Formation of clean dimers during gas-source growth of Si(001)

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Elevated temperature STM measurements have shown that one key phase during gas-source homoepitaxy of Si(001) is the formation of clean Si ad-dimers from hydrogenated ad-dimers, though the mechanism for this formation is unknown. We present *ab initio* density functional calculations designed to explore this mechanism. The calculations show that there is a pathway consistent with the experimentally observed reaction rates, which proceeds via a meta-stable intermediate, and is effectively irreversible. This result fills a vital gap in our understanding of the atomic-scale details of gas-source growth of Si(001).

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I. INTRODUCTION

Gas-source growth of Si(001) using hydrogen-based precursors (such as SiH_4, silane, and Si_2H_6, disilane) is of great scientific and technological interest[1,2,3,4] — in particular, hydrogen can act as an effective surfactant, and has been shown to reduce roughness and intermixing during growth of Ge/Si alloys and pure Ge on Si(001)[5]. Understanding the reactions that occur and the intermediate structures that are formed during this growth will enable greater control of surface and interfaces during growth. STM observations of the growth of Si(001) from disilane, both at room temperature following anneals[1,2] and at elevated temperature[3,4], along with careful electronic structure calculations[3,4,6] have mapped out the growth pathway. A key observation in this pathway is that the islands formed during growth are *clean*, while the substrate remains covered with a certain amount of hydrogen[3]. The fundamental building block in gas-source growth is the clean ad-dimer (as opposed to solid-source growth, where fast-moving ad-atoms are key[7]); yet, the mechanism to form such clean dimers from the hydrogenated dimers that occur naturally during gas-source growth is unknown. In particular, they are observed to form at 450K while desorption from the monohydride phase occurs at 790K, indicating that their formation must be completely different to the desorption of hydrogen from the monohydride phase. In this paper, we present a first-principles investigation of the mechanism for formation of clean ad-dimers from hydrogenated dimers, with the aim of explaining how these form at a comparatively low temperature.

Disilane (which is used in preference to silane as it decomposes more easily) adsorbs on Si(001) as SiH_3 (which soon breaks down to form SiH_2) or SiH_2[1], sometimes with accompanying hydrogen. These SiH_2 groups[6] start to diffuse at 400–500K[3]. When two groups are on adjacent dimer rows, they react to form a hydrogenated ad-dimer (that is, an ad-dimer with both dangling bonds saturated with hydrogen, illustrated in Fig. 1 (a)) over the trench between the dimer rows[3]. This then decomposes to form clean ad-dimers and hydrogen on the surface at around 450K[1,2,3], via a pathway to be investigated in this paper. A hydrogenated ad-dimer (which is the starting point) is illustrated in Fig. 1 (a), along with a partially hydrogenated ad-dimer (the result of the first part of the pathway) in Fig. 1 (b) and a clean ad-dimer (the final point) in Fig. 1 (c). Once formed, the clean ad-dimers diffuse[8] and form a square feature, which is believed to be the precursor to dimer strings[9], followed by short strings of dimers[2] which later increase to form larger islands[2,4].

The calculations to be presented are based on density functional theory (DFT) in the generalized gradient approximation (GGA), with a plane wave basis set and pseudopotentials. We have searched for possible pathways both by applying constraints to specific atoms (for instance constraining a hydrogen to lie in a given plane) and by using the nudged elastic band technique (NEB)[10,11] which allows accurate determination of reaction barriers given an initial approximation to a pathway. One key result is that the dehydrogenation proceeds via a meta-stable intermediate state (this is discussed fully in Section III and illustrated in Fig. 2).

The rest of the paper is organised as follows: the next section gives details of the computational techniques used; this is followed by a detailed discussion of the structure of the meta-stable state which plays a key role in the dehydrogenation; the diffusion pathways are then presented, looking at the mechanism for both hydrogens, followed by a conclusion section.

II. COMPUTATIONAL DETAILS

The theory underlying DFT[12,13] and their application to electronic structure calculations have been extensively reviewed[14], as has the use of pseudopotential and plane-wave techniques[15]. The calculations in this paper were performed using the VASP code[16], using the standard ultra-soft pseudopotentials[17] that form part of the code.

