Summary Abstract: Molecular dynamics studies of dynamical processes on the silicon {100} reconstructed surface

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Molecular beam epitaxial growth has provided tremendous flexibility for the production of novel as well as technologically important semiconductors. With this flexibility, however, comes 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. Even in the relatively simple case of homoepitaxial growth of silicon on silicon substrates, the strong surface reconstructions and associated rebonding of surface atoms found on different exposed faces can influence the epitaxial growth temperature for each face.[1]

In this summary, we report the results of molecular dynamics studies of the adatom induced unreconstruction of the silicon {100} symmetric dimer reconstructed surface. The interaction potential used for silicon was previously developed by Brenner and Garrison.[2] It is based on a variation of a valence force field[3] in which the proper energetics for dissociation of the silicon solid has been included. For the crystalline solid, it was shown that this dissociative valence force field (DVFF) accurately describes the phonon dispersion relations, cohesive energy and Debye–Waller factor as well as demonstrates lattice and temperature stability.

The bulk terminated {100} surface of the diamond lattice consists of surface atoms which can be thought of as having two unpaired or dangling bonds per atom. Pairs of surface atoms, which would be second neighbors in the bulk, can each satisfy one of their two dangling bonds by forming a new surface bond. Using the DVFF, the reconstructed surface is 2.1 eV per dimer more stable than the bulk terminated surface.[2] This value is in reasonable agreement with other theoretical estimates of 1.7–2.1 eV.[4,5] In order to epitaxially grow crystalline silicon on this surface, these extra surface dimer bonds must somehow be broken.

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 exposed surface so as to mimic an infinite crystal. The top layer was reconstructed into rows of dimers where there were sixteen total surface dimers. Taking into account the periodic boundary conditions, this arrangement comprised two independent rows of dimers repeating every eighth dimer. The bottom layer was held rigid and the slab was sufficiently thick so that subsurface strain generated by the surface reconstruction did not persist to the rigid layer.

A heat source/sink was simulated by dividing the slab into a reaction region consisting of the top four layers and a stochastic region consisting of five layers between the reaction region and the rigid layer. For atoms in the stochastic region, generalized Langevin friction and random forces were added in addition to the forces due to the atomic potential.[6–8] This maintained a temperature for both the reaction and stochastic regions which fluctuated around the 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 studies of the silicon {100} surface.[7]

The initial surface was defect free and was equilibrated to 900 K with the Langevin friction and random forces. Atoms were added perpendicular to the surface every picosecond with their velocities chosen from a distribution appropriate for an oven source at 2000 K. The excess energy released by the added atoms was dissipated to the stochastic region so that no surface heating was apparent and almost 90% of the incident atoms adsorbed on the surface. This is in agreement with the experimental sticking coefficient of almost unity.[9]

The addition of $1\frac{1}{2}$ monolayers of silicon atoms under the conditions given above did not result in the breaking of any of the surface dimer bonds. In order to study the breaking of these bonds, both the original substrate and the substrate with the adatoms were heated to 1800 K. Although this is just above the experimental melting point of silicon, it was below the estimated melting point for the DVFF.[2] For this temperature, it was found that the dimers on the clear reconstructed surface remained closed. However, for the surface with the adatoms, when silicon adatoms were bonded to both of the remaining dangling bonds on either side of a surface dimer, the dimer bond would occasionally instantaneously open, remain open for several femtoseconds to several picoseconds, and then close again. This opening and closing would continue unless either a third adatom inserted into the dimer or one of the adatoms bonded to the dangling bond anchored itself by bonding to an adjacent elongated dimer. In these two cases the dimer bond remained open. For the second case, a third atom could easily insert into the open dimer. All three of these adatoms then occupied bulk terminated sites.

In conclusion, it appears that this chemisorption induced and temperature activated instantaneous dimer opening, followed by insertion of a third atom, is the mechanism responsible for the layer by layer unreconstruction and epitaxial growth of silicon on the reconstructed silicon {100} surface. This is consistent with high-energy ion scattering and channeling and low-energy electron diffraction studies of the initial stages of silicon molecular-beam epitaxy performed by Gossman and Feldman,[1] where it was demonstrated that during epitaxial growth, the reconstruction remained at the growing surface even for very low coverages. The persistence

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of the surface dimer bonds in the calculations during the initial deposition was probably due in part to the short time scale of the simulation, and possibly also to the dimers being too stable with the DVFF. Since the breaking of the dimer bonds is an activated process, none of the bonds had sufficient time to break at the initial surface temperature used.

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