MICROSCOPIC MECHANISMS OF REACTIONS ASSOCIATED
WITH SILICON MBE: A MOLECULAR DYNAMICS INVESTIGATION

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A molecular dynamics simulation of the initial stages of the gas-phase epitaxy of silicon on the
silicon {100} symmetric dimer reconstructed surface has been performed. A diffusing adatom
induced rearrangement of the surface reconstruction is proposed as the reaction which leads to
good epitaxy. Surface diffusion is shown to play much less of a role in the reordering of the
reconstruction induced by an amorphous overlayer. The results of the simulation are used to
provide atomic-scale models which are consistent with experimental studies of the initial stages of
silicon growth on this surface.

1. Introduction

With the flexibility offered by modern crystal growth and processing techniques such as molecular beam epitaxy, chemical vapor deposition and reactive ion etching have come increasingly complicated chemical and physical processes. In particular, reactions involving the making and breaking of chemical bonds can play as large a role in growth as do the more traditional (and easier understood) concerns such as surface diffusion and nucleation. An example of this is the growth of solid silicon utilizing chemical vapor deposition of SiH₄. Here gas-phase SiH₄ molecules impinge on a silicon surface and decompose in a stepwise fashion [1]. The role of bond breaking, however, is not confined to growth with molecules, but also plays a part in the seemingly simpler growth of semiconducting crystals using single atoms as the source of added species. Semiconductors exhibit strong surface reconstructions which often involve the rebonding of surface atoms. To grow on these surfaces, even with atomic gas-phase species, the initial surface atoms must be rearranged to bulk positions. This means that specific reconstructions can influence a surface's potential for high-quality epitaxial growth [2,3].

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An example of surface reconstruction effects is the growth of silicon single crystals using silicon atomic beams incident on different crystallographic faces. Gossman and Feldman have performed a detailed study of this system by using high-energy ion scattering/channeling and low-energy electron diffraction to probe both the \{111\} and \{100\} surfaces of silicon during growth [3]. Their studies have indicated that the minimum substrate temperature needed to grow epitaxial crystalline layers on the \{100\} surface is 570 K while that needed for the \{111\} surface is 790 K. This difference in epitaxial growth temperatures was ascribed by them to be due to the differences in the energy required to reorder the different reconstructions on these surfaces. Despite the insight that was provided into the growth process, the experimental techniques that were used could not provide a detailed, atomic scale picture of the reordering of the reconstruction. The purpose of this study is to use molecular dynamics to elucidate the mechanisms of the adatom induced reordering of the silicon \{100\} reconstructed surface and to understand the role which these mechanisms play in the formation of amorphous versus crystalline overlayers.

In the next section, details of the reconstruction of the silicon \{100\} surface and examples of experimental methods for studying this surface are reviewed. The details and results of the simulation are contained in sections 3 and 4, respectively. A discussion of these results and how they relate to the study of Gossman and Feldman is given in section 5. Finally, a summary is presented in section 6.