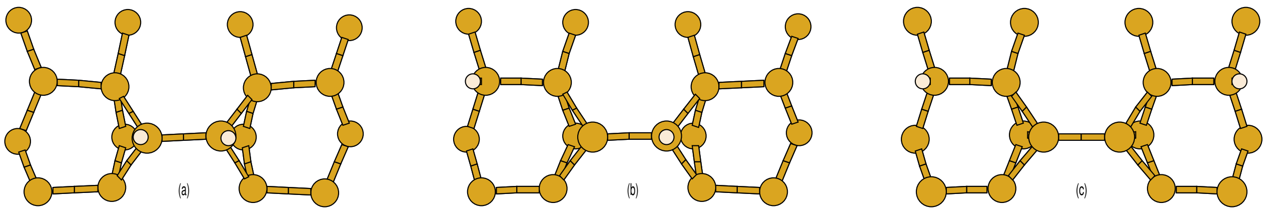

FIG. 1: Structures of: (a) the starting point, with a hydrogenated ad-dimer; (b) the end point for the first diffusion event with one hydrogen on the substrate; and (c) the final point with a clean ad-dimer and both hydrogens on the substrate.

The approximation we use for exchange-correlation energy is the generalised-gradient approximation (GGA) due to Perdew and Wang (PW91)[18,19]. We chose the GGA rather than the local density approximation (LDA) rather deliberately. As the barriers that we will be calculating are sensitive to bonding and stretched bonds, and the GGA is known to be rather more accurate in these situations (LDA generally overbinds), we considered its use to be essential for this work.

We use periodic boundary conditions, as is standard for DFT calculations with plane-waves, and we therefore used a periodic slab for the surface, with a vacuum layer between the slabs. Our simulations were performed within a unit cell two dimers long and two dimer rows wide, with five layers of Si (the bottom of which was terminated in hydrogen and constrained to remain fixed in bulk-like positions). The vacuum gap of 6.9 Å is equivalent to five atomic layers of Si, and provides sufficient isolation between vertical periodic images. We used a plane wave cutoff of 150 eV and a $2 \times 2 \times 1$ Monkhorst-Pack k-point mesh. All these parameters were tested, and found to converge energy differences to better than 0.01 eV. The system contains an even number of electrons, but has various saddle points which might involve unpaired electrons, so we checked the effect of performing spin-polarised calculations for these points. The effect was found to be negligible (both on energies and geometries) and so was not used in the calculations.

To investigate the diffusion pathways, we used two techniques: first, constraining the diffusing hydrogen to lie in a particular plane, and calculating static energies for different locations of the hydrogen; second, the Nudged Elastic Band method[10,11]. This second method requires the simultaneous relaxation of a number of images of the system, which can be done in parallel. However, this has the potential to become extremely computationally intensive, which is why we chose to use the smallest realistic unit cell (with four dimers in the surface).

The initial exploration of the system used the first method (static calculations, constraining the hydrogen). It was using this method that the meta-stable state (discussed in Sec. III) was found, and it is unlikely that it would have been found using the NEB without significant effort (for instance performing simulated annealing on the initial images of the system) or using a more complicated technique such as the dimer method[20]. The diffusion barriers presented in the paper were all calculated using a variant of the original technique which actively seeks the saddle point, the climbing image NEB[21], with 8 images relaxed in the chain.

While we have calculated the diffusion barriers, we have not calculated attempt frequencies, which have been assumed to be 10^{13} sec^{-1}, typical for diffusion processes. While DFT-GGA is sufficiently accurate to calculate reaction barriers to within 0.1 eV, it is not able to predict attempt frequencies accurately[22]; for instance, in previous work on solid-source growth of Si(001), it was shown that a factor of five in the attempt frequency was required to understand the results, but was not accurately predicted[23].

III. THE META-STABLE INTERMEDIATE

The lowest energy diffusion pathway, and the only one which has an energy barrier which is in line with the temperature at which the dehydrogenation is observed to occur, proceeds via a meta-stable intermediate. This is an unusual and rather important structure, and will be discussed in detail in this section. It is illustrated in Fig. 2, and should be contrasted with the hydrogenated ad-dimer illustrated in Fig. 1 (a).

