PHYSICAL REVIEW B VOLUME 50, NUMBER 8 15 AUGUST 1994-II

Tight-binding quantum molecular-dynamics simulations of hydrogen in silicon

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(Received 23 December 1993)

We have carried out molecular-dynamics simulations of neutral hydrogen in crystalline silicon using tight-binding (TB) quantum-mechanical total energies and forces. A well-established model due to Goodwin *et al.* is used for the Si-Si interactions. For the Si-H interactions, we have fit our Harrison-type TB model to the known properties of silane and to both theoretical and experimental information about hydrogen in crystalline silicon. Several simulations performed in the temperature range of 1050 to 2000 K yield a diffusion curve in good agreement with experiment. The H diffusion is found to be jumplike between bond-centered (BC) sites, and the trapping of H at the BC site is mediated by a metastable onefold coordinated H configuration which weakens adjacent Si-Si bonds, allowing the H to enter the BC site. Vibrational frequencies for hydrogen at the BC site are also calculated and isotopic frequency shifts are discussed.

I. INTRODUCTION

Hydrogen as an impurity in semiconductors has proven to be ubiquitous and versatile.[1,2] Because of its high mobility, H can readily diffuse into semiconductors, where by virtue of its high chemical reactivity, it may form complexes with many different intrinsic and impurity-related defects. Most notably, H can "passivate" shallow acceptors and donors in Si and III-V semiconductors, rendering these defects electrically inactive. The discovery of hydrogen's role in the passivation of these technologically important dopant impurities resulted in a vast amount of experimental and theoretical research into the effects of H on semiconductors and the microscopic mechanisms for these effects. In addition to the shallow-level impurities, hydrogen is known to interact with deep-level defects, such as transition-metal impurities, and also with various Si dangling bonds at surfaces, grain boundaries, and vacancies. The latter two are especially important to amorphous Si, in which the H passivation of intrinsic defects vastly improves the electronic properties of the material.

In addition to H passivation of existing defects, there is evidence that H may induce defects also. These include large "platelets" formed near the surface of Si exposed to a remote H plasma,[3] as well as H related gap states.[4]

Technological implications aside, the understanding of H in Si is important as a fundamental phenomenon in solid state physics. Hydrogen, the simplest atom, has proven to be anything but simple as an isolated impurity in Si. Experimentally, isolated H has been observed in EPR experiments[5] (the so-called "AA9" spectrum) and in muon spin resonance (μSR) experiments[6] (the Mu* spectrum). The μSR experiments complement the EPR experiments because "muonium," consisting of a positive muon and an electron, may be regarded as a very light ($\sim$ 1/9 the mass of H) isotope of H.[7] Both experimental techniques indicate that the H atom is situated at the center of a Si-Si bond, which has expanded to accommodate the H atom. I will refer to this site as the bond-centered (BC) site. The μSR experiments also find that muonium can exist in a state Mu that has an isotropic hyperfine interaction, indicating that it may be either at the tetrahedral site or perhaps moving about rapidly enough in the crystal so as to motionally average its spectrum.

A number of theoretical methods have been used to determine the possible microstructure of isolated H in Si.[8] In those calculations that allowed for the crucial lattice relaxation, the BC site is usually found[9–12] to be the global energy minimum for H^0. Two studies[13,14] utilizing semiempirical and *ab initio* Hartree-Fock cluster calculations predict that the H atom would be located in the midst of a Si-Si bond, but bonded more closely to one of the Si atoms. This asymmetric BC site is not inconsistent with experiment due to the zero point motion of H or μ. The other calculations place H at the geometric center of the Si-Si bond. Molecular-dynamics simulations of H$^+$ in Si have been performed using accurate local density pseudopotential total energies and forces.[15] These prodigious simulations yielded a diffusion curve at high temperatures which agrees well with experiment.

The immediate goal of the present work is to apply computationally efficient tight-binding (TB) total energies and forces to the molecular-dynamics simulation of H in Si, allowing us to learn more about the possible motion and diffusion of H in Si. More generally, the simulations presented here serve to explore the applicability of a class of TB methods to the study of defect dynamics.

This paper is arranged as follows. In Sec. II, we review the fundamentals of TB total energy and force calculations and provide details regarding the TB models used for the Si-Si and Si-H interactions. In Sec. III, we further refine the Si-H model to account for what is known about isolated H in Si. The static features of our model are then presented. Section IV provides the details of

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the MD simulations and the calculation of the hydrogen diffusion curve. Also, a microscopic mechanism for H trapping at the BC site is discussed. The calculated vibrational frequencies for H, ^{2}H, and ^{3}H at the BC site are presented in Sec. V. The paper closes with a discussion (Sec. VI) and summary (Sec. VII).