2. Structure of the silicon \{100\} reconstructed surface

The bulk terminated \{100\} surface of the diamond lattice consists of surface atoms which are two-fold coordinate rather than four-fold coordinate as in the crystalline solid. This surface is illustrated in fig. 1a, where the shaded surface atoms are shown in this undercoordinated configuration. Pairs of surface atoms, which would be second neighbors in the crystal, can each increase their coordination from two to three by bending toward each other and forming a new surface bond. This is illustrated in fig. 1c, where the shaded surface atoms are shown in their reconstructed configuration. This Schlier–Farnsworth dimer pairing mode [6] (including variations such as the asymmetric dimer [7–9] is the generally accepted reconstruction for the \{100\} surface of silicon [10–12] and has recently been directly observed by scanning tunneling microscopy [13,14]. The stabilization energy produced by this dimerization has been estimated theoretically to be 1.7–2.1 eV per dimer [8,15,16] This represents a substantial stabilization energy so dimer formation can be considered as the creation of a new and complete surface bond. In order to epitaxially grow on this surface, the atoms on the reconstructed surface must somehow be rearranged to bulk lattice sites.
The dimer reconstruction on the silicon \{100\} surface induces two major changes to the bulk terminated surface. First, it changes the symmetry of the surface so that a \((2 \times 1)\) rather than a \((1 \times 1)\) diffraction pattern is observed. Any modifications which may occur to this reconstruction (during the initial stages of growth, for example) can be studied experimentally with techniques such as low-energy electron diffraction (LEED) and reflectance high-energy electron diffraction (RHEED). These techniques, however, are sensitive to long-range order. For the study of a dynamically changing surface by computer simulation, which is generally restricted to a relatively small number of atoms, the long-range order is suppressed. This is true even when periodic boundaries are imposed, because these induce an artificial long-range order. Hence, direct comparisons between the results of diffraction experiments and surface structures produced by computer simulation are very difficult.
The second major effect of the dimer reconstruction is that the movement of the surface atoms induces a strain in the lattice. This strain is reduced by the displacement of subsurface atoms from their bulk lattice sites. Theoretical and experimental studies have indicated that the displacement of ~ 3–4 layers of subsurface atoms is required to completely relieve the surface strain [17–23]. The positions of the surface and subsurface atoms which are displaced due to the reconstruction can be studied with ion channeling/scattering [18,19]. For the reconstructed {100} surface of silicon, the number of backscattered ions which are initially aligned along major crystallographic orientations is a measure of the number of atoms which are displaced from bulk lattice sites. The greater the number of backscattered ions, the greater the number of atoms which are displaced due to the reconstruction. This technique then provides both a quantitative as well as qualitative measure of the surface reconstruction. Furthermore, since the results are sensitive to short-range order, they are amenable for interpretation with the aid of computer simulations.

3. Description of the simulation

In this section, the interaction of a single atom with the {100} surface is briefly explored using the interaction potential which is employed in the simulation. The details of the simulation conditions are then presented.

3.1. Interaction potential

The interaction potential which was used has been previously described [24]. It is based on a modification of Keating’s valence force field [25] where functional forms are used which properly describe the energetics for dissociation of the solid. For the crystalline solid, this dissociative valence force field (DVFF) has been shown to accurately describe the phonon dispersion relations, cohesive energy and Debye–Waller factor as well as demonstrate lattice and temperature stability.

In order to understand the simulation results presented in the next section, the energetics of the static surface should be discussed. Fig. 1a shows the top four layers of a bulk terminated (100) surface. Shown in fig. 1b are potential contours for the boxed region of (a). The energetics are given relative to a single adatom at infinity by summing the DVFF over a rigid surface with a single atom a distance above the crystal corresponding to the next bulk layer. For a full dynamical calculation with a moving substrate and other adatoms, this potential would be altered, but this contour plot still gives a feel for the surface potential. The deepest wells occur at the positions which correspond to lattice sites if the bulk were continued into the vacuum. There is also another
set of shallower wells at the sites between two surface atoms directly above a second layer atom. It is apparent that for a rigid system, the next layer of atoms would prefer to reside in epitaxial lattice sites. The position of the shallow wells would correspond to defects in the growing interface.

Shown in fig. 1c is the same (100) surface with a 2 × 1 symmetric dimer reconstruction. Periodic boundary conditions are used in the direction perpendicular to the surface and the atomic positions have been relaxed to the static equilibrium positions according to the DVFF. This potential yields a static surface dimer length of 2.39 Å and a dimer stability of 2.1 eV per dimer as compared to the bulk terminated surface. The latter value is in good agreement with other theoretical estimates of 1.7–2.1 eV per dimer [8,15,16]. The reconstructed surface also displays substantial subsurface distortions within the top four layers of the crystal. This result is in agreement with ion scattering studies of this surface [18–23].

