

## Diatomic-Hydrogen-Complex Diffusion and Self-Trapping in Crystalline Silicon

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We propose a new metastable diatomic hydrogen complex in crystalline Si. Our *ab initio* calculations show that the complex is about 1.2 eV more stable than two separated neutral hydrogen atoms in their most energetically favorable configurations. A novel diffusion mechanism, based on metastable and molecular hydrogen-complex formation and dissociation, is presented.

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The nature of hydrogen bonding and diffusion in crystalline<sup>1</sup> (and amorphous<sup>2</sup>) silicon has been the subject of many recent experimental and theoretical investigations because of its scientific and technological importance. The microscopic basis for hydrogen diffusion remains an open question, however. There is even controversy on the charge state and identity of the diffusing species, i.e., whether it involves monatomic or molecular hydrogen, or possibly some other complex.

Diffusion via primarily monatomic hydrogen is assumed in most studies<sup>1,3-12</sup> on crystalline Si. This assumption is reasonable in the region of low hydrogen concentrations, or at very high temperatures since molecular hydrogen (H<sub>2</sub>) has a large binding energy and a large diffusion barrier<sup>1,9</sup> of 2–3 eV. Recently, Johnson and Herring<sup>13,14</sup> found a highly immobile species with a diffusion coefficient of  $\leq 10^{-14}$  cm<sup>2</sup>/sec at 350°C, and they assigned it to molecular hydrogen. A deep-donor model<sup>3-7</sup> for hydrogen and observations of its electric-field-dependent diffusion<sup>3,4,13-15</sup> have provided strong evidence that atomic hydrogen diffuses as a positively charged unit H<sup>+</sup> in *p*-type samples.<sup>16</sup> In *n*-type Si, a negatively charged hydrogen H<sup>-</sup> has been suggested to be involved in both diffusion and in hydrogen-donor pair formation.<sup>11,15,17,18</sup> Although neutral hydrogen H<sup>0</sup> is also expected in diffusion, its presence would be difficult to reconcile with the general failure to observe an electron-spin-resonance (ESR) signal from it.<sup>19</sup> In addition, the large spread in the diffusion coefficient data and the difficulty in fitting it with a single activation energy suggest that hydrogen diffusion may not be as simple as envisioned by existing models.<sup>1,5,6,20</sup>

In this Letter a new metastable diatomic configuration of H in Si is proposed and its diffusion mechanism is examined. The metastable diatomic complex denoted by H<sub>2</sub><sup>\*</sup> is shown in Fig. 1(a). The hydrogen atoms in H<sub>2</sub><sup>\*</sup> occupy regions of high and low electronic charge densities. The results of our calculations for the diffusion barrier of this complex indicate that it should be an important source of hydrogen diffusion, particularly at high hydrogen concentrations and at low temperatures. We discuss the transformation of the H<sub>2</sub><sup>\*</sup> complex into an H<sub>2</sub> molecule, and its subsequent “dissociation” back into the complex.

*Ab initio* pseudopotential<sup>21</sup> calculations were done for monatomic, molecular, and other diatomic hydrogen complexes, using the Wigner interpolation formula<sup>22</sup> for the exchange and correlation potentials. A plane-wave basis set<sup>23</sup> with a kinetic-energy cutoff of 10 Ry was used for a supercell geometry with eighteen atoms per unit cell. For each configuration, the total energy was optimized by calculating the Hellmann-Feynman forces<sup>24</sup> and displacements of the first- and next-nearest neighbors of interstitial H atoms.

