

Energetics of hydrogen in amorphous silicon: An *ab initio* study

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Using *ab initio* density-functional calculations, we investigate the energetics of hydrogen in amorphous silicon. We compare a hydrogen atom at a silicon bond center site in *a*-Si to one in *c*-Si. In addition, we identify the energetics of the dominant traps for H in *a*-Si. The present calculations are used to elucidate many experiments and concepts regarding hydrogen in amorphous silicon including the role of H in equilibrium electronic defect formation. [S0163-1829(98)09119-X]

I. INTRODUCTION

Large concentrations of hydrogen (5–15 %) are needed to grow device quality films of amorphous silicon (*a*-Si:H). Hydrogen plays an important role in passivating electronic defects. The incorporation of hydrogen lowers the concentration of both the midgap states (by a factor 10^3 or more) and band tail states. However, hydrogen can also be a source of defects. For instance, in *a*-Si:H, the motion of hydrogen is linked to the generation of intrinsic and metastable midgap electronic defects.^{1–4} Determining the relationships of hydrogen to electronic defects is possible only if the mechanisms and energetics for H bonding and diffusion are well understood.

The details of hydrogen transport and bonding in amorphous silicon have been discussed extensively in the literature.^{5–12} Network disorder leads to a broadening of the energy levels.^{8–10} Therefore, it is appropriate to use a H density-of-states model⁹ where the hydrogen chemical potential energy would determine the occupancy of various hydrogen binding states. However, recent work suggests that the discrete trapping levels in Fig. 1 are sufficient to describe many aspects of H bonding and diffusion.⁷ The quantity E_a in Fig. 1 is the activation energy for long-range diffusion, E_m is the average migration barrier as H moves along the transport levels, and ΔE is the energy difference between the deep and shallow trap levels. For intrinsic *a*-Si:H, a large number of studies report that the activation energy (E_a) is 1.4–1.6 eV.^{6–8} Fewer studies produce estimates for E_m and ΔE , finding $E_m \approx 0.5$ eV (Refs. 8 and 11) and $\Delta E > 0.4$ eV.^{8,12} In addition, the microscopic structures responsible for the three trapping levels are not fully understood. Studies suggest that transport level diffusion in *a*-Si is similar to H diffusion in *c*-Si with the bond center site being the transport level.^{8,11} Regarding the shallow trap level, several studies indicate that the shallow traps are formed when hydrogen atoms break weak silicon bonds to form covalent Si-H bonds.^{8,13,14} However, the mechanisms and energetics of the H insertion are not well understood. Besides passivating weak bonds, hydrogen also passivates isolated coordination defects. These isolated defects constitute the deep traps for H in *a*-Si:H. In addition, the mechanisms for intrinsic and

metastable defect formation are still controversial. The defects are argued to be unpassivated isolated dangling bonds,^{4,9,15} weak bonds broken by one hydrogen atom,¹⁰ or overcoordinated bonds.^{16,17} The limits to the understanding of the role of hydrogen in *a*-Si are due in part to the lack of reliable theoretical calculations for the energetics of hydrogen in amorphous silicon.

Several structural models for hydrogenated amorphous silicon have been developed.^{18–23} Recently, for four of the *a*-Si:H structural models,^{18,20–22} we calculated several properties (structural properties, hydrogen vibrational spectra, electronic gap, etc.) and compared our results with the respective experimental observations.¹³ Although the model from Ref. 21 was produced from *ab initio* molecular dynamics, the final model had an unrealistically high number of coordination defects as discussed in Refs. 13 and 22. The models from Refs. 18 and 20 were the most realistic with no coordination defects and other properties in reasonable with experiment. For the present calculations of the energetics of H in amorphous silicon, we use the model developed by Guttman and Fong (see Ref. 20).

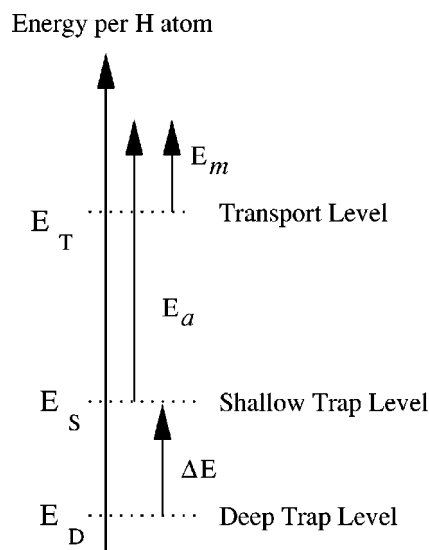


FIG. 1. Energy levels relevant to H in *a*-Si. See the text for details.

TABLE I. Tests of convergence for H in c -Si. The binding energies (in eV), as defined in the text, are reported for H at a bond center site and H at a hydrogenated vacancy. The calculations show that calculations with $E_c=16$ Ry and one high-symmetry point are converged to within 0.1 eV. The reference energy is chosen as the binding energy for a H bond center in column 2. Column 4 is equal to column 3 minus column 2. $\Delta E=H_{db}-H_{BC}$.

Energy	$E_c=18$ Ry, 8 \mathbf{k} points	$E_c=16$ Ry, 1 \mathbf{k} point	δ
$E(H_{BC})$	0.00	+0.69	+0.69
$E(H_{db})$	-2.19	-1.57	+0.62
ΔE	-2.19	-2.26	-0.07

Ab initio methods have been used to calculate the energetics of H in c -Si and the results have been applied to H in a -Si;^{8,9} however, *ab initio* calculations for the energetics of H in a -Si have not been performed previously. Previous studies of H in a -Si, based on semiempirical^{11,24} or approximate^{13,22} theoretical methods, were limited in scope and a consistent picture of H bonding and diffusion did not emerge. In several studies^{9,11,24-26} only single Si-H bonds were considered. In these studies, no consideration was given to the possibility that a strained Si-Si bond could be broken to form two Si-H bonds. Not considering the clustered Si-H bonds as a distinct phase makes it difficult for these studies to be consistent with a variety of experimental results. For instance, if only single Si-H bonds exist in a -Si:H, then as H evolves the dangling-bond concentration should be roughly equal to the evolved H concentration. However, it has long been observed that the dangling-bond concentration during evolution experiments stays orders of magnitude smaller than the evolved H concentrations.^{5,14}

A specific model for Si-H clusters, based on *ab initio* calculations for H_2^* in c -Si, is discussed in Ref. 8. The H_2^* model involves a (Si-H Si-H) configuration where one H atom is in a bond center site and one is in an anti-bonding site. A survey of several a -Si:H structural models did not find any structures similar to H_2^* , but instead found hydrogen clusters similar to a hydrogenated vacancy where in some cases a strained Si-Si bond would form upon the removal of two hydrogens.¹³ The energetics of these clustered hydrogens were calculated in Ref. 13 but, as noted by the authors, the approximate method used prevented quantitative analysis. For instance, the energy of the clustered hydrogens relative to either an H_2 molecule or a bond centered hydrogen atom could not be determined. The present calculations will quantify the trends found in Ref. 13.