Fig. 1d shows the potential contours for the reconstructed surface derived under the same conditions as fig. 1b. Several points are worth noting. First, the overall potential is much smoother than that for the bulk terminated surface. The dimers have “filled in” the deeper wells. The shallower wells, however, have not been greatly affected by the surface dimerization. There are also shallow wells in the center of fig. 1d which correspond to bulk terminated sites between two different dimers. While again the presence of surface motion would change the potential, it appears from this figure that the unreconstruction that would have to occur for epitaxial growth of a defect-free crystal would be initiated by surface atoms falling between dimers and pulling them apart. This is opposed to the simple insertion of a single atom into a dimer. Full dynamical calculations are presented in the next section which provide a detailed understanding of such mechanisms.

3.2. Details of the simulation

The reconstructed surface was simulated by using a finite slab ten layers thick with each layer containing 32 atoms. Periodic boundary conditions were imposed in the directions perpendicular to the surface normal in order to mimic an infinite crystal. The top layer contained sixteen surface dimers which were arranged into rows (fig. 2a). Taking into account the periodic boundary conditions, this arrangement produced two independent rows of dimers which repeated along the rows every eighth dimer. These were set diagonal to the periodic boundaries so that the two independent rows were offset.

The method used for simulating a heat source/sink of the infinite solid was based on similar methods which have been used to mimic dynamics on both surfaces [26,27] and in liquids [28,29]. The slab was divided into several regions according to the forces on the atoms. A reaction region consisting of the top four layers as well as the added atoms was maintained where the forces
Fig. 2. Silicon \{100\} surface as viewed from the vacuum. Periodic boundaries are imposed perpendicular to the surface. The dimerized surface atoms are drawn hatched. (a) View of the static surface prior to deposition. The four dimers which traverse the periodic boundaries are not numbered. (b) Snapshot of the simulation after deposition and subsequent heating of the substrate. The adatoms are drawn smaller than the substrate atoms for clarity. The numbers for each dimer as discussed in the text correspond to the numbers given in (a).

were due strictly to the interatomic potential. A stochastic region which consisted of five layers below the reaction region was included. For atoms in this region, generalized Langevin friction and random forces were added in addition to the forces due to the interatomic interaction. This maintained a temperature in the stochastic region (as well as the reaction region) which fluctuated around a desired temperature. The friction coefficient used was derived from the experimental Debye temperature of silicon and was the same value used by Lucchese and Tully in their theoretical studies of the silicon \{100\} surface [27]. Finally, a single layer at the bottom of the slab was held rigid. This kept the center of mass of the slab from moving and kept the bottom layer of stochastic from reconstructing.

The initial surface was defect free and was equilibrated to 900 K. A total of 48 atoms (1 ½ monolayers) was deposited by the addition of single atoms perpendicular to the surface every picosecond. The initial positions in the plane of the surface of the added atoms were chosen randomly and the atomic velocities were chosen from a distribution appropriate for an oven source at 2000 K. It should be emphasized that this flux is much greater than that used experimentally for crystal growth. The addition of atoms every picosecond allows each atom to come to local equilibrium with the surface and is not intended to mimic laboratory timescale growth. The excess energy released by the added atoms when they adsorbed on the surface dissipated to the stochastic region so that no global surface heating was apparent. Almost 90% of the
incident atoms adsorbed on the surface. This is in agreement with the experimental sticking coefficient of near unity [21].

Limited experimental results which yielded information as to the conditions needed to observe the reordering of the surface reconstruction were available prior to the simulation. Of concern was the optimum density of added atoms which should be present on the surface. The deposition of a total of $1\frac{1}{2}$ monolayers was chosen because it yielded both high and low densities of adatoms on the surface. It was hoped that this procedure would not bias the results, and that the variance in adatom density would allow the observation of the reaction mechanisms leading to the initial stages of both amorphous and crystalline overlayers.

