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Structural stability and vibrational properties of hydrogen complexes in silicon

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Abstract. The structural stability and vibrational properties of various hydrogen complexes in silicon are investigated using a total energy minimization scheme combined with the empirical tight binding method. The trends of hydrogen-induced relaxations of various complexes are basically in good agreement with the first-principles calculation. The vibrational properties of hydrogen complexes are re-evaluated in this calculational scheme. We will show that our calculated vibrational frequencies for metastable diatomic complexes are in a range of experimental values observed from various samples. Hence our model can be applied for further dynamical study of light-induced degradation in hydrogenated amorphous silicon.

1. Introduction

Structural stability associated with various hydrogen complexes in crystalline (c) and amorphous (a) silicon is a long-standing problem. Long exposure to light of hydrogenated a-Si leads to a decrease in photoconductivity and this change anneals at 150–250 °C where the material really returns to its original state. This is known as the Staebler–Wronski effect [1] and has been the subject of extensive experimental and theoretical investigations. It is generally believed that optical excitation creates Si dangling bonds which act as recombination centres and hence decrease the electrical conductivity of the material. It has been suggested that two hydrogen atomic complexes can account for various results better than bond switching and the Si–H bond-breaking model [2]. Many microscopic models [3–7] have been proposed in order to explain this phenomenon but the problem still remains unresolved since this involves temperature dependence, making theoretical approaches difficult. Among them metastable (bistable) diatomic hydrogen (known as H_2^*) proposed by Chang and Chadi [7] is a strong candidate for explaining light-induced degradation in hydrogenated amorphous silicon. It has also been suggested that hydrogen molecules are involved in this phenomenon [8].

Although it has been suggested that H_2^* may exist in n-type materials [9], to our knowledge no experiments have clearly identified it from other existing hydrogen complexes. One clue for clear identification is probably the measured vibrational frequencies. The vibrational frequencies of Si–H systems are mostly measured by IR, Raman, and EELS (surface) experiments on various a- and c-Si samples. Since the samples with hydrogen concentrations up to 25% were used under various experimental conditions, the possibility of H_2^* not being detected is low, assuming that H_2^*

really exists in these samples. The vibrational properties of H_2^* have been calculated previously [10]. However, the unexpectedly low bending frequencies at the bond centre (BC) site (220 cm^{-1}) and low stretching frequency at the antibonding T_d site (1480 cm^{-1}) calculated from first principles are hardly observable from experiments. Although the observed vibrational frequencies from various a- and c-Si samples range from $2000\text{--}2200 \text{ cm}^{-1}$ for stretching modes, and $500\text{--}700 \text{ cm}^{-1}$ for bending modes, the vibrational frequencies of H_2^* are not yet identified experimentally. We assume that the H_2^* exists and is detectable but not yet identified from the experiment. Thus the observed frequencies may involve the values of H_2^* . In this sense we call those experimental values. It is generally known that the first-principles calculations underestimate the vibrational frequencies [11]. Thus it is necessary to re-evaluate the vibrational frequencies of H_2^* by another method. In addition to this, the first-principles approaches are, computationally, very expensive to use to study for larger systems such as a-Si. Thus modelling with a new approach is necessary for practical purposes, to apply in a dynamical study of a hydrogenated silicon system. In this paper we propose a scheme of total energy minimization via an empirical tight binding (ETB) method. Since this method utilizes only valence electrons and ETB parameters for overlap integrals, it is much more efficient than the first-principles calculation. Since the necessary TB parameters of overlap integrals are fitted to experimental vibrational frequencies of a simple system, our method will provide accurate vibrational frequencies for more complex systems. The calculated vibrational frequencies of H_2^* are within the range of experimentally observed values from various samples. We expect that this model will be more appropriate for further application to unified tight binding molecular dynamics simulations, in order to investigate light-induced degradation involving temperature dependence. Vibrational properties of other complexes and related hydrogen-induced structural stability are further investigated.