II. TIGHT-BINDING MOLECULAR DYNAMICS

The rudiments of tight-binding molecular dynamics (TBMD) have been discussed elsewhere[16] and therefore will be presented here only briefly. The nuclei, or more accurately, the nuclei plus any core electrons, are treated as classical point masses, which are described by the total energy expression

$$E_{\rm tot} = \sum_I^N \frac{1}{2} m_I v_I^2 + E_{\rm BS} + E_{\rm corr}, \qquad (1)$$

where I is an atom index. The first term on the right-hand side is simply the kinetic energy of the nuclei and the remaining terms make up the potential energy. $E_{\rm BS}$ is the *band structure* energy and is defined as

$$E_{\rm BS} \equiv \sum_i^{\rm occupied} g_i \epsilon_i - \sum_j^{\rm occupied} g_j \epsilon_j^0 \,, \qquad (2)$$

where the g's are occupancy factors that are equal to 2 except for highest occupied state, where g may equal 1 or 2 depending upon the number of electrons. ϵ_i is a single-particle eigenvalue obtained by solving the single-particle Schrödinger equation. The eigenvalues ϵ_j^0 are obtained in the same manner, except that all interatomic interactions have been set to zero or, equivalently, all atoms have been moved to infinite separation. Defined in this way, the magnitude of $E_{\rm BS}$ represents the *binding* band structure energy among the atoms and is identically zero when all atoms are separated. Within the tight-binding approximation, the eigenvectors ψ_i are expanded in terms of localized, atomiclike basis functions ϕ_μ, $\psi_i = \sum_\mu c_\mu^i \phi_\mu$. The basis functions themselves are never explicitly defined; however, the electronic Hamiltonian matrix elements $\langle \phi_\mu | H_{el} | \phi_\nu \rangle$ are assumed to be of the general two-center Slater-Koster form.[17] Thus the matrix elements depend upon the spatial orientation between the two basis functions according to their symmetries. Their dependence upon the interatomic separation d is governed by a function whose form and magnitude are determined by fitting to experimental data or more rigorous theoretical calculations. We assume an orthornormal basis set $S_{\mu\nu} \equiv \langle \phi_\mu | \phi_\nu \rangle = \delta_{\mu\nu}$.

The last term on the right-hand side of Eq. (1) is a semiempirical "correction" for the double counting of electron-electron interactions in $E_{\rm BS}$ and also contains core-core interactions. $E_{\rm corr}$ is generally positive and serves to balance $E_{\rm BS}$, which is negative. In this work, we use a correction term of the general Chadi[18] type, where the correction energy is a sum of pairwise interatomic potentials

$$E_{\rm corr} = \frac{1}{2} \sum_{\substack{I,J \\ I \neq J}}^N V_{\rm corr}(d_{IJ}) \,. \qquad (3)$$

The forces on a given atom may then be calculated by taking the gradient of the total potential energy with respect to this atom's position. In TBMD, forces consist of two parts:[19] (i) a correction force, which is just the sum of two-body forces, and (ii) a band structure or Hellmann-Feynman force, which is a many-body force because of the many-body nature of $E_{\rm BS}$.

For the Si-Si interactions, the TB model of Goodwin, Skinner, and Pettifor[20] (GSP) was used. This model has been shown to provide a very good description of Si in various bulk phases, liquid Si,[21,22] and even intrinsic defects in c-Si.[23] For crystalline silicon, the TB parameters for this minimal sp^3 basis model are $\epsilon_p - \epsilon_s$ =8.295 eV, $V_{ss\sigma}(d_0) = -1.82$ eV, $V_{sp\sigma}(d_0)$ =1.96 eV, $V_{pp\sigma}(d_0)$ =3.06 eV, and $V_{pp\pi}(d_0) = -0.87$ eV. The hopping parameters $V_{ll'm}$ depend only upon the interatomic separation. In the GSP model, this distance dependence is given in terms of a scaling function f_s as

$$V_{ll'm}(d) = V_{ll'm}(d_0) \left(\frac{f_s(d)}{f_s(d_0)} \right)^2 \,, \qquad (4)$$

where

$$f_s(d) = \frac{1}{d} \exp[(d/d_s)^n] \,. \qquad (5)$$

Likewise, the interatomic correction potentials are defined as

$$V_{\rm corr}^{\rm Si-Si}(d) = V_{\rm corr}^{\rm Si-Si}(d_0) \left(\frac{f_s(d)}{f_s(d_0)} \right)^m \,. \qquad (6)$$

The remaining parameters of the GSP model have the following values: d_s = 3.67 Å, n = 6.48, m = 4.54, and $V_{\rm corr}^{\rm Si-Si}(d_0)$ = 3.4581 eV.