The initial addition of the $1\frac{1}{2}$ monolayers of silicon atoms to the substrate maintained at 900 K did not initiate any reordering of the surface. This is thought to be because the total time of the deposition ($\sim 8$ ps) was not sufficient to observe any temperature activated adatom insertion substrate reordering at 900 K. This premise is supported by the study of Gossman, Feldman and Gibson of the deposition of germanium on the {100} surface of silicon [2]. There they determined that the germanium induced reordering of the silicon surface is a temperature activated process. The similarity between this system and the deposition of silicon on the silicon surface has been established by Gossman and Feldman [3], so that the silicon induced reordering is probably also temperature activated. In order to observe reordering, the substrate was heated to 1800 K and maintained at that temperature for the duration of the simulation (500 picoseconds). While this is above the experimental melting point of silicon, it is well below the estimated melting point of the DVFF [24]. Furthermore, it was found that this heating did not affect the bonding of the initial reconstructed surface, i.e., the dimers on the clean surface remained closed. It was hoped that the heating would accelerate surface reactions and diffusion so that they could be better observed on the time scale required when molecular dynamics simulations are performed.

4. Simulation results

Shown in fig. 2b is a snapshot of the substrate and adatoms as viewed from the vacuum after the initial deposition and subsequent heating of the substrate. The larger atoms are those which comprise the initial substrate while the smaller atoms are the added atoms. The difference in sizes is for visual clarity. The hatched larger atoms are those which initially comprised the dimers (e.g. the top layer substrate atoms). The rows of initial dimer pairs are easily discernible by comparison with fig. 2a, where each dimer is identified by a number. When the substrate was maintained at 1800 K, it was observed that the dimers surrounded by adatoms would occasionally open from their recon-
structured length (~ 2.4 Å) to approximately that of the bulk terminated
distance (~ 3.8 Å). Examples of open dimers in fig. 2b are dimers numbered 5,
6, 9, and 12 in fig. 2a. Some dimers remained open for the duration of the
simulation while others remained open for less than a picosecond to ~ 150 ps.
The length of time these dimers remained open (and presumably their stabil-
ity) was found to be well correlated to the mechanism of opening and the final
configuration of the dimer atoms and adatoms. It will be proposed that the
final configurations can be associated with the initial stages of either the
formation of an amorphous overlayer or of epitaxial growth.

4.1. Stable dimer opening

Dimer openings which persisted for the duration of the simulation were
found to arise from two different mechanisms. The predominant mechanism
of the stable opening of a dimer is illustrated in figs. 3–5. Shown in fig. 3 is an
enlarged picture of the region which is boxed in fig. 2b. The atoms which
comprise dimer 7 are initially bonded to each other and two adatoms are
bonded to the remaining dangling bonds on dimer 7. The adatoms are also
bonded to other deposited atoms forming an overlayer network. Plotted in fig.
4 is the bond distance of dimer 7 and the distance from adatom A (labeled in
fig. 3) to the center of dimer 7 in its static position as a function of time
beginning at the configuration shown in figs. 2b and 3. The dimer pair opens
twice during the time shown. The first opening occurs for a short period of
time (0.4 ps) and is representative of an unstable opening discussed below. The
second opening is representative of the first type of stable dimer opening
mechanism. First, adatom A gets a kick from the lattice and diffuses toward
dimer 7. It accelerates towards the dimer until simultaneously the dimer opens

Fig. 3. Enlarged view of the boxed region of fig. 2b.
Fig. 4. Illustration of the stable opening of dimer 7 in figs. 2b and 3. (a) Bond distance of dimer 7 as a function of simulation time beginning at the configuration shown in fig. 2b. The initial distance is that of the closed dimer while the final distance corresponds to a bulk terminated surface. (b) Distance from adatom A in fig. 3 to the center of dimer 7 in its static position as a function of simulation time. The time corresponds to that for (a).