2. Theory

An efficient and reliable potential model has been proposed for the Si-H system [12]. The empirical tight binding scheme has been successfully applied to pure silicon and the carbon system [13]. We will show that this scheme is also adequate for the study of hydrogen complexes in c-Si.

In general, the total energy of an electron-ion system can be expressed as

$$E_{\text{tot}} = E_{\text{ee}} + E_{\text{ei}} + E_{\text{ii}} \quad (1)$$

where e and i stand for electron and ion, respectively. In first-principles calculations, E_{ee} and E_{ei} may be calculated with the local density approximation and pseudopotential methods, respectively. However, in an ETB this is rewritten as

$$E_{\text{tot}} = E_{\text{bs}} + U. \quad (2)$$

Here $E_{\text{bs}} = \sum_{n,\mathbf{k}} E_{n,\mathbf{k}} = E_{\text{ei}} + 2E_{\text{ee}}$ is the band structure energy consisting of a summation of occupied one-electron energy eigenvalues calculated by the Slater-Koster-type ETB [14] and

$$U = E_{\text{ii}} - E_{\text{ee}} \quad (3)$$

is a short-ranged repulsive pair-potential energy. E_{ee} is subtracted from the pair-potential energy due to double counting of electron-electron pairs. In evaluating the band structure energy we have used valence electrons with nearest-neighbour interactions only. Once the band structure energy is determined from the Slater-Koster ETB, the unknown pair potential may be determined by subtracting E_{bs} from E_{tot} which can be obtained either by first-principles total energy calculations or by experiments for any given system. Thus the most time-consuming routine is the diagonalization of the ETB matrix in which, in our case, only valence electrons are taken account of, and thus this model is efficient and can be applied to larger systems such as defects and various cluster problems.

In the Si-H system, three kinds of overlap integral parameters, Si-Si, Si-H and H-H, should be determined. For Si-Si pairs, we used the nearest-neighbour tight binding potential developed previously, in which the tight binding parameters are taken from Chadi's work [15]. These TB parameters are

$$\begin{aligned} E_s - E_p &= -6.45 \text{ eV} \\ V_{ss\sigma} &= -1.938(r_0/r)^2 \text{ eV} & V_{pp\sigma} &= 3.050(r_0/r)^2 \text{ eV} \\ V_{sp\sigma} &= 1.745(r_0/r)^2 \text{ eV} & V_{pp\pi} &= -1.075(r_0/r)^2 \text{ eV} \end{aligned}$$

where r is the interatomic distance and $r_0 = 2.36 \text{ \AA}$ is the nearest-neighbour distance of silicon in a diamond structure. Once the band structure energy is obtained for the bulk silicon problem through our ETB scheme with the above parameters, the repulsive pair-potential energy U is attained numerically by subtracting the band structure energy E_{bs} from the first-principles total energy calculation by Yin and Cohen [16]. Thus E_{bs} and U are determined separately for well known systems and this calculational scheme is used for further applications. These parameters reproduce the phonon vibrational frequencies and the bulk modulus within an error of about 10% from corresponding experimental values [13].

For Si-H pairs the TB parameters are fitted to the occupied eigenvalues and the vibrational frequencies of the silane (SiH_4) molecule and these are given below:

$$\begin{aligned} E_s &= -8.0 \text{ eV} \\ V_{ss\sigma} &= -3.63(r_{\text{H}}/r)^2 \text{ eV} & V_{sp\sigma} &= 4.63(r_{\text{H}}/r)^2 \text{ eV.} \end{aligned}$$