The rest of this paper is as follows. In Sec. II we present the calculational details including a discussion of the a -Si:H model that we use. In Sec. III we report our results for the energetics of bond centered H and the hydrogenated vacancy in c -Si. In Sec. IV our results for bond centered H in a -Si:H are presented. In Sec. V covalent (Si-H) binding in a -Si:H is examined. In Sec. VI we discuss our results in the context of a variety of experiments in a -Si:H. We draw our conclusions in Sec. VII.

II. CALCULATIONAL DETAILS

In this work we carry out *ab initio* total-energy calculations using a self-consistent, spin-averaged implementation of density-functional theory (DFT) within the local-density

approximation (LDA).²⁷ We use norm-conserving, nonlocal pseudopotentials developed by Troullier and Martins.²⁸ For the pseudopotentials, core radii of 2.25 and 0.2 Å are used for silicon and hydrogen, respectively. For the exchange-correlation potential in the LDA, we employ the established results of Ceperley and Alder²⁹ as parametrized by Perdew and Zunger.³⁰

For H in c -Si, periodic supercells with simple cubic symmetry are employed. Using the theoretical lattice constant, the cell length is 10.8 Å. The initial c -Si cell includes 64 Si atoms. Integrations over the first Brillouin zone are replaced by summations using a $2 \times 2 \times 2$ sampling that, depending on the symmetry of the configurations involved, reduces to 1–3 high-symmetry \mathbf{k} points in the irreducible wedge.³¹ For the plane-wave basis, a cutoff energy of $E_c=18$ Ry is found to be sufficient. For the calculations of interest, the above implementation of DFT is well converged and similar implementations have been widely used to investigate H in bulk c -Si.^{32,33}

Since our a -Si:H model is large and has no symmetry, a more efficient implementation of DFT is desirable. For our calculations of H in a -Si:H we modify our DFT LDA implementation as follows. Brillouin zone sampling is limited to one \mathbf{k} point at (0.5,0.5,0.5) and for the plane-wave basis an energy cutoff of $E_c=16$ Ry is used. Test calculations for H in c -Si were performed and are reported in Table I. Although the absolute energies differ by over 0.5 eV, the relative energy of a three-center bond (Si-H-Si) versus a Si-H bond is less than 0.1 eV from the converged results. Moreover, when comparing the energetics of a Si-H-Si bond in c -Si versus a -Si:H, the errors should be smaller still. For all calculations, we employ a conjugate gradient geometric minimization scheme to allow all the atoms to relax until each component of every atom's force is less than 0.1 eV/Å.

Starting from the a -Si:H model developed by Guttman and Fong in 1982,²⁰ we relax the coordinates and the lattice constant using the *ab initio* method described above. A ball and stick representation of the model is presented in Fig. 2. The model includes 54 Si and 6 H atoms giving a H content of 10%, which is consistent with device quality glow discharge films. The model has no coordination defects and has been found to be the best model of its size.¹³ The average silicon bond length is 2.35 Å, which is 0.02 Å longer than the silicon bond length in c -Si and the average silicon bond angle is 109.5°, the same as in c -Si. The fully relaxed Guttman-Fong model, at essentially 0 K, is found to have low network disorder with a root-mean-square silicon bond angle (and length) deviation of 6.2° (and 0.042 Å). These results are somewhat smaller than the results from experi-

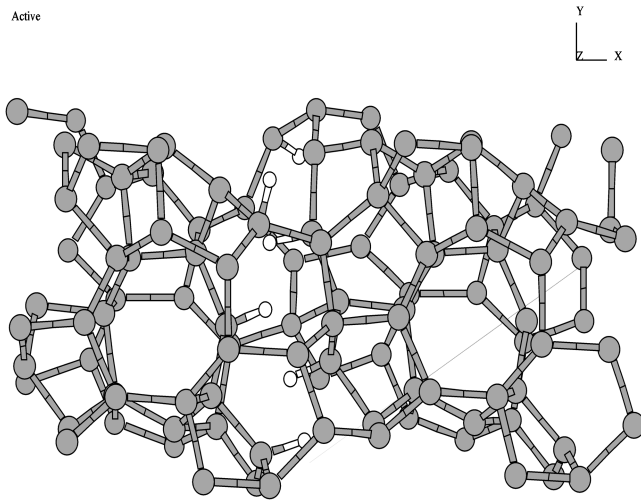


FIG. 2. Ball and stick representation of the model used for our calculations. The periodic cell has been partially repeated in the horizontal direction. The larger circles represent silicon atoms and the smaller circles represent hydrogen atoms.

ments performed at room temperature which include thermal as well as intrinsic contributions network disorder. To our knowledge, neither the bond length nor the bond angle disorder has been measured near 0 K. The Guttman-Fong model is relatively small (with 10.4 Å per side) which should overconstrain the network. Strained bonds show up as localized band tail states in real films. However, in such small supercells, band tail states will hybridize to become delocalized, having only the effect of reducing the electronic band gap. Although the model has the largest gap of the published *a*-Si:H models, the gap is smaller than in device quality films.³⁴

