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Transferable tight-binding model for Si-H systems

Qiming Li and R. Biswas
Microelectronics Research Center and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011

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We develop a tight-binding molecular-dynamics model for Si-H systems that incorporates relevant physics of charge-transfer and local-environment dependence of atomic interactions. Our model was fitted to silane, and yields electronic levels of disilane in good agreement with experiment and vibrational frequencies that are consistent with the experimental trend for SiH_n groups. The model describes well the formation energies and energy surfaces for the different charge states of H in *c*-Si, including the stability of the bond-centered site for positive and neutral charge states and the stability of the tetrahedral site for negative charge states. The model also describes well the structural and electronic properties of *a*-Si:H models. The present approach utilizes quantum-mechanical forces, incorporates important electronic effects, and is suitable for studying complex phenomena such as H diffusion and dynamics of *c*-Si or *a*-Si:H.

I. INTRODUCTION

It is well recognized that the presence of hydrogen strongly affects the electronic and optical properties of semiconductor microelectronic materials.[1] In crystalline silicon, hydrogen is a common impurity that is known to passivate the electrical activity of shallow dopants. On the other hand, in amorphous silicon a significant amount of H is necessary to passivate defects and produce electronic quality material with a high photoconductivity and low density of gap states. Porous silicon is another recent application where a large amount of H is also present and needed to increase luminescence efficiencies.[2] Many of these interesting phenomena, however, are not well understood.

The behavior of hydrogen in crystalline semiconductors has recently been understood by the pioneering calculations of Van de Walle *et al.*[3] who, using first-principles calculations, predicted that the stable position of H in *c*-Si depended on the charge state, with the tetrahedral (T) site being most stable for the negative charge state (n-type Si) and the bond-centered (BC) site being the stable state for the neutral and positive charge states (p-type Si). These and other similar calculations[6] incorporating H-dopant complexes have described well the passivation of dopants in Si by H and support the large body of experimental evidence in these systems.[4–6]

While such first-principles calculations have been very successful for predicting the properties of H in crystalline systems, there are a large variety of complex systems such as amorphous hydrogenated silicon (*a*-Si:H) or porous silicon where first-principles calculations are exceedingly difficult and virtually not feasible for large systems (i.e., hundreds of atoms). Problems in these complex systems include long-range H diffusion,[6] the nature of light-induced defects in *a*-Si:H,[7–9] the growth of realistic *a*-Si:H films, and the origin of the band gap in porous silicon. For such complex systems it is necessary to develop more robust methods that are computationally less intensive but contain the essential physics such that reliable information can be obtained.

Classical molecular dynamics (MD) with either two- and three-body potentials[10,11] or many-body potentials[12] have been developed for Si-H systems,[9,13–15] and used for computationally intensive molecular-dynamics simulations. However classical molecular dynamics cannot address purely quantum-mechanical phenomena involving electronic states, such as Jahn-Teller distortion or defect states in semiconductors.[1] A very promising simulation approach is the tight-binding (TB) method[16–18] which is intermediate between first-principles[19–21] and classical molecular-dynamics methods in the level of sophistication, and which contains the important aspects of the electronic properties.

Tight-binding molecular dynamics (TBMD) has emerged as a very robust method for simulating properties of pure C as well as Si systems. Recent successes include modeling properties of fullerenes[22] and development of models for Si (Ref. 23) which have shown promise in modeling the bulk phases and melting of silicon. These TB models for Si were based on the minimal sp^3 orbital basis set to model the electronic properties, and utilize quantum-mechanical forces in the molecular-dynamics simulation.

Previous TB approaches for Si-H systems by Allen and Mele[24] and subsequently an improved TB model of hydrogen silicon interaction by Min *et al.*,[25] both utilizing an s-orbital for H, were successful in describing silane and the lattice dynamics and structural properties of an H-covered Si(111) surface. We would expect a Si-H model to not only describe well the strong Si-H bonds but to also quantitatively describe the energy of weakly bonded H in *c*-Si, if it is to be reliable in simulating more complex systems such as *a*-Si:H. However, the simple extensions of previous TB models do not account for several important features of H in *c*-Si, especially the formation energies and energy surfaces for different charge states of H in *c*-Si.

