# Molecular Dynamics Studies of the Adatom Induced Rearrangement of the Silicon {100} Surface

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## ABSTRACT

A molecular dynamics simulation of the silicon adatom induced rearrangement of the silicon {100} symmetric dimer reconstructed surface has been performed. Surface diffusion is proposed to play a critical role in the reordering of this surface which leads to good epitaxy while it plays much less of a role in the reordering induced by an amorphous overlayer. These results are used to provide atomic-scale models which are consistent with high-energy ion channeling/blocking and LEED studies by Gossman and Feldman of the initial stages of silicon growth on this surface.

## 1. INTRODUCTION

In order to grow epitaxially on a reconstructed semiconductor surface, the substrate atoms in the surface region must be reordered to bulk lattice sites during deposition of the gas atoms. This means that different faces of the same substrate can exhibit very different growth behavior (including different epitaxial growth temperatures) which is due to various reconstructions. A well characterized example of this is the deposition of germanium and silicon on the silicon {111} and {100} surfaces. Using high-energy ion scattering/channeling and Low Energy Electron Diffraction (LEED), Gossman and Feldman have characterized contrasting growth behavior for these two surfaces[1,2]. They have ascribed these differences (including different epitaxial growth temperatures) to the initial reconstructions of each surface. The microscopic details of the effect which surface reconstructions have on the initial stages of epitaxial growth are not well understood. Furthermore, even if these details were understood for a few systems, they would be difficult to generalize to other systems. This is because of the vastly different reconstructions which the surfaces of semiconductors display. One must therefore go beyond traditional (and more system independent) approaches such as nucleation theory and examine the microscopic details of each system of substrate and added atoms individually. This includes an evaluation of both static structures and of surface dynamics.

The purpose of this study is to gain a microscopic understanding of the silicon adatom induced reordering of the reconstructed silicon {100} surface which occurs during the initial stages of growth. The {100} surface of silicon is believed to reconstruct by the bonding of surface atoms which would be second neighbors in the bulk to form surface dimers[3]. The formation of the new surface bond is accompanied by subsurface strain which results from the movement of the surface atoms[4]. This reconstruction has been theoretically estimated to be 1.7-2.1 eV per dimer more stable than the bulk terminated surface[5-7]. The dimer pairing can therefore be considered as the formation of a new and complete surface bond which must be broken in order to epitaxially grow on this surface.

In the past, molecular dynamics computer simulations have been useful for providing researchers an atomic scale picture of a variety of chemical and physical processes[8]. This technique typically follows atomic motion in real time by integrating classical equations of motion in small, discrete timesteps. These timesteps are usually on the order of a few

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femtoseconds or less, so simulating crystal growth on a monolayer per minute timescale is impossible with the current generation of computers[9]. Despite this, molecular dynamics simulations which use model as well as realistic potentials can produce estimates of static structures and surface dynamics. These estimates can then be used to develop models of chemical and physical processes which occur during crystal growth. Various aspects of these models, such as the feasibility of static structures, can be further explored at various levels of approximation. For example, the energetics of various structures suggested by computer simulations can be evaluated with *ab initio* total energy calculations.

A molecular dynamics computer simulation has been performed of the deposition of silicon on the silicon {100} surface. As mentioned above, the timescale which is inherent to this type of simulation prevents the mimicing of laboratory timescale growth. The events which were observed during the simulation, however, do provide input for models of both the amorphous layer reordering of the reconstruction as well as epitaxial growth on this surface. These models can be used to explain the experimental results of Gossman and Feldman of the initial stages of growth of this system[2].

## 2. OUTLINE OF THE COMPUTER SIMULATION

Details of the simulation will be presented in greater detail elsewhere[10], and so only an outline is given here. The interaction potential used is based on a valence force field where the functional forms for two- and three-body terms are rewritten so that the solid exhibits proper dissociation behavior[11]. It has been demonstrated that this potential accurately reproduces the vibrational properties of the solid as well as displays temperature and lattice stability. For the {100} surface, the potential yields a symmetric dimer stabilization energy of 2.1 eV per dimer. This value is in agreement with other theoretical estimates of 1.7-2.1 eV per dimer[5-7].