The bond length dependence of the hopping parameters is also assumed to follow the $1/r^2$ scaling law like the Si-Si pair. The Si-H ionic repulsive pair potential is extracted by subtracting the band structure energy from a parametrized form of the universal binding energy curve for the total energy E_{tot} of the SiH_4 molecule, i.e.,

$$E_{tot} = E_0[1 + (r - r_{\text{H}})/A]e^{-(r-r_{\text{H}})/A} \quad (4)$$

where $E_0 = -3.355 \text{ eV}$ is the average bond energy of Si-H clusters, $r_{\text{H}} = 1.48 \text{ \AA}$ is the Si-H bond length and $A = 0.4357 \text{ \AA}$ is the scaling length which is determined from the symmetric stretching frequency of silane. Thus the fitted parameters reproduce well the occupied eigenvalues and vibrational frequencies of the SiH_4 molecule [12]. The calculated vibrational frequencies of the hydrogenated silicon (111) surface give good agreement with experimental values [17]. Therefore, we expect that this model will provide accurate vibrational frequencies for more complex systems.

A similar procedure was used for H–H interactions. In this case, the H_2 molecule is adopted in order to fit the TB parameters. Only one parameter is needed, i.e. $V_{ss\sigma} = -4.55(r_0/r)^2$ eV where $r_0 = 0.742$ Å is the bond length of the hydrogen molecule. The corresponding parameters of the universal binding energy curve for H–H interactions are $E_0 = -4.454$ eV and $A = 0.2493$ Å which is fitted from the stretching vibrational frequency of the H_2 molecule [18].

The overall fitting procedures are simple. Having fitted to a simple, known system such as bulk and molecule, we proceed to calculate electronic properties for a complex system.

3. Results and discussion

Various hydrogen complexes in c-Si have been suggested. Some of those will be re-evaluated through our newly constructed tight binding method. We have used 54 supercell silicon atoms in this calculation, which is in practice a larger number than that of other calculations where Van de Walle *et al* [19] and Chang and Chadi [7] used 32 and 18 atoms, respectively. As noted in Van de Walle *et al*, the energy convergence was found to suffice, even for a 16-atom supercell, other than for some special hydrogen positions such as the bond centre (BC) site. Even for the BC site, 32 atoms are found to be accurate enough. Thus 54 atoms in our calculation should be large enough to eliminate the size effect.

Integration over the first irreducible Brillouin zone was performed by sampling 55 k -points uniformly over the zone. The convergence was checked using different numbers of sampling points. The absolute value of the energy was different for different numbers of k -points but the difference of energy between positions was less than 1 meV.

Because of the high symmetry the hydrogen atom takes its position along the (111) direction, with a lower energy cost. Thus the bonding BC and antibonding T_d positions are found to be the positions of minimum energy required. This has been suggested by Chang and Chadi [7]. Another stable diatomic hydrogen complex is H_2 located at a T_d site (figure 1). Once we have these configurations, hydrogen atoms and the neighbouring silicon atoms are allowed to relax. The stable configurations are determined from the total energy calculation. A few per cent of hydrogen atomic positions are changed in order to calculate the vibrational frequency after the stable configurations are found. These values are fitted to the harmonic function. It is noted [12] that the zero-point motion of the hydrogen atom due to its light mass plays an important role in the dynamical processes. Here we did not take account of this effect but this motion will be incorporated in future dynamical studies.

3.1. Bond centre site

Shown in figure 1(a) is the simplest single hydrogen interstitial in c-Si. At the BC site the hydrogen atom breaks the nearest-neighbour Si–Si bond and forms a new three-centre Si–H–Si bond. Two neighbouring silicon atoms are allowed to relax. Two silicon atoms move out by over 0.43 Å, giving an Si–H bond length of 1.60 Å where the hydrogen atom locates at the centre of two neighbouring silicon atoms. As a result, the neighbour distance between silicon atoms becomes 2.25 Å shorter than the ideal bond length of 2.35 Å where the second nearest-neighbour distance was fixed in this calculation. Our calculation agrees with previous *ab initio* pseudopotential

