Anisotropic Spread of Surface Dimer Openings in the Initial Stages of the Epitaxial Growth of Si on Si{100}

D. Srivastava and B. J. Garrison
Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

D. W. Brenner
Code 6119, Naval Research Laboratory, Washington, D.C. 20375
(Received 31 March 1989)

The initial stages of the epitaxial growth of the dimer-reconstructed Si{100} surface are modeled via molecular-dynamics simulations using the Tersoff many-body potential. We report a novel anisotropic spread of surface dimer openings in the direction perpendicular to the original dimer rows. This correlated reaction mechanism dramatically increases the crystal growth process in one direction as confirmed by recent scanning-tunneling-microscope studies.

PACS numbers: 68.55.Bd, 68.35.Fx, 82.20.Wt

The recent availability of realistic many-body potentials for materials such as silicon,[1] germanium,[2] and carbon[3] allows the calculation of chemical reaction dynamics at surfaces. In this Letter we report the results of molecular-dynamics (MD) computer simulations where thermally deposited Si atoms are allowed to react with a dimer-reconstructed Si{100} surface. The results reveal a *novel* mechanism of cooperative motion where dimers simultaneously open in adjacent rows. This mechanism predicts that there should be single rows of dimers rather than isolated dimers in the first epitaxial layer. Concurrently with these calculations the anisotropic growth of Si{100} during molecular-beam epitaxy (MBE) has been reported by Hamers, Köhler, and Demuth[4] with scanning tunneling microscopy (STM). A total of 4–5 monolayers (ML) of epitaxial silicon has been grown in the simulation. In accordance with the experimental results, we find that the highest overlayer structures occur in the regions of epitaxial rather than amorphous growth,[4] and that the reconstruction remains at the growing interface.[5] Thus these simulations are the first that both establish a microscopic mechanism of anisotropic growth and mimic the macroscopic features of the MBE growth on the dimer-reconstructed Si{100} surface.

The Si surface used in the MD simulation is shown in Fig. 1(a). The total sample consists of a slab of 10 layers of 32 atoms each with periodic boundary conditions in the horizontal directions and is the same as described previously.[6] The gas-phase Si atoms are randomly deposited on the substrate that is maintained at a constant temperature. The forces on the top five layers of atoms and the adatoms are taken directly from the interaction potential described below. The next four layers (stochastic region) are constrained by the forces from the interaction potential as well as by a friction that maintains thermal equilibration of the entire system.[7] The final layer is anchored so that no reconstruction occurs at this interface. The adsorption of the atoms on the surface is an exothermic process so the excess energy must eventually be dissipated into the stochastic region of the sample. In these studies the deposition rate of one atom per 3 ps was found to be sufficiently slow so that the sample is at the desired temperature when the next atom is deposited. If the gas-phase atoms are deposited too quickly then melting occurs,[8,9] masking the structural influence on the MBE growth process.

As there are several interaction potentials that have been developed for describing bulk silicon, some procedure must be devised for choosing among them. In most of our work on MBE growth, we have equilibrated the system for about 0.5 ns after each deposition of 1.5 ML of material. During this period if any physically interesting phenomenon was observed then the simulation was extended to longer time durations. During these initial stages of the use of MD simulations with realistic potentials we note that this is the most efficient way of using the available computer time for exploring as many physical properties as possible. In this testing we examined two of Tersoff's potentials[10,11] and the Brenner-Garrison potential.[12] In the simulations using the older Tersoff potential,[10] atoms deposited at thermal temperatures exhibited a tendency to implant and disorder the surface at 300 K. We did not feel that this was realistic. The later Tersoff potential[11] is similar in functional form to the earlier one,[10] but the parametrization has been improved so that the potential better describes the elastic properties of Si. The potential has been tested extensively for bulk and surface properties, and describes the energetics of point defects in crystalline solids rather well. To our knowledge, however, it has not been used to simulate surface dynamics. It should be pointed out that both potentials[10,11] reproduce the energetics of the Si{100} surface within an acceptable range but that the earlier potential[10] is better for the Si{111} surface. The Tersoff potential[11] has two advantages over the Brenner-Garrison potential.[12] First, the surface dimer stabilization energy is smaller (1.45 vs 2.1 eV), thus re-