For use in MD supercell simulations, it is necessary to define a cutoff distance for the Si-Si interactions, beyond which the matrix elements and correction potentials rapidly vanish.[21] We acheived this by using a "cutoff" function of the form

$$f_c(d) = \{1 - \exp[(d - r_c)/s]\}^{-1} \,, \qquad (7)$$

by which the matrix elements and correction potentials are multiplied. The parameter r_c is the cutoff distance and s controls the sharpness of the truncation. We used the values r_c =3.6 Å and s =0.04 Å for the Si-Si interactions.

The GSP model defines only the difference between the Si self-energies ϵ_s and ϵ_p and not their absolute values. This is adequate for dealing with a homonuclear Si system, but to introduce hydrogen TB parameters, we must choose some energy reference. We have chosen this reference to be the vacuum (ϵ = 0), relative to which the top of the Si valence band is -5.1 eV.[24] This fixes the Si self-energies at $\epsilon_s = -11.64$ and $\epsilon_p = -3.34$ eV.

For the Si-H interactions, we use a Harrison-type $1/d^2$ distance dependence for the hopping parameters.[25] The

H atom was assumed to have one s orbital. The TB parameters were adjusted so as to reproduce the energies of the occupied molecular orbitals $a_1^+ = -18.20$ eV and $t_2^+ = -12.70$ eV and the E mode bond-bending vibrational frequency $\nu_E = 975.9\ \text{cm}^{-1}$ of the silane molecule SiH_4.[26] The H-H interactions were ignored, as the H-H distance in silane is 2.4 Å, and therefore much larger than the H_2 dimer bond length of 0.74 Å. This yields the following TB parameters: $\epsilon_h = -8.36$ eV, $V^{\text{Si-H}}_{ss\sigma}(d_0) = -4.02$ eV, and $V^{\text{Si-H}}_{sp\sigma}(d_0) = 5.52$ eV. The equilibrium Si-H bond length is $d_0 = 1.48$ Å in silane.

To obtain the correction potentials for the Si-H interactions, we followed the procedure used by Min *et al.*[27] Using the breathing mode distortion of silane, we define

$$V^{\text{Si-H}}_{\text{corr}}(d) = E^{\text{per bond}}_{\text{tot}}(d) - E^{\text{per bond}}_{\text{BS}}(d) \qquad (8)$$

where

$$E^{\text{per bond}}_{\text{tot}}(d) = -E_0\left(1+\frac{d-d_0}{l_s}\right)\exp\left(-\frac{(d-d_0)}{l_s}\right) . \qquad (9)$$

Equation (9) is called the "universal binding curve" and its minimum value $-E_0$ is determined from experiment to be -3.355 eV. The parameter l_s was adjusted so that the A_1 (breathing mode) vibrational frequency obtained from a low temperature ($T = 3$ K) MD simulation yielded the experimental value of 2187 cm^{-1}. With the $1/d^2$ distance dependence, it was necessary to cut off the Si-H matrix elements and correction potentials to prevent the unphysical overcoordination of H in the Si lattice. The cutoff function given in Eq. (7) was used with $r_c^{\text{Si-H}} = 2.0$ Å and $s = 0.10$ Å.

III. STATIC FEATURES OF OUR TB MODEL

Using the model as described above, a single H atom was introduced into a cubic supercell 10.86 Å wide containing 64 Si atoms, arranged in a diamond lattice with a lattice constant of 5.43 Å. (The 64 Si supercell was found to be adequate for determination of total energies and bond lengths. The results obtained with the 64 atom supercell were very similar to those obtained with 216 Si and 512 Si supercells.) The total number of valence electrons was fixed at 4×(number of Si atoms)+1×(number of H atoms), so that the entire supercell remained electrically neutral. For the calculation of E_{BS} and the Hellmann-Feynman forces, we used the Γ point ($\vec{k} = 0$) of the supercell, which is equivalent to sampling 32 points from the first Brillouin zone of diamond structure Si. The eigenvalues and eigenvectors were evaluated using direct diagonalization of the Hamiltonian matrix. To search for stable and metastable sites for the H atom, several MD simulations were performed in which the average temperature of the supercell was slowly decreased, via rescaling of the velocities, until all atoms were in positions of stable equilibrium. Using this "simulated annealing" technique and parameters thus far described, the global minimum for the H atom was found to be at the tetrahedral interstitial (T) site, which is inconsistent with experimental evidence and most theoretical calculations, as noted earlier.