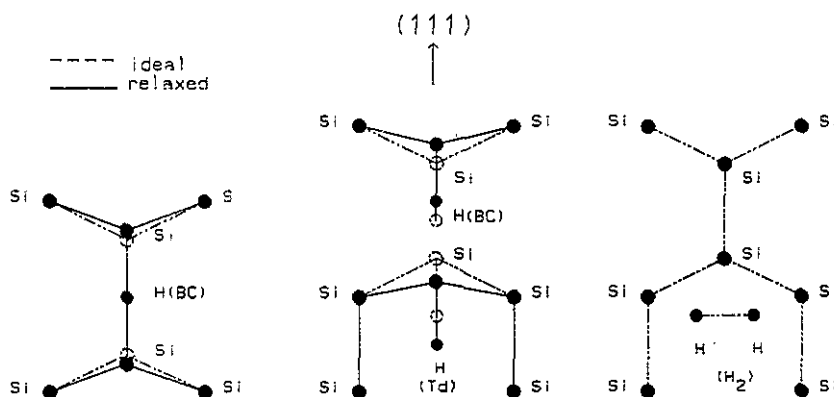


Figure 1. Sketch of various hydrogen complexes: (left) single hydrogen atom at bond centre site, (centre) diatomic metastable complexes H_2^* that have one hydrogen at the bond centre site and one at the antibonding T_d site, (right) an H_2 molecule located at a T_d site. The dotted lines are ideal configurations and the solid lines are fully relaxed configurations.

calculations [19] where the Si-H distance is equal to 1.63 Å. It is also reported that MNDO calculation gives an asymmetric hydrogen position, i.e., one of the bond lengths of Si-H is larger than the other [20]. We believe that the asymmetric result comes from the finite size of the cluster they used. Because of the high symmetry of c-Si, the asymmetric position of hydrogen requires a large energy cost. However, in a-Si it may be possible to have not only an asymmetric position but also the position of hydrogen deviating from the (111) direction (Si-H-Si) due to symmetry-broken networks [21]. The fully relaxed configurational energy where the Si-H bond length is 1.60 Å is 0.44 eV lower than the unrelaxed one where the Si-H bond length is 1.48 Å. Once the silicon atoms are fully relaxed, the total energy is obtained for different hydrogen positions and then the energy difference is fitted to the parabolic function. Figure 2(a) illustrates the stability of Si-H bond stretching at the BC site. The calculated vibrational stretching frequency is 1912 cm^{-1} , reproducing well the *ab initio* pseudopotential calculation (1945 cm^{-1}) [19]. Experimental values for the single H atomic stretching frequency in a- and c-Si range between 2000–2200 cm^{-1} [22]. Thus our new TB scheme produces correct BC site stability to within a numerical error of about 5%.

3.2. Metastable diatomic hydrogen complexes

Even though very complex hydrogen clusters are found in silicon [23], the energetics and dynamics are believed to occur in a single atomic form since more complex forms such as the H_2 molecule (though it exists inside microvoids of a-Si) are electrically inactive and structurally hard to diffuse. The proposed simple diatomic complex is the H_2^* ; one hydrogen atom locates at the BC site and the other at the T_d site. The two atoms are stable and hence it is called a bistable or metastable complex, H_2^* . It has been suggested that this complex may play an important role in light-induced degradation in a-Si by either dissociation or reassociation. However, the calculated vibrational frequencies are somewhat implausible. Here we will re-evaluate the physical properties of the H_2^* complex.

We first test hydrogen at the BC site while the other hydrogen locates at the T_d