The atom labelled 'A' in Fig. 2 is one of the substrate dimers, to which the hydrogenated (and clean) ad-dimer is bonded; 'B' is a second layer atom in the substrate, to which the substrate dimer is normally bonded (for instance in Fig. 1 (a)); and 'C' is the ad-dimer atom itself, which is now clean (having started hydrogenated). The hydrogen is now bonded to 'A', which has broken its bond to 'B', while 'C' has formed a bond to 'B' (not easily seen, owing to the geometry).

In terms of the bonding of the atoms, the atoms A, B and C are all saturated as they are in Fig. 1 (a) — the bonding has merely cycled around (so that the A–B bond is now an A–H bond and a B–C bond, while the C–H bond is now a C–B bond). It is this saturation that gives the structure its stability. While some of the bond angles are rather strained (in particular, the bonds associated with B and C make 60° angles) the bond lengths are all close to equilibrium, and there are no further broken bonds, leading to an energy difference of 0.57 eV rel-

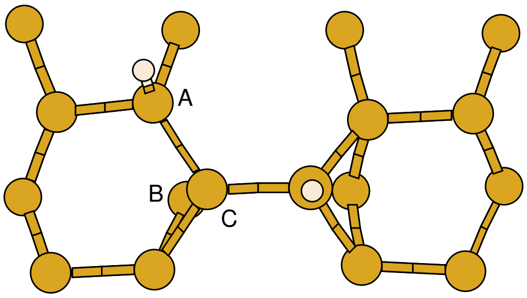

FIG. 2: The structure of the meta-stable state which provides a low energy pathway for dehydrogenation. The diffusing hydrogen is bonded to a substrate dimer (A), which has broken one bond to a second-layer silicon (B). The ad-dimer (C) is now partly clean, and has formed a bond to the second-layer silicon (B) left by the substrate dimer.

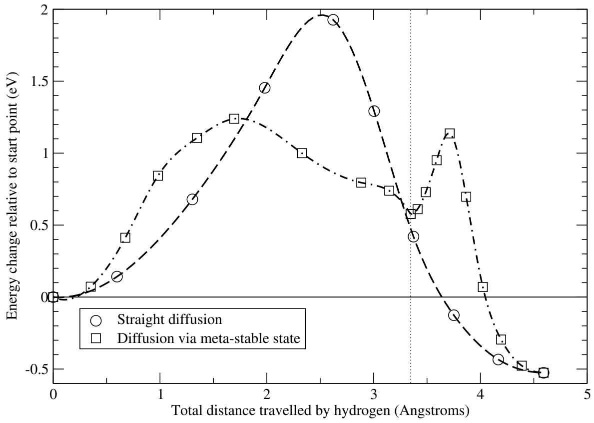

FIG. 3: A graph showing energy barriers for the diffusion for the first hydrogen off the ad-dimer. The energies are given relative to the starting point, while the x-axis gives the distance from the starting point of the hydrogen. The open circles show direct diffusion (proceeding without the meta-stable intermediate state). The open squares show the diffusion via the meta-stable state (whose position is marked with a vertical dotted line at 3.35Å, and whose structure is shown in Fig. 2). The lines (long dashes for direct diffusion and dash-dotted for diffusion via the meta-stable state) are spline fits to the data, and are given as guides to the eye.

ative to the starting point, but no more. It is interesting to note that there are other structures where 60° bond angles are found during growth of Si(001), which also exhibit stability which might seem counter-intuitive[6].

In terms of the formation of this structure, as we shall see in the next section, there is not a large barrier. The H never has to move a long distance from either A or C, leading to relatively strong bonds being present at all times; the second-layer atom B moves up slightly; and while the substrate dimer atom A and the ad-dimer atom C do move up and down respectively, they do this gradually while maintaining their bonding. It is this relatively small perturbation on the overall structure, and the ease with which it is reached, which allows the formation of this state, and gives it its importance.

IV. DIFFUSION PATHWAYS

In this section, we describe the diffusion pathways that we have explored with DFT calculations. For simplicity, and because it is likely to be physically realistic, we allow the hydrogens on the ends of the dimer to diffuse off independently — i.e. we consider the diffusion off one end of the ad-dimer while the other hydrogen remains on the ad-dimer. Then we allow the remaining hydrogen to diffuse off the now partially-hydrogenated ad-dimer onto the substrate. In order to avoid the complications of spin and half-filled bands, we maintain both hydrogens in the unit cell at all times (the first hydrogen to diffuse off stays on the substrate, illustrated in Fig. 1(b)). The three stable points of the process (fully hydrogenated ad-dimer, partially hydrogenated ad-dimer with a hydrogen on the substrate and clean ad-dimer with both hydrogens on the substrate) are illustrated in Fig. 1. The atomic positions during the diffusion pathways are presented below in an aggregated form (due to space constraints): only the position of atoms which move significantly are shown. All of the atomic structures at each step in all the diffusion pathways are available elsewhere[24].

