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Hydrogen diffusion on Si(001) studied with the local density approximation and tight binding

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Abstract. As computational power increases, it becomes easier to model complex reactions. It is important to understand where the limitations of different modelling methods lie, and what each can be used for. The diffusion of hydrogen on the Si(001) surface is presented, studied with the local density approximation (LDA) to density functional theory (DFT) and tight binding. A new parametrization for tight binding is presented, and its fitting described. Tight binding is found to describe the diffusion reaction well, once a correction has been applied.

1. Introduction

The diffusion of hydrogen on Si(001) is an interesting system to study for two main reasons: first, it is a prototypical system for diffusion, which is easy to image in STM, and there are therefore comparative data available [1]; secondly, it plays an important role in the growth of silicon from silane and disilane, growth sources of increasing importance in Si and SiGe/Si industries. At low temperatures, the silicon growth rate is limited by the hydrogen desorption rate [2, 3] since the hydrogen adsorbed on the surface can block incoming disilane molecules or fragments, although growth can proceed slowly on a hydrogen-saturated surface [4]. Adsorbed hydrogen can also influence the rate of diffusion of Si atoms [5, 6], which then affects the morphology and the rate of growth. Thus the diffusion of hydrogen in the presence of small islands is an important question to address; computer modelling is an ideal way to investigate this.

While *ab initio* methods play an important role in computer modelling, the requirement for large amounts of computer time, or massively parallel computing facilities, can make them impractical for many applications. A good compromise between speed and accuracy is achieved by the tight-binding method [7], which retains a quantum mechanical description of bonding, but parametrizes the Hamiltonian. With the development of linear scaling methods which are applicable to many different systems [8], tight binding becomes a powerful method, capable of modelling many thousands of atoms on a workstation, which will enable modelling of systems including large defects, steps etc. However, the parametrization used is

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of vital importance, and there has been little work on parametrizations specifically designed for diffusion, where long bonds become important. This paper describes such work, and proposes a parametrization which rectifies these problems for the H–Si(001) system.

The basic chemistry of H on Si(001) is reasonably well understood. Hydrogen adsorbs on the (001) surface of silicon by breaking the π-bond of the silicon dimer [9] and bonding to one of the dangling bonds thus created. The remaining half-filled dangling bond appears as a bright blob in the STM, while the hydrogen at the other end is relatively dark [10], due to the bonding energy gain. Hydrogen adsorbs randomly at coverages of less than 0.1 ML [11, 12], but after that it pairs up onto single dimers [13]. This arrangement, with one hydrogen on each end of a silicon dimer, is the most stable phase for adsorption, as the silicon atoms are both four coordinate, with no dangling bonds. Widdra *et al* [13] found that this pairing occurs at adsorption temperatures between 150 K and 600 K, and that the amount of pairing was independent of temperature; they proposed a mobile precursor mechanism (similar to that proposed by Sinniah *et al* [14] for desorption) to explain this. In this mechanism, the incoming hydrogen atom is in an excited, band state with a finite lifetime, which will sample several different adsorption sites. If the lifetime allows it to sample, say, ten sites, then for coverages below 0.1 ML, the hydrogen distribution will appear random, and above that it will be almost entirely paired. Confirming that the diffusion barrier is sufficiently high to prevent diffusion on adsorption over a good part of the temperature range used (150–600 K) would lend weight to this argument. These experiments by Widdra *et al* [13] suggest that the diffusion barrier is sufficiently high to prevent diffusion upon adsorption. Recent STM experiments and *ab initio* modelling [1] have shown that the diffusion barrier is 1.7 ± 0.2 eV. Confirming the reliability of the parametrization against these results will enable confident modelling of new systems which require extremely large unit cells, for instance diffusion of hydrogen up or down a step.

2. Parametrizations for Si(001) and H diffusion

There are already several parametrizations for both Si–Si and Si–H bonds which are used in the literature [15–21]; it might be reasonable to ask why another parametrization is necessary. The answer which emerges is that the parametrizations which are available are all unsuitable in one way or another for the systems which are to be studied in this paper. The Si–Si parametrization will be described first, followed by the Si–H parametrization and tests of the two.

