MECHANISMS OF MOLECULAR BEAM EPITAXIAL GROWTH ON RECONSTRUCTED Si{100}: THERMAL AND ENERGIZED BEAMS

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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. For example, 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 [1,2]. The Si{001} surface, if bulk terminated, would have each atom bonded to two other silicon atoms in the second layer (Fig. 1). There would be two dangling bonds each with one electron, and the nearest-neighbor distance on the surface would be ~3.84Å. Since Si prefers higher coordination environments two surface atoms react and form a bond (i.e. "dimerize") - with a distance of ~2.4Å (Fig. 1) [3].

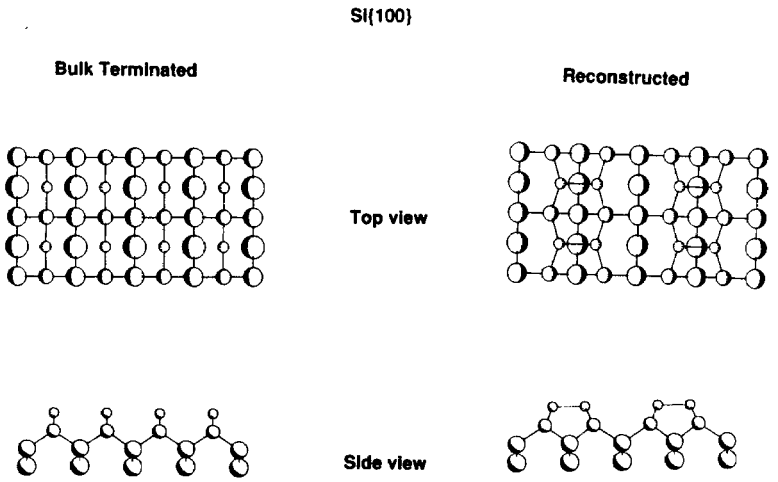

Fig. 1. In all cases the first layer atoms are smaller with the size increasing as the atoms are deeper in the crystal.

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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. Gossmann 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 [1-2]. 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 detailed, atomic scale pictures of the reordering of the reconstruction. It has also been proposed that the beam of atoms that are being deposited, if energized, could enhance layer by layer growth without allowing interlayer diffusion [4-9]. It has been shown that for Si beam deposition of energies 10-65 eV on Si{100} good epitaxial growth is obtained for colder temperatures that when thermal atom beams are used [8]. For energies above 100 eV crystal damage is observed as far as 400 Å below the surface. The kinetic energy enhanced epitaxial growth process is not completely athermal, that is, the quality of the films increases with increasing substrate temperature [8]. 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 in both the thermal and 5-20 eV energy regimes and to understand the role which these mechanisms play in the formation of amorphous versus crystalline overlayers. Although other investigators [10-11] have examined aspects of the adsorption process, none have emphasized the microscopic mechanisms of surface reordering.

DISCUSSION AND RESULTS

A molecular dynamics simulation was used to examine the reaction mechanisms which lead to reordering of the atom-pairing reconstruction on the Si{100} surface during atom deposition.[12] The simulations incorporated a dissociative valence-force-field potential [13-14]. The actual prescription used to maintain temperature control in the dynamics is described elsewhere [12]. The surface consisted of 10 layers of 32 atoms per layer thus there were 16 dimer pairs on the original reconstructed surface. For the thermal energy deposition 1.5 monolayers of Si adatoms were deposited on the surface. For the enhanced kinetic energy processes only 10-12 Si atoms were deposited per surface.

Thermal Energy Deposition

After the deposition of the 1.5 monolayers the surface was annealed at a high temperature for a total of 500 ps. The most notable feature of the deposition of the thermal energy Si atoms on the {100} surface is that the initial atoms attach to the remaining dangling bonds of the surface dimers. During the dynamics two modes of surface dimer opening ('unreconstruction') were observed. In the first mode the distance between the two atoms in a dimer pair would intermittently change between that corresponding to the reconstruction (~2.4 Å), and the distance corresponding to the bulk terminated surface (~3.84 Å). This mechanism, termed an unstable opening, resulted when a surface dimer was surrounded by several randomly positioned atoms. Because the atoms surrounding the open dimer were not in lattice sites (Fig. 2), this mode of dimer opening is proposed as being the initiation of an amorphous overlayer which reorders the reconstruction. Also, since diffusion did not play a large role, this was associated with the low temperature growth mode proposed by Gossmann and Feldman [1-2].

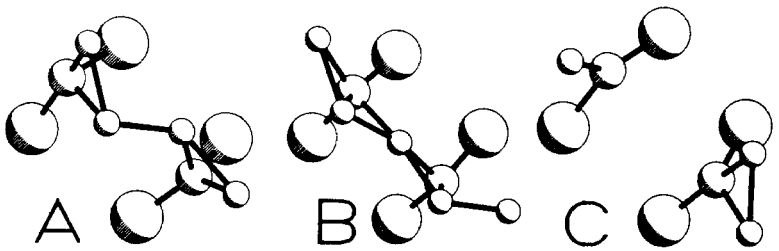

Fig. 2. Examples of atomic configurations which induce unstable dimer openings. Adatoms are randomly positioned around the dimers. (a,b) Opening induced by more atoms than is required for a crystalline overlayer. These dimers remained open for ~50-150 ps. (c) Examples of an atomic configuration which induces an even less stable opening. These dimers remained open for ~0.1-25 ps.