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In this paper, we develop a tight-binding model for Si-H that is suitable for studying formation energies of H in *c*-Si including the dependence on the charge states of H, and for hydrogenated amorphous silicon systems. Our starting point is our recently developed Si tight-binding model.[23] While the basic strategy is to use experimental data and first-principles calculations to fit the Si-H parameters, we found that the simple sp^3 tight-binding formulation does not model properties of H interstitials in *c*-Si well. We introduce terms to represent the physics of charge transfer and the dependence of H-Si interactions on the atomic environment. With these new pieces of physics, the formation energy of H at different locations in the crystalline silicon lattice qualitatively agrees with first-principles calculations, including the predicted stability of bond-centered H for H^+, and H^0, and the *T*-site for H^-. We also calculated the pair correlation function and bond angle distributions for hydrogenated amorphous Si configurations. The model describes well the structure and electronic properties of *a*-Si:H. Our tight-binding model will be presented in Sec. II along with results for simple Si-H molecules (silane, disilane) and the vibrational frequencies of SiH_n groups. In Sec. III, we present our results for the formation energy of H in *c*-Si. Properties of hydrogenated amorphous silicon networks with our new TB model are described in Sec. IV. Conclusions and discussions are given in Sec. V.

II. TIGHT-BINDING MODEL FOR HYDROGEN SILICON INTERACTIONS

In the tight-binding molecular-dynamics scheme,[18] the motion of atoms is described by the Hamiltonian

$$H_0 = \sum_{i\alpha} \frac{P_{i\alpha}^2}{2m_{i\alpha}} + \sum_{n}^{\mathrm{occ}} \langle \psi_n | H_{\mathrm{TB}} | \psi_n \rangle + E_{\mathrm{rep}} + \sum_{\alpha} N_\alpha E_{0\alpha}. \tag{1}$$

The first term is the kinetic energy of the atoms, the second term (E_{TB}) is the electronic energy usually calculated by summing up the eigenvalues of all occupied states of H_{TB}, the third term is the repulsive potential representing the ion-ion interaction and correcting for the double counting of the electron-electron interaction of the second term. E_0 is a constant energy shift. α denotes the type of atom (indexed by i). All the electronic information is contained in the tight-binding Hamiltonian H_{TB} with a minimal basis set. The construction of the tight-binding parameters and their distance dependence is an art and involves judicious *a priori* experience. Once the tight-binding parameters are known, the repulsive energy can be obtained by subtracting the band energy E_{TB} from the total energy of a system for which the first-principles results are available. The classical dynamics of the system is simulated from integrating Newton's equations of motion. The quantum-mechanical contribution to the atomic force is evaluated via the Hellmann-Feymann theorem with eigenfunctions obtained by direct diagonalization. The TBMD is a simplification of the *ab initio* Car-Parrinello approach and incorporates the most important aspects of the electronic and atomic interactions.

For Si-H systems, there are three types of interactions: Si-Si, Si-H, and H-H. We have neglected H-H interactions in this study as the H-H distance in systems of interest here is much larger than the H_2 molecule bond distance of 0.74 Å. We start with the previously developed transferable tight-binding model of Si-Si interactions with the parametrization described in detail in Ref. 23. That model describes well the total energies of different bulk crystalline Si structures, elastic constants, and formation energies of vacancies and interstitials in *c*-Si, as well as the melting of Si and the short-range order in liquid silicon.[23,26] Two primary features of the model are the Goodwin-Skinner-Pettifor (GSP) short-range scaling functions[27] for the tight-binding hopping parameters and the embedded atom type of approach to the repulsive potential. Specifically, all the overlap integrals h_α scale as

$$h_\alpha(r) = h_\alpha(r_0) \left(\frac{r_0}{r}\right)^n \exp\left\{ -n \left[\left(\frac{r}{r_c^\alpha}\right)^{n_c^\alpha} - \left(\frac{r_0}{r_c^\alpha}\right)^{n_c^\alpha} \right] \right\}, \tag{2}$$

where α denotes the four tight-binding overlaps ($ss\sigma$, $sp\sigma$, $pp\sigma$, and $pp\pi$). The large value of the exponents n_c^α guarantees a short-range interaction that is numerically advantageous for molecular-dynamics simulations. The second important feature of the Si model is that the total repulsive interaction of an atom with all other atoms in the system is a nonlinear function of the sum of the repulsive pair potentials between that atom and its neighbors, i.e.,

$$E_{\mathrm{rep}} = \sum_i F\left(\sum_j \phi(r_{ij}) \right), \tag{3}$$

where $\phi(r_{ij})$ is the repulsive pair potential between atoms i and j that also has the GSP scaling form. F is a fitted function with a polynomial form. This way of constructing the total repulsive potential is analogous to the embedded atom approach where the contribution of one atom to the total energy is a nonlinear function of the local properties of the atom. Similar expressions have also been used in recent TB models of carbon.[18] It turns out that the second feature has nontrivial consequences when multicomponent systems are concerned, because the total repulsive energy is now no longer the sum of the pair potentials and depends on the partitioning of the pair potentials between the individual species, an aspect that will be discussed later.