2.1. Si–Si bonding

The parametrization of Goodwin, Skinner and Pettifor [15] (GSP) was designed to fit to various phases of silicon at equilibrium bond lengths—notably including the metallic phases. This was achieved in the simple sp^3, orthogonal tight-binding model by artificially increasing the separation between E_s and E_p beyond that appropriate for the silicon atom, and introducing a rescaling to the distance variation of the hopping parameters:

$$f(r) = \left(\frac{r_0}{r}\right)^n \exp\left\{n\left(-\left(\frac{r}{r_c}\right)^{n_c} + \left(\frac{r_0}{r_c}\right)^{n_c}\right)\right\} \quad (1)$$

where n, r_c and n_c are suitably chosen constants and r_0 the nearest-neighbour distance. Unfortunately, the increased on-site E_s–E_p separation (from 6.4 to 8.3 eV) weakens the π-bonding of silicon dimers on Si(001) and renders it unsuitable for modelling the chemistry of the Si(001) surface—where the π-bond plays an important role. The weakening can

be seen quite simply by modelling two unit cells: a clean Si(001) surface, and a Si(001) surface with one hydrogen adsorbed on one end of a dimer. The dimer which has had hydrogen adsorbed on one end should be longer, as the π-bond in the dimer has been broken (and, indeed, in the LDA modelling described in section 3.1, the bond length for a clean dimer is 2.28 Å, and for a partially hydrogenated dimer 2.43 Å). Unfortunately, the GSP parametrization predicts that the bond *shortens* when a hydrogen adsorbs; this suggests that the next available orbital after the σ-bond is the σ^* anti-bonding orbital (rather than the π-orbital), which is emptied when the hydrogen adsorbs, leading to the shortening. This conclusion is reinforced by the fact that when modelling the clean surface, the dimer bond length is 2.42 Å long as compared to a bulk bond length of 2.35 Å.

Table 1. Parameters for Si–Si interactions. The parameters from the Goodwin, Skinner and Pettifor (GSP) parametrization [15] are shown for comparison.

	E_s	E_p	$h_{ss\sigma}$	$h_{sp\sigma}$	$h_{pp\sigma}$	$h_{pp\pi}$	ϕ_0
	−12.2	−5.75	−1.938	1.745	3.050	−1.075	3.445 66
(GSP)	−12.2	−3.91	−1.82	1.96	3.06	−0.87	3.45
	r_0	r_c	d_c	n	n_c	m	m_c
	2.35	3.8661	3.8521	1.9771	6.8702	4.7104	7.0531
(GSP)	2.35	3.67	3.67	2.0	6.48	4.54	6.48

Table 2. Fitting results for the silicon–silicon interactions. Energies are in eV, lattice constants in ångströms and elastic constants in Mbar. LDA results are from [33], elastic constants from [34].

	Diamond					β-tin	
	a_0	Energy	B	C'	C_{44}^0	a_0	Energy
TB	5.43	0.00	0.998	0.363	1.099	4.842	0.266
Experiment/LDA	5.43	0.00	0.990	0.510	1.110	4.822	0.266

The early parametrization of Chadi [16] described the band structure rather well, and had the correct separation of E_s and E_p, but gave poor elastic constants, due to the assumption of $1/r^2$ scaling for the repulsive potential. The parametrization of Kwon *et al* [17] is rather more complicated, and uses a cut-off which is more than nearest neighbour, which degrades the performance of linear scaling methods enormously. This parametrization and the GSP parametrization, in attempting to be transferable to all phases of silicon, are less suited to a detailed study of one aspect of silicon chemistry. For this reason, a new parametrization was created specifically for the Si(001) surface.

The aim of the parametrization presented here was to reproduce well the chemistry of the Si(001) surface, as well as bulk Si. This led to a number of requirements: a good fit to the bulk band structure; good elastic constants; the correct separation of E_s and E_p; and accurate reproduction of small distortions of the structure. As Chadi's parametrization [16] has the correct separation of E_s and E_p, and reproduces the band structure well, the values he chose for the energy levels and equilibrium hopping parameters were adopted. The scaling rules must now be fitted; the GSP form for scaling (1) was used, and the following criteria fitted to:

(i) the diamond and β-tin structure absolute volumes;
(ii) the diamond-β-tin energy difference;
(iii) the bulk modulus, B, and the elastic constants C' and C_{44}^0.

This fitting yielded the parameters shown in table 1 with the GSP parameters shown for comparison. The quality of the fit is shown in table 2. Various tests of the model, which involved both Si–Si interactions and Si–H interactions, are given in section 2.3. It is worth noting here that, with the exception of the C'-constant (which is normally at least this inaccurate in a minimal-basis-set and nearest-neighbour model), the fit is extremely good.

