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Ab initio temperature dependent studies of the homoepitaxial growth on Si(001) surface

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Abstract

We performed ab initio zero temperature and finite temperature molecular dynamics calculations to investigate the homoepitaxial growth on the Si(001) surface. How do the deposited atoms (adatoms) form addimers and how do the addimers reach their favorable positions at the nucleation site of the growth process are presented. Once two epitaxial addimers, one over the dimer row and oriented perpendicular to the surface dimer bonds and the other over the adjacent trough, are aligned at high temperature, the nucleation site of the growth process is formed. The concerted bond exchange between these addimers and the reconstructed surface dimers is found to be the atomistic mechanism that leads to the homoepitaxial growth. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Because of the importance for using silicon (Si) in microelectronics, a great deal of experimental [1–18] and theoretical [19–28] effort has been devoted to the investigation of its epitaxial growth process. The understanding of the atomic scale growth mechanism in the simpler case which is along the [001] direction has still been a chal-

lenging subject of research owing to its complexity. One of the crucial ingredients for unfolding the enigma is to tracking down the motions of the deposited atoms (adatoms) and the atoms of the substrate. Remarkable progress has been made by using scanning tunneling microscopy (STM) to provide direct information about the kinetics of the growth processes as a function of the temperature at the Si(001) surface. For example, even at $T = 160$ K adatoms on top of the reconstructed dimer row are mobile and nearly half of the adatoms at a coverage $\Theta = 0.02$ form dimers [7]. At $T \sim 300$ K adatoms are quickly paired to form strongly bound addimers [11,12]. While addimers readily diffuse along the substrate dimer row at $T \sim 300$ K, the diffusion over the trough between

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two adjacent dimer rows is favored at elevated temperatures [1,8]. In fact, addimers over the trough become mobile at $T \sim 400$ K and form non-epitaxial strings or “dilute dimer” rows [8]. It has been shown [1,2] that “dense dimer” rows perpendicular to the existing substrate dimers can grow into epitaxial strings by using molecular beam epitaxy when the substrate temperature $T \sim 500$ K. It is clear that the substrate temperature is crucial in various precursor stages leading to the epitaxial nucleation. At finite temperature, the kinetics of adspecies and several substrate atoms at the close proximity may favor a process involving certain pathways which are different from that calculated to be energetically most favorable at $T = 0$ K. Therefore, the temperature factor has to be taken into account in the calculations modeling the epitaxial growth process. Theoretically, several studies [6,10,19–28] have contributed significantly to the understanding of the initial stages and various processes in the growth of the Si(001) surface, and have guided the experimental works. In those studies, *ab initio* (self-consistent pseudopotential method within the density functional theory) [10,19–27], empirical tight binding [27] and empirical potential [6,28] methods have been used to calculate the energetics of adatoms and addimers adsorbed at various places on the substrate surface and to determine the optimized atomic structure. Based on these calculations possible pathways for rotational and/or translational motion of addimers with low energy barrier, and also for their combinations to form nucleation sites (such as cross-structure, dilute dimer, etc.) or grown islands have been proposed [19,28]. Yet, the temperature related complexities of heat generation and heat dissipation at the close proximity of moving adspecies, and the associated non-equilibrium and stochastic behaviors have not been incorporated. Thus, a complete picture for the microscopic mechanism about the layer formation of the growth processes remain to be elucidated. In particular, the elementary processes which initiate the epitaxial nucleation occurring at high temperature have not been well understood yet.

In this paper we studied the epitaxial growth of the Si(001) surface by using *ab initio* molecular

dynamic (MD) method [29]. In addition to static and $T = 0$ K calculations we also performed finite temperature calculations [30]¹. We proposed an elementary process and demonstrated that it, in fact, can initiate an epitaxial nucleation site and can form dense-dimer row. The finite temperature *ab initio* MD calculation can access information related to various effects of temperature, which are not available to static and $T = 0$ K calculations. Furthermore, one can make an efficient search for the kinetics together with the relevant pathways, and study the thermal behavior of the surface. In Section 2, we give a brief description of the atomic structure of the slab representing the substrate and the method of calculation. In Section 3, we first address various precursor stages (or processes) which can take place in the course of growth. Combining these precursor processes, we show how the proposed elementary process has led to an epitaxial nucleation. In the same section we briefly compare other atomistic elementary processes proposed earlier with the present one. In Section 4, we present the discussion of our results and, in Section 5 we summarize our conclusions.