The charge state of atomic hydrogen and its stable interstitial position are strongly affected by the position of the Fermi level. In *p*-type samples where the Fermi level is close to the valence-band maximum, atomic H<sup>+</sup> is most stable at the bond-center (BC) site of two neighboring Si atoms, whereas in *n*-type Si atomic, H<sup>-</sup> at the tetrahedral (*T<sub>d</sub>*) site is most stable. These results are generally consistent with other calculations.<sup>11,12</sup> Therefore, hydrogen can be either a donor or an acceptor in *p*- and *n*-type Si, respectively.<sup>12,25</sup>

The activation energies for the H<sup>+</sup> and H<sup>0</sup> diffusion were calculated to be about 0.1–0.3 eV along the high-density channels which connect neighboring BC positions, while H<sup>-</sup> has an activation energy of 0.3 eV in the low-density regions going through the interstitial *T<sub>d</sub>* and hexagonal sites.<sup>11,12</sup> Although H<sub>2</sub> is an inactive species which is not easily accessible to experimental tests, recent findings of an extremely immobile species even at 350°C provide strong evidence for its existence in crystalline Si.<sup>13,14</sup> It is generally accepted that hydrogen diffuses by an atomic mode at very high temperatures of around 1000°C.<sup>20</sup> The results of a very recent experiment<sup>26</sup> show the existence of a rapidly diffusion species in B-doped Si, even at room temperature and at very low hydrogen concentrations of 10<sup>14</sup> cm<sup>-3</sup>. Since the measured activation energy and the diffusivity in this experiment are similar to those obtained from the high-temperature measurements,<sup>20</sup> the diffusing species is most likely atomic in origin.

In the following we investigate new hydrogen diffusion modes which can be operative at low temperatures and at high hydrogen concentrations. We consider the neutral and ESR-inactive diatomic H<sub>2</sub><sup>\*</sup> complex shown in Fig. 1(a). The complex has C<sub>3v</sub> symmetry and its two

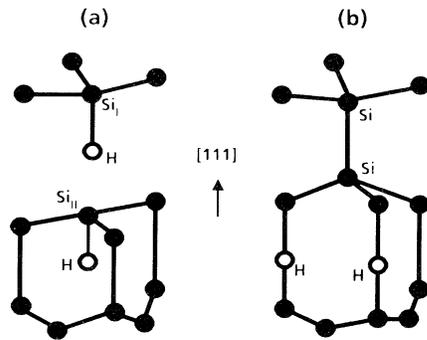


FIG. 1. Two atomic complexes of hydrogen. The hydrogen atoms in (a) occupy the bond-center (BC) and  $T_d$  sites along the [111] axis while in (b) they are at BC sites of neighboring Si-Si bonds parallel to the [111] axis.

hydrogen atoms occupy a BC site and a neighboring  $T_d$  site. The total energy for  $H_2^*$  is found to be lower by  $\approx 1.2$  eV than that of two isolated neutral hydrogen atoms. It is also lower by 1.15 eV when compared to a combination of positively and negatively charged hydrogen atoms in their most favorable atomic configurations. However,  $H_2^*$  is 0.4 eV higher in energy than an  $H_2$  molecule in its lowest-energy configuration at a  $T_d$  site.

The H atom at the BC site of the  $H_2^*$  complex is strongly bonded to its adjacent  $Si_I$  atom (see Fig. 1), which is well separated from the other H atom at the  $T_d$  site. The  $Si_I$ -H bond length is 1.53 Å and the  $Si_I$  atom relaxes 0.24 Å towards the antibonding region. However, the  $Si_{II}$  atom bonded to the H atom at the  $T_d$  site has a larger relaxation from its ideal position, moving by 0.79 Å to the interstitial position, lying on the plane of its three neighboring Si atoms. The  $Si_{II}$  atom is also well separated from the hydrogen atom which occupies the BC site. The  $H_2^*$  complex, therefore, involves the formation of two strongly bonded H atoms. If the combination of each Si-H pair is considered to be approximately equivalent to that of an As atom, the bond-breaking configuration for the  $H_2^*$  complex is similar to that for the metastable As-antisite defect in GaAs.<sup>27</sup>

In the other diatomic complex shown in Fig. 1(b), the two neutral H atoms occupy neighboring BC sites aligned along the same crystalline axis.<sup>28</sup> The elongation of these Si-H-Si bonds has been suggested to be the source of H-induced microdefects observed in  $n$ -type materials.<sup>29</sup> The energy for this complex is found to be 1.8 eV higher than for  $H_2^*$ .