The simulation involved the deposition of 1 1/2 monolayers of silicon atoms onto a reconstructed {100} surface. The initial substrate was composed of ten layers with each layer containing 32 atoms. Periodic boundary conditions were imposed perpendicular to the surface and the bottom layer of the slab was held rigid. The latter constraint kept the bottom of the slab from reconstructing. The top layer was initially composed of 16 dimers which were arranged in rows. This structure has been directly observed by scanning tunneling microscopy[12] and is the structure which is believed to yield the commonly observed (2x1) LEED pattern. The initial substrate was maintained at a temperature of 900 K by the inclusion of Langevin friction and random forces on subsurface atoms[13]. The 1 1/2 monolayers were deposited by adding single atoms to the surface every picosecond. While the growth rate was much higher than typical laboratory timescale growth, this procedure does allow each atom to come to local equilibrium with the surface. The atoms were aimed at random positions on the surface with velocities perpendicular to the surface chosen from a distribution which is appropriate for an oven source at 2000 K.

After the initial deposition, very little diffusion of the adatoms was apparent and no dimer bonds were broken. The latter observation is inconsistent with experimental results, where it has been concluded that the reconstruction is reordered by the addition of overlayers[2]. This discrepancy is probably because the total time for the deposition was only ~48 picoseconds. It is thought that this was not sufficient time to observe dimer opening, i.e. adatom-induced dimer opening is a temperature activated process which requires longer time to be observed. This is supported by studies of Gossman, Feldman and Gibson of the deposition of germanium on the silicon {100} surface[1]. There it was determined that

the reordering is temperature activated. In order to observe surface reactions on the timescale required for feasible simulations, the surface was heated to 1800 K for a duration of 500 ps. While this is above the experimental melting point of silicon, it is below the estimated melting point of the potential[10]. Furthermore, no change in the reconstruction was observed when a clean surface was heated to this temperature. It was hoped that this heating would increase surface reactivity and would not significantly influence the resulting microscopic mechanisms.

## 3. RESULTS AND DISCUSSION

During the simulation, it was observed that surface dimers would spontaneously open from their equilibrium distance (~2.4 Å) to the bulk terminated second-neighbor distance (~3.8 Å). Some of the open dimers would tend to fluctuate between opened and closed, and some would remain open for the duration of the simulation. It was observed that the amount of time the dimers remained opened (and presumably their stability) correlated with the opening mechanism and with the final configuration of adatoms in the vicinity of the original dimer.

The majority of dimer openings where the dimer would remain open were found to arise from a diffusing adatom induced rearrangement of the closed dimer. This is illustrated in Figure 1. First, the two atoms which comprise the dimer are bonded to one adatom each (Fig. 1A). This increases the coordination of the atoms which comprise the dimer to the bulk value of four. Also, a more favorable configuration is for one or both of the adatoms to be bonded to other adatoms on the surface. A third adatom then diffuses to the end of the dimer and 'bumps' one of the adatoms into the dimer (Fig. 1B). This single adatom insertion stabilizes the opening. The diffusing adatom then occupies the position vacated by the adatom which inserted into the dimer. The three adatoms and the atoms which comprise the open dimer occupy final sites which are characteristic of either a bulk terminated surface or a surface where a new reconstruction is beginning to form (Fig. 1C). If an adjacent dimer should open with the same mechanism, the adatoms which occupy bulk terminated sites are in position to continue the same reconstruction on the new surface, albeit rotated by 90°. It appears that this mechanism is responsible for epitaxial growth on a defect and step free surface.

For unstable dimer opening (where the dimers fluctuated between being opened and closed), the adatoms were randomly positioned around the dimers and no significant movement of adatoms were observed during opening. Furthermore, it was found that the larger the number of adatoms which surrounded these dimers, the longer they remained open. This is proposed to be the initiation of an amorphous overlayer which has reordered the surface reconstruction. Both this mechanism and the diffusion induced stable dimer opening can be shown to be provide models which explain experimental results for the growth of this system.