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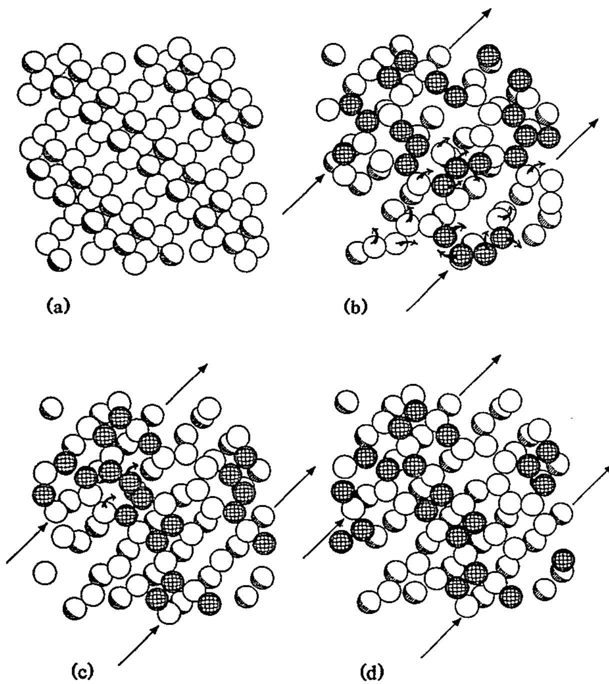

FIG. 1. Si{100} surface used in the MD simulations. (a) Original surface at 800 K. The shaded circles represent the surface dimer atoms. The open circles represent the next two subsurface layers. Periodic boundary conditions connect the top and bottom of the surface and the left and right. The dimer rows proceed from the upper left of the diagram to the lower right. (b) The surface after deposition of 1.5 ML. The original surface dimer atoms are shown as shaded circles. The subsurface atoms shown in (a) are no longer displayed. The hatched circles are the topmost deposited atoms and the open circles are the remaining deposited atoms. The curly arrows indicate the directions that the atoms move in the next 512 ps. The straight arrows on the sides of the crystal are a guide to the periodic boundary conditions and the correlated motion mechanism discussed in the text. (c) The surface after 512 ps of equilibration at 800 K. The atom representations are the same as in (b). The lower half of the surface has grown epitaxially as well as part of the top, which is connected to the bottom by the periodic boundary conditions. (d) Surface after another 476 ps of equilibration. The total time of the simulation was 1.1 ns.

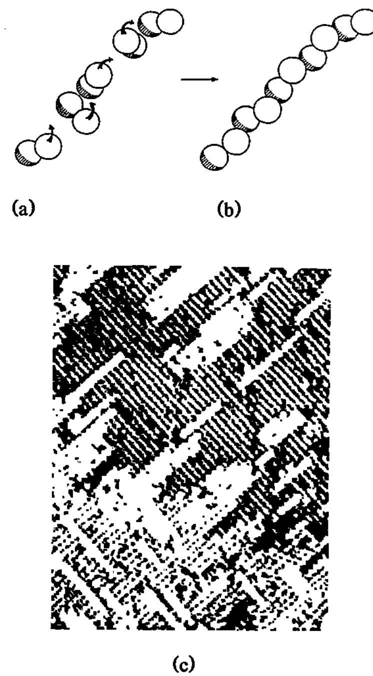

FIG. 2. Anisotropic dimer opening mechanism. (a) Position of dimer atoms (shaded circles) and adatoms (open circles) before opening. (b) Position of atoms after equilibration. (c) Section of an STM image taken during MBE (from Ref. 4 and supplied by R. Hamers). The original surface had a single-height step that goes from the upper left corner to the lower right corner of the figure. Therefore, the original dimer rows on the lower step terrace (upper right corner) go parallel to the step edge, whereas those on the upper terrace (lower left corner) are perpendicular to the step edge. Only a few tenths of a monolayer of Si atoms have been adsorbed on the surface. The lighter the atoms the higher they are.

actions will proceed faster. Second, the compatible potentials for C and Ge have also been developed[13] so that future studies of heterosystems can be performed.

