

KINETIC ENERGY ENHANCED MOLECULAR BEAM EPITAXIAL GROWTH OF Si{100}Barbara J. GARRISON¹, Mitchell T. MILLER*Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, USA*

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For kinetic energy enhanced molecular beam epitaxial growth of Si{100} we show that there are direct mechanisms of dimer opening, i.e. unreconstruction, that lead to epitaxial growth. These unreconstructions occur on the femtosecond timescale rather than requiring the long times associated with surface diffusion processes. The optimal energy range appears to be 5–10 eV.

In molecular beam epitaxy (MBE) of semiconductors the goal is to synthesize a highly ordered crystalline film layer by layer so that the arrangement of atoms is well defined. For example, one might want to construct superlattices which consist of alternate bands of GaAs and AlAs which are four atomic layers thick [1] or to dope boron into silicon in a highly controlled fashion. To obtain epitaxial growth it has been observed that the sample must be held above a certain critical temperature. If the sample is below this epitaxial temperature, amorphous growth occurs. The problem with high sample temperatures is that interlayer diffusion can also occur, thus possibly destroying the desired structure. The nature of the surface reconstruction influences the epitaxial growth temperature [2,3]. Gossman and Feldman have shown that the epitaxial temperature for Si{111} is ≈ 790 K whereas it is ≈ 570 K for growth on Si{100} [3]. They propose that it is harder to reorder the Si{111}(7 \times 7) surface than to unreconstruct the surface dimers on Si{100}(2 \times 1). As displayed in fig. 1 ($t=0$ fs), two surface atoms on Si{100} that would be next-nearest atoms in bulk Si bond together into a dimer with a bond length ap-

proximately that of the nearest-neighbor spacing in the bulk.

It has been proposed that the beam of atoms that are being deposited, if energized, could provide a very *localized* heating source for the surface, thus enhancing layer by layer growth without allowing interlayer diffusion [4–16]. 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 than that when thermal atom beams are used [15]. 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 [15].

In this Letter we show from molecular dynamics calculations of the energetic deposition of Si atoms on Si{100} that distinct non-thermal mechanisms of epitaxial growth can occur. We find for energies between about 5 and 10 eV that there can be direct insertion of a Si adatom into the dimer bond on the Si{100} face. We also find a direct knocking apart of the dimer bond. These mechanisms both occur on the femtosecond timescale and have not been observed in calculations of purely thermal energy deposition [16,17].

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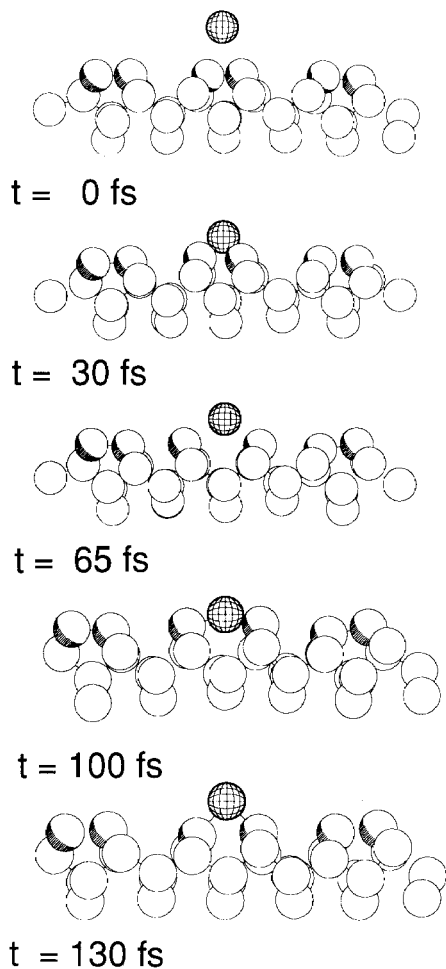


Fig. 1. Insertion mechanism of dimer opening as a function of time in femtoseconds. The adatom started with 7.5 eV of kinetic energy and oriented perpendicular to the surface. The hatched circles represent the adatoms, the shaded circles the original surface dimer atoms and the open circles the substrate atoms. Only four layers of the ten used in the simulation are shown.

The initial stages of thermal energy MBE growth were previously modeled via molecular dynamics simulations in order to understand the reaction mechanisms of growth of both amorphous and crystalline overlayers on the dimer reconstructed Si{100} surface [17]. For thermal energy deposition of Si atoms on Si{100} the adatoms initially occupy dangling bond sites as shown in fig. 2. We found that other adsorbed Si atoms diffused to these dimers and induced an opening of the dimer with all the atoms in epitaxial positions [17]. Alternately we have re-

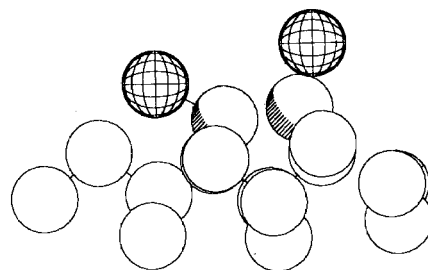


Fig. 2. Surface dimer with adatoms occupying dangling bonds. The deposition of adatoms was at 0.026 eV. The hatched circles represent the adatoms, the shaded circles the original surface dimer atoms and the open circles the substrate atoms. Only four layers of the ten used in the simulation are shown.

cently observed a mechanism of dimer opening in which the dimer is pulled open by the adatom on the dangling bond also bonding to a dangling bond of an adjacent dimer. Of note is that these processes occur on the tens to hundreds of picosecond timescale and that the first step is the occupation of the dangling bonds by Si adatoms. A higher surface temperature enhances both diffusion and bond opening allowing epitaxial growth to proceed.