2. Method

The Si(001) surface is modeled by a periodic slab and a vacuum region within a supercell geometry. The slab has seven atomic planes with each plane consisting of 16 Si atoms. Si atoms of the bottom plane are kept at their optimized bulk positions and are saturated by 32 hydrogen (H) atoms along tetrahedral directions. A total of 148 atoms in the supercell including adspecies (i.e. Si adatoms or addimers), 112 Si and 32 H atoms of the substrate are considered. Adspecies and the 96 Si atoms in the top six layer of the supercell are relaxed to obtain the optimized initial configuration. The vacuum spacing between slabs along the [001] direction is taken 9.58 Å.

Calculations have been carried out in momentum space with the ionic potentials for Si and H acting on a valence electron approximated by

¹ We used the computer code JEEP provided by Dr. F. Gygi.

norm conserving pseudopotentials [31]. The electron–electron interaction is treated within the local density approximation (LDA) of density functional theory. We used the Ceperley–Alder [32,33] exchange correlation potential and the generalized gradient approximation (GGA) by using the form given by Perdew et al. [34]. The cutoff energy, $|\mathbf{k} + \mathbf{G}|^2$, is 15.0 Ry. We used a single $\mathbf{k}(0, 0, 0)$ -point in the supercell Brillouin zone to calculate the charge densities. The large size of the supercell allows us to achieve $\mathbf{k}$ -sampling quality comparable to those calculations which used two $\mathbf{k}$ -points. Since no symmetry is used, the ions are allowed to move without any constraint.

We calculated the energetics of optimized structures at $T = 0$ K. We also studied certain growth processes occurring at high temperature by performing finite temperature ab initio MD calculations, whereby we explored the reaction pathways. For a given initial geometry we first obtained self-consistent solutions of the wave function by wave function dynamics, and then we carried out the structure optimization at $T = 0$ K. Finite temperature calculations started with random initial velocities of ions and were performed by using the Nosé thermostat [35]. Si ions in the bottom layer and saturating H ions were frozen, but the rest of the Si ions in the following six layers and the ions of the adspecies on the surface were allowed to move under the forces acting to those *dynamic* ions. The ionic motions were realized in time steps of $\Delta t \sim 5 \times 10^{-16}$ s. The freezing of the bottom ions creates a temperature gradient; the effect of it will be discussed in Section 4. At each temperature, the system is equilibrated for a suitable time interval which is determined by examining the energy vs. time curve. We have studied various processes at a given temperature in the range of 1–2 ps. In finite temperature calculations, the simulations are usually carried out at temperatures higher than the experimental ones in order to compensate for the small time scale in ab initio MD [21,30]. This way the statistics is enhanced, hence the time required for a process to occur is shortened. Here, we achieved thermal motion at relatively lower temperatures by relaxing more atoms at the close proximity of the adspecies and also by using relatively larger Δt . The value of

Δt has been determined after several test calculations.

We started with the Si(001) surface with the $p(2 \times 2)$ reconstruction for the clean case. By optimizing the atomic structure at $T = 0$ K, the well-known surface structure with 0.7 Å alternating buckled dimer in the growth direction was obtained. We considered the $p(2 \times 2)$ reconstruction as the initial surface in our study. Note that at room temperature $c(4 \times 2)$ and $p(2 \times 2)$ geometries can coexist and within the accuracy of the calculations they are almost energetically degenerate [36]. The ab initio calculations at $T = 0$ K predicted that the $c(4 \times 2)$ structure is 45 meV/dimer more energetic than the $p(2 \times 2)$ structure [37]. However, these regular reconstruction geometries have to be disturbed at finite temperature in the presence of adspecies, and hence which surface reconstruction, ($p(2 \times 2)$ or $c(4 \times 2)$), we start with should not affect our conclusion in any essential manner. The top two layers of the $p(2 \times 2)$ reconstructed surface are shown in Fig. 1. The atoms forming the buckled dimer bonds are indicated by S_1 and S_2 , which make the surface dimer rows along the $[1\bar{1}0]$ direction. The open circles are atoms at the next lower layer. Following the convention, the adatom adsorption sites [19] (M, H, B and D) and four type of addimers [16,27] (A, B, C, and D) are shown in Fig. 1. A and D addimers are perpendicular to, while B and C addimers are parallel to the existing (S_1 – S_2) surface dimers. Thus A and D are oriented parallel to the epitaxial dimer bonds to be grown perpendicular to the existing dimer row. A and B are over the surface dimer row, but C and D are over the trough between two adjacent dimer rows.