Next, we will briefly discuss two important and well-known shortcomings of density-functional theory (DFT) within the local-density approximation (LDA). First, the LDA is not appropriate for systems where the charge-density gradients are large. Thus the LDA tends to overbind solids relative to molecules and atoms. For instance, cohesive energies are over 10% too large for semiconductors such as silicon.³⁵ Although the binding energies of small molecules have not been systematically studied, results suggest that the LDA overbinds molecules relative to atoms. Using all-electron, local orbital calculations with the commercial package GAUSSIAN94, we find H-H and H-SiH₃ LDA binding energies to be only 3–5% larger than experiment.³⁶ These results are consistent with the pseudopotential, plane-wave calculations by Van de Walle.³³ In contrast, Perdew *et al.*³⁷ studied more complicated hydrocarbons and found that the LDA gave atomization energies 10–15% too high. To compensate for these shortcomings, extensions of the LDA including gradient corrections have been developed by a number of researchers including notably Perdew and Wang,³⁸ whose PW91 functional is perhaps the best currently available. Using PW91, Perdew *et al.*³⁷ find the atomization energies for hydrocarbon molecules to be only 2–4% higher than experimental results improving upon the LDA results. Also, hydrogen dissociation barriers [H₂ from Si(100):H surfaces (Ref. 39) or H exchange with H₂ (Ref. 40)] are greatly improved with gradient corrections to the LDA. In general,

using PW91 will give better energetics; however, we find that PW91 overcorrects the binding energies of H-H and H-SiH₃, giving results 3–4% below experiment.³⁶ Since we are primarily interested in the relative binding energies of Si-H bonds in *a*-Si, we conclude that the LDA will be appropriate and extensions of the LDA such as PW91 (Ref. 38) will not necessarily improve the results.

Another well-known shortcoming of DFT LDA calculations is that conduction-band states, although qualitatively correct, are shifted down in energy. For instance, the LDA band gap for silicon is 0.5–0.6 eV compared to the experimental result of 1.13 eV.³⁵ This error should not effect calculations in which conduction-band levels remain unoccupied since unoccupied bands do not contribute to the total energy of the system. The accuracy of total-energy LDA calculations for systems including occupied band-gap defect levels has garnered some attention in the literature.³² We will discuss these issues in the relevant section below (Sec. VI D). Unfortunately, extensions beyond the LDA, such as PW91, do not improve on the DFT LDA band-gap result.³⁵

Finally, the uncertainties of our calculated energies are similar in magnitude to those of the measured values with which we compare. The sources of uncertainty fall into three main categories. First, our implementation of DFT within the LDA has some uncertainty associated with it.³² Also, because of limitations of the LDA, we can only be qualitative in our discussion of electronic gap states.³⁴ The second source of uncertainty is from the relatively small model we use to approximate the amorphous silicon network. The increase in network strain will mostly affect the relaxation energetics. The third source of uncertainty involves the small number of bonded H atoms examined. The model has only six covalent Si-H bonds, which prevents a statistical analysis of the Si-H binding energetics. In addition, the distribution of binding sites in the model cannot fully represent the actual distribution. For relative trapping energies in *a*-Si:H, we estimate ±0.2 eV to be the uncertainty in our calculations. Despite the uncertainties involved, the present study quantifies the effects of the disordered network and provides a microscopic picture of important mechanisms for hydrogen bonding and diffusion in *a*-Si:H.

III. HYDROGEN IN CRYSTALLINE SILICON

The calculations for H in *c*-Si reported below have in part been previously performed by Van de Walle³³ using a smaller 32-atom supercell. Binding energies are typically reported as positive if bonding is favored. In these calculations, we will report energies relative to the bond energy of a H atom at a silicon bond center site in *c*-Si. Let $E(X)$ designate the total relaxed energy of supercell labeled X ; then the bond energy for H at a silicon bond center site (H_{BC}) in *c*-Si is

$$E_{bond}(H_{BC}^{c-Si}) = E(c-Si + H_{BC}) - E(c-Si). \quad (1)$$

Using this convention, the bond energy of one (Si-H) bond at a hydrogenated vacancy is given by

$$E_{bond} = [E(VH_4) - E(VH_3)] - E_{bond}(H_{BC}^{c-Si}), \quad (2)$$

where VH_4 represents a fully hydrogenated vacancy and VH_3 represents a vacancy where three of the four dangling

TABLE II. Energies for H at analogous sites in *c*-Si and *a*-Si. (Si-H)_{*c*} represents Si-H bonds that are clustered. In *c*-Si, the cluster is a hydrogenated vacancy.

Site	Energy (eV)	
	<i>c</i> -Si	<i>a</i> -Si
H _{<i>BC</i>}	0.00	−0.21
(Si-H) _{<i>c</i>} with Si-Si	−1.93	−1.25
(Si-H) _{<i>c</i>} without Si-Si	−2.04	−1.79

bonds are passivated by a H atom. We have chosen the sign such that a negative value of the bond energy represents a bound state relative to H_{*BC*}. Some caveats to Eq. (2) are discussed in Ref. 41. We find the bond energy of Si-H at a hydrogenated vacancy to be −2.04 eV (row 2 in Table II), which is close to −2.13 eV as calculated by Van de Walle.³³ We have also calculated $E(V)$, the energy of a relaxed vacancy. Our value for the formation energy of a silicon vacancy relative to *c*-Si is 3.51 eV, which is consistent with other values found in the literature (see Refs. 42 and 43 and references therein). The average bond energy for the Si-H bond at a vacancy can be defined as

$$E_{bond} = \left[\frac{E(\text{VH}_4) - E(V)}{4} \right] - E_{bond}(\text{H}_{BC}^{c-Si}). \quad (3)$$

The average bond energy for Si-H at a vacancy is 1.93 eV, where Jahn-Teller-like silicon reconstructions⁴³ account for the average being higher than the single Si-H binding energy. We find that the energy per reconstructed bond is 0.05 eV. The above results are included in Table II, which will be discussed below in the context of our calculations for H in *a*-Si.

IV. BOND-CENTERED HYDROGEN IN AMORPHOUS SILICON

Because of disorder, the structure and energetics of Si-H-Si bonds in *a*-Si vary from site to site. In order to capture this variation, we examined 13 bond center sites. Since *a*-Si has no crystallographic symmetry, the bond center site is not

unambiguously defined. Also, the Si-H-Si bond may not be a stable configuration. For the 13 sites examined, we first placed the H midway between a Si-Si bond and then allowed all the atoms to relax. Below we examine the structure, energetics, and electronic structure of H_{*BC*} in *a*-Si.