Upon examining the contributions to the potential, we find that the Si-H correction term is responsible for repelling the H away from the Si atoms toward the T site, which is the largest void in the Si lattice. To make our model consistent with what is known of isolated H in Si, we thus decreased the strength of the Si-H correction potential by using a multiplicative factor χ. Shown in Fig. 1 is the total energy of a fully relaxed Si_{64}H_1 supercell for various hydrogen sites as a function of χ. The BC site becomes the global minimum at $\chi \sim 0.84$ and continues to decrease in energy as χ is lowered. For $\chi < 0.82$, we find that the H atom becomes so deeply trapped at the BC site as to prevent its migration even at high temperatures. We have chosen 0.83 as the optimum value of χ, which allows H migration while maintaining the BC site as the global minimum. Our value of χ is somewhat arbitrarily chosen, but chosen from a narrow range of physically meaningful values. In a phenomenological way, the parameter χ accounts for differences between the silane environment, from which the TB parameters and correction potentials were obtained, and the environment of the Si crystal. With $\chi = 0.83$, the model is optimized for H in c-Si, but when applied to silane, the Si-H bond is underestimated by 16% and the A_1 frequency is overestimated by 5%.

With the inclusion of χ into our Si-H model, the nature of the H potential energy surface in Si has changed dramatically. When H is placed at the center of a Si-Si bond and all atoms are relaxed so as to minimize the interatomic forces, the H remains at the bond center while the two nearest Si atoms relax outward forming two Si-H

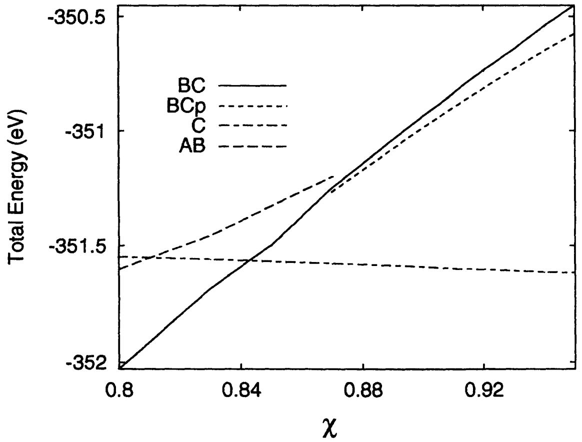

FIG. 1. The total energy of a Si_{64}H_1 supercell for different H sites and varying correction reduction factor χ. BC is the bond-centered site, BCp is a bond-centered site in which the H is displaced off the Si-H-Si axis, and C denotes a site near the center of a rhombus formed by three Si lattice sites and a tetrahedral interstitial site. The T (tetrahedral interstitial) site is nearly equivalent in energy to the C site and is not shown on the graph. AB is an "antibonding" site along the [111] direction, opposite a Si-Si bond. The range $0.82 < \chi < 0.84$ preserves the BC site as the global minimum while still allowing the H to migrate at elevated temperatures.

bonds 1.53 Å long. This site will be referred to as the BC site and has C_{3v} symmetry about the Si-H-Si axis. Of course, the BC site is now the global minimum, but not the only stable site for H. Nearly equivalent in energy to the BC site is an asymmetric BC site, wherein the H atom bonds more closely (1.25 Å) to one Si than to the other (2.04 Å). The existence of the asymmetric BC site was unanticipated during the construction of our Si-H TB model. The fact that it exists in addition to the symmetric BC site is a result of the delicate balance between repulsive (correction) and attractive (band structure) forces in the three center bonds. As noted in Sec. I, some researchers' calculations predict the symmetric BC site and others an asymmetric BC site. We regard the existence of the asymmetric BC site in our model as an artifact caused by cutting off the Si-H interactions at $r_c^{\text{Si-H}} = 2.0$ Å; increasing this cutoff distance eliminates the asymmetric BC site altogether while the symmetric BC site remains stable.

In addition to the BC region, there are two metastable configurations for H in our model. The "*C*" site, which lies close to the *C* site in the undistorted Si lattice, is 0.13 eV above the BC region. Here the H atom is very weakly bound to two Si atoms and lies just outside the cutoff distance from a third Si. The metastable site highest in energy is the "antibonding" or AB site and it is 0.22 eV above the BC region. In the AB configuration, the H atom is bonded to one Si atom at 1.44 Å, directly opposite a Si-Si bond, which is now weakened. This weakened bond, at 2.57 Å, is longer than the perfect Si-Si crystal bond of 2.35 Å.

The major features of the model are readily seen in the adiabatic H potential energy surface shown in Fig. 2. To generate this surface, the H atom was moved about in the (110) plane of the Si lattice. For each H position, the Si atoms were relaxed until all interatomic forces fell below a threshold of 0.1 eV/Å, which provides total energies converged to within ±0.05 eV. In the figure, one can clearly see the large potential wells that are associated with the BC sites. Although qualitatively similar to the *ab initio* potential energy surface calculated by Van de Walle *et al.*,[9] our BC region is much wider, due to the existence of the asymmetric BC sites in our model. The flatness of the BC region indicates that the three BC sites (one symmetric, two asymmetric) associated with a particular Si-Si bond are not separated by an appreciable energy barrier. The adiabatic reaction pathway between adjacent BC regions has a minimum barrier, located near the *C* site, of ~ 0.23 eV. The *C* sites are manifested as very small wells and the AB and *T* sites are very broad valleys.