To formulate the Si-H interaction, we first follow the approach of earlier workers.[24,25] In these approaches, only the s orbital of H is considered, resulting in two overlap integrals between Si and H, $V_{ss\sigma}^{\mathrm{SiH}}$ and $V_{sp\sigma}^{\mathrm{SiH}}$. The three electronic parameters consisting of the hydrogen s orbital energy, E_s^{H}, and the magnitude of the two overlap integrals (at the Si-H bond length) are determined by fitting the two occupied eigenvalues (−18.2 eV and −12.7 eV) and the symmetric bending mode (ω_a = 976 cm^{-1}) of the silane (SiH_4) molecule. We then assume the distance dependence of the TB overlaps is given by Harrison's $1/r^2$ scaling,[17] truncated by a cutoff function beyond 2.40 Å. The pair repulsion energy $\phi^{\text{Si-H}}(r)$ is then obtained by subtracting the electronic energy of silane from the universal binding curve,[25,28]

$$\phi^{\text{Si-H}}(r) = \tfrac{1}{4}[E_{\text{tot}}(r) - E_{\text{band}}(r)].$$

The curvature of the binding energy at the equilibrium position of r_0 = 1.48 Å determines the vibrational frequency of the symmetric stretching mode of silane. Following Min *et al.*[25] the curvature of the universal curve is chosen such that the symmetric stretching frequency from a frozen phonon calculation is 40 cm^{-1} (5 meV) higher than the experimental value of ω = 2189 cm^{-1} to compensate for the overestimation of vibrational frequencies by frozen phonon calculations due to the light mass of the hydrogen atom. This simple extension of the previous tight-binding approaches used for group IV elements (Si and C) produces good results on the energy levels and vibrational frequencies of the disilane molecule and hydrogenated Si(111) surfaces. However, we found it is not sufficient to describe the formation energy of H in *c*-Si. For example, only in the positive charge state, the BC site is found to be lower in energy than the T site (by about 0.4 eV compared with 1 eV from *ab initio*). A more serious problem, however, is that the antibonding site is found to be much lower in energy than both the BC site and the T site. These are in contrast to the conclusions from *ab initio* calculations[3] that established BC sites as the global energy minimum for both the positive and neutral charge states and the T site the stable configuration in the negative charge states, in agreement with experiment.

The aforementioned problems may be traced to two deficiencies of the simple tight-binding approach. One of the deficiencies relates to the simple fact that charge transfer is not correctly described within the tight-binding formalism and it is also absent from the data base from which the tight-binding model is constructed. However, the T site configuration involves large charge transfer because the H *s*-orbital energy is in the valence band of the Si and, therefore, hydrogen tends to be doubly occupied. Clearly such charge transfer should be penalized due to electron-electron interaction. To correctly describe the physics of charge transfer, we introduce a Hubbard term on the H atom,

$$H_U = \tfrac{1}{2}U(n - n_0)^2, \tag{4}$$

where $n_0 = 1$. The resulting energy expression is

$$H = H_0 + \frac{1}{2}U\sum_i^{\text{H}}(n_i - n_0)^2. \tag{5}$$

In this work, we treat H_U within the Hartree approximation. The *s*-orbital energy of H is shifted by an amount proportional to the hydrogen charge. The charge is calculated self-consistently through an iteration by taking the output from the previous iteration step as an input for the next step. This increases the computer time for MD simulation by a factor equal to the average number of iterations required to achieve the desired accuracy. In practice, only three iterations are needed in relaxation calculations. For MD simulations, the self-consistent loop may not be required except at the beginning of the simulation since the charge difference between two consecutive MD steps is small in general. The value of U will be treated as a parameter. We find the choice U = 1.5 eV, in conjunction with other parameters, produces reasonable energy differences between the T site and the BC site.