We now focus on the diffusion of  $H_2^*$  because of its low-energy configuration. The diffusion paths shown in Fig. 2 consist of high- and low-density channels along which the H atoms become positively and negatively charged, respectively. It should be noted, however, that the  $H^+$  species at the BC site becomes a neutral one in the configuration of Fig. 1(a) because of charge transfer from the relaxed  $Si_{II}$  atom to  $H^+$ . As the H atom moves

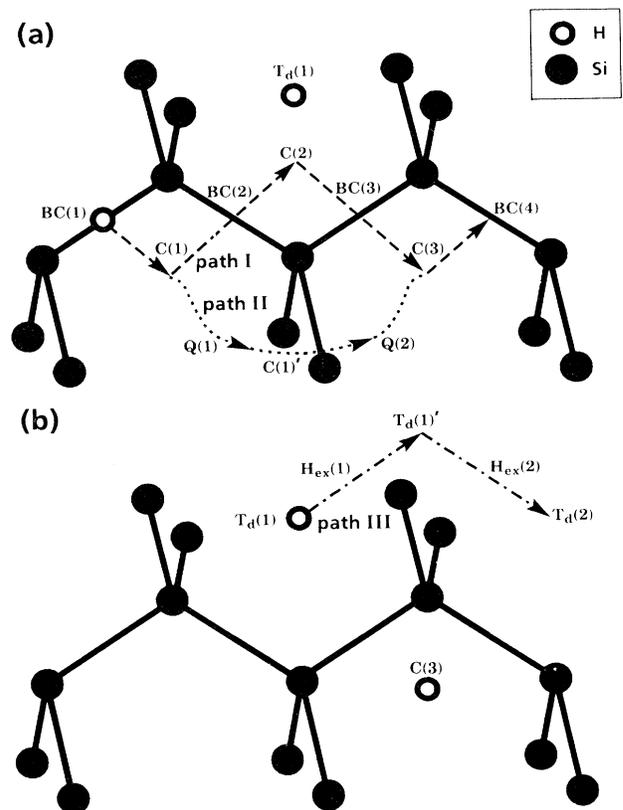


FIG. 2. Possible diffusion paths are marked by arrows for the (a)  $H^+$  and (b)  $H^-$  species which are interacting. Relaxation effects are neglected. Paths I, II, and III are drawn by dashed, dotted, and dot-dashed lines, respectively.

away from the BC site and follows the high-density region, it regains its positive charge state because the ionized  $Si_{II}$  atom which was bound to the  $H^-$  relaxes back to its original position and forms a normal Si-Si bond.

For the diffusion step of the  $H^+$  atom of the complex, we assume that its  $H^-$  counterpart remains fixed at the  $T_d(1)$  site, but all Si atoms are relaxed at each step. In Fig. 3 we show the variation of the total energy for  $H^+$  diffusion along various paths. The  $H^+$  ion can be self-trapped by the metastable  $H_2^*$  configuration at the BC(1) site prior to the start of diffusion. After the hydrogen atom occupying the BC(1) site has overcome the 0.8-eV energy barrier to migrate to the neighboring C(1) site [defined by the center of the rhombus formed by the two neighboring Si-Si bonds lying on a (110) plane], two different diffusion paths become possible: The C(1)-BC(2)-C(2)-BC(3)-C(3) labeled as path I in Fig. 2 is almost identical to the diffusion path for monatomic  $H^+$  (Ref. 12), whereas the C(1)-Q(1)-C(1)'-Q(2)-C(3) labeled as path II is more or less parallel to the Si-Si bond chains. In this case, the paths actually cross the points close to the C and C' sites, where C' has the same symmetry as C and is on the plane perpendicu-

