer numbers of these complexes.

V. SUMMARY

We have calculated the energies for various configurations of interstitial hydrogen in Si using a first-principles pseudopotential method. Monatomic hydrogen is predicted to behave as a weak negative-U center, leading to a temperature-dependent ESR signal from H in undoped Si. However, the stability of diatomic hydrogen complexes may provide an explanation for the failure to detect an ESR signal. We have discussed the effects of temperature, hydrogen concentration, and dopant on hydrogen diffusion. At very high temperatures, the diffusion mode is predominantly through an atomic species, assuming that diatomic hydrogen and dopant-hydrogen complexes dissociate. Even at low temperatures, if the hydrogen concentration is sufficiently low so that the formation of hydrogen complexes is avoided, the

atomic diffusion mode is likely to occur, especially in *p*-type Si. However, the diffusion mode in *n*-type Si is suggested to be of a diatomic complex nature in which the H atoms occupy regions of high and low electronic charge densities. In contrast to the atomic diffusion mode, the activation energy is higher and the diffusivity is lower for the diatomic complex diffusion. These results provide, therefore, a better framework for understanding the differences in the diffusivity of hydrogen between *n*- and *p*-type Si. Atomic H is more diffusive in *n*-type than in *p*-type Si than previous models dealing with purely atomic or molecular hydrogen diffusion have indicated. Future molecular dynamics studies should provide a more complete picture of hydrogen diffusion in Si.

ACKNOWLEDGMENTS

This work was supported in part by the U.S. Office of Naval Research through Contract No. N00014-82-C-0244.

[1]S. J. Pearton, J. W. Corbett, and T. S. Shi, Appl. Phys. A **43**, 153 (1987).

[2]A. Van Wieringen and N. Warmoltz, Physica **22**, 849 (1956).

[3]A. J. Tavendale, D. Alexiev, and A. A. Williams, Appl. Phys. Lett. **47**, 316 (1985).

[4]N. M. Johnson, Appl. Phys. Lett. **47**, 874 (1985).

[5]N. M. Johnson and M. D. Moyer, Appl. Phys. Lett. **46**, 787 (1985).

[6]N. M. Johnson, Phys. Rev. B **31**, 5525 (1985).

[7]C.-T. Soh, J. Y.-C. Sun, and J. I.-T. Tzou, J. Appl. Phys. **54**, 5864 (1983).

[8]J. I. Pankove, R. O Wance, and J. E. Berkeyheiser, Appl. Phys. Lett. **45**, 1100 (1984).

[9]N. M. Johnson, C. Herring, and D. J. Chadi, Phys. Rev. Lett. **56**, 769 (1986).

[10]C. H. Seager and R. A. Anderson, Appl. Phys. Lett. **53**, 1181 (1988).

[11]S. J. Pearton, in *Proceedings of the Thirteenth International Conference on Defects in Semiconductors,* edited by L. C. Kimerling and J. M. Parsey, Jr. (Metallurgical Society of AIME, New York, 1984), p. 737.

[12]M. Capizzi and A. Mittiga, Appl. Phys. Lett. **50**, 918 (1987).

[13]S. T. Pantelides, Appl. Phys. Lett. **50**, 995 (1987).

[14]J. W. Corbett, S. N. Sahu, T. S. Shi, and L. C. Snyder, Phys. Lett. **93A**, 303 (1983); T. S. Shi, S. N. Sahu, J. W. Corbett, and L. C. Snyder, Sci. Sin. **27**, 98 (1984).

[15]G. G. DeLeo, M. J. Dorogi, and W. B. Fowler, Phys. Rev. B **38**, 7520 (1988).

[16]P. Deak, L. C. Snyder, and J. W. Corbett, Phys. Rev. B **37**, 6887 (1988).

[17]C. G. Van de Walle, Y. Bar-Yam, and S. T. Pantelides, Phys. Rev. Lett. **60**, 2761 (1988).

[18]N. M. Johnson and C. Herring, Phys. Rev. B **38**, 1581 (1988).

[19]N. M. Johnson and C. Herring, in *Proceedings of the Fifteenth International Conference on Defects in Semiconductors, Budapest, 1988,* Vols. 38–41 of *Materials Science Forum,* edited by G. Ferenczi (Trans Tech, Aedermannsdorf, 1989).

[20]N. M. Johnson and C. Herring (unpublished).

[21]K. J. Chang and D. J. Chadi, Phys. Rev. Lett. **60**, 1422 (1988).

[22]J. I. Pankove, D. E. Carlson, J. E. Berkeyheiser, and R. O. Wance, Phys. Rev. Lett. **51**, 2224 (1983).

[23]J. I. Pankove, P. I. Zanzucchi, C. W. Magee, and G. Lucovsky, Appl. Phys. Lett. **46**, 421 (1985).

[24]Y.-C. Du, Y.-F. Zhang, G.-G. Qin, and S.-F. Weng, Solid State Commun. **55**, 501 (1985).

[25]M. Stavola, S. I. Pearton, J. Lopata, and W. C. Dautremont-Smith, Appl. Phys. Lett. **50**, 1086 (1986).

[26]M. Stavola, K. Bergman, S. I. Pearton, and J. Lopata, Phys. Rev. Lett. **61**, 2786 (1988).

[27]K. J. Chang and D. J. Chadi, Phys. Rev. Lett. **62**, 937 (1989).

[28]M. L. Cohen, Phys. Scr. **T1**, 5 (1982).

[29]*Theory of the Inhomogeneous Electron Gas,* edited by S. Lundqvist and N. H. March (Plenum, New York, 1983), and references therein.