The second deficiency has to do with a more general problem of the standard tight-binding approach. In the simplest form, the tight-binding overlap integral is only a simple function of the local environment that depends on the bond lengths of the neighbor pairs, independent of the local environment. Physically, if a H atom approaches an already four coordinated silicon atom, the H-Si overlap interaction should be much weaker than that in a H-Si bond. Without the weakening of the H-Si interaction, the antibonding (AB) site is the lowest energy for the H-interstitial in *c*-Si. The lack of information on the existing bonding structure of the neighbor atoms in the simple tight-binding model tends to produce overbonded structures, for example, during quenching. The previously developed Si TB model favors four coordination when only Si is present. To represent the favored four-coordinated bonding nature of the Si when Si-H bonding is present, we introduce local-environment dependence of the tight-binding overlap integral

$$h_\alpha(r_{ij}) = h_0\left(\frac{r_0}{r_{ij}}\right)^2 f\left(\sum_k g(r_{jk})\right), \tag{6}$$

where i represents H and j Si, and $f(b)$ is a monotonically decreasing function that smoothly varies from one at small b (i.e., $b < 4$), to zero for $b > 5$. g is a bond counting function that counts the contribution to the overall coordination from each neighbor, recognizing that the weak bonds should contribute less than the normal bond. For simplicity we choose the Fermi distribution functions for g,

$$g(b) = \frac{1}{1 + \exp(\frac{r - r_b}{\Delta r})}, \tag{7}$$

where r_b is the cutoff distance for nearest neighbor bond counting and Δr represent a smoothing range. We use r_b = 2.9 Å, Δr = 0.2 Å and r_b = 2.3 Å, Δr = 0.1 Å, for Si-Si bonds and Si-H bonds, respectively. In this work, the function $f(b)$ is chosen to be

$$f(b) = \begin{cases} 1 & \text{for } b < 4 \\ \frac{1}{2} + \frac{1}{2}\cos((b-4)\pi) & \text{for } 4 \le b \le 5 \\ 0 & \text{otherwise.} \end{cases} \tag{8}$$

We have verified that the results are relatively insensitive to small changes in the parameters used in defining the f and g functions. Such a choice does not mean a

TABLE I. Tight-binding parameters for Si-H interactions.

E_s^{H}	$V_{ss\sigma}^{\text{SiH}}$	$V_{sp\sigma}^{\text{SiH}}$	n	n_c	c	U
−8.33 eV	−3.554 eV	4.46 eV	2	0	0.1	0.75 eV

five-coordinated configuration is not possible, but if such a configuration exists, it has to be energetically less favorable. Our approach here resembles the classical MD model of Tersoff,[12] in which the attractive part of the pair potential associated with bonding is a monotonically decreasing function of the coordination. An alternative approach[29] proposed recently takes local environments into account by varying the local orbital energies with local configuration, rather than the overlap integrals. In this alternate approach[29] the extra H atom approaching an already four-coordinated Si atom would increase the orbital energies of both the H and Si atom more than the energy lowering from the H-Si bonding interaction, leading to an effective repulsion between the H and Si.

As remarked earlier, the repulsive energy is a nonlinear function of the Si-Si pair potential [Eq. (3)] and when Si-H interactions are included it is ambiguous as to how much of the Si-H pair potential is to be included in the operand of Eq. (3). To be consistent with the spirit of that approach, we have partitioned the Si-H repulsive pair potential into two parts. A fraction c of ϕ^{SiH} is added to the summation of Eq. (3). The rest is classified as belonging to the H atoms. The total repulsive potential now becomes

$$E_{\text{rep}} = \sum_i F\left(\sum_j^{\text{Si}} \phi^{\text{Si-Si}}(r_{ij}) + c\sum_k^{\text{H}} \phi^{\text{Si-H}}(r_{ki})\right) + (1-c)\sum_k^{\text{H}}\sum_i^{\text{Si}} \phi^{\text{Si-H}}(r_{ik}), \tag{9}$$

where i and j represent Si atoms and k the H atoms.

After incorporating these new physical effects, we find that the new tight-binding model is able to correctly describe the formation energy of H in c-Si for the different charge states as will be discussed in the following section. Our choice of parameters is summarized in Table I. We first show results for the disilane molecule (Table II) and for small Si-H clusters with different polyhydride groups (Table III). Since the model was fitted to silane, the electronic levels and vibrational frequencies of disilane are a natural test and are shown in Table II, together with experimental values and results of previous TB models. The present calculation agrees within 3% of the experimental electronic levels typical of the other tight-binding models. Notably, the energy level of the highest filled state a_g agrees better than previous TB models. Correcting the 40 cm^{-1} overestimate from the frozen phonon calculation, the stretching frequencies are in good agreement with experiment.