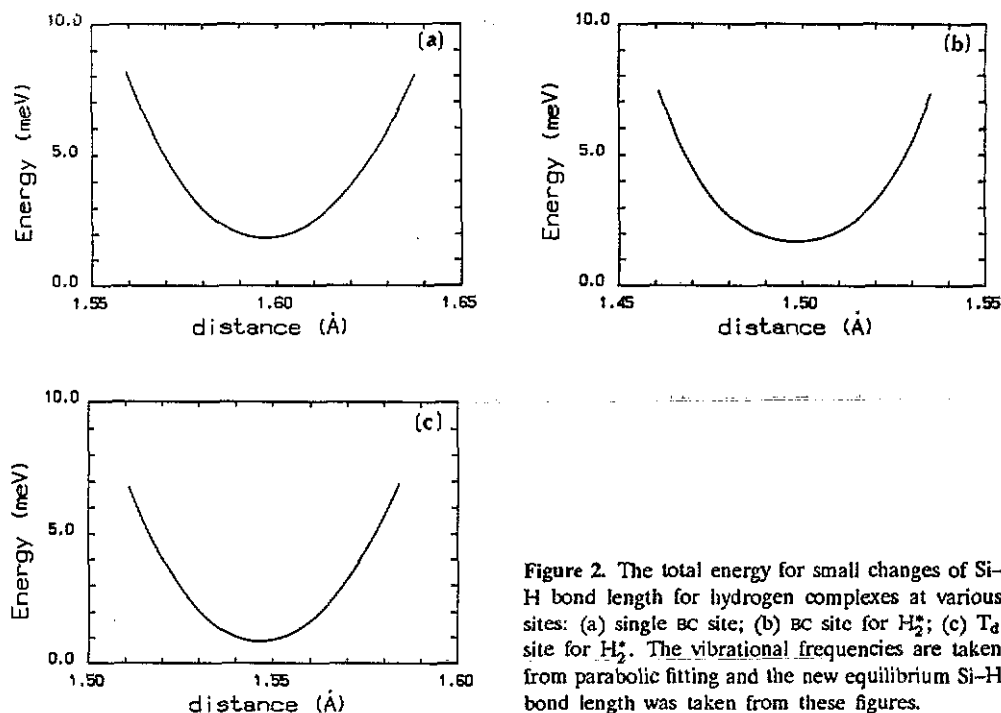


Figure 2. The total energy for small changes of Si-H bond length for hydrogen complexes at various sites: (a) single BC site; (b) BC site for H_2^* ; (c) T_d site for H_2^* . The vibrational frequencies are taken from parabolic fitting and the new equilibrium Si-H bond length was taken from these figures.

site. The nearest-neighbouring silicon atoms only are allowed to relax. The BC centred hydrogen pushes the neighbouring silicon atom towards the antibonding site by 0.05 \AA along the (111) direction, giving the nearest-neighbour distance between silicons of 2.33 \AA , while the tetrahedrally bonded hydrogen atom pulls the neighbouring silicon atom 0.53 \AA along in the (111) direction from its ideal position such that the hydrogenated silicon atom is nearly coplanar with neighbouring silicon atoms, giving a nearest-neighbour distance between silicons of 2.23 \AA , i.e., the hydrogen-induced relaxation at the T_d site changes the hybridization of sp^3 silicon atoms into almost sp^2 (figure 1(b)). These relaxations are very similar to Chang and Chadi's results [7] but a little underestimated, which was expected from the previous surface calculation result [12] that the relaxed hydrogen bond length on the silicon (111) surface is 1.50 \AA compared to 1.53 \AA from *ab initio* pseudopotential calculation. This may come from strong bonding of a tight binding nature.

It is interesting to see how much energy is required to relax the neighbouring silicon atom with the insertion of a hydrogen atom for each site. The total energy for the fully relaxed geometry of the BC site in H_2^* is lowered by 13 meV compared to its unrelaxed geometry (i.e. $d_{\text{Si-H}} = 1.48 \text{ \AA}$ and $d_{\text{Si-Si}} = 2.36 \text{ \AA}$), using most of its energy relaxing the neighbouring silicon atom. The energy for the T_d site is then lowered by 0.88 eV compared to that for unrelaxed geometry, using 0.85 eV for relaxing the neighbouring silicon atom. Thus the relaxation energy comes mostly from relaxation of the silicon atom. The energy cost of the T_d site is even larger than that of a single BC site and hence the metastable H_2^* complex is more stable than a single BC site.