First, the structural properties of H_{*BC*} in *a*-Si are similar to those of H_{*BC*} in *c*-Si. In *c*-Si, our results indicate that the relaxed Si-H bond length is 1.58 Å and the Si-H-Si bond is linear with a bond angle of 180°. In *a*-Si, the average bond length (bond angle) is 1.66 Å (163.9°) with 0.02 Å (8.8°) being the root-mean-square deviation. In Table III we report both the Si-H bond lengths and the Si-H-Si bond angle for all 13 cases examined. There are only three sites whose final configuration suggest that a three-center bond may not have formed. In one case (site 10 in Table III), the Si-H-Si bond angle (at 137.9°) diverges significantly from 180°; in another (site 12 in Table III), one Si-H bond length (at 1.56 Å) is significantly shorter than the other (at 1.78 Å); in the third and exceptional case (site 13 in Table III), both of the above conditions hold. In the two cases where the Si-H-Si bond angle is less than 140°, it may be possible that a weak Si-Si bond persists after we insert the H atom. However, in both cases the final Si-Si distance is over 3.0 Å, which is inconsistent with silicon bonding.¹³ In all 13 cases, the initial Si-Si bond is broken by the H atom and, as will be discussed below, the electronic structure is similar to a three-center bond (Si-H-Si). Fedders²⁵ also inserted H into silicon bonds using a high-quality *a*-Si:H model. However, he found that two of eight attempts failed to produce a three-center bond, which is somewhat contrary to our results. These differences may be attributed to the approximate calculational method used by Fedders.²⁵ Moreover, the method has recently been shown to overestimate the Si-Si strain energies¹³ so the Si-H-Si bond will be more sensitive to the network strain; therefore, the Si-H-Si bond will be less likely to form in cases where the local network strain is compressive in nature. Our results suggest that the three-center bond in *a*-Si is a locally stable configuration.

In Table III we also report relaxed bond energies for H_{*BC*} in *a*-Si given by

$$E_{bond} = [E(a\text{-Si} + \text{H}_{BC}) - E(a\text{-Si})] - E_{bond}(\text{H}_{BC}^{c-Si}), \quad (4)$$

TABLE III. Details of the calculations of H at bond center sites in *a*-Si.

Site	E_{bond} (eV)	$d_{Si-Si}^{initially}$ (Å)	d_{Si-H} (Å)	$\Theta_{Si-H-Si}$ (deg)
1	−0.50	2.46	1.74, 1.65	173.7
2	+0.01	2.33	1.69, 1.65	173.6
3	−0.23	2.36	1.60, 1.71	151.3
4	−0.16	2.33	1.68, 1.60	162.6
5	−0.03	2.31	1.60, 1.69	160.8
6	−0.28	2.34	1.63, 1.63	172.9
7	−0.35	2.39	1.68, 1.68	169.7
8	−0.14	2.33	1.64, 1.64	174.5
9	−0.19	2.34	1.65, 1.61	177.2
10	−0.33	2.34	1.66, 1.66	137.9
11	−0.31	2.38	1.67, 1.73	171.4
12	−0.22	2.29	1.56, 1.78	169.5
13	−0.03	2.30	1.56, 1.74	132.2

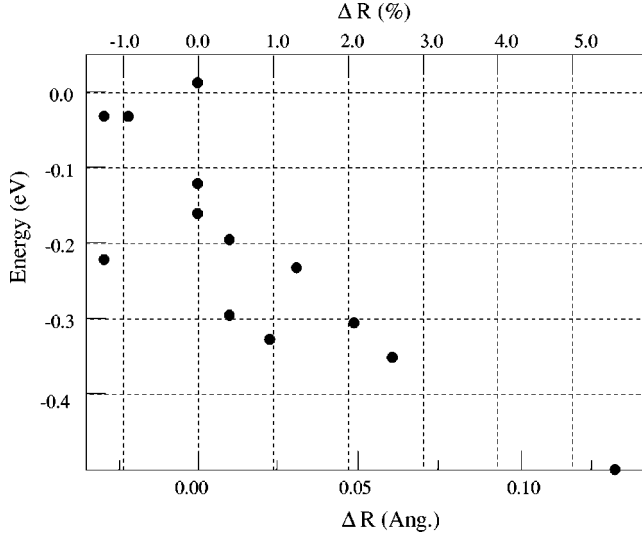


FIG. 3. Energy (in eV) of H at bond center sites verses the bond length relative to *c*-Si.

where *a*-Si designates the Guttman-Fong model. The bond energies range from +0.01 to -0.50 eV. We find that the average H_{BC} bond energy, for H in the neutral charge state, is -0.21 eV (also reported in Table II) with a standard deviation of 0.05 eV. Fedders²⁵ reports an average bond energy of -0.52 eV and a bond energy range of 1.0 eV. The study of Li and Biswas²⁴ was not directly aimed at calculating the average H_{BC} in *a*-Si relative to *c*-Si. However, for silicon bond lengths similar to those reported here, the results of Ref. 24 indicate a bond energy range of nearly 2.0 eV. Since all *a*-Si:H models are of similar quality, quantitative differences may be attributed to the approximate methods used in Refs. 24 and 25.

The first two columns of data from Table III are reported in Fig. 3 where along the *x* axis is ΔR , the silicon bond length in *a*-Si relative to 2.33 Å (the bond length for silicon bonds in *c*-Si). For the longest Si-Si bond length examined (2.46 Å), the H_{BC} bond energy is -0.50 eV, which corresponds to -0.38 eV per 0.1 Å increase in bond length, assuming a *y* intercept at 0.0 eV. This result appears to be consistent with the -0.4 eV per 0.1 Å increase in bond length reported by Van de Walle and Nickel.⁴⁴

To examine these results more closely, we also fit the 13 data points in Fig. 2 to the line given by

$$E(\Delta R) = E_0 - \alpha \Delta R, \quad (5)$$

where E_0 is the bond energy at $\Delta R = 0$, α is a constant in units of eV/Å, and ΔR is the difference from the *c*-Si bond length (in angstroms). We find $E_0 = -0.17 \pm 0.03$ eV and $\alpha = 2.6 \pm 0.6$ eV/Å. The error bars indicate the 95% confidence of the linear fit. These results contradict the results of Li and Biswas,²⁴ who found $E_0 = 0.0$ eV and $\alpha \sim 6.3$ eV/Å; however, it should be noted that the study of Li and Biswas was more concerned with cases where $\Delta R > 0.1$ Å, whereas all but one of our calculations are for $\Delta R < 0.1$ Å. Closer to our results are the results of Van de Walle and Nickel,⁴⁴ who used *ab initio* DFT LDA calculations to examine the energy of H in strained Si-Si bonds in a *c*-Si environment. They found $E_0 = 0.0$ eV (by construction) and $\alpha = 4.0$ and 4.6 eV/Å for the bond angle and bond length strain, respectively.