The experimental data that we are comparing against comes from two separate experiments: first, where the Si(001) surface was exposed to a dose of disilane (Si_2H_6), annealed at different temperatures for different times, and then observed at room temperature in STM[1,2]; second, where an elevated-temperature STM was used to observe the results of dosing with disilane in real time at different temperatures[3,4]. The results of both these types of experiment are identical: around 450K, clean, non-rotated dimers are formed over the trench between dimer rows. In other words, the monohydride dimers lose their hydrogen to the substrate in a matter of minutes at this temperature (for instance, an anneal to 470K for two minutes led to the dehydrogenation of all ad-dimers[2]). Assuming an attempt frequency of 10^{13} sec^{-1} and a successful dehydrogenation rate of 1/60 Hz, we obtain a barrier of 1.28 eV. This changes by about 0.03 eV if the rate is doubled or halved, giving us a good estimate of the likely reaction barrier.

A. The First Hydrogen

There are two diffusion paths considered for the first hydrogen diffusing off the ad-dimer: a direct diffusion path; and diffusion via the meta-stable considered in Sec. III and shown in Fig. 2. We will discuss these separately, starting with the direct diffusion, and then contrast their results.

The diffusion barrier for direct diffusion is shown in

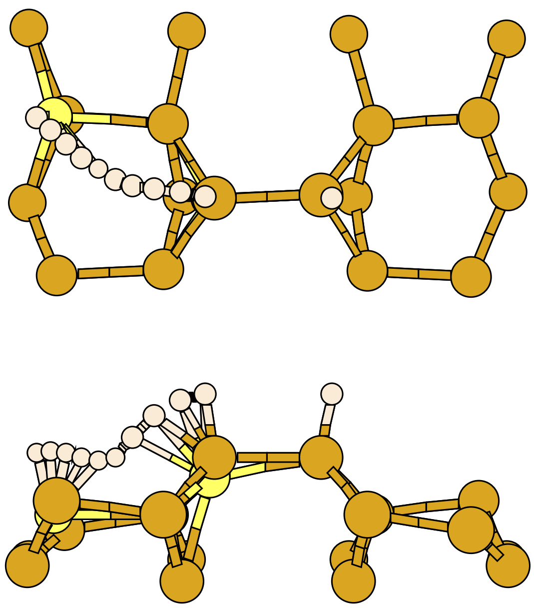

FIG. 4: The path of the first hydrogen in the direct diffusion path from above (top) and the side (bottom). All the hydrogen positions are shown, along with the initial and final positions of the atoms to which the hydrogen bonds (with the final position shown in a lighter shade). The final position of the ad-dimer cannot be seen in the top image since it is directly below the initial position. Bonds (or lack of bonds) are produced by the imaging software, and should not be taken as definite indications.

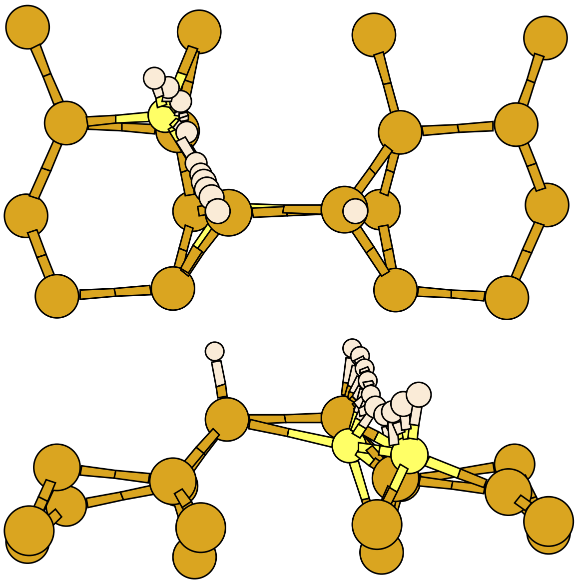

FIG. 5: The path of the first hydrogen from the ad-dimer to the meta-stable state shown in views from above (top) and the side (bottom). All the hydrogen positions are shown, along with the initial and final positions of the atoms to which the hydrogen bonds (with the final position shown in a lighter shade). The side view is shown rotated by 180° relative to the view from above as the image is clearer. The final position of the ad-dimer cannot be seen in the top image since it is directly below the initial position. Bonds (or lack of bonds) are produced by the imaging software, and should not be taken as definite indications.