2.2. Si–H bonding

As has been explained above, it has been necessary to create new parametrizations for Si–Si and Si–H, although such sets already existed. The reasons for the rejection of the Si–H parametrizations previously published now follow. The parametrization of Panzarini and Colombo [18] for H–Si interactions uses the GSP silicon parametrization, and thus will not work well at surfaces for two reasons: firstly, because the Si–Si π-bonds are poorly described, and secondly because the gap between the silicon E_s (or, equivalently, the silicon E_p) and the hydrogen E_s will be incorrect. Also, they did not fit the scaling terms to any H–Si stretched bonds, which is appropriate for the bulk diffusion that they were investigating, but is inappropriate for surface diffusion. The parametrization of Min *et al* [19] used poor Si–Si parameters, and was not fitted to extended bonds. Boucher and DeLeo [20] used the GSP parametrization for their Si–Si interactions, while Li and Biswas [21] used the longer-range Si–Si parameters of Min *et al* [19]; both of these parametrizations were therefore unsuitable. Again, a new parametrization was created to fit to the following situations: extended bonds, and interactions at the Si(001) surface.

In the SiH_4 molecule, the only bonding involved is between Si and H. As it is also tetrahedral, the molecule is ideal for modelling Si–H interactions. The electronic eigenstates are available from experiments; theoretically, the Hamiltonian for the silane molecule can be solved analytically; the bonding (s_b, t_b) and anti-bonding (t_a, s_a) eigenvalues are given by

$$s_b = \frac{1}{2}\left[(E_s^{\mathrm{Si}} + E_s^{\mathrm{H}}) - \sqrt{(E_s^{\mathrm{Si}} - E_s^{\mathrm{H}})^2 + 16h_{ss\sigma}^2}\right] \tag{2}$$

$$t_b = \frac{1}{2}\left[(E_p^{\mathrm{Si}} + E_s^{\mathrm{H}}) - \sqrt{(E_p^{\mathrm{Si}} - E_s^{\mathrm{H}})^2 + \frac{16}{3}h_{sp\sigma}^2}\right] \tag{3}$$

$$t_a = \frac{1}{2}\left[(E_p^{\mathrm{Si}} + E_s^{\mathrm{H}}) + \sqrt{(E_p^{\mathrm{Si}} - E_s^{\mathrm{H}})^2 + \frac{16}{3}h_{sp\sigma}^2}\right] \tag{4}$$

$$s_a = \frac{1}{2}\left[(E_s^{\mathrm{Si}} + E_s^{\mathrm{H}}) + \sqrt{(E_s^{\mathrm{Si}} - E_s^{\mathrm{H}})^2 + 16h_{ss\sigma}^2}\right]. \tag{5}$$

These can be inverted, to give the hopping parameters in terms of the energy levels of hydrogen and silicon. The hopping parameters will be written in terms of the bonding eigenvalues, and the on-site energies for silicon and hydrogen:

$$h_{ss\sigma} = \frac{1}{16}\sqrt{\left[(E_s^{\mathrm{Si}} + E_s^{\mathrm{H}}) - 2s_b\right]^2 - (E_s^{\mathrm{Si}} - E_s^{\mathrm{H}})^2} \tag{6}$$

$$h_{sp\sigma} = \frac{3}{16}\sqrt{\left[(E_p^{\mathrm{Si}} + E_s^{\mathrm{H}}) - 2t_b\right]^2 - (E_p^{\mathrm{Si}} - E_s^{\mathrm{H}})^2}. \tag{7}$$

If no energy zero is defined, then there are three energy differences available for fitting (e.g. $s_a - s_b$, and the other levels relative to s_b), and three variables to fit (E_s^{H}, $h_{ss\sigma}$ and $h_{sp\sigma}$). A perfect fit to these requires the silicon E_s and E_p splitting to be reduced to 5.45 eV; as the Si–Si parameters have already been fitted, with the splitting between E_s and E_p fixed at 6.45 eV, the requirement for reducing E_{sp} will be disregarded. The minimal-basis tight-binding model which is being used rarely reproduces excited states well, so only the occupied (bonding) eigenvalues were fitted to, as shown in (6) and (7), which should not greatly affect the quality of the modelling. The other electronic degrees of freedom are the separation of the hydrogen E_s- and silicon E_s-levels, and the absolute level of the silicon E_s-level relative to the experimental eigenspectrum (all other energy levels are taken relative to the silicon E_s-level). The scaling of the Si–H bond for small displacements was fitted to the binding energy curve for the silane molecule. The final degree of electronic freedom (the absolute value of the silicon E_s-level) can be understood more easily when it is noted that the hopping terms, $h_{ss\sigma}$ and $h_{sp\sigma}$, depend on E_s^{Si}.