As mentioned above, Gossman and Feldman have studied the initial stages of the growth of silicon on silicon substrates using LEED and high energy ion scattering/channeling[2]. For the deposition of silicon on the {100} surface, they determined that at least two substrate temperature dependent growth modes exist. For room temperature growth, they concluded that the deposited silicon simultaneously forms an amorphous layer while also reordering the reconstruction. Furthermore, they speculated that it requires the equivalent of three monolayers of deposited material to completely reorder the initially reconstructed surface atoms to bulk lattice sites. They proposed a model where the three subsurface layers which are displaced due to the reconstruction require the equivalent of three monolayers to be reordered. The observation from the computer simulation that the stability of the unstable dimer opening increases with an increasing number of randomly positioned adatoms in the vicinity of the

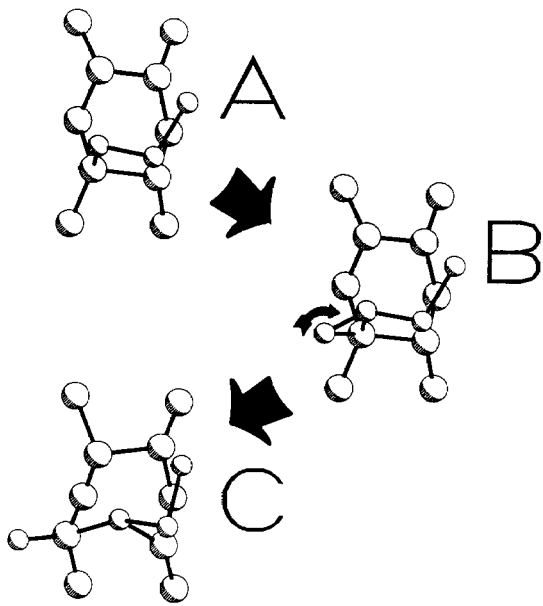


Figure 1. View From Above the Surface of Epitaxial Dimer Opening. Two dimers are shown with the lower one eventually opening. The adatoms are drawn slightly smaller than the substrate for clarity. A) Adatoms bonded to dimer atoms. B) Diffusing adatom 'bumps' one adatom into dimer bond. C) Single adatom insertion stabilizes opening. Final positions of adatoms and dimer atoms lead to epitaxial growth.

dimer suggests an alternate model for this result. As the adatoms are deposited on a room temperature substrate, at any one time a certain proportion of dimers are open. As more atoms are added, the dimers tend to remain open longer and a larger number of dimers are opened. This continues for the deposition of the equivalent of three monolayers after which essentially all of dimers remain open.

For deposition of silicon on a high temperature substrate (temperatures greater than 570 K), Gossman and Feldman determined that epitaxial growth occurs, and that the reconstruction remains at the growing vacuum-solid interface[2]. It appears that no atoms in excess of that needed to form an epitaxial layer are required to reorder the surface reconstruction. It can also be concluded that a higher temperature process is required to initiate epitaxial growth over that which simply reorders the surface reconstruction. The computer simulation based mechanism for epitaxial opening is consistent with these observations. First, for the stable dimer opening, no adatoms in excess of that which occupy lattice sites are required for stable reordering of the reconstruction. Hence, a single monolayer can induce epitaxial growth while continuing the same reconstruction at the vacuum-solid interface. Second, a diffusing adatom,

which provides kinetic energy, is required to induce this dimer opening. This yields an explanation for the higher temperature process which is required for epitaxial growth over that which simply reorders the reconstruction.

In order to further evaluate the configurations which were observed in the simulation during stable dimer opening, the energetics of static structures were calculated. This was performed with both the potential used in the simulation[11] and a potential which has been developed for silicon by Tersoff[14]. The latter potential yields unrealistic minima in some cases[14-16], and so its use for molecular dynamics simulations is limited. Nonetheless, this potential has been found to produce accurately structural energies which agree with total energy, *ab initio* calculations for various surface reconstructions[14]. This provides an independent test of the structural energetics. Shown in Figure 2 are several local energy minima configurations for three adatoms positioned around a dimer. These were generated by starting with configurations which were observed in the simulation during the stable dimer opening. These were then allowed to relax to the local minimum energy configurations. In each case the Tersoff potential yielded configurations (and associated bond connectivity) which matched that found with the initial potential. The numbers next to the configurations correspond to their energy. The first set of numbers are for the potential used in this simulation while the numbers in parenthesis are for the Tersoff potential. The zero of energy is arbitrary. The two most stable configurations are those which correspond to final configurations observed for the epitaxial dimer opening discussed above (Figs. 2B and 2C). The other configuration is that for the precurser to the epitaxial dimer opening mechanism (Fig. 2A). It appears that the bond connectivity and the stability of the open dimer configurations relative