TABLE II. Eigenvalues (in eV) and the vibrational frequencies (in cm^{-1}) of disilane molecules, Si_2H_6.

	Experiment[a,b]	Allan and Mele[c]	Min *et al.*[d]	Present calculation
a_g	-10.7	-10.93	-11.07	-10.50
e_g	-12.1	-12.38	-12.28	-12.44
e_u	-13.3	-12.85	-13.23	-13.26
a_u	-17.3	-17.27	-16.65	-16.82
a_g		-19.18	-18.71	-18.70
Stretch	2152		2226	2225
Bend	909			791
Wag	379–625			415

[a] See K. C. Pandey, Phys. Rev. B **14**, 1557 (1976).
[b] See Ref. 35.
[c] See Ref. 24.
[d] See Ref. 25.

TABLE III. Vibrational frequencies of SiH_n (in cm^{-1}) using finite cluster calculations. Calculated values are shown in parentheses while experimental values in upper rows. With the consideration of zero point motion, the calculated stretching frequency should decrease by about 40 cm^{-1}.

SiH	stretch	bend			
(r = 1.477 Å)	2080	630		⟵	expt.[a]
	(2107)	(548)		⟵	(present calculation)
SiH_2	stretch	bend	roll	twist	rock
(r = 1.471 Å)	2128	877	625–720	655	380
	(2184)	(874)	(752)	(754)	(298)
SiH_3	stretch	bend	wag		
(r = 1.469 Å)	2187	876	502		
	(2204)	(756)	(418)		

[a] See Ref. 33.

The calculated frequencies of SiH_n species obtained from finite Si-H clusters, $Si_{13}H$, Si_9H_2, and Si_5H_3 for $n = 1, 2, 3$, respectively are shown in Table III. In these calculations the Si atoms are fixed in the diamond configuration and only H is allowed to relax. Clearly the experimental stiffening of the SiH stretching frequency from the monohydride, dihydride, and trihydride species is reproduced, although all stretching frequencies are slightly higher than experiment. The Si-H bond gets stronger in the polyhydrides, as indicated by progressively shorter SiH bond lengths. Although the bending frequencies are somewhat low compared with experiment, the overall agreement is satisfactory, and the ordering of the different SiH_2 and SiH_3 modes agrees well with experimental trends.

III. INTERSTITIAL H IN c-Si

The formation energy of H in c-Si for different charge states has been performed with a single H interstitial atom in a crystalline silicon supercell. Supercell sizes of 64 and 216 Si atoms have been investigated. The H position in this supercell is fixed and all the Si atoms except those at the outermost shell are then relaxed with a steepest-decent algorithm. The positive and negative charge states of H correspond to removing one electron from and adding one electron to the neutral system, respectively. The relaxation is usually achieved when the force on each atom is less than 9.2×10^{-12} N, typically within 40 steps. We find that the BC site is the global energy minimum for H^+ and H^0 while the T site is the stable site for H^-, in agreement with the *ab initio* calculation of Van de Walle *et al.*[3] Relaxation of the host lattice around the impurity is essential to accommodate the hydrogen atom at the BC site and other high charge density sites. For the H^+ BC site, the two Si atoms symmetrically relax outward to reach an equilibrium distance of 1.65 Å from the hydrogen atom in good agreement with the *ab initio* value of 1.60 Å.[3] The large strain energy is compensated by the energy gain in forming the Si-H-Si three centered bond, which lowers the energy of the bonding state.[31,32,34] As found in the *ab initio* calculations, the three centered configuration also creates an antibonding state just below the conduction band (about 0.2 eV with respect to the bottom of the conduction band for the 64 Si atom supercell). This state is empty, singly occupied, and doubly occupied in H^+, H^0, and H^-, respectively. This difference in the occupation of electronic states results in somewhat different relaxations of the lattice, but the differences in the overall equilibrium structures are minor. We note that the charge on the hydrogen atom in the BC site is almost neutral in all three charge states. The removed or added charge actually involves the valence electrons of the Si atoms.

At the T site, the H atom only weakly interacts with the host lattice owing to the large distance of about 2.36 Å before the relaxation and about 2.47 Å after the relaxation. The state created by H lies within the valence band and H is almost doubly occupied, in all three charge states. Again the removed or added charge is from Si but now involves the state at the top of the valence band. This difference in the occupation of different levels explains why the T site is actually lower in energy than the BC site in the negative charge state of H.