The experimental data being fitted to are the electron energy levels of the molecule and the frequency of the symmetric bending mode. The other data come from *ab initio* calculations: the binding energy curve about equilibrium from a fully self-consistent LDA calculation. There are two electronic degrees of freedom (the absolute position of the silicon E_s-level, and the relative position of the hydrogen E_s-level with respect to the silicon E_s-level), which are fitted to four pieces of data, while there are seven scaling degrees of freedom (using GSP scaling as shown in (1), there are n, n_c and r_c for hopping and repulsive terms and ϕ_0) which are fitted to a 26-point binding energy curve.

Table 3. The parameters for Si–H interactions.

E_s	E_p	$h_{ss\sigma}$	$h_{sp\sigma}$	$h_{pp\sigma}$	$h_{pp\pi}$	ϕ_0
−8.4	N/A	−3.834	4.734	N/A	N/A	7.4399
r_0	r_c	d_c	n	n_c	m	m_c
1.474	3.4	3.4	2.6752	20.0	4.2302	20.0

The parameters obtained from the fitting are shown in table 3. In this situation, the GSP-style rescaling is used to obtain a clean cut-off at 3.4 Å (a requirement found from fitting to extended bonds; the simple r^{-n}-scaling for the hopping and repulsive parameters reproduced the binding energy curve extremely well, making the rescaling GSP terms unnecessary, and hence available to provide a smooth cut-off). The tests of the parametrization are described in the next section.

The fitting to extended bonds is somewhat harder; a fictitious but appropriate reaction has been chosen. The process used consisted of SiH_4 and SiH_3 (separated by 5 Å) transferring a hydrogen from the SiH_4 to the SiH_3 along the threefold axis so that the end product is SiH_3 plus SiH_4. The entire system remains frozen during this transfer, with the hydrogen placed at different points between the two Si atoms. The Si–H interaction is completely negligible once the distance is more than 3.4 Å (i.e. the charge density between the two is zero, and the energy does not change once this distance is increased, hence the cut-off mentioned above). An additional constraint upon the fitting was that the equilibrium curvature of the binding energy curve should remain the same, so as not to disturb the vibrational modes already fitted. As it turned out, the parameters as already fitted gave a good fit to the *ab initio* energies, as shown in figure 1. The forces from LDA and the tight-binding fit are

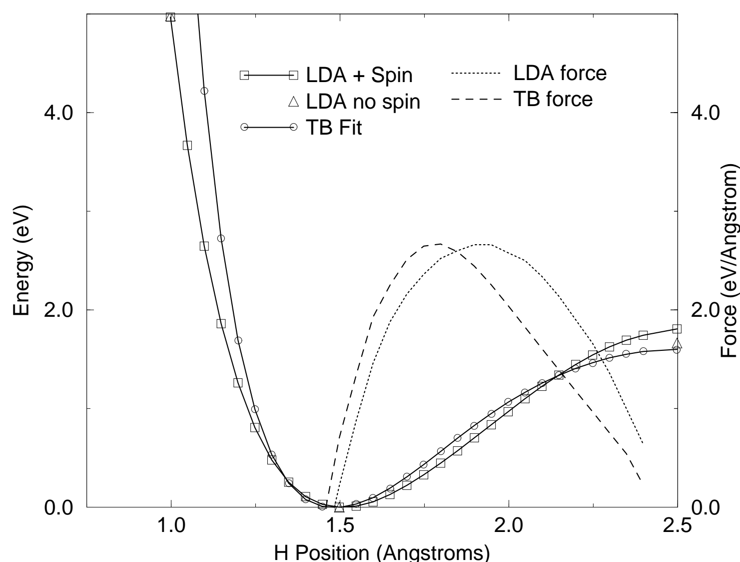


Figure 1. The energy for a fictitious reaction, $SiH_4 + SiH_3 \rightarrow SiH_3 + SiH_4$, with the coordinates of all of the atoms except the central hydrogen kept fixed. The results from LDA and tight binding are shown, along with three points to indicate the effect of spin, and the force (by numerical differentiation of the energy curves).

also shown in this figure, and are in remarkably good agreement.