Figure 3, with open circles and long dashes. The barrier is 1.93 eV, which is extremely high; the reason for this can be seen from the atomic positions, which are illustrated in Figure 4. At the saddle point, the ad-dimer bond is extended greatly (from 2.51 Å at the start to 2.82 Å) while the bond from the hydrogen to the ad-dimer is more extended (from 1.51 Å at the start to 1.85 Å). Inspecting the charge density, it is clear that the ad-dimer remains bonded (though weakly) and that the H has made a weak bond to the substrate dimer (which is 2.32 Å away) as well as maintaining a slightly weakened bond to the ad-dimer. It is this lengthening and weakening of bonds at the saddle point that causes the high barrier. Assuming Arrhenius behaviour and an attempt frequency of 10^{13} Hz, we find a hopping rate of $\sim 10^{-10}\text{sec}^{-1}$ at 450K, which is many orders of magnitude below the observed rate.

The diffusion barrier into and out of the meta-stable state is also shown in Fig. 3, with open squares and a dot-dashed line. The barrier from the start to the meta-stable state is 1.24 eV, while the barrier from the meta-stable state to the end is 0.56 eV (and the reverse path, from the meta-stable state to the start is 0.66 eV).

The pathway from the starting position to the meta-stable state (shown in Fig. 5) involves considerable rearrangement: first, the hydrogen inserts into the bond between the ad-dimer (labelled ‘C’ in Fig. 2) and the substrate dimer (labelled ‘A’ in Fig. 2); at the saddle point, the hydrogen is 1.65 Å from the ad-dimer, and 1.94 Å from the substrate dimer (compared to an equilibrium distance of 1.51 Å), while the distance between the ad-dimer and the substrate dimer is 3.10 Å (compared to 2.48 Å at the start); second, after the hydrogen has transferred to the substrate dimer, the ad-dimer bonds to a *second layer* atom in the substrate (labelled ‘B’ in Fig. 2); third, the substrate dimer bonds back to the ad-dimer and breaks its bond to the second layer atom in the substrate. The first part of this rearrangement is the area where most of the energy change happens: the energy actually falls by about 0.6 eV during the second and third parts of the rearrangement.

The pathway from the meta-stable state to the end position (shown in Fig. 6) is much simpler, involving only the movement of the hydrogen from one end of the substrate dimer to the other, while the substrate dimer ‘C’ reforms its bond to the second layer atom ‘B’. At the saddle point, the hydrogen is 1.72 Å from the substrate atom and 2.05 Å from the end atom.

The barrier of 1.24 eV from the starting point to the meta-stable state fits extremely well with the observed temperature behaviour: at 450K with an attempt fre-

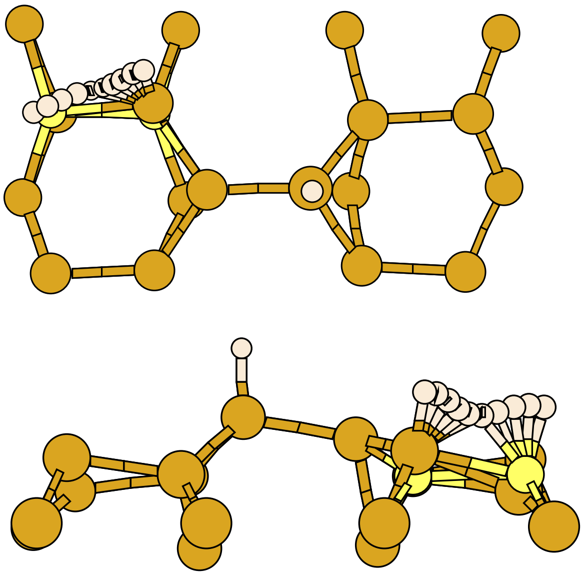

FIG. 6: The path of the first hydrogen from the meta-stable state to the substrate dimer shown in views from above (top) and the side (bottom). All the hydrogen positions are shown, along with the initial and final positions of the atoms to which the hydrogen bonds (with the final position shown in a lighter shade). The side view is shown rotated by 180° relative to the view from above as the image is clearer. Bonds (or lack of bonds) are produced by the imaging software, and should not be taken as definite indications.