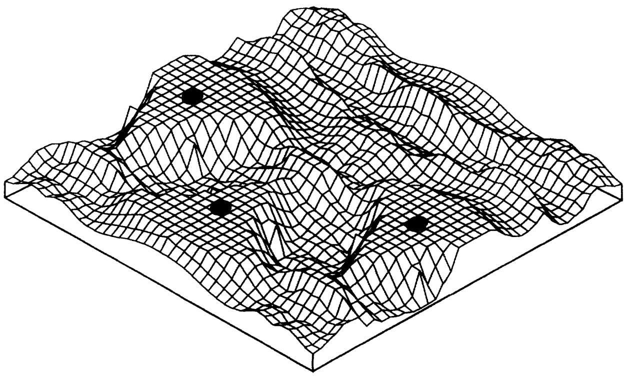

FIG. 2. The adiabatic potential energy surface for H in the (110) plane of the Si lattice. The perfect Si lattice sites are indicated by the dots. The energy surface has been cut off above $E_{BC} + 0.8$ eV.

Because the TB method is quantum mechanical, we may comment on the electronic structure of H in Si. For H at the BC site, our results are similar to the molecular orbital picture due to Fisch and Liccardello[28] and Cox and Symons.[29] The H *s* orbital and the Si-Si bond orbital form a bonding and antibonding pair of molecular orbitals. The bonding state lies below the valence band and is doubly occupied whereas the antibonding state lies in the conduction band and is therefore unoccupied. The remaining unpaired electron resides in a hostlike state just below the edge of the conduction band. (The calculation of accurate occupancy level positions is beyond the scope of this work because that would require a charge-state-dependent correction term.) As shown in Ref. 29, this arrangement is consistent with results of μSR experiments. Due to the similarities between the μSR and EPR hyperfine tensors,[5] this molecular orbital picture is also consistent with the EPR results mentioned earlier.

IV. SIMULATION DETAILS AND RESULTS

Using the Si-Si and Si-H interactions discussed in Secs. II and III, we have performed MD simulations using the $Si_{64}H_1$ supercell. For the integration of the equations of motion, the velocity form of the Verlet algorithm[30,31] was used with a time step of $\delta t = 0.35 \times 10^{-15}$ s. To calculate the electronic structure, direct diagonalization of the Hamiltonian matrix was used for each time step. The number of particles and the supercell volume were held constant and the total energy was conserved to within 0.02 eV over the course of the highest temperature simulation. Thus the simulations correspond to microcanonical (N, V, E) ensembles. The temperatures reported represent time-averaged temperatures, as the instantaneous temperature fluctuates about this mean value in a microcanonical ensemble. To prepare the diffusion simulations, the Si atoms were placed at their perfect lattice sites and the H was placed at a tetrahedral interstitial site. The particles were given speeds corresponding to a Boltzmann distribution at the target temperature. After short initial simulations of 2000–5000 time steps, required to achieve stable mean temperatures, data were taken. To implement the simulations, IBM RS6000 (models 340 and 350) workstations were used. The longest simulations (~ 120 000 time steps) took approximately 14 CPU days.

From the trajectory of the H atom, we may calculate a hydrogen diffusion constant by using the Einstein relation

$$D = \lim_{\tau \to \infty} \langle |\vec{R}(t+\tau) - \vec{R}(t)|^2 \rangle / 6\tau \, . \tag{10}$$

Of course, the infinite time limit must be approximated by the limit $\tau \to \tau_{\rm max}$, $\tau_{\rm max}$ being the total simulation time. In practice, the above expression gives unreliable results, in that one is looking at the trajectory of just one atom. It is possible for this one atom to eventually approach its original position, making the $\tau \to \tau_{\rm max}$ limit essentially zero. We therefore take the diffusion constant to be the statistically weighted average

$$D_{\rm av} = \frac{1}{M} \sum_{\tau_{\rm min}}^{\tau_{\rm max}} \frac{1}{6\tau} \sum_{t=0}^{\tau_{\rm max}-\tau} |\vec{R}(t+\tau) - \vec{R}(t)|^2 . \qquad (11)$$

M, the total number of data points, is simply equal to the sum from $\tau = \tau_{\rm min}$ to $\tau_{\rm max}$ of the quantity $(\tau_{\rm max} - \tau)/\Delta\tau$. The data were recorded every fifth time step, so that $\Delta\tau = 5\delta t$. The equation above weights smaller values of τ more heavily because there are more time origins t contained in the second summation than there are for large values of τ. The statisically insignificant values of D for $\tau \sim \tau_{\rm max}$ thus do not affect $D_{\rm av}$ very much. The average is begun at $\tau_{\rm min}$ =1 ps so as to avoid averaging over very short portions of the H trajectory, which contain no information about the long-time diffusive processes.