In Fig. 1(a) we show a (2×1) dimer-reconstructed surface of Si{100} which has been equilibrated at 800 K. Top layer (shaded circles) and two inner-layer (open circles) atoms are shown. Of note is that none of the surface dimers are open. The result of depositing 1.5 ML of Si atoms on the surface over a time span of 144 ps is shown in Fig. 1(b). About half of the deposited atoms bind to sites of dangling bonds. The remaining atoms are either at the level of the second deposited layer or form a random overlayer at the level of the first deposited layer. The observation that the deposited atoms first attach to dangling-bond sites is identical to that found in a previous study[6] which used a different many-body interaction potential.[12]

During the deposition process four of the original surface dimers were found to open. For two of the openings the adatoms at the dangling-bond sites stabilized the open dimer, an adatom that was deposited later on eventually inserted between the two original dimer atoms in the epitaxial growth position. The other two openings were due to a diffusing adatom-induced mechanism observed previously.[6] In one of these latter cases the adatom actually replaced one of the original dimer atoms.

The surface covered with 1.5 ML of Si adatoms is shown in Fig. 1(b). The curly arrows indicate the atomic motion that occurs in the next 512 ps of equilibration at 800 K. At this later time the majority of the original surface dimers have opened [Fig. 1(c)]. One sequence of relevant motion starts in the direction of the straight arrow at the bottom of crystal shown in Fig. 1(b). The adatoms move stepwise in the direction of the arrows with dimers opening along the way. Because of the presence of periodic boundary conditions the continuation of

the motion (follow the straight arrows) proceeds to the upper left part of Fig. 1(b). This string of open dimers is perpendicular to the original dimer rows [Fig. 1(c)]. The correlated motion of adatoms inducing a dimer opening does not appear to be dependent on the periodic boundary conditions. This can be seen in another set of correlated motions, which initiate the lower left corner of the surface in Fig. 1(b) and is terminated only when an amorphous region is encountered as is shown in the upper right corner of Fig. 1(b). An isolated picture of these events is shown in Figs. 2(a) and 2(b). Initially the adatoms are bonded to dimer atoms at the dangling-bond positions [Fig. 2(a)]. A cooperative or correlated motion occurs in which the atoms move perpendicularly to the original dimer rows. The final configuration is shown on the right side of the picture. All the adatoms are in the epitaxial positions and all the original surface dimers are open [Fig. 2(b)]. We note that some correlated motion mechanisms were observed in the overlayer structures also, and they too were terminated only when they encountered an amorphous region.

Recent experiments[4] that examine the MBE growth on Si{100} using the STM have observed surface structures that are indicative of our mechanism of anisotropic growth. Shown in Fig. 2(c) is a portion of one of the scanning tunneling micrographs of a Si{100} surface (see the figure caption for a description of the surface). The first epitaxial layer is partially present. One of the most striking features in this figure is the long single rows of dimers on both the lower and upper terraces. Based on our simulations these single dimer rows can readily occur because of the correlated adatom motion that leads to dimers opening in a direction perpendicular to the original rows. It is of note that the second layer has already started to form [middle of the very top of Fig. 2(c)] even though the first epitaxial layer is not complete.

In Fig. 1(d), we show the sample of Fig. 1(c) after allowing equilibration for another 476 ps. One more dimer has opened due to the correlated adatom motion [see curly arrows in Fig. 1(c)]. Some of the adatoms at the level of the first and second deposited layers have started to form new surface dimers. Of note is that the empirical potentials do not predict that the ordered rows of dimers, as in the (2×1) reconstruction, have a lower energy than an equivalent number of random dimers. Thus some of the atoms in the topmost layer are randomly paired into dimers. In Fig. 3, we show the epitaxial growth of up to 4 ML of the deposited material. This was achieved by two repetitions of depositing of 1.5 ML of Si atoms and equilibrating the system for about 1 ns. The initially deposited atoms in this sample have therefore been present for 3.4 ns. For clarity, some of the atoms at the level of the fifth and sixth deposited layers are not shown. The total number of atoms in the third and fourth deposited layers is thus about 0.8 ML per layer. In the epitaxial region initiated by the dimer openings shown in Fig. 1 the reconstruction stays constantly at the vacuum-solid interface while the next to the last layer is constantly rearranging. This observation is in agreement with the results from Rutherford backscattering experiments.[5] In addition, we also note that the epitaxial growth characteristics of the first deposited layer are continuously passed onto the growth characteristics of the later deposited layers. This means that the domains of good epitaxial growth in the first four deposited layers are roughly in the same area of the original surface in which the dimer atoms had rearranged back to their bulk positions.