quency of 10^{13} $\sec^{-1}$, it would correspond to a hopping rate of 0.044 Hz, or one hop every 23 seconds. But this is only *into* the meta-stable state, and there are *two* low energy paths out of that. The hopping rate from the meta-stable state to the end state is $\sim 4\times10^6$ Hz, while from the meta-stable state to the start state is $\sim 2\times10^5$ Hz, so that only 10% of meta-stable states would return to the starting point. We also expect that the equilibrium populations of the start and end states would differ, since the end state is 0.53 eV lower than the start (roughly, at 450K, we would expect a relative population about 10^6 times higher in the lower state). There is also the question of whether the hydrogen could return, via the meta-stable state, from the end to the start. The barrier from the end point *back* to the meta-stable state it is 1.66 eV, making it extremely unlikely that the hydrogen would return to the meta-stable state (and even if it did, it would be ten times more likely to drop back to the end state than to return to the start state). Clearly, it is the low barrier from the starting state to the meta-stable state that allows the first part of the dehydrogenation of the ad-dimer to proceed, and the energy difference between the start and end points, as well as the high barrier out of the end state that makes the reaction effectively irreversible.

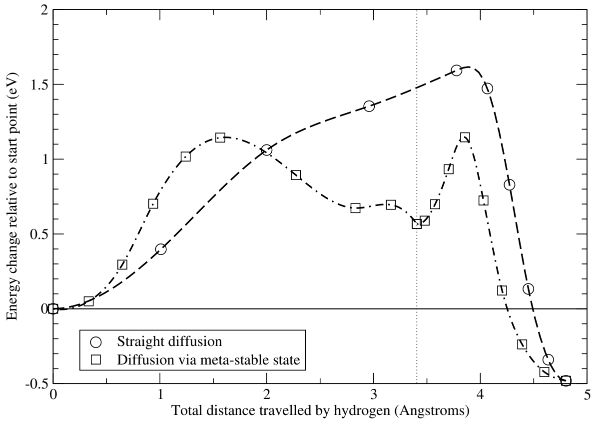

FIG. 7: A graph showing energy barriers for the diffusion of the second hydrogen off the ad-dimer (with the first hydrogen already on the substrate). The energies are given relative to the starting point, while the x-axis gives the distance from the starting point of the hydrogen. The open circles show direct diffusion (proceeding without the meta-stable intermediate state). The open squares show the diffusion via the meta-stable state (whose position is marked with a vertical dotted line at 3.41Å, and whose structure is shown in Fig. 2). The lines (long dashes for direct diffusion and dash-dotted for diffusion via the meta-stable state) are spline fits to the data, and are given as guides to the eye.

B. The Second Hydrogen

Once the first hydrogen has diffused off the ad-dimer, we retain it on the substrate, as shown in Figure 1(b). This is computationally convenient (as it maintains a filled set of bands) but also physically reasonable: hydrogen does not begin diffusing along the dimer rows on Si(001) at an appreciable rate until about 550K with a barrier of 1.68 eV[25].

As with the first hydrogen, the second hydrogen can diffuse either directly, or via a meta-stable state, which is exactly equivalent to the meta-stable state for the first hydrogen (shown in Fig. 2) and therefore not illustrated here. As before, we will discuss these results separately, starting with the direct diffusion.