To estimate the diffusion curve for H^0 in Si, ten simulations were performed in the temperature range of 1047 to 2003 K. The data are shown in Fig. 3. Using a least-squares fit to the semilogarithmic data, we obtain the following Arrhenius curve:

$$D = 6.91 \times 10^{-3} \exp(-0.45\ {\rm eV/kT})\ {\rm cm^2/s} . \qquad (12)$$

Our value of E_a =0.45 eV for the activation energy is in good agreement with the experimental result of 0.48±0.05 eV due to Van Wieringen and Warmoltz,[32] which is the only diffusion data available for elevated temperatures. Buda *et al.*[15] obtained a value of $E_a = 0.33 \pm 0.25$ eV in *ab initio* MD simulations of H^+ in Si. Although their data indicate a greater mobility than either the present study or experiment, diffusion in the real material would likely be hindered by the trapping of H^+ at defects such as acceptors. (See Fig. 3.) Our smaller mobilities are due to a larger effective cross section of the BC site as a trap for the migrating H atom.

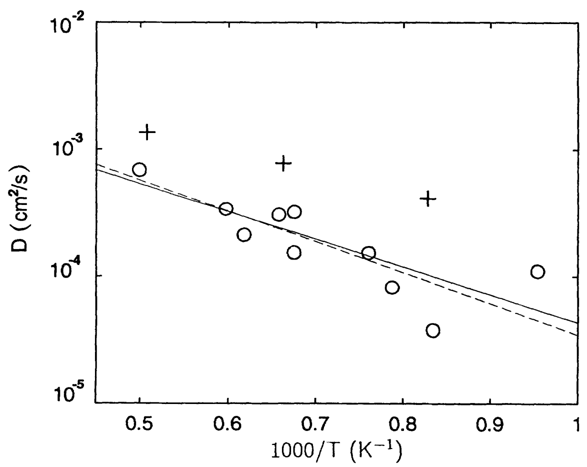

FIG. 3. Our data are indicated by the circles and the Arrhenius fit to our data is shown as a solid line. The experimental curve from Ref. 32 is shown as a dashed line. The crosses are MD simulation data for H^+ from Ref. 15.

It is important to note that in both the present work and that of Buda *et al.*, the activation energies obtained by MD simulation are larger than those obtained adiabatically, which were, for Buda *et al.*, < 0.2 eV and, for the present work, 0.23 eV. This should be expected because, while the adiabatic potential energy surface provides one with the lowest energy barrier for H diffusion, those reaction pathways are very unlikely dynamically because they require significant Si relaxation and the heavier Si atoms cannot be expected to follow adiabatically the motion of the lighter H atom. The effective dynamic activation energy will therefore be greater than that obtained adiabatically. In both the work of Buda *et al.* and the present study, the activation energy represents, as it should in the real crystal, an average of the barriers associated with various different paths that the H atom takes while diffusing. Our simulations indicate that the H atom spends the majority of its time trapped at BC sites and relatively little time in the interstitial regions. It has been suggested[15] that scattering experiments may provide information about the average local environment of the H atom. Our results indicate that this environment would be predominantly BC in character, even at elevated temperatures.

The most remarkable capability of MD simulations is their ability to elucidate the correlated motions of the individual atoms. Looking at the H trajectories in Fig. 4, one can see that the H atom traverses the interstitial regions of the crystal very rapidly, but is very easily "trapped" at a BC site, where it may remain for several picoseconds at lower T (~ 1000 K). This behavior raises a question: If the Si atoms must relax substantially for H to be stable at the BC site, should we expect them to do so adiabatically? To answer this, we analyzed some trapping and detrapping "events" that occurred during our simulations. At T ~ 1000 K, a typical Si-Si bond may stretch up to 2.60 Å while oscillating about its equilibrium value of 2.35 Å. Dynamically, one might expect that the light H would have to wait for the heavier Si atoms to separate themselves, opening a "doorway"[34] through which the H may enter the BC region. Within our model, however, the BC region becomes a stable site for H only at Si-Si separations of 2.85 Å or larger. Therefore, such

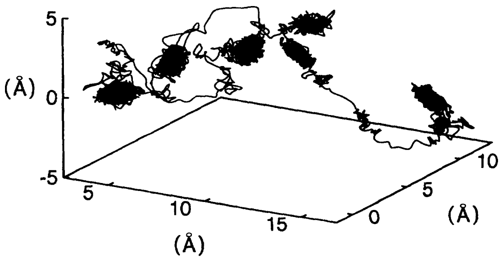

FIG. 4. A H trajectory for our simulation at T =1050 K. The jumplike nature of the H motion can clearly be seen; the H spends most of its time trapped at BC sites (the dense, globular structures in the graph), but traverses the interstitial regions quickly. For clarity, the Si atoms are not shown. The total time encompassing the graph is 34.65 ps.

doorways would be too rare, even at elevated temperatures, to account for the frequency of H trappings.