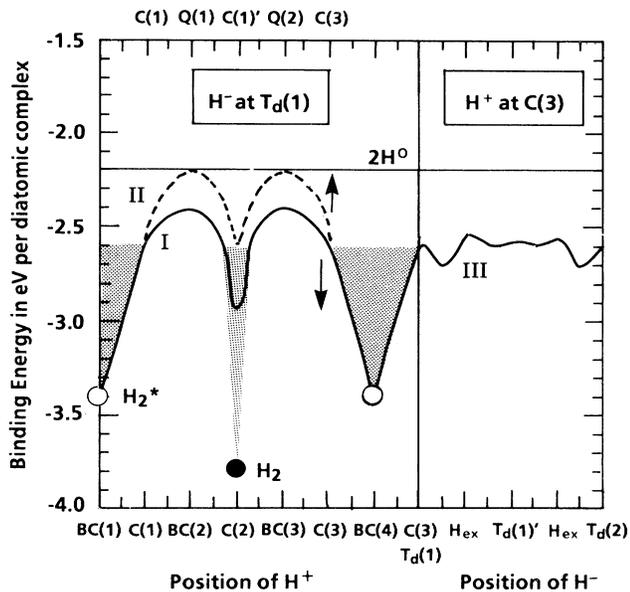


FIG. 3. Calculated binding energies of the diatomic complex for diffusion paths I, II, and III shown in Fig. 2. The energies for  $H_2$  and  $H_2^*$  are marked by open and closed circles while the horizontal line denotes the energy for two isolated neutral hydrogen atoms. Shaded areas represent self-trapping regions induced by  $H_2$  and  $H_2^*$  formations.

lar to a (110) plane. The  $Q(1)$  and  $Q(2)$  sites are displaced from the midpoints of the  $C-C'$  line segments by  $0.93 \text{ \AA}$  towards neighboring  $T_d$  sites.

Along path I, the  $H^+$  ion experiences a low activation barrier. However, molecular  $H_2$  formation is highly likely at the  $C(2)$  site because of the proximity of the H atoms of the diatomic complex. In this case, the energy is reduced by  $0.9 \text{ eV}$  by moving the complex  $0.54 \text{ \AA}$  along the [001] direction and contracting the bond length to  $0.85 \text{ \AA}$ . Since the resulting energy for  $H_2$  is lower by  $0.4 \text{ eV}$  than  $H_2^*$ , the molecule acts as a deeper trap than the  $H_2^*$  configuration in Fig. 1(a). Along path II, the energy barrier is found to be higher by  $0.2 \text{ eV}$  than that of path I. The maximum energies occur at the  $Q(1)$  and  $Q(2)$  sites while the intermediate  $C(1)'$  site is at a local minimum of the energy, similar to those at the  $C(1)$  and  $C(2)$  positions.

Since the molecule formed at the  $T_d(1)$  site is almost immobile, its dissociation and other complex formation reduce its activation barrier for diffusion. If the  $H^+$  species occupies the  $C(3)$  position either after being detrapped from an  $H_2$  molecule (or if it has avoided molecular formation), the  $H^-$  unit would diffuse through the low-density channel denoted by path III [ $T_d(1)-H_{ex}(1)-T_d(1)'$ - $H_{ex}(2)-T_d(2)$ , where  $H_{ex}(1)$  and  $H_{ex}(2)$  are the hexagonal sites and  $T_d(1)'$  is an intermediate tetrahedral site]. Such a diffusion path is similar to path II for  $H^+$ . However, the maximum energy barrier is lower by about  $0.2\text{--}0.4 \text{ eV}$  and the total-energy variation along path III

is only  $0.15 \text{ eV}$  which is much smaller than that for  $H^+$  diffusion.