[30]E. Wigner, Trans. Faraday Soc. **34**, 678 (1938).

[31]D. R. Hamann, M. Schluter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

[32]M. T. Yin and M. L. Cohen, Phys. Rev. B **26**, 5668 (1982).

[33]K. J. Chang and M. L. Cohen, Phys. Rev. B **30**, 5376 (1984).

[34]K. J. Chang and M. L. Cohen, Phys. Rev. B **31**, 7819 (1985).

[35]R. M. Wentzcovitch, K. J. Chang, and M. L. Cohen, Phys. Rev. B **34**, 1071 (1986).

[36]J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4401 (1979).

[37]H. Hellmann, *Einführung in dir Quanten Theorie* (Deuticke, Leipzig, 1937), p. 285; R. P. Feynman, Phys. Rev. **56**, 340 (1939).

[38]Y. Bar-Yam and J. D. Joannopoulos, Phys. Rev. B **30**, 1844 (1984).

[39]S. B. Zhang and D. J. Chadi (unpublished). Our more recent calculations give a hydrogen bonding configuration with a slightly (i.e., 0.1 eV) lower energy than the structure in Fig. 5. In the new configuration the Si nearest-neighbor of the donor which is closest to the hydrogen atom break its bond with the donor and moves towards the hydrogen atom and bonds with it. This configuration is very similar for the diatomic complex shown in Fig. 2(d), particularly if the Si_I plus the H atom attached to it are considered to be chemically equivalent to a donor atom. None of the conclusions of this paper regarding the energetics of various reactions are affected by the new geometry.

[40]A. Mainwood and A. M. Stoneham, J. Phys. C **17**, 2513 (1984).

[41]B. D. Patterson, E. Holzschuh, R. F. Kiefl, K. W. Blazey, and T. L. Estle, Hyperfine Interact. **17-19**, 399 (1984).

[42]R. F. Kiefl, M. Celio, T. L. Estle, S. R. Kreitzman, G. M. Luke, T. M. Riseman, and E. J. Ansaldo, Phys. Rev. Lett. **60**, 224 (1988); R. F. Kiefle and T. L. Estle, in *Hydrogen in Semiconductors,* edited by J. I. Pankove and N. M. Johnson (Academic, New York, in press).

[43]V. A. Gordeev, Yu. V. Gorelkinskii, R. F. Konopleva, N. N. Nevinnyi, Yu. V. Obukhov, and V. G. Firsov (unpublished); Yu. V. Gorelkinskii and N. N. Nevinnyi, Pis'ma Zh. Tekh. Fiz. **13**, 105 (1987) [Sov. Tech. Phys. Lett. **13**, 45 (1987)].

[44]F. A. Ponce, N. M. Johnson, and J. C. Walker, in *Proceedings of the 5th Oxford Conference on Microscopy of Semiconductor*

Materials, edited by A. G. Cullis and P. D. Augustus (Institute of Physics, Oxford, 1987), p. 49; N. M. Johnson, F. A. Ponce, R. A. Street, and R. J. Nemanich, Phys. Rev. B **35**, 4166 (1987).
[45]J. B. Boyce and M. Stutzmann, Bull. Am. Phys. Soc. **30**, 354 (1985).
[46]P. Briddon, R. Jones, and G. M. S. Lister, J. Phys. C **21**, L1027 (1988).
[47]D. J. Chadi and K. J. Chang, Phys. Rev. Lett. **60**, 2187 (1988).
[48]D. J. Chadi and K. J. Chang, Phys. Rev. Lett. **61**, 873 (1988).
[49]M. Stutzmann, Phys. Rev. B **35**, 5921 (1987).
[50]J. I. Pankove, C. W. Magee, and R. O. Wance, Appl. Phys. Lett. **47**, 748 (1985).
[51]A. D. Marwick, G. S. Oehrlein, and N. M. Johnson, Phys. Rev. B **36**, 4539 (1987).
[52]B. Bech Nielsen, J. U. Anderson, and S. J. Pearton, Phys. Rev. Lett. **60**, 321 (1988).
[53]M. L. W. Thewalt, E. C. Lightowlers, and J. Pankove, Appl. Phys. Lett. **46**, 689 (1985).
[54]K. Bergman, M. Stavola, S. J. Pearton, and J. Lopata, Phys. Rev. B **37**, 2770 (1988).
[55]G. G. DeLeo and W. B. Fowler, Phys. Rev. B **31**, 6861 (1985).
[56]L. V. C. Assali and J. R. Leite, Phys. Rev. Lett. **55**, 980 (1985).
[57]M. Stavola, S. J. Pearton, J. Lopata, and W. C. Dautremont-Smith, Phys. Rev. B **37**, 8313 (1988).
[58]C. P. Herrero and M. Stutzmann, Phys. Rev. B **38**, 12 668 (1988).
[59]M. Stavola, K. Bergman, S. Pearton, and J. Lopata, Phys. Rev. Lett. **61**, 2786 (1988).
[60]P. I. N. Denteneer, C. G. Van de Walle, Y. Bam-Yam, and S. T. Pantelides, in Ref. 19.
[61]M. Stavola, K. Bergman, S. J. Pearton, J. Lopata, and T. Hayes, in Ref. 19.
[62]F. Buda, G. L. Chiarotti, R. Car, and M. Parrinello, in *Proceedings of the 19th International Conference on the Physics of Semiconductors, Warsaw, 1988,* edited by W. Zawadski (Institute of Physics, Polish Academy of Sciences, Warsaw, 1988), p. 1159.