Fig. 5. Predominant mechanism of stable dimer opening which leads to epitaxial growth. The adatoms, initially dimerized atoms and the second layer substrate atoms are drawn with different sizes for clarity. Bonds are arbitrarily drawn between atoms which are 3 Å or less apart. (a) Dimer and adatoms before opening. Two of the adatoms occupy the remaining dangling bonds. The adatoms shown are also bonded to other adatoms on the surface. (b) A concerted rearrangement of the dimer is induced by a diffusing adatom. One of the adatoms initially occupying a dangling bond is inserted into the dimer while the diffusing adatom occupies the vacated dangling bond. (c) Final configuration of the stable single-atom insertion. The initially dimerized atoms and the adatoms occupy sites which are characteristic of a bulk terminated lattice. The atoms are in position to form a new surface dimer reconstruction.
and adatom A stops diffusing. Hence, a diffusing adatom initiates the stable dimer opening. This mechanism is further illustrated in fig. 5. An adatom diffuses to a dimer (whose remaining dangling bonds are occupied by other adatoms) with sufficient momentum to induce a concerted rearrangement. This rearrangement involves the insertion into the dimer of one of the adatoms which initially occupied a dangling bond (fig. 5b). The diffusing adatom then occupies the vacated dangling bond (fig. 5c). The diffusion induced single atom insertion sufficiently stabilizes the open dimer so that it remains open for the course of the simulation (500 ps). Furthermore, after opening, both the two atoms which initially comprised the dimer and the three adatoms which induced the stable opening occupied sites which were characteristic of a bulk terminated lattice. Dimers 6 and 9 of fig. 2b also opened via this mechanism.

The less dominate stable dimer opening mechanism is illustrated in fig. 6. This mechanism again began with a dimer whose two remaining dangling bonds were each occupied by an adatom. In this case, the dimer would thermally open (fig. 6a). The adatoms apparently induced this temporary opening as no thermal opening was found when a clean surface was heated to 1800 K. The first opening which is apparent in fig. 4 is characteristic of this unstable opening. In most cases, such an opening would be unstable and close after a short period of time. However, if an adatom diffused into the open dimer, this single atom insertion would sufficiently stabilize the open dimer so that it remained open for the course of the simulation. As in the first stable dimer opening mechanism described above, after the opening the two initially dimerized atoms and the three adatoms occupy positions which are characteristic of a bulk terminated overlayer. The stable opening induced by this single atom insertion occurred much less frequently than the mechanism described above because of the short period of time in which the thermally opened dimer would remain open. Hence, there was a small probability of an adatom diffusing into the open dimer.

Fig. 6. Less dominate mechanism of stable dimer opening. (a) Dimer thermally opens. (b) Insertion of diffusing adatom. (c) Final atomic configuration is the same as that illustrated in fig. 5.
Fig. 7. Examples of atomic configurations which induce unstable dimer openings. Adatoms are randomly positioned around the dimers. (a, b) Opening induced by more atoms than is required for a crystalline overlayer. These dimers remained open for \( \sim 50-150 \) ps. (c) Examples of an atomic configuration which induces an even less stable opening. These dimers remain open for \( \sim 0.1-25 \) ps.

4.2. Unstable dimer opening

Configurations of adatoms around the dimers other than those discussed above were also found to induce dimer opening. This opening, however, was unstable, i.e. the dimers would fluctuate between being open and closed. Examples include dimers 5 and 12 of fig. 2b. Additional snapshots of some of these configurations are shown in fig. 7. Configurations 7a and 7b illustrate open dimers where more than one adatom has inserted into the dimer bond. This type of opening is reasonably stable, up to a duration of \( \sim 50-150 \) ps. These configurations do not, however, lead to adatoms which occupy lattice sites. This reordering is less dependent on surface diffusion, but requires a larger number of atoms in the vicinity of the opened dimer than is needed for the stable opening discussed above. Configuration 7c shows an example of a dimer which has temporarily opened. Again, the addition of more adatoms in the vicinity of these dimers will induce greater stability of the open dimers. As opposed to what we have termed above as stable opening, however, these configurations do not lead to the deposited atoms occupying lattice sites.