Similarly to H_{BC} in *c*-Si, for all 13 cases, we find the H_{BC} in *a*-Si has a donor state near the conduction-band edge, which is consistent with the results in Refs. 24 and 44. For all 13 final configurations, the deconvolution of the eigenvectors was calculated. In all cases except one (site 13 in Table III), the donor state that resulted from the H_{BC} is localized on the two Si atoms and one H atom that form the three-center bond. The exceptional case (site 13 in Table III) is associated with a Si-H-Si structure where the bond is far from linear and one Si-H bond is 1.56 Å with the other Si-H bond length being rather long (1.78 Å).

V. COVALENTLY BONDED HYDROGEN IN AMORPHOUS SILICON

As previously mentioned, there are six covalently bonded hydrogen in the Guttman-Fong *a*-Si:H model. All six hydrogen atoms interact with at least one other hydrogen atom and the degree of H-H interaction is unique in each case. For the relaxed hydrogenated vacancy in *c*-Si, each hydrogen atom is 1.8 Å from three other H atoms. In the *a*-Si:H model, each hydrogen atom is 2.0–2.8 Å from one or two other H atoms. Information regarding the six covalently bonded hydrogen atoms is presented in Table IV. In columns 4 and 5 of Table IV, the number and distance of nearby H atoms are reported. By comparing NMR linewidths of the H atoms in the Guttman-Fong model with the linewidths measured by H NMR experiments, we find that three of the H atoms (at sites 1, 2, and 3 in Table IV) are bonded in a manner comparable to the clustered phase hydrogens in device quality *a*-Si:H.¹³ In Fig. 2 these three hydrogen atoms are the second, third, and fourth hydrogen atoms from the bottom of the picture. The bonding of two of the other three H atoms (at sites 4 and

TABLE IV. Details of the calculations of Si-H bonds in *a*-Si.

Site	E_{bond} (eV)	d_{Si-H} (Å)	No. of H atoms nearby	
			$d_{H-H} < 2.5$ Å	$2.5 \text{ Å} < d_{H-H} < 3.0$ Å
1	-1.84	1.54	2	0
2	-1.81	1.54	1	1
3	-1.71	1.54	1	0
4	-2.01	1.56	0	1
5	-2.05	1.56	0	1
6	-1.48	1.55	0	1

5 in Table IV) are more representative of isolated Si-H bonds.

Similarly to our calculations for the hydrogenated vacancy in *c*-Si, we have investigated the binding of single Si-H bonds by removing one H atom at a time from the *a*-Si:H model and then fully relaxing the structures. The bond energies (E_{bond}) for all six hydrogen atoms are reported in Table IV, where

$$E_{bond} = [E(a\text{-Si}) - E(a\text{-Si} - 1\text{H})] - E_{bond}(\text{H}_{BC}^{c\text{-Si}}). \quad (6)$$

Three of the hydrogen atoms at sites 1, 2, and 3 in Table IV were notably higher in energy (at -1.84 , -1.81 , and -1.71 eV, respectively) than two H atoms at sites 4 and 5 (at -2.01 and -2.05 eV, respectively).⁴⁰ The H atom at site 6 was highest in energy (-1.48 eV) and is discussed separately. In contrast to our results, Fedders²⁵ calculates Si-H bond energies between -2.03 and -3.06 eV;⁴⁰ again, differences may be attributed to the approximate method used by Fedders.²⁵ For cases 1–5 in Table IV, removing one hydrogen left an undercoordinated silicon atom and the midgap electronic defect level was occupied by one electron. The defect state is sp^3 in character and is highly localized on the silicon dangling bond. The average binding energy (-1.79 eV) of sites 1–3 are reported in Table IV in row 2 labeled $(\text{Si-H})_C$ without Si-Si, which is short for a clustered Si-H bond without Si-Si bond reconstructions; this value in *a*-Si is 0.3 eV lower than in *c*-Si.

For case 6 in Table IV, breaking the Si-H bond caused the Si atom to bind to a nearby Si atom, making the latter fivefold coordinated; moreover, a mid-gap defect level forms. The eigenstate is localized on the five neighbors of the overcoordinated Si. The silicon from which the H atom was removed has the largest localization. Interestingly, one of the five neighbors has a defect charge density that is locally *d*-like in character. The defect level is occupied by one electron. Figure 4 includes the local configuration before and after the H atom is removed. Atoms labeled 1 and 2 in Fig. 4 form a bond once the hydrogen is removed. Also included in Fig. 4 are the bond lengths between a few important atoms. Atom 2 in Fig. 4(b) participates in five bonds with two bonds being particularly long at 2.53 and 2.58 Å. If the the bond length between atoms 1 and 2 in Fig. 4 were longer, there would be some ambiguity as to whether atom 2 is a fivefold-coordinated defect or atom 1 is a threefold defect. Such a situation was introduced by Pantelides¹⁶ to explain measurements of electrically active dominant defects in *a*-Si:H which we will discuss in Sec. VI C.