For the energetic beam deposition of Si adatoms on the dimer reconstructed Si{100} surface we used the same configuration of atoms as used for the thermal energy studies [17]. The reconstructed surface as simulated by using a finite slab ten layers thick with each layer containing 32 atoms. We used the dissociative valence force field (DVFF) interaction potential for bulk silicon [18] with a modified short-ranged portion of the Si-Si interaction^{#1}. In the calculations presented here the solid was maintained at 1200 K, which is a lower temperature than used in the previous simulation [17] and is lower than the melting point predicted by our potential [18]. The beam of atoms was monoenergetic and directed toward the surface at a specified angle using randomly generated aiming points.

For each simulation ten Si adatoms were deposited on a fresh Si{100} dimer reconstructed surface. The deposition of each adatom was monitored for about 4 ps before another adatom was deposited. For the adatom energies of 0.026, 5.0, 7.5 and 10.0 eV, two simulations were performed at each energy. As

^{#1} The modification made by Brenner is published in ref. [19].

shown schematically in fig. 2 deposition at 0.026 eV resulted in the adatoms bonding to dangling bonds of the dimers with none of the dimers having opened on this timescale. For the 5.0–10.0 eV simulations dimers opened on this short timescale. As with the thermal energy deposition many of the remaining adatoms occupy dangling bond sites. Finally for 15–20 eV (fig. 3) we did not observe dimer opening but did observe implantation of the Si adatoms. This observation is consistent with the fact that the displacement energy of Si is ≈ 17 eV [20].

The results presented in figs. 1, 2 and 3 are highly representative of many simulations we have performed. It is interesting that for the 5–10 eV range approximately $10 \pm 5\%$ of the adatoms open a dimer bond without first having the dangling bonds saturated. A time sequence of one insertion mechanism is shown as a side view in fig. 1. The adatom initially has 7.5 eV of kinetic energy. This is sufficient energy to break the dimer bond in approximately 60 fs. In this case the adatom actually penetrates into the first layer before coming to rest in the epitaxial position. These same initial starting positions were rerun with the adatom having kinetic energies of 1, 2, 4, 6, and 9 eV. The 2–7.5 eV runs all resulted in dimer opening with the adatom inserting into the dimer. The 1 eV simulation did not result in dimer opening, which is not completely surprising since the bond strength is ≈ 2 eV [18]. At 9 eV the adatom opened the dimer but bounced out with the dimer closing and the adatom coming to rest on the dangling bond. As the timescale of this process is on the order of 100 fs, we do not believe that the surface temperature should affect this insertion mechanism.

Two other examples of direct dimer opening were observed in the simulations. In one mechanism the energetic adatom knocked open the dimer and then

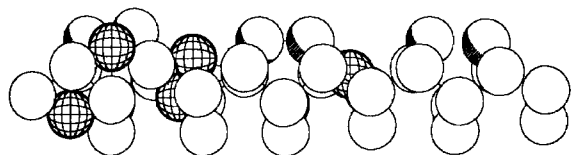


Fig. 3. Si adatoms implanted at 15 eV. The hatched circles represent the adatoms, the shaded circles the original surface dimer atoms and the open circles the substrate atoms. Only four layers of the ten used in the simulation are shown.

bonded to one of the dimer atoms and the adjacent dimer dangling bond, thus holding the dimer open without an inserted atom. In the second case the adatom actually replaced one of the dimer atoms, which then became the inserted atom. In all three of the mechanisms discussed above the openings occurred on the 20–100 fs timescale and did not require the dangling bonds to be occupied.

Calculations were performed for an angle of incidence of 45° at azimuthal angles parallel and perpendicular to the dimer rows and at energies of 10 and 20 eV. At this time there is no obvious angle effect in the direct dimer opening. As observed for the perpendicular approach of the energized beam, some of the 20 eV particles implanted into the substrate.

Of note for kinetic energy enhanced crystal growth is that the energetic beam does more than supply a localized heating source. An energetic Si atom can directly open a dimer on the Si{100} face thus leading to epitaxial growth on a femtosecond timescale rather than requiring the long times associated with surface diffusion processes. From these simulations it appears that the optimal energy range is 5–10 eV and that energies > 15 eV induce damage. It is impossible to ascertain from these simulations whether these defects can be easily annealed out. However, for heterostructures there will be mixing of the layers.

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