3. Homoepitaxial growth model

Because of the fourfold coordination of each Si atom, the dimer rows of the new epitaxial layer should be oriented perpendicular to the existing surface dimer row along the $[1\bar{1}0]$ direction. The bonds of the existing surface dimers, in turn, have to be broken and the atoms S_1 and S_2 to be incorporated into the subsurface layer when the

Fig. 1. Top view of the Si(001)- $p(2 \times 2)$ surface comprising four reconstructed cells. Positions of adatoms are designated by M, H, B, D... according to the labeling of Ref. [19]. Different adatom–adatom combinations forming A, B, C, D-type dimers (with the labeling used in Refs. [5] and [15]) are indicated by arrows. A_1 and A_2 (D_1 and D_2) are the Si atoms forming the A (D) addimer. Large, medium and small filled, empty circles denotes, respectively, adatoms (or addimers), raised and lowered surface dimer atoms (S_1 , S_2), subsurface atoms. Reconstructed surface dimer bonds in the rows along the $[1\ 1\ 0]$ direction are indicated by thick lines.

growth of a new epitaxial layer is completed. Based on this physical evidence, we expect that with our model of the (001) surface the parallel alignment of the A and D addimers as shown in Fig. 1 will form a crucial nucleation site for the epitaxial growth of the new top layer around $T = 500$ K. In order to confirm this new model, we shall show that (i) different types of addimers co-existing on the Si(001) surface can transform eventually to A and D above a certain temperature by translational and rotational motions; (ii) it is energetically favorable for a D addimer at the close proximity of A to be aligned parallelly with it; (iii) once they are aligned the bonds of the reconstructed surface dimer formed by S_1 – S_2 (Fig. 1) at both sides of A are eventually broken and concomitantly A and D are transformed to become new surface dimer bonds. Before we demonstrate

that these three essential ingredients of the above model can occur, we first address three stages which are precursors to the epitaxial nucleation. They can take place either sequentially or concomitantly depending upon the growth conditions. Some of the individual atomic processes in these stages were obtained by earlier theoretical or experimental studies. We, however, note that in the earlier static and $T = 0$ K calculations based on the transition state theory (TST) analysis, either the energetic and the formation energy of the ad-species relative to a reference system (e.g. isolated ad-species and substrate surface) was calculated and/or ad-species were moved on certain pathways to find the lowest energy barrier Q . The present finite temperature calculations, on the other hand, can show how an elementary process occurs, and which pathways are taken in the concerted motion

of several involved atoms. Therefore, the present calculations are complementary to the previous studies, and also give some idea about in what capacity the finite temperature calculations can be used in the study of the growth.

(1) In the first stage Si adatoms are equilibrated with the Si substrate and eventually adsorbed preferentially at non-epitaxial sites [7] after complex phononic and electronic dissipation processes in the course of the deposition. Earlier, potential energy surface $E(x,y)$ of a single Si adatom were calculated by using the *ab initio* MD method at $T = 0$ K and various local minima (possible binding sites) and saddle points were identified [19]. Our calculated relative energies of a single Si atom adsorbed at various positions at $T = 0$ K are in agreement with the results given in Ref. [19]. The site of global minimum is designated as M in Fig. 1. The next energetic site is determined to be near the center of the hexagon (H-site in Fig. 1.) and is ~ 0.2 eV above the global minimum. Other relatively less energetic sites are indicated in the same figure by B and D.