We find that while moving through the interstitial regions, the H can easily form a bond with a single Si atom. Because very little Si relaxation is needed for this binding to take place, it can occur almost instantaneously. The resulting configuration is similar to the AB site described earlier, although the H atom need not be on a ⟨111⟩ axis. Thus the H is one fold coordinated, but does not intrude upon a Si-Si bond. This configuration, which I will refer to as the "precursor" site, is therefore distinctly different from the asymmetric BC site described earlier. Recall that within our model a configuration such as the AB or precursor site leads to the weakening of an adjacent Si-Si bond, which then begins to lengthen. Assisted by thermal vibrations, this weakened Si-Si bond can easily stretch enough so as to allow the H atom to enter the BC region which, due to the Si-Si relaxation, is now favorable energetically. It is the precursor site which allows the H to be trapped so effectively at the BC site. In a manner of speaking, the Si-Si doorway must still be opened before the H can occupy a BC site, but the H atom itself possesses the key to that door.

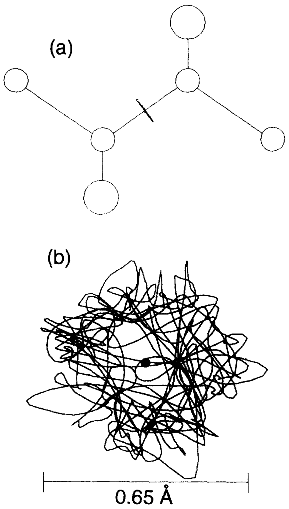

FIG. 5. The trajectory of H at the symmetric BC site at $T = 3$ K. (a) A view perpendicular to the Si-H-Si bond [the page lies in a (110) plane] showing that the H trajectory is confined to a thin disk which is centered on the bond and perpendicular to it. The Si atoms are shown as circles at their perfect lattice sites, although they were allowed to move during the simulation. (b) A view along the bond axis; the Si atoms are not shown. The dot in the center indicates the position of the bond axis.

V. VIBRATIONAL FREQUENCIES

The vibrational frequencies for atoms in an MD simulation may be easily obtained by Fourier transforming the velocity-velocity autocorrelation function.[30] For H at the symmetric BC site, a simulation was performed at $T=3$ K and the Si-H bond stretching frequency ν_S was found to be 1291 cm^{-1}. (The vibrational spectrum for the symmetric BC site at 300 K yields $\nu_s \sim 1285$ cm^{-1}, although this is a much noisier spectrum than that obtained at 3 K. We therefore limited our vibrational studies to low temperatures, where the frequencies can be determined with more accuracy.) This frequency depends weakly upon the parameter χ, ranging from 1240 to 1330 cm^{-1} for the entire range of physically meaningful values, $\chi = 0.82$ to $\chi = 0.84$. This value of ν_S is significantly lower than the value of 1945 cm^{-1} calculated by Van de Walle *et al.*,[9] but higher than that calculated by others.[11,13] Experimentally, an ir absorption band near 1990 cm^{-1} is one likely candidate for ν_S, but this has not been positively identified.

The H vibration perpendicular to the Si-H-Si bond (a "wagging" mode) is very erratic, as can be seen in Fig. 5. Consequently, we could not determine a particular dynamical frequency ν_W for the H transverse motion, only a broad band in the 50 to 100 cm^{-1} range. This frequency range is extremely low for such a light atom as H. There has been speculation,[33] based on low frequency sidebands which appear in the H-Al ir spectrum of Si, that hydrogen does indeed have a very soft wagging mode frequency when in such bond-centered configurations.

Both the stretching and wagging frequencies calculated using full MD (all atoms freely vibrating) differ from those obtained by holding the Si atoms fixed at their relaxed sites and allowing only the H atom to freely vibrate with an average kinetic energy corresponding to a temperature of 3 K. We label such frequencies as MD* and they are listed in Table I. The origin of the H atom's errant behavior in the transverse mode can now be understood to be a result of the thermal motions of the nearby Si atoms. In our model, the potential energy surface for H motion perpendicular to the bond is not only very flat, but also strongly affected by even small displacements of the nearest neighbor Si atoms. The thermal motion of the Si atoms at $T = 3$ K is sufficient to smear the transverse frequencies.