The formation energies at other high-symmetry interstitial sites are also calculated. They are listed relative to that of the T site in Table IV, for different charge states. H is the hexagonal interstitial site and C is midway between two next-nearest-neighbor Si sites. AB is an antibonding site with a Si-H separation of about 1.9 Å and lying in direction opposite to a Si-Si bond. The M site is located midway between a BC site and a neighboring H site, or equivalently between two C sites. For comparison, we also listed the *ab initio* results at the BC site. The overall agreement is very good, with the exception of the H site, which has a higher energy in the present calculation. This is partially due to the strong tail part of the Si-H repulsion at a H site, which has 6 Si neighbors with distance of 2.26 Å in the unrelaxed geometry. Notably the stability of the BC relative to the T site by -0.73 eV and -0.26 eV for H^+ and H^0 agrees well with *ab initio* results of -1.0 eV and -0.3 eV. The T site is 0.24 eV lower in energy than BC in H^-, somewhat lower than the *ab initio* value of 0.7 eV, partly due to the Coulomb repulsion for the T site.

The adiabatic energy surface of H^+ in the (110) plane through the atoms in *c*-Si is shown in Fig. 1, with the darkness of the shading indicating the energy required to insert a proton at each position, allowing full relaxation of the host lattice. The energy surface was constructed by a plane-wave expansion of the potential energy of H on a grid of positions in the (110) plane, calculated with a 64 atom cell with periodic boundary conditions. The calculated energy of the hexagonal H site was not included in the figure, since it does differ from the *ab initio* values.[3] For clarity of the picture, the high-energy portion of the surface was cut off and replaced by a flat surface. The absolute energy difference between the highest energy (dark ovals surrounding the Si atoms) and the lowest energy (at the BC site) is 1.35 eV. Clearly evident in Fig. 1 is the low-energy path passing through the BC sites, with an energy barrier of about 0.5 eV, located near the C site.

TABLE IV. Formation energies (in eV) of H in c-Si in different charge states.

	H^+	H^0	H^-
H	0.71	1.46	1.87
AB	0.35	0.44	0.13
T	0.00	0.00	0.00
C	-0.22	0.31	1.37
M	-0.53	-0.03	0.51
BC	-0.73	-0.26	0.24
BC[a]	-1.0	-0.3	0.7

[a] See Ref. 3.

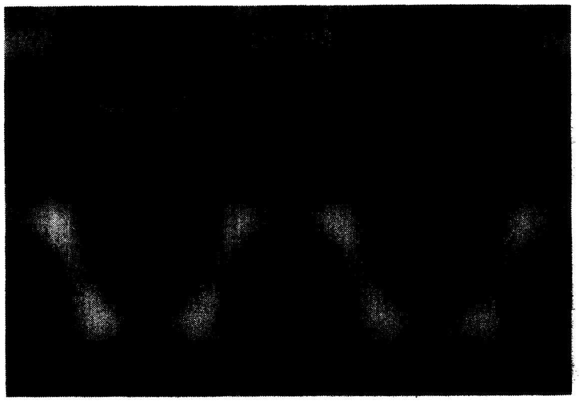

FIG. 1. The adiabatic energy of H^+ in the (110) plane through Si atoms, obtained by a low order plane-wave expansion with energy input from 12 sites. The darkness of the shading indicates the energy required to insert a proton at that position. The dark ovals show the high-energy cutoff regions surrounding the Si atoms. The lightly shaded regions between two neighboring Si atoms show the low-energy diffusion channels passing through the bond-centered (BC) sites. A low energy region also appears near the C' site. The difference in energy between the BC sites and the dark ovals is 1.35 eV. Since the H site energy was not given accurately in the tight-binding model, it was not used as an input in the expansion. This figure is only intended to show the overall features of formation energy of hydrogen in *c*-Si because of the low order of the expansion. Not all high symmetry sites are labeled.