(2) In the second stage the adatoms become mobile at finite temperature and form different types of addimers. Addimers were observed first by Dijkkamp et al. [4], and later van Dam et al. [11,12] studied the room temperature deposition by STM and observed that highly mobile adsorbed Si monomers are quickly combined to form Si dimers. Different types of addimers were identified based on the first principle theoretical studies [20,21], and their energetics were obtained by both *ab initio* [21,24] and empirical potential [6,18] calculations. A more extensive treatment of energetics was provided by Smith and Jonsson [23]. We investigated the processes for the formation of the four addimers shown in Fig. 1 by considering simple pathways: A pair of Si atoms co-adsorbed at the adjacent H-sites with interatomic distance $d = 3.83$ Å become mobile at $T = 100$ K. They first rise and one of them moves over the separating reconstructed surface dimer bond. Eventually, this pair is transformed into an A-type addimer (Fig. 1) with the total energy lowered by ~ 1 eV. At the same time, the tilt angles of the adjacent reconstructed surface dimer are reduced from 17° to $\sim 10^\circ$. Similarly, one Si atom adsorbed

at the H-site migrates to one of its adjacent sites at $T = 100$ K by passing over the separating surface dimer. This atom can dimerize with a Si atom at the M-site to form a B-type addimer (Fig. 1). Two Si atoms adsorbed at the M-sites at both sides of the same trough can also dimerize and form a C-type addimer (Fig. 1) with 0.9 eV energy gain. A pair of Si atoms adsorbed at adjacent B (not bold faced in Fig. 1) sites again with $d = 3.83$ Å form a D-type dimer. Our results suggest that the potential energy surface and the energy barriers between the local minima which was calculated for a single adatom can be modified significantly, if two Si adatoms are co-adsorbed at nearby sites. This also indicates that other more complicated pathways are possible. By optimizing the two atoms forming an addimer and the 96 Si atoms in the first six layers of substrate at $T = 0$ K, we calculated the total energies of A, B, C and D addimers. We summarize our results: The average height of A is ~ 0.3 Å greater than that of B. The relative energies of the isolated addimers A, B, C and D are 119, 0, 261, and 1540 meV with LDA; while with GGA they are 18, 0, 367, and 1832 meV, respectively. For the sake of comparison with the earlier works, these energies were calculated with the cutoff energy, $|\mathbf{k} + \mathbf{G}| = 12$ Ry. Earlier experimental and theoretical results on the order of these energies have been at variance. While the *ab initio* calculations [10,21,24] found the dimers forming over the dimer row (i.e. A and B) more energetic than those forming over the through (i.e. C and D), the calculations based on the empirical potential found the opposite [6]. Moreover, the *ab initio* calculations [10,21,23,24] by themselves have been in conflict on the order of A and B. Experimentally [6,8], A was found to be an order of magnitude more populated than that of B. Here, our study brings up an interesting aspect of the issue of ordering, that is the convergence with respect to the energy cutoff. The ordering of our energies above finds B more stable than A for the cutoff energy 12 Ry. However, the ordering is reversed by using energy $|\mathbf{k} + \mathbf{G}|^2 \gtrsim 16.5$ Ry in the GGA calculations, so that A becomes (4 meV) more energetic than B as found experimentally. The difference of total energies, $\Delta E_{AB} = E_{T,A} - E_{T,B}$ is, nevertheless, small. We note, however, that

both the ordering of addimer energies and the difference of total energies (i.e. relative stabilities) and even the energy barriers between them may change at finite temperature.

(3) The third stage involves the motion of addimers and hence their transformation from one type to another. The possibility of transforming either $\mathbf{A} \rightarrow \mathbf{B}$ or $\mathbf{B} \rightarrow \mathbf{A}$ through a rotation was pointed out first by Brocks and Kelly [20] and also demonstrated by using finite temperature calculations [21]. The rotation of $\mathbf{A}$ and $\mathbf{B}$ was confirmed with empirical potential calculations [6] and with STM experiments [8]. Swartzentruber et al. [10] obtained quantitative results on the dynamics of rotation by using the data obtained from atom tracking experiments. They estimated the energy barriers $Q_{\mathbf{B} \rightarrow \mathbf{A}}$ and $Q_{\mathbf{A} \rightarrow \mathbf{B}}$ to be 0.68 and 0.78 eV, respectively. This implies that the transformation, $\mathbf{B} \rightarrow \mathbf{A}$ by rotation is more favorable than the transformation, $\mathbf{A} \rightarrow \mathbf{B}$. Physically, any rotation for either $\mathbf{A}$ or $\mathbf{B}$ addimer requires the breaking of several bonds. Hence, it is surprising that rotations of addimers can be achieved with energies much smaller than the ~ 2.3 to 2.7 eV energy necessary to break a Si–Si covalent bond. We found the underlying mechanism for the small estimated [10] energies by performing finite temperature MD calculations.