It is interesting to compare these results for H at a fivefold defect with similar examples in *c*-Si. Although in *c*-Si there are no examples of a single overcoordinated atom with a midgap level, there are several Si interstitials that lead to overcoordinated configurations. The split interstitial is closest to the fivefold Si defect calculated here. The split interstitial and its interactions with H have been investigated theoretically by Van de Walle and Neugebauer.⁴⁵ They find the split interstitial can be passivated with two H atoms such that the two fivefold-coordinated Si atoms become fourfold coordinated and all gap levels are removed. The binding energy (per H atom) is reported at -1.35 eV relative to the H BC bond center in *c*-Si, compared to the -1.48 eV calcu-

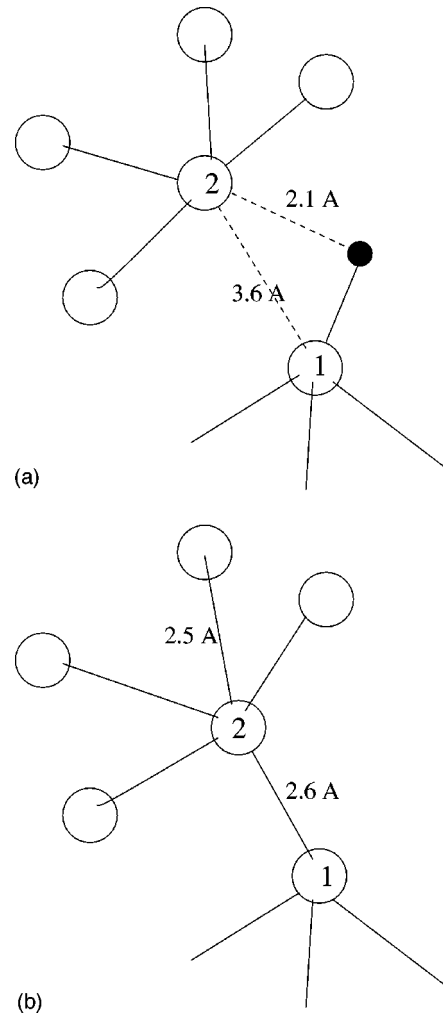


FIG. 4. H at a fivefold defect. Sketch of the local configuration (a) before and (b) after the hydrogen atoms are removed and bond reconstructions occur. The silicon atoms are represented by large open circles and the hydrogen atoms are represented by small filled circles. The distance between some atoms are given for each case. Solid lines between atoms indicate bonding and dashed lines indicate nonbonded states. Not all bonds are shown.

lated here for the H passivating a single fivefold defect. Van de Walle and Neugebauer suggested that similar H related structures may exist in *a*-Si. Indeed, our calculations support this suggestion. The possibility of H passivating fivefold defects in *a*-Si was suggested by Pantelides.⁴⁶ Also, Mousseau and Lewis¹⁹ passivated with hydrogen overcoordinated Si atoms in their atomistic model of *a*-Si:H. However, to our knowledge, we are the first to investigate the energetics of these structures using *ab initio* calculations.

In two cases, a Si-Si bond reconstructs upon removing two hydrogens. These two cases involve the three H atoms that are more representative of the clustered phase hydrogen. In Fig. 2, these three hydrogen atoms are the second, third, and fourth hydrogen atoms from the bottom of the picture. The H atoms form in roughly a vertical plane perpendicular to the page. The silicon reconstructions occur across the plane. Reported as item $(\text{Si-H})_C$ with Si-Si in Table II, the average bond energy per H atom for the two H pairs is -1.24 eV. Due to silicon reconstruction, the clustered bond energies are higher than single Si-H bond energies. In both

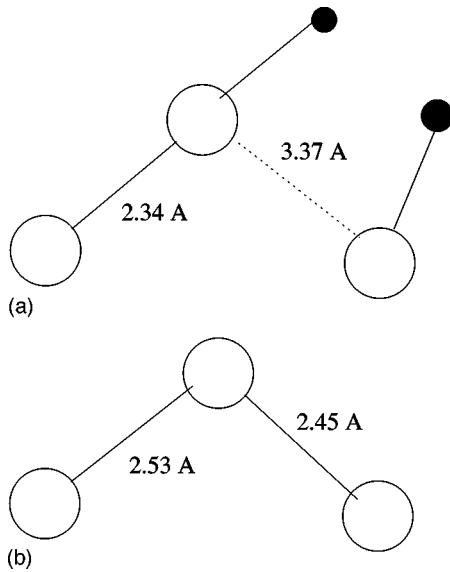


FIG. 5. H at a weak bond defect. A sketch of (a) the initial configuration and (b) the configuration after two hydrogen atoms are removed and bond reconstructions occur. The silicon atoms are represented by large open circles and the hydrogen atoms are represented by small filled circles. The bond distance for the silicon atoms are given for each case. Not all bonds are shown.

cases, a long (~ 2.45 Å) reconstructed Si-Si bond forms and one of the back bonds lengthens to ~ 2.5 Å. The initial and final reconstructed configurations are sketched in Figs. 5(a) and 5(b), respectively. In *a*-Si we find that the energy of silicon bond reconstruction is ~ 0.5 eV, which is much larger than in *c*-Si. In both cases, the electronic structure involves a localized state introduced near the valence-band edge. In both cases, the defect state is occupied by two electrons and is localized primarily on the back bonded silicon atom as shown in Fig. 4.

VI. DISCUSSION

A. Hydrogen energy levels

Using our results from Tables II–IV we can identify the energy of the trapping levels listed in Fig. 1. As in Table II, the bond energy of H_{BC} in *c*-Si is the reference for all energies reported below. The transport level trap, associated with the average bond center site in *a*-Si, has an energy (E_T in Fig. 1) of -0.21 eV. The shallow trap is associated with clustered Si-H bonds, which form by passivating strained silicon bonds, and has an average energy (E_S in Fig. 1) of -1.25 eV. The deep traps in *a*-Si may be associated with an isolated Si-H bond. Using the values from Table II, the deep trap energy (E_D in Fig. 1) is $-(1.71-2.05)$ eV. However, the energy of H at sites 4 and 5 in Table IV are a lower bound to the deep trap energy since these configurations best represent the isolated Si-H bonds. A truly isolated Si-H bond may be lower in energy, but not by much. For instance, the energy of an isolated Si-H bond both in a *c*-Si environment and on a *c*-Si (111) surface is -2.50 eV, according to *ab initio* calculations by Van de Walle.³³ Also, a recent study by the present authors found that the isolated Si-H energy in *a*-Si is higher than an isolated Si-H in *c*-Si.¹³ The combined results suggest -2.0 eV $\geq E_D > -2.5$ eV and $\Delta E \geq 0.7$ eV.