The Si-H bond stretching mode is nearly harmonic, as indicated by the near equivalence of the MD* frequencies and those obtained using a harmonic approximation (labeled SO in Table I). For all H isotopes, there is a clear increase in the stretching frequency when the Si atoms are allowed to move. The Si motion leads to an effective mass of the H defect which is slightly smaller than the mass of H itself.

TABLE I. Calculated vibrational frequencies for H at the symmetric BC site. SO are harmonic approximation (small oscillation) frequencies for H with the Si atoms fixed at their relaxed positions. Those labeled MD* also have the Si atoms fixed but the H moves freely. MD indicates full molecular dynamics with all atoms freely moving.

	Frequencies (cm^{-1})					
	Stretching			Wagging		
Isotope	SO	MD	MD*	SO	MD	MD*
^{1}H	1283	1291	1282	103		110
^{2}H	907	915	906	73		78
^{3}H	740	752	740	60		64

VI. DISCUSSION

The proposed diffusion mechanism is one in which the H atom plays a very active role in creating its own stable interstitial environment. Such behavior may help to explain the formation of H-induced defects.[1–3] The qualitative features of this mechanism, a metastable onefold coordinated H defect and the corresponding weakening of adjacent Si-Si bonds, remain intact for a large range of parameter values. We therefore expect that the mechanism is at least qualitatively valid, but may be augmented by charge-state effects, which were not included in this study.

From the isotope shifts of the stretching frequency, we can clearly see that the lattice is participating in the defect motion as though it has a rather large "equivalent" mass. (That is, the defect's effective mass is nearly that of the H isotope alone.) Such effects have been seen in the spectra of other light atom impurities.[35] In Fig. 5, we see that the H atom is often off axis, where the "force constant" for the bond stretching motion may be slightly different than that for an on-axis H atom. Such thermal motion tends to broaden the spectrum for the Si-H stretching mode. Also, the frequency resolution of our MD spectra, being inversely proportional to the total simulation time, is roughly $\pm 0.5\ \text{cm}^{-1}$. An accurate determination of the "equivalent lattice mass" and an understanding of its origin require much higher frequency resolution and a careful consideration of thermal effects. This is a possible future application of the methods presented herein. Also, we hope that other total energy methods will be applied to this problem. Likewise, further experimental information regarding the vibrational behavior of H at the BC site would be of great help.

As this work is a preliminary study on the use of TB for MD simulations of defects, we used a very simple empirical TB approach. Our goal was not the basic development of TB methods. As stated in Sec. III, our Si-H model lacks some transferability in that it cannot simultaneously provide an accurate description of both silane and H in the Si lattice. This lack of transferability stems from the simplicity of our phenomenological model. We determined most of the parameters of our model from the energy levels and vibrational frequencies of silane, which are accurately known, and used the primarily qualitative information on H in Si to further refine our empirical model through the use of the correction energy reduction factor χ. Although more sophisticated environment-dependent correction potentials could be envisioned, one would need more detailed experimental data regarding H in Si to obtain parameters for such potentials. There is ongoing research into improving the transferability of TB methods,[36–38] and such improvements will undoubtedly lead to the use of TB for MD simulations of many other defects. Though simple, the TB models used here nevertheless provided us with a very computationally efficient means of obtaining a quantum-mechanical total energy which is in good agreement with accurate local density pseudopotential (LDA) calculations on H in *c*-Si. This efficiency allows one to perform MD simulations of systems of ~ 100 atoms on desktop workstations rather than the supercomputers needed for the more rigorous LDA MD simulations. This makes TB methods attractive especially for larger systems, longer simulation times, and isotopic studies.

VII. SUMMARY

In summary, we have presented results of semiempirical tight-binding molecular-dynamics simulations of neutral H in crystalline Si. Several high-temperature simulations in the temperature range of 1050 to 2000 K yield a diffusion curve in good agreement with experiment. The dynamic H migration paths seen in these simulations are significantly different from that which might be inferred from a zero-temperature adiabatic calculation. This concurs with the local density pseudopotential molecular dynamics simulations of H^+ in Si performed by Buda *et al.* In contrast to their work on H^+, we find that H^0 can be easily trapped at the bond-centered site, even at high temperatures. This trapping occurs as a result of a metastable onefold coordinated H configuration which weakens the adjacent Si-Si bonds, allowing the H to slowly enter the bond-centered site. From simulations performed at low temperature, vibrational frequencies for H at the BC site were calculated. The effects of both H isotopic substitution and Si motion on these frequencies were discussed. One positive aspect of a MD approach is that such effects are included in a natural, direct way.

ACKNOWLEDGMENT

This work has been supported by the Office of Naval Research under Contract No. N00014-89-J1223.

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