The rotation $\mathbf{B} \rightarrow \mathbf{A}$ was realized at the temperatures $T = 300$ and 600 K. For the low temperature case, the change of the bond length of the addimer is not large, but the heights of the atoms forming this addimer vary significantly during the rotation. On the other hand, the bond is stretched significantly in the course of rotation at high temperature $T = 600$ K. The involved bond-breaking and bond-forming processes between the addimers and the atoms forming the substrate during rotation are clearly seen by examining the motion of atoms and the corresponding charge density at the close proximity of the addimers [38]. Snapshots in Fig. 2 illustrate how $\mathbf{B}$ is transformed into $\mathbf{A}$ by rotation at $T = 300$ K. In this figure the height of an atom is coded by the contrast of the ball representing this atom. Sticks stand for the bonds. As the rotation angle increases, the distance of the bond between one atom of the $\mathbf{B}$ dimer and that of the surface dimer (S_1) increases and hence the corresponding bond is weakened. On the other hand, the same atom of $\mathbf{B}$ approaches one atom of the other adjacent surface dimer (S_2) and starts to form a new bond. The latter bond is the precursor for the bond formation between the $\mathbf{A}$ addimer and its nearby substrate atoms. The second atom of the rotating $\mathbf{B}$ addimer undergoes similar processes with the corresponding atoms of

Fig. 2. (a)–(f) Snapshots for the rotation $\mathbf{B} \rightarrow \mathbf{A}$ taken from ab initio finite temperature MD simulations at $T = 300$ K. The height of atoms in this and following figures is coded with the contrast of the corresponding balls. Sticks between balls denote the bonds, and are made by the RASMOL programme plotting these figures for the guide to the eye. Some of the sticks are deleted to provide a better view of subsurface atoms.

the surface dimers. During the rotation the **B** addimer moves also upward and other existing bonds are reformed to comply with its motion. During any rotation, the correlated motion of substrate dimers and subsurface atoms is crucial. We attribute it to be a concerted motion of these atoms which leads to the bond exchange and hence makes the transformation possible. In fact, a concerted motion of the substrate dimers in the course of the diffusion of Ge on the Ge(100) surface was observed by using STM [18]. The rotation, **A** $\rightarrow$ **B** required relatively higher temperature and involved also the translational motion along the top of the surface dimer row, suggesting that the rotation, **B** $\rightarrow$ **A** occurs more easily than the rotation of **A** $\rightarrow$ **B**. This is in conformity with the experimental results [10,13] finding $Q_{A \rightarrow B} > Q_{B \rightarrow A}$.

Recently, Borowsky et al. [16] observed that addimers can also diffuse across the surface dimer row at $T \sim 450$ K. They estimated the energy barrier for the transformation of **C** to **B** to be 1.36 eV. This result is smaller than the calculated barrier (1.8 eV at $T = 0$ K) obtained by Yamasaki et al. [24] but agrees reasonably well with Lee et al. [27] who found a path with a relatively smaller barrier (i.e. $Q_{C \rightarrow B} = 1.39$ eV). Apparently, the transformation of **C** to **A** can be accomplished by **C** first transforming to **B** at a proper temperature [16,24,27], subsequently **B** itself transforming to **A** by rotation. Goringe and Bowler investigated the