5. Discussion

As mentioned in section 1, the initial stages of growth of both amorphous and crystalline silicon overlayers on the silicon \{100\} surface have been studied by Gossman and Feldman using high-energy ion scattering/channeling and LEED [3]. For the former technique, 0.5 MeV He\(^+\) ions were used which were aligned along major crystallographic orientations. These experiments provided information about the nature of the silicon induced reordering of both the surface and subsurface regions.
For growth where the substrate was maintained at temperatures above 570 K, Gossman and Feldman observed that the total backscattered ion intensity remained constant and that a steady \((2 \times 1)\) LEED pattern was maintained. They concluded that for these conditions, a crystalline epitaxial overlayer is formed and that the dimer reconstruction remains at the surface of the overlayer. It can also be concluded that the reordering of this surface is induced by a crystalline overlayer which is composed of a monolayer or less of added atoms.

In the simulation, it was observed that stable dimer opening was induced by two-step mechanisms. The first step is the occupation of the two remaining dangling bonds on a surface dimer by adatoms. This is followed by a second step which involves the diffusion of a third atom to the site of the dimer opening. After this opening, both the added atoms and the two atoms which comprised the dimer occupy sites characteristic of the solid being continued into the overlayer. These atoms are then in position to form the same reconstruction (albeit rotated by 90°) as the original surface. For example, dimer 6 in fig. 2b has epitaxially opened. The three adatoms in the vicinity of this dimer are in position to form the new reconstruction after dimer 7 has opened as illustrated above. This mechanism appears to be responsible for the initiation of epitaxial growth on a defect- and step-free reconstructed surface. All of the atoms which were involved in the two different mechanisms occupy crystalline lattice sites after the stable dimer opening. Thus no atoms in excess of that in the crystalline overlayer are required to completely re-der the surface. This is consistent with the experimental studies, where it was concluded that the reconstruction remains at the growing vacuum–solid interface. Also, the role that surface diffusion plays in this dimer opening is apparent. It does not act simply as a means of mass transport. Instead, the diffusing atom actually induces the rearrangement. This means that energetic surface atoms (and hence relatively high substrate temperatures) are required for reactions leading to epitaxial growth.

For the addition of silicon atoms to a substrate maintained at room temperature (300 K), Gossman and Feldman observed that the backscattered ion intensity remained at the initial value characteristic of the clean reconstructed surface for the deposition of the equivalent of three monolayers. With further deposition, however, the intensity of the surface peak increased with a slope characteristic of the formation of an amorphous overlayer. This may be interpreted as being epitaxial growth for the first few layers followed by deposition of amorphous material. Gossman and Feldman, however, argue against this based mainly on the LEED pattern. They observed a conversion of the LEED pattern from \((2 \times 1)\) for the initial reconstruction to a disordered pattern for the deposition of less than a monolayer of silicon atoms. The LEED pattern then changed to \((1 \times 1)\) for the deposition of more than about one monolayer. They felt that while the disordered pattern and the \((1 \times 1)\)
pattern did demonstrate that the symmetry of the exposed surface had changed due to the overlayer, neither provided sufficient information to identify a surface structure or a reordering mechanism. They proposed instead that the \((1 \times 1)\) pattern was due to some unknown long-range order. Rather than initial epitaxial growth, Gossman and Feldman proposed that the adatoms simultaneously form an amorphous (or polycrystalline) surface layer while also reordering the reconstruction. The constant backscattered ion intensity was a result of the increased channeling of the incoming ions as the dimerized surface atoms reorder to bulk lattice sites which is cancelled by increased blocking of the channels as amorphous layers are deposited. It then requires the equivalent of three monolayers of amorphous silicon to completely reorder the surface. They proposed a model where the equivalent of one monolayer of amorphous silicon reorders the surface reconstruction so that the atoms in one strained subsurface layer return to their bulk lattice sites. The three subsurface layers which are displaced because of the reconstruction then require three amorphous (or polycrystalline) layers to be completely reordered to bulk lattice sites.