In contrast to the diffusion of atomic hydrogen, the hydrogen atoms in the complex, separated by  $0.85\text{--}4.25 \text{ \AA}$  during diffusion, are interacting and their energies are generally lower than those of isolated hydrogen atoms as shown in Fig. 3. The interacting hydrogen atoms migrate via a zig-zag motion, i.e., repeating paths I (or II) and III for the  $H^+$  and  $H^-$  species, respectively. The calculated activation energy for the diffusion of a diatomic complex is about  $0.5 \text{ eV}$  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  $0.9 \text{ eV}$ , respectively. Therefore, the activation energy for diatomic-complex diffusion is higher and its diffusivity is lower than that for atomic hydrogen.<sup>20</sup> Comparing the energies of stable atomic hydrogen (i.e.,  $-1.85 \text{ eV}$  for  $H^+$  in  $p$ -type and  $-1.55 \text{ eV}$  for  $H^-$  in  $n$ -type Si),<sup>25</sup> with that of the metastable diatomic complex, and with that of hydrogen-dopant pairs,<sup>18</sup> we suggest that the formation of the diatomic complex is most likely at high hydrogen concentrations and at low temperatures because the complex easily dissociates into atomic hydrogen at high temperatures. The possibility of atomic hydrogen diffusion at low hydrogen concentrations cannot be excluded, however. Since the maximum energy in path II is similar to that for two isolated hydrogen atoms, the dissociation of the complex is likely to occur at the peak positions in Fig. 3.

We also like to point out that dopants can affect the formation of an  $H_2^*$  complex, thus influencing the efficiency of hydrogen diffusion. The formation of an  $H_2^*$  complex from charged hydrogen atoms resulting from compensation by free carriers involves the reactions  $H^0+H^+\rightarrow H_2^*+h^+$  and  $2H^+\rightarrow H_2^*+2h^+$  in  $p$ -type Si and  $H^0+H^-\rightarrow H_2^*+e^-$  and  $2H^-\rightarrow H_2^*+2e^-$  in  $n$ -type Si, where  $h^+$  and  $e^-$  denote a free hole and an electron, respectively. We find that the energy of the metastable  $H_2^*$  complex is lower than that of  $2H^-$  in  $n$ -type Si while it is higher than that of  $2H^+$  in  $p$ -type Si. Therefore, the diatomic-complex diffusion is more likely to occur in  $n$ -type than in  $p$ -type Si. In addition, since  $H_2^*$ -complex formation competes with H-dopant pair formation, a smaller binding energy for a H-P as compared to a H-B pair<sup>18</sup> also helps in  $H_2^*$  (and  $H_2$ ) formation in  $n$ -type Si. An excess of  $H_2^*$  complexes increases the formation of  $H_2$  molecules because the atomic geometries of these two complexes are closely related to each other and the energy barrier of  $1.0 \text{ eV}$  from  $H_2^*$  to  $H_2$  is not very high.

Our results suggest that hydrogen diffusion in  $p$ -type Si at very low hydrogen concentrations is dominated by the ionized atomic mode, and this prediction is in good agreement with recent experimental results.<sup>26</sup> In  $n$ -type Si, analysis of recent experimental data provides strong evidence that diffusion involves more than just an atomic hydrogen species and some type of hydrogen-complex

diffusion was inferred.<sup>14</sup> This result is again consistent with our theoretical predictions. To detect atomic hydrogen diffusion in *n*-type Si, one has to do experiments at very low hydrogen concentrations, which are similar to those of Ref. 26 for *p*-type Si.

As we mentioned earlier, a diatomic H<sub>2</sub><sup>\*</sup> complex is ESR inactive, consistent with the experimental failure to detect any ESR signal from H in Si. Our theory predicts that hydrogen should also be ESR inactive in *undoped* Si. If atomic hydrogen were more stable than the diatomic complex, then a strong ESR signal from H would be expected in pure Si since atomic hydrogen would occur in large numbers in the neutral and spin-active state. The negative-*U* reaction 2H<sup>0</sup> → H<sup>+</sup> + H<sup>-</sup>, which is found to be weakly exothermic by ≈ 0.05 eV, would also lead to a temperature-dependent ESR signal which has not been experimentally observed.

We hope that our theoretical results will provide a better framework for understanding the differences in the diffusivity of hydrogen in *n*- and *p*-type Si than previous models dealing with purely atomic or molecular hydrogen diffusion.

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<sup>1</sup>S. J. Pearton, J. W. Corbett, and T. S. Shi, Appl. Phys. A **43**, 153 (1987).