translation [25] and rotation [26] of **C** in the trough by using ab initio TST calculations at $T = 0$ K. For the translational motion they found that the **C** dimer is very likely to break up first, and resulting monomers diffuse sequentially and then rebind. The minimum energy barrier is found to be 1.15 eV. Since the dimers and their orientations relative to the existing surface dimers are essential for the epitaxial nucleation, they also examined the rotation of **C** into **D** [26]. The energy barrier to this motion of addimer, $Q_{C \rightarrow D}$ is found 1.4 eV. The energy barrier to the rotation in the opposite direction, $Q_{D \rightarrow C}$ was 0.45 eV lower. These barriers are calculated at $T = 0$ K, and their values and forms are expected to undergo significant changes at high temperature. Clearly both types of motion are crucial and might occur at high temperature. Our ab initio MD calculations at $T = 600$ K suggest that **C** can also transform to **D**. The atomic mechanism of this rotation is illustrated in Fig. 3 by the snapshots taken from the calculations. The addimers and the surrounding atoms have significant movements and bond alterations as seen in Fig. 3(b) and (c). The sticks representing bonds between atoms are made by the image program based on certain criteria for the guide to the eye. The actual bond formation has been investigated by the analysis of SCF-charge density. It should be noted that the rotation of **C** to **D** at high temperature does not exclude the occurrence of the rotation in the opposite direction which, in fact,

Fig. 3. (a)–(e) Snapshots for the rotation **C** $\rightarrow$ **D** taken from MD simulations at $T = 600$ K. For further details see Fig. 2.

seems to be energetically favorable according to energetics and barrier energies calculated at $T = 0$ K. Not being able to perform several simulations at different temperatures to extract a statistical distribution of dimer transformations, we cannot tell at this moment which rotation (i.e. $C \rightarrow D$ or $D \rightarrow C$) occurs more frequently at a given temperature. Nevertheless, from the above results one concludes that various kind of addimers coexisting on the substrate surface can transform from one to another and these transformations can be controlled by the growth temperature. This situation is essential for the homoepitaxial growth of Si. In what follows we show how the atomistic mechanism we propose can lead to homoepitaxial growth.

The epitaxial growth nucleates when **A** and **D** are aligned as shown in Fig. 1. As a matter of fact, the alignment of these two addimers is energetically favorable. To show this we calculated the total energies of the two systems, namely one having **A** and **D** aligned (as in Fig. 1), second having **D** shifted in the same trough and hence separated from **A** in the $[1\ 1\ 0]$ direction by $a\sqrt{2}$ (a being the lattice constant of the bulk crystal). We found that the aligned configuration is favorable by 87 meV; this value is further lowered as explained below. In spite of the fact that the aligned configuration is energetically favorable based on the total energies of the initial and final configurations, the separated **A** and **D** cannot be aligned by themselves at $T = 0$ K due to an energy barrier. However, the situation can be different at high temperature. In fact, finite temperature calculations showed that **A** and **D** which are separated by $a/\sqrt{2}$ along the $[1\ 0\ 0]$ direction, can move to approach each other, and eventually become aligned at $T = 600$ K. Interestingly, such an alignment of **A** and **D** cannot occur at relatively lower temperatures. In compliance with the present results, it was also found experimentally that the diffusion of addimers along the trough is favored at high temperature [8]. By using STM van Dam et al. [11] deduced a similar kind behavior between addimers (**B** and **B**, or **A** and **A**) in adjacent surface dimer rows. They were able to activate the motion by increasing tip-sample voltage to obtain clusters from the diffusing dimers.

The addimer **D** is also bonded to the surface atoms S_1 and S_2 , even though the binding is somehow different from the other addimers. Once **A** and **D** are aligned, they become bonded to the same surface atoms. This situation induces an interaction that weakens the existing surface dimer bond (S_1-S_2) (Fig. 4(a)). The interaction can be initiated and get carried away by the random oscillatory thermal motion of **A**, **D** and the involved surface dimers. In the end, the adjacent surface dimer bonds are weakened and eventually broken. The atoms forming the surface dimer, S_1 and S_2 (as labeled in Fig. 1) are displaced towards their bulk ideal positions. Concomitantly, S_1 and S_2 strengthen their bonds with the atom A_1 and also they form new bonds with D_1 (Fig. 4(b) and (c)). Since **D** is raised, $S_2-D_1-S_1$ and also $S_1-A_1-S_2$ bonds become more bulk like, and thus they become stronger. Same arguments are also valid for the atoms A_2 and D_2 at the other side of **A** and **B**. The final configuration shown in Fig. 4(c) is favorable by ~ 1 eV as compared to the initial configuration (separated **A** and **D**), and occurs through the concerted bond exchange. The snapshots in Fig. 4 (a)–(c) summarize these atomic processes involving concerted bond exchange during the formation of nucleation site. Previously, Pandey [39] showed that the self-diffusion of Si atoms can be realized preferably by the concerted bond exchange without the assistance of the vacancy.