The overall energy barrier for this diffusion path, however, may be located on the *M* site,[3] which is only 0.2 eV higher in energy than the BC site (the *M* site is not on the surface shown in Fig. 1). The stretching frequency of H in the direction of Si-Si at the BC site is calculated to be 1500 cm^{-1}. The lower value, compared with the experimental value of 2000 cm^{-1} and *ab initio* result[3] of 2210 cm^{-1}, reflects a slightly larger Si-H distance in the present work. For comparison, it is worth noting that other cluster calculations[36–38] produce a low vibrational frequency of around 800 cm^{-1}. The wagging frequency perpendicular to the Si-H-Si direction is very low, about 160 cm^{-1} in our model. In the energy surface, the *T* site appears as a high-energy feature adjacent to the *C* site. The features of this energy surface agree very well with the *ab initio* calculations of the energy surface.[3] Our calculated energy surface indicates another low-energy path passing through the *C′* sites that is approximately 0.3 eV higher in energy than the path through the BC sites and similar to the *ab initio* result. However, the energy barrier for diffusion along this alternative path is not well estimated due to the higher energy found for the *H* site in our calculations.

IV. *a*-Si:H PROPERTIES

In addition to the previous tests in *c*-Si we have applied this tight-binding model to disordered structures where H is strongly bonded to Si, in contrast to the weaker binding of the H interstitials in *c*-Si. We study the structural and electronic properties of *a*-Si:H network models. We have chosen the Guttman-Fong *a*-Si:H model[30] with 10% H and all H in monohydride bonding configurations, containing a total of 60 atoms with periodic boundary conditions. In several earlier studies, this model was found to be a good representation of local structural properties of *a*-Si:H. We have also tested another *a*-Si:H network model containing 22% hydrogen and both monohydride and dihydride species, derived by us from another Guttman-Fong network and having 68 atoms (with three dihydride and eight monohydride groups). Since these network models were developed with classical potentials, the stability and applicability of these models to the quantum-mechanical TB method is important.

The 60 atom monohydride model with 6 hydrogen atoms was fully relaxed with our tight-binding model, including the relaxation of overall cell size. The H was found to remain tightly bonded to the network, with a narrow rms distribution of Si-H bond length of 0.034 Å (2.3%), and a rms Si-Si bond length distribution of 0.056 Å (2.2%) at 300 K. The corresponding pair correlation function $g(r)$ for Si-Si and Si-H is shown in Fig. 2. The molecular-dynamics simulation was carried out at 300 K for 8 ps with a time step of 0.27 fs, small enough for accurate MD simulations of Si-H systems. Notably there are no weak Si-Si bonds (with bond length greater than 2.6 Å) indicated by a complete absence of neighbors between 2.6 Å and 3.3 Å in Fig. 2, a feature that is qualitatively different from classical simulations. The broad second-neighbor Si-Si feature occurs around 3.9 Å.

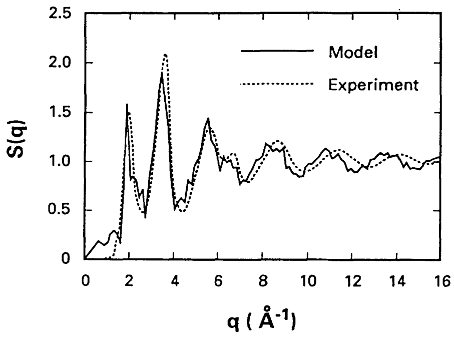

FIG. 3. The Si-Si partial structure factor of *a*-Si:H at 300 K for the theoretical model (solid line) compared with neutron scattering experiment (Ref. 39).

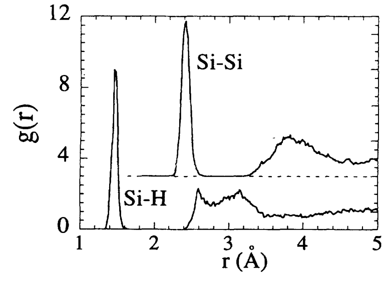

FIG. 2. The Si-Si and Si-H pair correlation functions of *a*-Si:H at 300 K.

The Si-H $g(r)$ displays the sharp first-neighbor peak centered around 1.47 Å and split second-neighbor Si-H feature. The first feature of this split peak is from Si-H separations where Si is a second neighbor of the H. The second feature occurs from Si-H pairs where Si is not a second neighbor of the H but (or bonded to the monohydride) in the proximity of the monohydride.

The calculated Si-Si structure factor $S(q)$ (Fig. 3) agrees very well with neutron scattering measurements[39] for the entire range of wave vectors including the second peak in $S(q)$ being slightly larger than the first peak, and the small splitting of the third peak. The first two peaks of $S(q)$ represent a convolution of the order in $g(r)$ whereas the period of the large q peaks represent the interatomic separation of Si-Si.