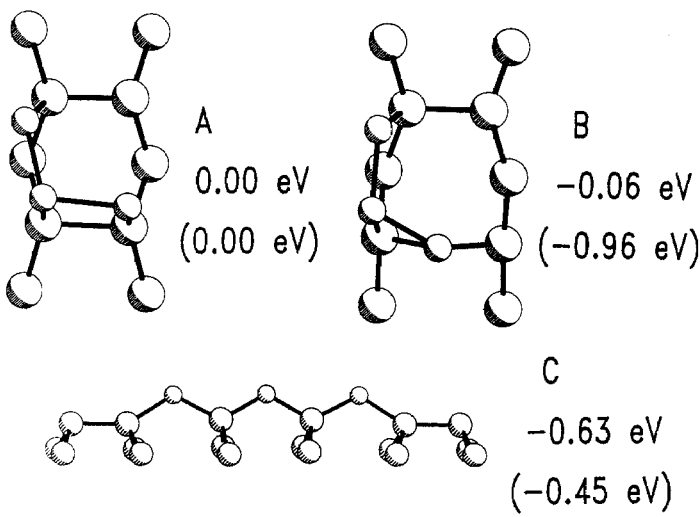


Figure 2. Local minimum energy configurations for three adatoms positioned around a dimer. The numbers refer to the energy of each configuration. The first value refers to the potential used in the simulation and the second value in parenthesis refers to the minimum energy using the Tersoff potential[14]. A) Example of a configuration prior to stable opening. B,C) Examples of configurations after stable dimer opening. Configuration (C) is a side view.

to the closed dimer configuration for the epitaxial opening mechanism are not potential dependent and are characteristic of the real system. The structure and stability of these configurations as well as additional ones suggested by the simulation are currently being explored with a variety of potentials[14-16].

In conclusion, models for both the amorphous layer induced reordering and epitaxial reordering of the silicon {100} reconstructed surface during the initial stages of deposition have been proposed. The models were based on a molecular dynamics computer simulation of growth. For the amorphous layer reordering, it is proposed that randomly positioned adatoms cause surface dimers to fluctuate between being opened and closed. Furthermore, it appears that the larger the number of adatoms in the vicinity of the dimer, the more stable the opening. This model accounts for the experimentally based conclusion that the equivalent of three monolayers of amorphous material is required to complete the reordering of the reconstruction. A second model which requires a rapidly diffusing adatom has been proposed for the epitaxial opening of surface dimers. This mechanism provides a higher temperature process which is required for epitaxial growth over that which reorders the reconstruction

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REFERENCES

1 H.-J. Gossman, L.C. Feldman and W.M. Gibson, Surf. Sci. 155, 413 (1985).
2 H.-J. Gossman and L.C. Feldman, Phys. Rev. B 32, 6 (1985).
3 R.E. Schlier and H.E. Farnsworth, J. Chem. Phys. 30, 917 (1959).
4 J.A. Applebaum and D.R. Hamann, Surf. Sci. 74, 21 (1978).
5 M.J. Cardillo and G.E. Becker, Phys. Rev. B 21, 1497 (1980).
6 M.T. Yin and M.L. Cohen, Phys. Rev. B 24, 2303 (1981).
7 K.C. Pandy, in Proceedings of the Seventeenth International Conference on the Physics of Semiconductors, edited by D.J. Chadi and W.A. Harrison (Springer-Verlag, New York, 1985), p.55.
8 See for example a) F.F. Abraham, Adv. Phys. 35, 1 (1986); b) W.G. Hoover, Molecular Dynamics (Springer-Verlag, Berlin, 1986).
9 See reference 8a, p. 91.
10 D.W. Brenner and B.J. Garrison, to be published.
11 D.W. Brenner and B.J. Garrison, Phys. Rev. B 34, 1304 (1986).
12 R.J. Hamers, R.M. Tromp and J.E. Demuth, Phys. Rev. B 34, 5343 (1986).
13 See for example a) S.A. Adelman, Adv. Chem. Phys. 44, 143 (1980);
b) R.R. Lucchese and J.C. Tully, Surf. Sci. 137, 570 (1983).
14 J. Tersoff, Phys. Rev. Lett. 56, 632 (1986).
15 B.W. Dodson, Phys. Rev. B 35, 2795 (1987).
16 J. Tersoff (private communication).