Note that, the final structure in Fig. 4(c) is the configuration evolved by starting from one pair of **A** and **D**, and eventually nucleated a dense dimer row. We also found that the energy of the system can further be lowered if the nucleation sites extend on both side by sequential incorporation of more **A** and **D** addimers into the process. Interestingly, an initial configuration consisting of a row of **ADAD**... addimers (in the $[\bar{1}\ 1\ 0]$ direction perpendicular to the existing surface dimer row in the $[1\ 1\ 0]$ direction) has transformed into a new epitaxial dimer row in the $[\bar{1}\ 1\ 0]$ direction even at $T = 0$ K, while the existing surface dimers are incorporated into the subsurface (001) atomic plane. The final structure is more stable and hence corresponds to a lower minimum on the Born–Oppenheimer (BO) surface. The final configura-

Fig. 4. (a)–(c) Snapshots for the nucleation of new epitaxial surface dimers perpendicular to the existing rows, when **A** and **D** are aligned. (d) Formation of new epitaxial row of surface dimers from the row **ADAD**... along the $[\bar{1}10]$ direction. For further details see Fig. 2.

tion of simulations are presented in Fig. 4(d). It should be noted that the growth of a perfect new layer, as such that each dimer row along the $[\bar{1}10]$ direction is separated from the next neighbor row by a trough, cannot be guaranteed by the above model. Since the nucleation site may initiate randomly at any cell (or hexagon in Fig. 1) in the surface dimer row, a situation can occur where one dimer row can start to grow in the trough adjacent to the row that already started to grow along $[\bar{1}10]$ direction. Under these circumstances these two rows stop growing when their growing ends meet. Even the growth of long epitaxial dimer strings cannot occur because of random distribution of addimers. This growth mode shall lead to the formation of dislocated dimer strings of finite length and other structural defects at the epilayer.

Different types of intermediate structures, which may form at temperatures relatively lower than the temperature favoring the growth of epitaxial dimer rows and change into the epitaxial islands, have been proposed. These are the cross- [21] and tie-structures [17]. The former consists of a **C** addimer and two monomers at the other sides of the adjacent dimer rows. This structure nucleates the formation of the dilute dimer rows and is proposed to be an intermediate structure for strongly anisotropic epitaxial growth [11,12,21]. The tie-structure is formed by a **A** addimer and two monomers at two adjacent through. The tie-structure has been observed to grow into a six-atom island which are energetically favorable rebonded step edges on both ends [17]. The importance of epitaxial orientation of addimers subsequent to the

nucleation site have been pointed out by various authors [24,26]. Yamasaki et al. [24] found the dense dimer row configuration, whereby two epitaxial dimer bond is nucleated over and (perpendicular to) the existing surface dimer row, is the most stable cluster as compared to similar four atom clusters [24]. This is in conformity with the present results. Furthermore, they proposed a pathway based on the TST calculations at $T = 0$ K starting from two nearest parallel **A** addimers. One of these dimers is rebonded in the surface, but another dimer exchanged from the surface atoms moves to the trough to form the dense dimer row. The minimum energy barrier for this pathway is 1.3 eV. The present model differs from the model by Yamasaki et al. [24], and starts from the aligned **A** and **D**.

4. Discussion

In our study of the homoepitaxial growth of Si(001) we found that the finite temperature approach allows an individual atom experiencing the temperature effects, and hence simulates more realistically the experimental condition. Crucial features for simulating the growth processes which are missing in the static and $T = 0$ K calculations relevant to the TST analysis are: (i) A global energy exchange. That is, an increase of the total energy in a local region around an adspecies can be compensated by a lowering of an energy barrier around a local minimum on the BO surface associated with another region of the growth front. This situation can best be described in terms of the concerted motion of adspecies together with the substrate atoms located in a number of surface atomic planes. (ii) Access to various type of concerted motion. The finite temperature calculations comprising adspecies and substrate atoms can sample larger number of concerted motion. (iii) Effects of local energy fluctuations. For example, with one of the crucial factors, i.e. the non-equilibrium distribution of phonons created locally or local energy fluctuations, it becomes relatively easy for an adspecies to overcome an energy barrier and to become more mobile as compared to the case for $T = 0$ K. Accordingly, in the Arrhenius-type