Table 1 shows the calculated vibrational frequencies of hydrogen complexes. Since ETB parameters are fitted to the stretching frequency of the SiH_4 molecule that has the

Table 1. Vibrational frequencies of various hydrogenated silicons and their related relaxations. Experimental values are taken from various a- and c-Si samples. These are not assigned to H_2^* yet. All units of frequency are in cm^{-1} and those of length are Å. The ideal H-Si bond length of the silane molecule is 1.48 Å.

Species	Bond length		Stretching frequency			Bending frequency		
	Ours	<i>Ab initio</i>	Ours	<i>Ab initio</i>	Expt.	Ours	<i>ab initio</i>	Expt.
Si(111):H	1.50	1.53 ^a	2128	1978 ^a	2085 ^a	597	569 ^a	630 ^a
BC site	1.60	1.63 ^b	1912	1945 ^b				
H_2^* BC site	1.50	1.53 ^c	2132	2070	2000~	544	220 ^c	500~
H_2^* T_d site	1.55	1.62 ^c	1933	1480 ^c	2200 ^d	589	690 ^c	700 ^d
H_2 molecule	0.74	0.74	4396(fit)		4396 ^e			
H_2 molecule in T_d site	0.74	0.86	4396					

^a [11].

^b [19].

^c [10].

^d [22].

^e [18].

highest vibrational frequency among Si-H clusters, the calculated stretching frequency on the silicon (111) surface is larger by 3% than the experimental results, whereas the bending frequency is in excellent agreement with experiment [12]. Therefore, we believe that the calculated vibrational properties of hydrogen complexes in bulk c-Si are accurate to within an error of 3%. Even if we consider 3% an overestimation for the stretching modes, our results are still in good agreement with experimental values. Figures 2(b) and (c) illustrates the stability of each hydrogen in H_2^* with a parabolic shape, giving bistability of both sites. It is noted that the calculated bending frequencies of H_2^* are in excellent agreement with experimental values measured from various samples. This is expected because our TB parameters are fitted to experimental vibrational frequencies of the silane molecule. It is emphasized that our calculation reproduces observable vibrational frequencies for both stretching and bending modes of experiments. Despite the fact that the vibrational frequencies of H_2^* in our calculation are within the range of observed values from various samples, it is still difficult to identify H_2^* from other existing complexes due to the closeness of the calculated vibrational frequencies. However, we suggest that these frequencies may play a crucial role in the identification of H_2^* since both first-principles calculations and ours give systematically lower values than the observed values for various Si-H clusters (Si-H, SiH_2 , SiH_3 , and SiH_4). Thus the dissociation of H_2^* into two isolated Si-H bonds will result not only in increasing the dangling bonds of silicon atoms but also increasing the values of vibrational frequencies of the system. These conditions may be achieved either by thermal annealing or by light illumination. One may have to measure both the spin densities and the frequencies for the measurement of dangling bonds at the same time in order to identify the H_2^* complex during the dissociation process. The Si-H bond lengths in all our calculations are basically in good agreement with the first-principles calculation.

4. Conclusion

A complete model for the Si-H system is constructed using an empirical tight binding total energy minimization scheme. Hydrogen complexes have been investigated with our newly constructed tight binding method. The stability of the hydrogen complexes is re-evaluated. It is shown that H_2^+ complexes are indeed stable and that the hydrogen produces a large relaxation of the neighbouring silicon atoms. The calculated vibrational frequencies—in particular, the bending mode of the BC site (544 cm^{-1}) and the T_d site (589 cm^{-1}), and the stretching mode of T_d (1933 cm^{-1})—are within a range of experimental values observed for various a- and c-Si samples but are consistently a little lower than any of those for Si-H clusters. Hence our model can be applied to further dynamical properties. Extension of this method to a molecular dynamics study of temperature-dependent properties will be our next project.

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