B. Hydrogen chemical potential

In device quality *a*-Si:H, the majority of hydrogen are in the clustered phase. We find that when the clustered phase Si-H bonds form, silicon bonds are broken and network strain is relieved. As proposed in Refs. 8 and 15 the chemical potential for H (μ_H) in *a*-Si:H will be pinned at the average binding energy per H atom of the clustered Si-H bonds. Therefore, the H chemical potential will be the average shallow trap energy, $\mu_H = E_S = -1.25$ eV. Calculations place the bond energy of H_2 in bulk Si at -0.9 eV so the clustered hydrogen atoms in the Guttman-Fong model are stable to the formation of H_2 . To our knowledge, no experimental estimate for μ_H in bulk *a*-Si:H exists. However, based on observations of the etching of some *a*-Si:H films in the presence of H_2 , Jackson and Tsai⁸ conclude that μ_H near the surface cannot be far from the bond energy of H_2 in free space, which is -1.26 eV, relative to $E_{bond}(H_{BC})$.³³ These results, based on experimental observations, are in good agreement with our estimate. Also, Van de Walle and Street⁹ argue that the chemical potential for H can be associated with the energy of the isolated Si-H bond minus the energy to create a silicon dangling bond from the *a*-Si network. Using *ab initio* calculations for H in *c*-Si, their estimate for the hydrogen chemical potential in *a*-Si:H is -1.12 eV, in agreement with our estimate.

On the other hand, using tight-binding calculations, Li and Biswas investigate the energetics to remove a single H from a Si-H bond and place it into a strained Si-Si bond.²⁴ They use the results within a density-of-states model to explicitly calculate the silicon dangling-bond concentration. Based on their calculations, the H chemical potential is roughly -2.0 eV, relative to H_{BC} in *c*-Si, which is not in accord with the above results. Li and Biswas use a model derived from the Guttman-Fong model, so the model is similar to the one we use for the present calculations. However, in order to sample low-probability long Si-Si bonds, Li and Biswas²⁴ dilated their *a*-Si:H model. In real *a*-Si:H, low-probability, long Si-Si bonds typically will be surrounded by a normal silicon network, whereas the long silicon bonds in the dilated model were surrounded by long silicon bonds. Therefore, the Si-H-Si bond energy calculated is likely to be low. These considerations, in addition to the uncertainties of the empirical tight-binding methodology, explain the low estimate by Li and Biswas²⁴ for the hydrogen chemical potential.

C. Midgap electronic defects

The role of H in midgap defect formation in *a*-Si:H is still controversial. These defects are paramagnetic and have been studied by electron spin resonance experiments and electron spin hyperfine experiments.⁴⁷ The midgap defects are thermally activated at temperatures above 200 °C with activation energies around 0.3 eV. Also, the the equilibration time of the defects have the same activation energy and kinetics as the diffusion coefficient for H in *a*-Si:H and evolution of H is correlated to the increase in electronic defects.¹⁵ Such observations have led to many H related models for defect creation,^{9,10,15,24} indeed, no H-free defect model is able to explain all of the above-mentioned observations.¹⁵ Although the midgap defects are commonly attributed threefold-

coordinated silicon atoms, some argue that the experimental results favor fivefold-coordinated atoms.⁴⁸ Following the notation of Adler,⁴⁹ we label n -fold-coordinated Si as T_n . For the past decade, studies have examined the arguments for and against each model.^{48,50–54} Yet no definitive answer has emerged. Several factors prevent definitive tests of the competing structural models. One difficulty is that concentration of midgap defects in device quality material is roughly 10^6 times lower than the silicon concentration. Also, disorder allows for great variations in the local geometry surrounding coordination defects. Such variations can significantly effect the energy and electronic structure of a particular atomistic model. In addition, in amorphous silicon T_3 - T_5 structures may exist where the coordination of the defect may be ambiguous. For instance, if a coordination cutoff radius of 2.55 Å is used for the configuration in Fig. 4(b), then atom 1 is a threefold-coordinated Si atom, whereas, if 2.65 Å is used, then atom 2 is a fivefold-coordinated Si atom. We discuss the competing defect models in the context of our present calculations.

Several researchers argue that the dangling-bond creation process involves exciting a H atom out of an isolated Si-H bond to the hydrogen chemical potential, leaving behind a silicon dangling-bond midgap defect.^{4,9,15,24} The energy for such a process would be ΔE (as discussed above and in Fig. 1). The dangling-bond defect state in a -Si:H is known to be over 3 Å from any H atoms.^{47,55} For all Si-H bonds in the Guttman-Fong a -Si:H model, removing one H atom leaves a dangling bond that is within 3 Å from at least one H atom. Although more isolated Si-H bonds are not present, we can with confidence place an upper bound on their energy. For E_D we should use the lowest energies reported in Table IV (sites 4 and 5) since the corresponding configurations best represent the isolated Si-H bond. From our calculations $\Delta E \geq 0.7$ eV, whereas experimental observations give a value of 0.3 eV (Ref. 4) for the dangling-bond creation process in a -Si:H. The differences between our calculations and the experimental observations are larger than the uncertainties involved. However, the dangling-bond concentration is roughly five orders of magnitude smaller than the hydrogen concentration. A small fraction of isolated Si-H bonds may have an energy ~ 0.3 eV lower than $\mu_H (= E_S)$. In order for the Si-H bond energy to differ from our estimate, there would have to be significant relaxations of the silicon, strengthening the three back bonds. However, Stutzmann and Biegelson⁵⁶ find that the T_3 model can only be consistent with their hyperfine measurements if they assume at least one of the back bonds is a weak bond. Therefore, it appears unlikely that isolated dangling bonds are the source of midgap defects in amorphous silicon.

Another proposal for midgap defect creation is that a weak silicon bond could be broken by one H atom such that an isolated dangling bond forms.¹⁰ We have attempted to create such an isolated dangling bond starting with the strained Si-Si structure shown in Fig. 5(b) and one long Si-Si bond (site 1 in Table III). In one instance, a midgap dangling bond was created that was far from the H used to create the dangling bond. However, the energy of the defect creation process was 0.8 eV, which is much larger than observed. Our results appear to contradict the H passivating a Si-Si bond

mechanism for midgap defect creation. However, since we have considered only a few cases, it is difficult to form a definitive conclusion.