expression, $\omega = v_0 \exp(-Q/k_B T)$, the apparent energy barrier Q shall be reduced by the “local temperature”. As for the question whether the energy generated locally can be transferred to the diffusing adspecies, we refer to the recent works [40–42] where it is predicted that the non-equilibrium phonon distribution is dissipated through harmonic and anharmonic couplings within picoseconds. In the present work using time steps shorter than a femtosecond, the thermal motions of the atoms can be enhanced by the local heating before it dissipates. In the actual situation, where the jump frequencies of diffusing atoms are in the range of $\sim 10^{-14}$ s, the thermal motion of atoms at the close proximity are affected.

Our results provide evidence that the potential energy surface and also potential barrier for a given atomic process can undergo changes at high temperature. As a result, atomic processes and reaction paths may be affected by these changes. The implications of these changes may not necessarily be included in the analysis based on the static calculations. This argument can be very well corroborated by the following cases: For example, it is observed that the addimers over the trough (i.e. **C** and **D**) appeared in greater numbers after gentle annealing at ~ 400 K [6]. This brings up an apparent contradiction between static calculations performed at $T = 0$ K within density functional theory (including also present static calculations) which have found the addimers over the dimer row (i.e. **A** and **B**) were more stable and experiments (also empirical potential calculations [6]) have suggested **C** and **D** were more stable. In addition to this example, a structure formed by adatoms, which is known as cross structure, was observed [8] at temperature ($T \sim 400$ K) relatively lower than the temperature at which epitaxial growth sets in. Interestingly, the same structure is found energetically unfavorable as compared to other structures at $T = 0$ K [24]. These examples demonstrate that the stability of a structure as revealed by static calculations may not prevail at elevated temperature.

With regard to the present approach we comment on the following aspects: Firstly, the fixing of atoms at the bottom layer of the supercell corresponds to bringing the base of the slab in contact

with the heat reservoir at $T = 0$ K. This, in turn, creates a temperature gradient that may restrict the thermal motion. In fact, we have found that by allowing the atoms only at the top two layers to move but freezing the rest of the slab, the extent of concerted motion was dramatically reduced. This artifact nevertheless is weakened by allowing atoms in the top six layers to move. Second, in finite temperature calculations the rotation of addimers or other similar processes are realized in a time scale much shorter than estimated by STM experiments due to reasons explained in Section 2. On the other hand, we note that the time scales obtained by STM can be modified by the tip-sample interaction effects [11,12,43,44]. Furthermore, events taking place in a time scale shorter than the threshold time for STM cannot be observed. Third, the energies obtained by finite temperature calculations are not directly comparable with those obtained from static, $T = 0$ K calculations. For the reason explained above, the temperature of the calculations may not correspond to the actual temperature at which a particular process is observed.

Finite temperature *ab initio* MD methods by themselves require further development in the areas, such as the implementation of the stochastic behavior, development of new and more realistic schemes to achieve simulation of an actual processes taking place in a time interval much longer than the integration time Δt ; inclusion of the energy transfer from external sources (i.e. *incoming atoms, contact with the heat reservoirs*, etc.) and energy dissipation. Nevertheless, it is shown that the finite temperature calculation can provide information about a particular process which is complementary to the analysis carried out by using TST calculations. These calculations appear to be a promising tool in the study of certain processes [21,30,45,46] and in the exploration of the effect of surfactant and associated atomistic mechanisms.

5. Conclusions

In conclusion, we performed an extensive first-principles analysis of the dynamics aspects for the epitaxial growth of Si(001) surface. By carrying

out the MD calculations at finite temperature we investigated the energetics and the motion of adatoms and addimers, and the formation of addimers and their transformation among themselves through rotational and translational motions. The transformations among various kind of addimers on the surface are controlled by the growth temperature. We further demonstrated that the epitaxial growth can be nucleated when **A**- and **D**- type dimers are aligned parallelly in neighboring sites. Finally, we identified that the concerted motion of adspecies with the substrate atoms to exchange bonds is the essential mechanism for the epitaxial growth.

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