<sup>2</sup>R. A. Street, C. C. Tsai, J. Kakalios, and W. B. Jackson, Philos. Mag. B **56**, 305 (1987).

<sup>3</sup>A. J. Tavendale, D. Alexiev, and A. A. Williams, Appl. Phys. Lett. **47**, 316 (1985).

<sup>4</sup>N. M. Johnson, Appl. Phys. Lett. **47**, 874 (1985).

<sup>5</sup>N. M. Johnson and M. D. Moyer, Appl. Phys. Lett. **46**, 787 (1985).

<sup>6</sup>M. Capizzi and A. Mittiga, Appl. Phys. Lett. **50**, 918 (1987).

<sup>7</sup>S. T. Pantelides, Appl. Phys. Lett. **50**, 995 (1987).

<sup>8</sup>J. W. Corbett, S. N. Sahu, T. S. Shi, and L. C. Snyder, Phys. Lett. **93A**, 303 (1983).

<sup>9</sup>T. S. Shi, N. Sahu, J. W. Corbett, and L. C. Snyder, Scientia Sinica **27**, 98 (1984).

<sup>10</sup>A. Mainwood and A. M. Stoneham, J. Phys. C **17**, 2513

(1984).

<sup>11</sup>P. Deak, L. C. Snyder, and J. W. Corbett, Phys. Rev. B **37**, 6887 (1988).

<sup>12</sup>C. G. Van de Walle, Y. Bar-Yam, and S. T. Pantelides, Phys. Rev. Lett. **60**, 2761 (1988).

<sup>13</sup>N. M. Johnson and C. Herring, Phys. Rev. B **38**, 1581 (1988).

<sup>14</sup>N. M. Johnson and C. Herring, in Proceedings of the Third International Conference on Shallow Impurities in Semiconductors, Linköping, Sweden, 1988 (to be published).

<sup>15</sup>N. M. Johnson and C. Herring, in Proceedings of the Fifteenth International Conference on Defects in Semiconductors, Budapest, Hungary, 1988 (to be published).

<sup>16</sup>For H at the bond-center site in *p*-type Si, the H-related energy level in the gap results from the antibonding combination of the Si and H orbitals; thus its ionized state is not a bare proton but a positively charged state of a Si-H complex.

<sup>17</sup>N. M. Johnson, C. Herring, and D. J. Chadi, Phys. Rev. Lett. **56**, 769 (1986).

<sup>18</sup>K. J. Chang and D. J. Chadi, Phys. Rev. Lett. **60**, 1422 (1988).

<sup>19</sup>V. A. Gordeev, Yu. V. Gorelkinskii, R. F. Konopleva, N. N. Nevinnyi, Yu. V. Obukhov, and V. G. Firsov (to be published). These authors reported an ESR signal from H-implanted Si, but the signal may be due to defects created during implantation.

<sup>20</sup>A. Van Wieringen and N. Warmoltz, Physica **22**, 849 (1956).

<sup>21</sup>D. R. Hamann, M. Schluter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

<sup>22</sup>E. Wigner, Trans. Faraday Soc. **34**, 678 (1938).

<sup>23</sup>J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4401 (1979).

<sup>24</sup>H. Hellmann, *Einführung in die Quanten Theorie* (Deuticke, Leipzig, 1937), p. 285; R. P. Feynman, Phys. Rev. **56**, 340 (1939).

<sup>25</sup>K. J. Chang and D. J. Chadi (to be published).

<sup>26</sup>C. H. Seager and R. A. Anderson, Appl. Phys. Lett. **53**, 1181 (1988).

<sup>27</sup>D. J. Chadi and K. J. Chang, Phys. Rev. Lett. **60**, 2187 (1988).

<sup>28</sup>The atomic complex in Fig. 1(b) would be ESR inactive if the exchange interaction is larger than a magnetic splitting.

<sup>29</sup>F. A. Ponce, N. M. Johnson, J. C. Walker, and J. Walker, in *Proceedings of the Fifth 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).