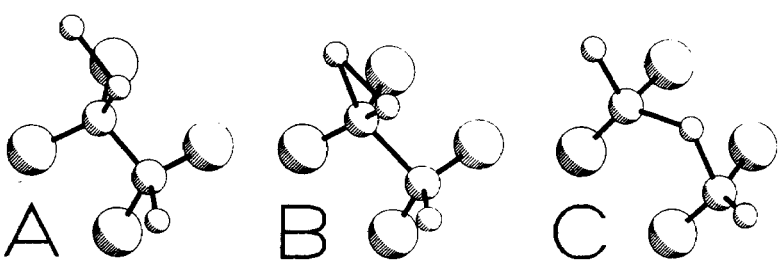

Fig. 3. Predominate mechanism of stable dimer opening which leads to epitaxial growth. The adatoms, initially dimerized atoms and the second layer substrate atoms are drawn with different sizes for clarity. Bonds are arbitrarily drawn between atoms which are 3 Å or less apart. (a) Dimer and adatoms before 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.

The second dimer-opening mode observed resulted when a surface atom diffused to the site of a surface dimer and 'bumped' a nearby atom into the center of the dimer. This mechanism resulted in atoms which occupied lattice sites, and produced a surface dimer which remained open for the course of the simulation (Fig. 3). Because the final atomic positions corresponded to lattice sites, and because a high rate of surface diffusion was required to produce the 'bump', this mechanism was associated with the high-temperature epitaxial growth mode identified by Gossmann and Feldman.

Kinetic Energy Enhanced Growth

In a separate calculation silicon atoms with energies of 0.026-20 eV were deposited on a silicon {001} dimer-reconstructed surface. For atomic energies of 0.026 eV and perpendicular incidence, the atoms in the beam remained on the surface, and no significant motion of the dimer reconstructed surface atoms occurred. For energies in the range of 5-10 eV, however, significant motion of the surface atoms was observed which lead to epitaxial atomic configurations. One mechanism which occurred in this energy range was the direct insertion of the incoming atom into the dimerized pair of surface atoms (Fig. 4). In a second mechanism, the incoming atom replaced one of the atoms in a surface dimer pair, which then became the inserted atom. Finally, the incoming atom could also knock open the dimer, and bind to the surface so that the dimer remained open. Each of these mechanisms took place on a timescale of ~100 fs (1fs=10^{-15} second), and so they are best characterized as direct dimer opening processes. This is opposed to a thermal process where many vibrations might be required. Although not all trajectories in this energy range produced open dimer pairs, the results of the simulation indicate that the energy range of up to 10 eV would enhance epitaxial growth without introducing subsurface defects.

In addition to the 5-10 eV energy range, incoming atoms with energies of up to 20 eV were also explored. These atoms were observed to implant into the lattice, and presumably produce damage in a growing film. This conclusion agrees with that of Dodson [9], where a majority of atoms incident perpendicular to the {111} with energies of 10 eV implanted. These studies indicate that for perpendicular incidence, atoms with energies in the range 5-10 eV would be the most effective for producing low-temperature epitaxial films.

SUMMARY

Molecular dynamics simulations have been performed that examine the microscopic mechanisms of rearrangements of atoms on the Si{100} surface due to deposition of gas phase atoms. For thermal energy deposition we find that the gas atoms initially attach to dangling bonds of the surface dimer atoms. The dimer 'unreconstruction' is due to a diffusion event on the surface, thus is temperature activated. We also find that dimers may open in regions of the surface where there are several atoms not at lattice sites, thus a low temperature amorphous structure. For 5-10 eV deposition there are direct mechanisms of dimer opening that occur on the 50-100 fs timescale. For energies greater than 15-20 eV there is implantation of the silicon atoms which leads to subsurface damage.

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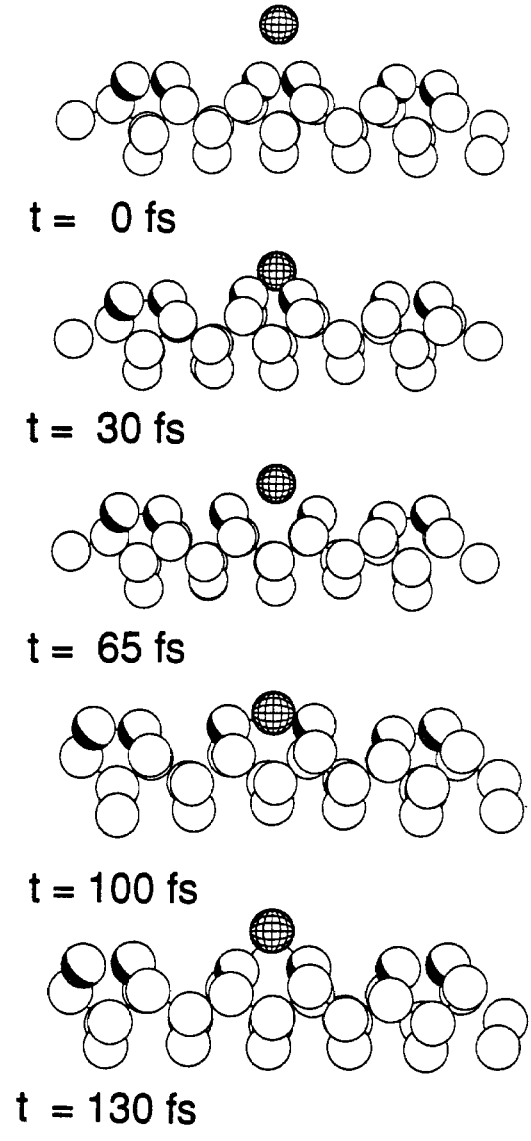

Fig. 4. Insertion mechanism of dimer opening as a function of time in femtoseconds(fs). The adatom started with 7.5 eV of kinetic energy and oriented perpendicular to the surface. The hatched circles represent the adatoms, the shaded circles the original surface dimer atoms and the open circles the substrate atoms. Only four layers of the ten used in the simulation are shown.

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