As will be discussed in detail in section 3.2, there is one remaining problem with the modelling of diffusion on the surface. When there is a long, weak bond, there is little charge density between the two atoms (e.g. between a hydrogen and the atom towards which it is diffusing), which means that physically there is little interaction. Unfortunately, in tight binding, the repulsive term is sufficiently large that, rather than a weak attraction between the atoms, there is a weak repulsion. This means that the barriers calculated using tight binding are rather high; however, they should all suffer from about the same effect, meaning that comparisons between different barriers in different environments should be accurate. An estimate of the effect of the repulsion, and a correction to the barriers calculated, is developed in section 3.2.

2.3. *Tests of the parametrizations*

The parametrizations have been tested on a number of different systems, and perform extremely well. The asymmetric bending mode of the silane molecule is modelled as 108 meV, where experimentally it should be 113 meV. The four lowest eigenvalues and stretching modes for disilane are given in table 4, and the bond lengths and angles for disilane and disilene are given in table 5. These results indicate that the parametrization is extremely good for Si–H bonds in a range of environments; along with the parametrization for C–H bonds by Horsfield *et al* [22], it indicates that tight binding can achieve remarkable results given a relatively low level of computational effort.

The above calculations of molecules show remarkable agreement with experiment, but do not tackle a large system with a surface. Three of these are offered as tests of the parametrization. First, the single missing-dimer defect of the Si(001) surface [23]. The

Table 4. Eigenvalues and stretching modes for the disilane molecule, from tight binding and experiment. Eigenvalues are in eV, stretching modes in meV.

Eigenvalue	TB	Experiment
One	−16.6	−17.3
Two	−13.1	−13.3
Three	−12.1	−12.1
Four	−10.5	−10.7
Vibrational mode	TB	Experiment
Symmetric stretch	286	265
Symmetric bend	114	112
Asymmetric bend	107	105
Wag	74	78
Twist	55	62
Si–Si	56	54

Table 5. The bond lengths and angles for disilane (Si_2H_6) and disilene (Si_2H_4). Experimental values are given in brackets. Lengths are in ångströms, angles in degrees.

Molecule	Si–H	Si–Si	H–Si–H	H–Si–Si
Disilane	1.48 (1.49)	2.32 (2.33)	109.7 (108.6)	109.2
Disilene	1.48 (1.49)	2.25 (2.22)	110.7 (110)	116.3

LDA results show the rebonded defect to be 0.42 eV more stable than the unbonded one; this parametrization gives it as 0.45 eV more stable. Secondly, the SiH_2 fragments resulting from the adsorption of disilane [24] are correctly ordered in stability by this parametrization, with one exception. The fragment can adsorb between two dimers in the same row, on top of a single dimer (leaving the σ-bond intact), in a single dimer (breaking the σ-bond) or between two dimers in adjacent rows. The only inaccuracy when compared to LDA results is for the on-dimer fragment (which, with a 60° bond angle, is a difficult system for tight binding to model) and is not sufficiently stable compared to the other structures. Thirdly, the stability of Si ad-dimers in different adsorption sites on the Si(001) surface is correctly ordered by this parametrization. There are two positions in which the dimer can sit (on the dimer row or over the trench) and two orientations for each: epitaxial (perpendicular to the substrate dimers) and non-epitaxial (parallel to the substrate dimers). The trench dimers are less stable than the row dimers, and the non-epitaxial orientation is more stable than the epitaxial one. The parametrization correctly predicts these facts, though the trench dimers are more stable than they should be according to LDA; this is again a feature of the 60° bond angles formed in the row dimer case, which are too far from what was fitted to be modelled accurately. So with the exception of structures with approximately 60° bond angles, the parametrization is extremely good for the Si(001) surface, and its interactions with Si and H.

3. Atomistic modelling of single-atom diffusion

There have been many theoretical investigations of hydrogen diffusion on Si(001), which have not proved conclusive. Wu and Carter have performed cluster calculations using CI

techniques and initially [25] predicted diffusion barriers of 2.0 eV along the dimer rows and 2.7 eV across the dimer rows. However, they used a small cluster consisting of 9 silicon atoms terminated with 12 ‘pseudo-hydrogen atoms’, and did not allow the substrate to relax during diffusion, which suggests that their barrier will be a poor approximation to the actual barrier. The CI method finds a very accurate answer, but the use of clusters (which is necessary to limit the number of atoms modelled) will introduce errors due to the edge effects inherent in such a technique. When they later performed different calculations [26] using empirical potentials (based on the Stillinger–Weber potential) which they had generated from SCF-LCAO calculations, and allowed the slab substrate to relax, they found a significantly lowered barrier of 1.5 eV for diffusion along the dimer row and a slightly lowered value of 2.5 eV for diffusion across dimer rows.