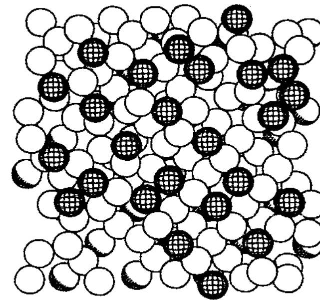

FIG. 3. Si{100} surface after the deposition of 4.5 ML of Si atoms and a total equilibration time of 3.4 ns at 800 K. The atoms in the fourth deposited layer are shown as hatched circles, whereas the atoms in the first, second, and third deposited layers are shown as open circles. This simulation took 800 h of IBM 3090 computer time.

To study the temperature behavior of the proposed model of epitaxial growth, we performed analogous simulations at 300 K. Two open dimers were formed during the deposition process. However, no new dimer openings, due to a diffusion-induced mechanism, were observed during the equilibration period of 0.5 ns. Therefore, we note that the proposed anisotropic mechanism does in fact have a temperature dependence, but a definite conclusion about the nature of this temperature dependence cannot be made until the simulations at other temperatures and for longer duration of equilibration times are made. The simulation at 800 K (Fig. 3) ran for 3.4 ns and took 800 h of IBM 3090 central-processing-unit time. This is already pushing the current limit of such simulations.

In a similar study[6] of epitaxial growth using a different interaction potential,[12] the diffusing adatom-induced mechanism of stable dimer opening was found to be the main mechanism of surface reactions leading to epitaxial growth. However, no correlated motion of the chemical reactions was observed during the equilibration period. We believe that the higher surface stabilization energy of that potential[12] (2.1 eV per dimer) versus that of the Tersoff potential[11] (1.45 eV per dimer) and the shorter equilibration times (0.5 vs 1.1 ns) may have prevented the observation of anisotropic growth. In the

earlier study[6] some unstable open dimers were found to occur with two or more adatoms inserted into the dimer. These structures were not observed in the present simulations.

In another study of MBE growth of Si{100}, Gawlinski and Gunton report epitaxial growth for up to 4 ML, but they did not examine the microscopic mechanisms of dimer opening.[8] As has been subsequently pointed out,[9] the deposition rate in their study was too fast to allow for complete dissipation of the energy from the exothermic reaction. This energy effectively destroyed the structure of the interface of the originally reconstructed surface and the layers of the deposited material. The effect of a long-time equilibration after the deposition, therefore, is more like a simulation of crystallization from a liquid state.

In conclusion, our MD simulations of the reaction dynamics of atoms deposited on the dimer-reconstructed Si{100} surface predicts a correlated reaction mechanism that can result in anisotropic epitaxial growth. This is in agreement with the recent STM results which show that the epitaxial layer should grow preferentially in a direction perpendicular to the original dimer rows on the surface. We have also achieved the epitaxial growth of a thin film of up to 4-ML thickness. Our simulations indicate that a layer-by-layer growth mode,[5] in which the top layer is constantly reconstructing and the atoms in the next to the top layer are constantly returning to bulk sites, is a correct description of the mechanism of good epitaxial growth.

Two of the authors (D.S. and B.J.G.) graciously thank the Office of Naval Research, the National Science Foundation, the IBM Program for the Support of the Materials and Processing Sciences, and the Camille and Henry Dreyful Foundation for financial support. Pennsylvania State University supplied a generous grant of computer time for this work. R. Hamers sent us a copy of his work prior to publication.

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