The simulation results suggest a somewhat different model. In our simulation unstable dimer opening was observed to occur when adatoms were positioned randomly around the dimers. It is proposed that the randomly placed adatoms are the initial stages of the formation of an amorphous overlayer which has reordered the reconstruction. Furthermore, it was observed in the simulation that a larger number of adatoms are required for the unstable dimer opening than is required for stable dimer opening. The more adatoms which are present, the more stable the reordering of the surface reconstruction. Although the average number of the randomly positioned adatoms needed to complete the reordering of the surface is difficult to quantify from this simulation, it does appear that more added atoms are required to induce the unstable dimer opening than is required when the added atoms occupy lattice sites. This result provides a basis for an alternate model which accounts for the experimental observation that more than a single layer is needed to completely reorder the surface reconstruction. During the experimental deposition of amorphous layers, the dimers are fluctuating between being opened and closed. At any one time during the initial deposition, only a fraction of the total surface dimers are open. Hence, incomplete reordering occurs. As additional randomly positioned adatoms are deposited, the fraction of open dimers increases until all of the dimers remain open. This would occur after the deposition of more than a single layer. Furthermore, since the deposited atoms would not occupy lattice sites, this mechanism would not lead to epitaxial growth. The role of diffusion in this model is also clear. It simply provides a means of mass transport and does not play a major role in the reordering mechanism. Hence this type of reordering could occur with high fluxes and relatively low substrate temperatures.
While the models which have been derived from the molecular dynamics simulation correlate very well with the experimental results described above, one additional point about this work should be addressed. Even though the potential used here has been previously shown to provide a very good description of crystalline silicon as well as the dimer stabilization energy of the \{100\} silicon surface, it is still based on an expansion about equilibrium for a perfect crystal. Hence, it is designed only for tetrahedral bonding. The occupation of the remaining dangling bonds by the adatoms may then be overemphasized since the orbitals of the atoms on a real silicon surface are most likely somewhat rehybridized. A classical interaction potential developed for silicon by Tersoff, which is fully described in ref. [32], is quite good for describing the structure and energetics of undercoordinated configurations. With this potential, it was found that for the static surface there is at least a local potential minimum for two adatoms occupying the remaining dangling bonds on the dimers. Furthermore, the bonding connectivity and relative stability of open dimer configurations compared to the closed dimer configurations have been shown to be comparable for the two potentials [33]. It appears that the initial configuration which occurs before the reordering is not potential dependent, and is representative of the real system.

6. Conclusions

The silicon adatom induced reordering of the symmetric dimer reconstructed \{100\} silicon surface has been studied with a molecular dynamics simulation. The simulation employed a dissociative valence force field for silicon which has been previously described [24]. The simulation consisted of the deposition of single silicon atoms up to a total of $1\frac{1}{2}$ monolayers on a silicon substrate that was maintained at a temperature of 900 K. This was followed by heating of the surface to 1800 K. The latter process was performed in order to accelerate surface reactivity.

Two distinct categories of surface dimer opening were observed. The first was a stable dimer opening in which once a dimer opened, it remained open for the duration of the simulation. This was found to be induced by two different two-step mechanisms, both of which required in the second step the diffusion of an adatom to the site of the opening. Both the three added atoms and the two dimer atoms involved occupied final positions which were characteristic of the formation of a crystalline overlayer. This is proposed to be the initiation of epitaxial growth where the reconstruction remains at the growing vacuum–solid interface. Furthermore, the diffusion provides an explanation for the higher substrate temperature which is required for epitaxial growth over that which yields amorphous overlayers.
The second category was an unstable opening. This was induced when a dimer was surrounded by three or more randomly positioned adatoms, and is proposed to be the initiation of an amorphous overlayer which reorders the reconstruction. This mechanism differs from what we have termed stable opening in that the deposited atoms do not occupy lattice sites. This is consistent with the experimental result that amorphous (or polycrystalline) overlayers reorder the reconstruction for growth on a room temperature substrate. It was also observed that additional added atoms are required to induce the reordering than what would be present for a single crystalline overlayer. This observation provides the basis for a model which explains the experimental result that an excess of a single layer of amorphous material is required to complete the reordering.

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