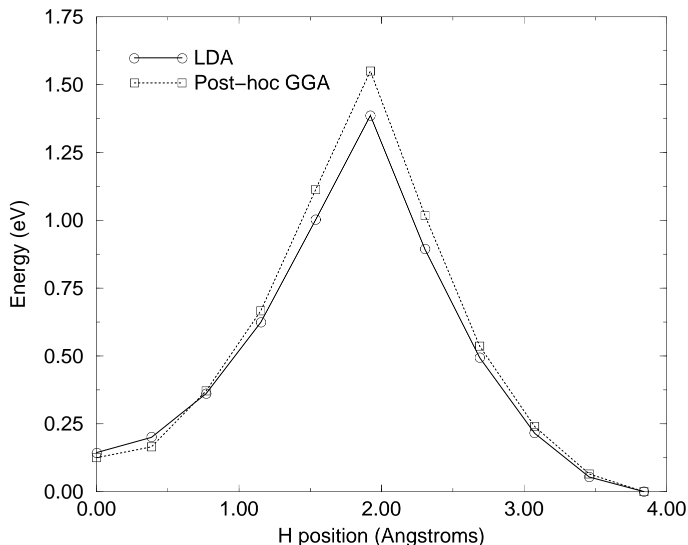
This lower barrier fits with LDA calculations by Vittadini, Selloni and Casarin [27] who found a barrier of 1.3 eV, though we would argue that using empirical potentials (as Wu, Ionova and Carter did [26]) to model a process where the bond breaking is vital will introduce large error bars on a calculation. Vittadini, Selloni and Casarin used LDA, and a repeated slab for their calculations, and allowed the top four layers of the slab to relax. They claim that the major difference between their calculations and those of Wu and Carter [25] is the lack of surface relaxation in Wu and Carter’s work. They attempt to estimate the magnitude of this effect by performing their diffusion calculations *without* allowing the substrate to relax, and conclude that the effect can be as large as 1 eV.

Recent calculations using gradient corrections [1] find a barrier of 1.25 eV from LDA (allowing the slab to relax) and 1.55 eV from GGA, which is within experimental error of the value of 1.68 eV found by STM measurements. The addition of spin herein is found to raise the barrier to 1.6 eV. The tight-binding calculations carried out in this paper find a barrier of 1.66 eV, all of which suggest that the process is now well understood, and that there can be no thermal diffusion upon adsorption for temperatures up to 500 K, lending weight to the mobile-precursor model for adsorption.

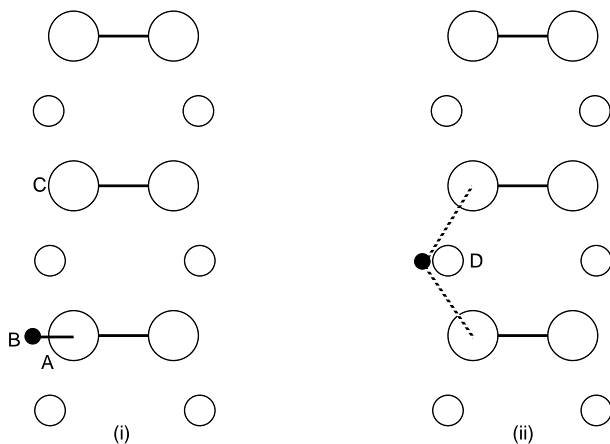
In this paper, the problem has been approached from two directions: that of LDA and GGA, and that of tight binding. The former have been used for this problem essentially to validate the tight-binding calculations, and for comparison with experiment; once the tight-binding parameters have been validated, larger systems than can be tackled with LDA may be addressed, such as diffusion on the saturated surface [28] and steps and defects [29, 30].