Pantelides¹⁶ proposed that the midgap defects are fivefold- instead of threefold-coordinated silicon atoms. We find, in one case (site 6 in Table IV), that a fivefold-coordinated silicon forms upon removing a hydrogen from a Si-H bond. The bond energy of the H atom is -1.48 , as reported in Table IV. Therefore, the energy needed to excite this H atom to μ_H is on average 0.23 ± 0.2 eV, which is consistent with the measured 0.3-eV activation energy for midgap defect formation. Indeed, our calculations indicate that the fivefold-coordinated silicon defect has a midgap energy level. The midgap state is localized on the five neighbors of the fivefold-coordinated silicon. Biswas *et al.*,⁵⁰ using a tight-binding approach, examined two T_5 and three T_3 defects in an atomistic model of a -Si. From explicitly calculating the hyperfine splitting for the T_n defects, they found that the T_5 defect wave functions were too delocalized (and the T_3 defects were too p -like) to account for the experimental results. However, the T_5 defects examined by Biswas *et al.*⁵⁰ are qualitatively different from the one examined here. As depicted in Fig. 4(b), our T_5 defect has three bonds of length 2.3–2.4 Å and two long bonds between 2.5 and 2.6 Å, whereas the T_5 defects they examined had all bond lengths between 2.3 and 2.4 Å. Also, a qualitative comparison of the defect wave functions suggests that the T_5 defect may be more localized, which is consistent with the differences in bond lengths. These considerations suggest that the T_5 defect of Fig. 4(b) may be consistent with all experimental measures of midgap defects. An explicit calculation of the hyperfine splitting would be useful, but such a calculation is beyond the scope of the present study. The defect sketched in Fig. 4(b) is perhaps better categorized as a T_3 - T_5 defect pair. Our results suggest that such defects should be considered as viable candidates for intrinsic midgap defects in a -Si:H.

D. Long-range diffusion

Our calculations are consistent with the following picture of long-range H diffusion in amorphous silicon: Si-H bonds break in pairs, leaving reconstructed silicon bonds behind as the H atoms hop along bond center sites. Referring to the energies in Fig. 1, the activation energy for long-range diffusion is E_a , where $E_a - E_m = E_T - E_S$. We did not examine migration barriers for H in a -Si, so we do not have a theoretical result for E_m . If we use a previously established value of $E_m \approx 0.5$ eV,^{8,11} then our estimate for E_a is $+1.25 - 0.21 + 0.5 = 1.54$ eV, which is within the experimental range 1.4–1.6 eV.⁶

Other researchers have proposed that the hydrogen diffusion instead occurs only by single Si-H bonds.^{9,11,24–26} As discussed in the Introduction, these proposals are inconsistent with well-known experimental results. For instance, deep and shallow H traps have been observed by several groups.^{12,8,57} Also, it has long been observed that the dangling-bond concentration during evolution experiments stays orders of magnitude smaller than the evolved H concentrations.^{5,14} Thus most H atoms must leave behind

reconstructed Si-Si bonds. It is difficult to reconcile these experimental facts with H diffusion controlled by single Si-H bonds.

Since isolated Si-H bonds are stronger than clustered phase Si-H bonds, it is difficult to directly observe trapping or detrapping of H from isolated Si-H bonds in the presence of clustered phase Si-H. A recent experiment by Mahan *et al.*¹² measured the Si-H ir stretching mode absorption as H evolved from an *a*-Si:H sample. They found that the decrease in ir absorption was thermally activated in two regimes. Initially, the activation energy was 1.4 eV, which is consistent with evolution being limited by long-range H diffusion as discussed above. Then, after $\sim 70\%$ of the hydrogen evolved, the activation energy was 2.1 eV. In general, there may be a continuum of bonding states between shallow and deep traps. The fact that two discrete activation energies fit the Mahan *et al.*¹² data suggests that between the shallow and deep trap sites there is a significant reduction in the density of Si-H bonding states. Our calculations show that the reduction in bonding states is natural since two distinct traps are involved: Shallow traps are highly strained silicon bonds and the deep traps are silicon dangling bonds. To compare our calculations with evolution experiments one should note that H atoms associated with the shallow trap level will evolve first and so cannot also be associated with the deep trap level. Thus the calculated value of ΔE relevant to evolution studies is, from our analysis, $\Delta E \geq 0.7$ eV, assuming the deep traps are primarily isolated silicon dangling bonds. The analysis of Mahan *et al.*¹² indicates $\Delta E \sim 0.7$ eV. Mahan *et al.* find an activation energy of 2.1 eV for the diffusion for the majority of the deep trap H atoms (at a concentration $\approx 10^{21} \text{ cm}^{-3}$). For much lower H concentrations, the activation energy should be even larger than 2.1 eV, as suggested by our results. Indeed, a recent study found diffusion kinetics at H concentrations $\approx 10^{19} \text{ cm}^{-3}$ have an activation energy of 2.7 eV.⁵⁷

Finally, Van de Walle and Street,⁹ using results from *c*-Si, calculated E_a in a manner similar to our calculation above. Both estimates assume that the total energy of the H_{BC} is not affected by the LDA band-gap problem (see Sec. II). However, since H_{BC} in both *a*-Si and *c*-Si has an occupied conduction-band-related defect level, the LDA results may be in error. Also, for *p*-type and intrinsic *a*-Si:H the positively charge H_{BC}^+ may be energetically more favorable since the defect electron can reduce its energy by dropping from

the defect level to the Fermi level, as discussed in Ref. 32. Preliminary results suggest that the estimate to E_a is reasonable, but that it is H_{BC}^+ , not H_{BC} , that will be the hydrogen species diffusing along transport levels. To resolve these issues, one of us plans to participate in a collaboration to explore the H_{BC} calculation using accurate many-body quantum Monte Carlo calculations.⁵⁸

VII. CONCLUDING REMARKS

We have performed *ab initio* calculations for the structure, energetics, and electronic structure of hydrogen in amorphous silicon. We compare our calculations for H in *a*-Si with analogous calculations for H in *c*-Si (see Table II). Our results are quantitatively compared with other theoretical studies. We provide estimates for the energies of hydrogen trap levels (E_T , E_S , and E_D in Fig. 1). The transport level, shallow trap, and deep trap can be associated with the Si-Si bond center site, highly strained Si-Si bonds, and isolated dangling bonds, respectively. Also, analysis of our results compares well with observations in *a*-Si:H regarding H evolution and long-range diffusion. Finally, the present calculations provide some insight into the H bonding states that may be involved in the formation of electronic defects in *a*-Si:H. Given the limited size of the model used for the present study, reliable results are not guaranteed. Nevertheless, the agreement between our theoretical calculations and experiments encourages confidence that we have examined important features of device quality *a*-Si:H.

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