The diffusion barrier for direct diffusion is shown in Figure 7, plotted with open circles and dashes. The shape is much broader than for the first hydrogen's direct path, with a lower barrier of 1.59 eV. The reason for this can be seen in part in the atomic positions, which are shown in Figure 8. This is a little more confusing than previous plots, as the positions both of the hydrogen and the ad-dimer atom to which it is bonded have been plotted. As the hydrogen moves across towards the substrate dimer (the end point), the bond between the silicon atoms in the ad-dimer breaks, with the atom that the hydrogen is bonded to following the hydrogen as it diffuses. At the saddle point, the hydrogen is 1.67 Å from the ad-dimer and 2.03 Å from the substrate dimer, while the distance between ad-dimer atoms is 4.48 Å. Beyond this

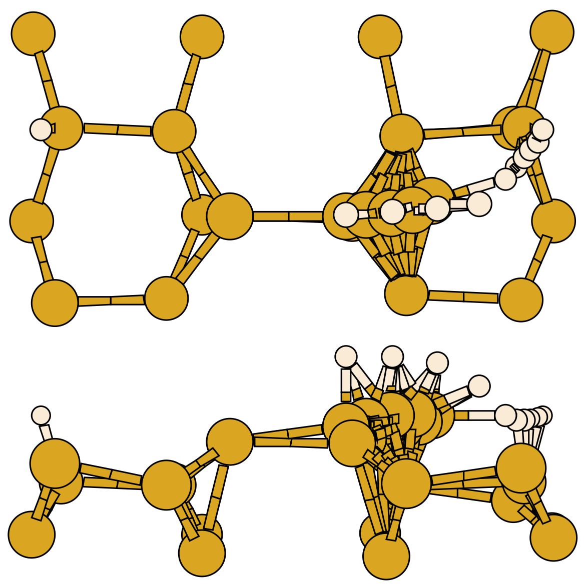

FIG. 8: The path of the second hydrogen in the direct diffusion path shown in views from above (top) and the side (bottom). All the hydrogen positions are shown, as are the positions of the atoms to which the hydrogen bonds. Bonds (or lack of bonds) are produced by the imaging software, and should not be taken as definite indications.

point, the hydrogen transfers to the substrate, and the ad-dimer reforms slowly.

The bond in the clean or partially clean ad-dimer is not as strong as the other bonds to the substrate, which explains why the energy cost for breaking it is relatively small, and why this pathway is followed in contrast to the pathway for the first hydrogen. Even with the reduced barrier, the hopping rate at 450K will be $\sim 4 \times 10^{-6}$ sec^{-1}, which is still far too low to be consistent with the experimental observations.

The diffusion barrier into and out of the meta-stable state is also shown in Figure 7, plotted with open squares and dot-dashed lines. The barrier from the start to the meta-stable state is 1.14 eV, while the barrier from the meta-stable state to the end is 0.58 eV (and the reverse path, from the meta-stable state to the start is also 0.58 eV). The atomic positions are almost identical to those for the first diffusion (shown in Figs. 5 and 6) and are not shown (though these figures, and many other pieces of supplementary information such as animations of the processes can be found elsewhere[24]).

The barrier of 1.14 eV is 0.1 eV lower than the barrier for the first hydrogen, suggesting that once the first hydrogen has diffused off the ad-dimer, the second will follow slightly more quickly; it is still in excellent agreement with observed experimental behaviour. The barriers from the meta-stable state to the start and end states are now identical, meaning that 50% of meta-stable states will return to the starting state. However, the end state is 0.48 eV lower in energy than the start, so that (as before with the first hydrogen) we would expect the population in thermal equilibrium at 450K to be about 10^6 times higher in the end state than the start state. The barrier from the end state back to the meta-stable state is 1.63 eV, which again makes the reaction effectively irreversible. Of course, the clean ad-dimer can also diffuse away along the trench between dimer rows, with a barrier of 1.15 eV[8], which would make the reforming of the hydrogenated ad-dimer impossible.

V. CONCLUSIONS

We have presented *ab initio* calculations, modelling the diffusion of hydrogen off a hydrogenated ad-dimer, which is a key stage in gas-source growth of Si(001). We have shown that the diffusion proceeds via a meta-stable intermediate, and that the energy barriers calculated (1.24 eV for the first hydrogen and 1.14 eV for the second hydrogen) are in excellent agreement with temperatures at which these features are observed in experiment.

We have used the climbing image nudged elastic band method to find the diffusion barriers, and have found it to be extremely effective, particularly for the direct diffusion which was difficult to model simply by picking a single constraint. However, the problem of exploring phase space is still a difficult one, as the existence of the meta-stable state (which was discovered through application of a single constraint) shows. There are techniques for exploring energy surfaces, such as the dimer method[20] and variants on hyperdynamics[26], but there is still a large amount of work to be done in this field.

Acknowledgments

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