3.1. DFT calculations

The hydrogen diffusion was modelled using LDA to obtain coordinates and charge densities, and both LDA and post hoc GGA to obtain the energies. The unit cell which was used was two dimer rows wide, each of which contained two dimers. The hydrogen atom which was to diffuse was placed on one end of a dimer in one row, and to prevent the system from having an unfilled band, a hydrogen atom was also placed on the other side of the other dimer row. This hydrogen atom played no part in the diffusion (except to obviate the need for a subspace rotation at every step to correctly half-fill one band). There were five layers of silicon, with the bottom layer constrained to lie in bulk-like positions, and terminated with hydrogen. The only other constraint applied to the system was to force the hydrogen atom to remain in a plane of constant y (in figure 2(b), the y-axis runs vertically up the page), which was moved along the dimer row at each point in the calculation. A plane-wave cut-off of 200 eV and a single k-point at (0, 0.25, 0) were used, which are sufficient for energy difference convergence [24]. The energies from both LDA and GGA



(a)



(b)

Figure 2. (a) The energy for a hydrogen atom diffusing on the Si(001) surface, calculated using LDA and post hoc gradient corrections (GGA). The barriers are 1.55 eV from GGA and 1.39 eV from LDA. (b) The process indicated schematically. The letters A, B and C refer to figure 4, and the letter D is for reference in the discussion of the tight-binding results.

calculations are shown in figure 2(a).

The mid-point ((ii) in figure 2(b)) is highly unstable, as shown by the sharp peak in the graph. This is not unreasonable, as the hydrogen is bonded to two silicon atoms at this point, which is not an energetically favourable state for a $1s^1$ atom to be in. The distances between the hydrogen and the two silicon atoms are shown in the next section, in figure 4; these show that once the hydrogen is past the mid-point it bonds strongly to the atom towards which it has been diffusing, and less strongly to the atom on which it started. The energies obtained (1.55 eV from GGA and 1.39 eV from LDA) are a little smaller than the experimental value (1.68 eV), but bring home the point that gradient corrections can be important in obtaining

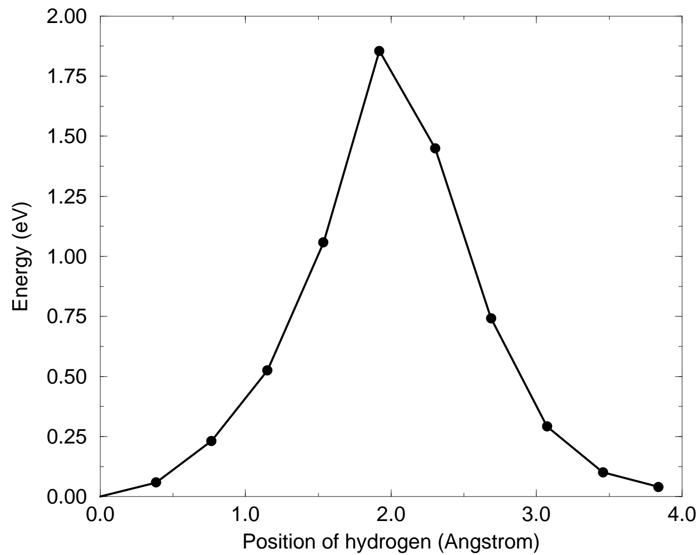


Figure 3. The TB energy for a hydrogen atom diffusing on the Si(001) surface. The barrier is 1.86 eV (see the text for a discussion of a correction to be applied to this). The process is illustrated schematically in figure 2(b).

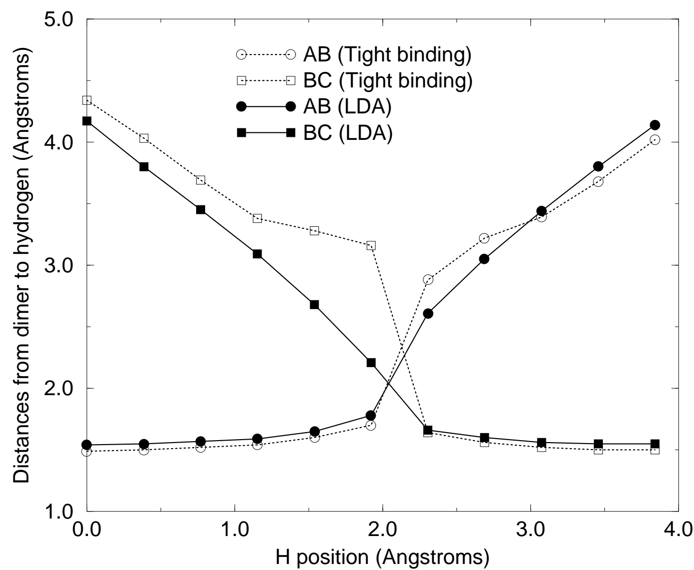


Figure 4. The distance from the two Si atoms which bond to the hydrogen, as calculated using tight binding and LDA, as the hydrogen moves. All distances are in ångströms. The letters refer to the atoms shown schematically in figure 2(b).