The bond angle distribution on the Si sites (Fig. 4)

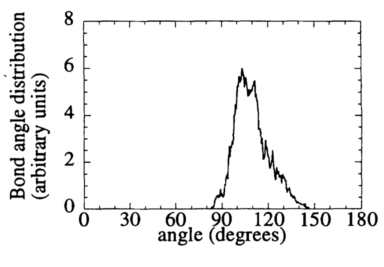

FIG. 4. The Si-Si-Si bond angle distribution function of the *a*-Si:H model at 300 K.

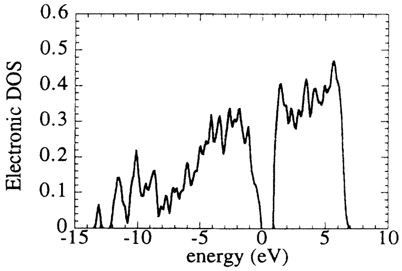

FIG. 5. The electronic density of states of the *a*-Si:H model.

have a rms deviation of 11.4° typical of theoretical models. We have verified that the Si-Si-H angles has a slightly narrower rms angle deviation of $\approx 9^\circ$ resulting from the greater structural freedom of the H to reorient itself at the monohydride site.

The total electronic density of states (Fig. 5) displays a well-defined gap. The magnitude of the gap (1.5 eV) is somewhat lower than experiment owing to the underestimation of the gap of *c*-Si in the tight-binding model. While most of the electronic states are extended the few states in the band tail show only partial localization from an analysis of their inverse participation ratio. These results for the pair correlation functions and electronic densities of states are very similar for the dihydride *a*-Si:H network model and are not displayed separately.

V. DISCUSSION AND CONCLUSIONS

We have developed a tight-binding model for Si-H systems that incorporates the relevant physics of charge-transfer and local-environment dependence of the tight-binding overlap integrals. Utilizing the previously developed Si-Si interactions, the model is able to describe a variety of systems ranging from Si-H molecules to hydrogenated amorphous silicon. More importantly the model correctly describes the energetics of formation of H in *c*-Si in different charge states in good agreement with first-principles results, a stringent test indeed for a tight-binding model. This success extends the applicability of the quantum-mechanical tight-binding model to new frontiers including an array of interesting physical phenomena such as the H diffusion in crystalline or amorphous silicon and the light-induced generation of defects (Staebler-Wronski effect) in *a*-Si:H. Understanding the mechanisms underlying these phenomena has important implications not only in terms of device applications, but also from the fundamental physics point of view. Similar physics is also involved in C-H systems and the present approach to incorporate new interactions for Si-H can be equally applied to C-H systems. Similar considerations should also be applied to Si-Si interactions, at least when charge transfer become important, for example when dealing with negatively charged dangling bond defect states and this is an aspect for further work. The tight-binding model we presented in this paper for Si-H interaction together with the Si-Si interaction developed earlier will be very useful for molecular-dynamics simulations of large systems, longer times and problems of a quantum-mechanical nature.

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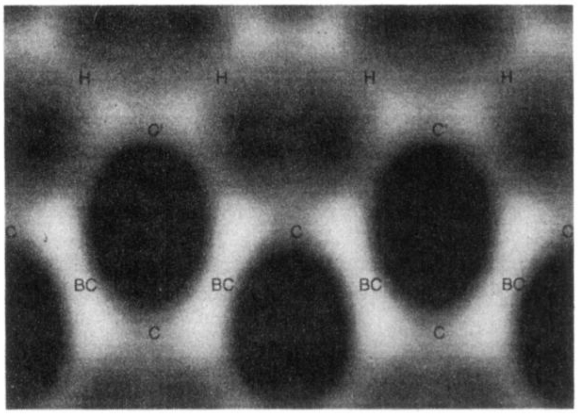

FIG. 1. The adiabatic energy of H^+ in the (110) plane through Si atoms, obtained by a low order plane-wave expansion with energy input from 12 sites. The darkness of the shading indicates the energy required to insert a proton at that position. The dark ovals show the high-energy cutoff regions surrounding the Si atoms. The lightly shaded regions between two neighboring Si atoms show the low-energy diffusion channels passing through the bond-centered (BC) sites. A low energy region also appears near the C' site. The difference in energy between the BC sites and the dark ovals is 1.35 eV. Since the H site energy was not given accurately in the tight-binding model, it was not used as an input in the expansion. This figure is only intended to show the overall features of formation energy of hydrogen in *c*-Si because of the low order of the expansion. Not all high symmetry sites are labeled.