the correct value of barrier heights, for the GGA result agrees to within experimental error. The barrier is increased to 1.6 eV with the addition of spin to the calculation, which brings the calculated value well within experimental errors. Another point worth raising here is that of attempt frequencies: the experimental value of 1.68 eV was found from *hopping*

rates and assuming an attempt frequency of 10^{13} s^{-1}, while another frequency which fits perfectly well (10^{14} s^{-1}) gives a barrier of 1.80 eV. It is certainly accepted that LDA cannot predict attempt frequencies accurately (Smith and Jónsson [31] state that a factor of 5 is too sensitive for LDA to correctly model; see reference [32]), and so it has been decided that the prefactor relevant for comparing LDA/GGA hopping rates should be taken as 10^{13} s^{-1}. This fits well with values from the literature found using, for example, experimental vibrational mode studies. This is the first *ab initio* study of this system to predict a barrier which agrees well with the experimental value.

3.2. TB calculations

To calculate the energy of a hydrogen atom diffusing on the Si(001) surface using tight binding is a difficult task. In particular, the bonding at the saddle point will be highly non-equilibrium and therefore test the fitting of the parametrization greatly.

The unit cell used for this calculation was six dimers long, and one dimer wide, with ten layers of silicon in the slab. The bottom five layers of silicon were constrained to lie in bulk-like positions and the final layer was terminated in hydrogen. The only constraint applied to the system was the same as for the LDA modelling, i.e. constraining the hydrogen to lie in planes of constant y. The hydrogen was allowed to bond to only two silicon atoms—the one it started on and the one it ended on. The other atom to which it could bond is the second-layer atom to which the two dimers are bonded (marked as 'D' in figure 2(b)). Tests showed that if this atom was allowed to bond to the hydrogen, the bond energy was almost zero, but the repulsive energy was high; this was clearly unphysical and solved by removing the interaction. Examining surfaces of constant charge density from the LDA calculations showed that there was almost no charge between these two atoms, indicating that any interaction is negligible and that the above approximation is good. The start and end points are not exactly symmetrical, as the cell is $p(2 \times 2)$, but the energy difference is small.

The anomalous repulsion manifests itself again when the hydrogen is approaching the mid-point. The hydrogen is bonded strongly to the atom which it is leaving, and weakly to the atom which it is approaching, and again the repulsive term is too large. The error induced by this repulsion has been calculated as 0.2 eV; this was found by taking the unit cell at the mid-point, and comparing the energy for the cell both as it is and after re-relaxing *without* the interaction between the hydrogen and the second atom (C in figure 2). This correction of 0.2 eV should be applied when hydrogen diffusion processes are modelled using this parametrization. The energy for the diffusion reaction is shown in figure 3, and the bond lengths between the hydrogen and the two atoms to which it bonds are shown, along with the equivalent LDA lengths, in figure 4. This latter figure displays the effects of the anomalous repulsion: when the hydrogen is just within bonding range of the second dimer, instead of a slight attractive interaction (as seen in LDA) there is a slight repulsive one (shown by the knee in the TB curve, and caused by the same effect as that alluded to above for the second-layer Si atom—a high repulsive term where there is a low electron density). This is due to the fact that TB cannot take into account screening—the physical interactions represented by the TB repulsive term are very small, but this is not reflected in the relatively large repulsive interaction. Taking the correction into account makes the overall barrier $1.66\ \text{eV} \pm 0.15$ eV, which is much more in line with experiment. Indeed, in further calculations for diffusion barriers in a variety of different environments [29, 30] this correction brought the calculated barriers into good agreement with available experimental data.

4. Conclusions

A new tight-binding parametrization for Si(001) surfaces and their interactions with hydrogen has been described, and shown to be in good agreement with both experiment and *ab initio* calculations. The cause of an anomalous repulsion in tight binding has been described, and a correction which can be applied found. This modelling indicates that, with the correct parametrization fitted to long bonds, tight-binding modelling of diffusion processes can be accurate and useful.

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