Dynamics of Growth of Silicon on Vicinal Si (001) Surface

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Using the *ab initio* molecular dynamics approach we have studied the initial stages of silicon growth on a vicinal Si(001) surface. We find that for this surface the equilibrium structure is a double-layer stepped surface with atoms rebonded to the upper surface. The rebonding energy is approximately 0.7 eV/bond, which is about half the dimer formation energy (1.6 eV/bond). We then studied the growth process dynamically. This involved a sequence of bond breaking and bond forming which generates a new rebonded step edge. From the results of our simulation we suggest that this double-stepped Si(001) surface is most suitable for good quality layer growth.

The structure of a stepped Si (001) surface has been studied intensively not only because of its technological importance in the homo- and heteroepitaxy processes, but also because of the rich variety of structures it exhibits [1–3]. A flat Si(100) surface is known to reconstruct, leading to the formation of a dimer. In the presence of a step, which can be single (S) or double (D), the dimer can align either parallel (A) or perpendicular (B) to the step edge [4]. When it aligns perpendicular to the surface, S_B or D_B rebonding occurs, which eliminates the dangling bonds. This causes the formation of dimer-like bonds with the atoms at the edge of the upper terrace. A stepped surface can be generated by cutting a slightly misoriented (vicinal) surface. The technological interest in these surfaces arises from the possibility they offer to allow regular crystal growth. In fact the stable reconstruction of flat Si(001) surfaces strongly hinders an ideal growth process [5,6]. The use of a surfactant such as As, Sb or Bi has been proposed [4] as a solution to this problem. However, part of these surfactant molecules might diffuse away from the interface and alter the properties of the system. Stepped surfaces are free of this problem and provide numerous absorption sites in the vicinity of the step, thus allowing the epitaxial process to proceed with regularity. In spite of this technological relevance, vicinal Si(001) surfaces are not yet completely understood, let alone the process of growth. From a theoretical point of view, realistic simulation of growth on complicated surfaces is challenging because of the difficulty of constructing a correct surface potential of the substrate and thus generating accurate trajectories of adsorbed atoms. To date, most theoretical calculations have been done with model classical potentials [7]. Furthermore, none of the calculations has been done on the growth of the vicinal Si (001) surface.

In this letter, we study for the first time the atomic structure of a fully relaxed vicinal Si (001) surface misoriented in the (110) direction by 9°. We explicitly show by *ab initio* molecular dynamics that the adatoms break into the rebonded atoms at the step to generate a new step edge in the (110) direction.

In this calculation the surface is simulated by periodically repeated slabs of Si atoms in which six atomic layers (unreconstructed geometry) are included, with one side terminated by hydrogens and the other followed by a vacuum region of $\simeq 12$ Å. We have chosen a triclinic supercell with lattice vector $\vec{a}$ ($\sqrt{2}$, 0, 0), $\vec{b}$ ($-\sqrt{2}/4$, $9\sqrt{2}/4$, $1/2$) and $\vec{c}$ ($\sqrt{2}/4$, $-\sqrt{2}/4$, $3/2$) in units of a lattice constant which include 54 Si atoms and 18 H atoms in the cell. In this way, the number of layers of the upper and lower terraces are kept equivalent in order to prevent any unnecessary effects on either terrace surface. These unusual periodic boundary conditions are necessary to simulate a stepped surface with a limited number of atoms. The vicinal Si (001) surface with this periodicity will favor a double-stepped surface with a step length of l = 17.278 Å in the (110) direction and a step height of h = 2.715 Å in which three dimers and a step edge are included. This gives the misorientation angle $\gamma = \tan^{-1}(h/l) = 9°$, which is approximately the maximum angle for the stable vicinal surface. Note that it is known experimentally that for $\gamma \geq 7°$ only double steps are present.

Our calculations have been performed using the Car-Parrinello approach [8]. The interaction between ionic cores and valence electrons was described by a fully nonlocal pseudopotential with s-only nonlocality [9]. We used a plane-wave basis set with a typical cutoff kinetic energy of 8 Ry (corresponding to about 5000 plane waves) and Bloch functions only at the Γ point of the supercell surface Brillouin zone [10].

We started from an ideally (unreconstructed) stepped Si (001) surface as shown in Fig. 1(a). Two silicon layers from the bottom H layer in addition to the bottom H layer were not allowed to move in order to prevent any spurious forces from being emitted by the hydrogen bonds. Each surface atom on the Si(001) surface has two unpaired electrons. The distance between the surface atoms is 3.84 Å, which is the next-nearest neighbor distance. Owing to the presence of dangling bonds, this structure is unstable. We searched for an energy minimization using a steepest descent approach. Figure 1(b) shows the structure thus obtained. The top surface atoms are stabilized by forming dimers with their next-nearest neighbors whereas the atoms (r_1 and r_2) at the step edge rebond to the upper terrace atoms. This reduces two dangling bonds at the step edge. Two dimers (d_1 and d_2) are formed on the upper terrace and one dimer (d_3) on the lower terrace. These are in fact neighboring dimers with the periodic boundary condition of a triclinic cell, i.e., dimer d_3 is the neighbor of dimer d_1. The dimer in the middle (d_1) has an asymmetry of Δz = 0.52 Å in good agreement with experimental results [11]. The asymmetric values of dimers d_2 and d_3 are 0.35 and 0.23 Å respectively, which are smaller than that of a centered dimer (d_1). The asymmetry Δz changes its sign along the dimer row. One notes that the dimers d_2 and d_3, which are close to the step edge, show less asymmetry than does d_1, the centered one. This may suggest that the asymmetry of the dimers is associated with the dimer interactions in the same row. This trend is similar to calculated results [12]. Atoms r_1 and r_2 rebond to the neighboring atoms of the upper terrace, confirming Chadi's suggestion that the rebonded configuration is favored over the nonbonded one at the step edge [4]. The rebonded bond lengths are larger while the dimerized bond lengths are smaller (see Table I) but all are close to an ideal bond length of 2.35 Å. Those dimers close to the step edge have less asymmetry Δz and a lower dimer energy than the dimer far from the step edge because the asymmetric dimer energy is lower than the symmetric dimer energy. The energy gain with the rebondings is approximately 0.7 eV/bond, which is about half a dimer energy (1.6 eV/bond) [13]. This suggests that the rebonded step edge is the energetically favorable site over other regular dimers of the surface in the molecular beam epitaxy or chemical vapor deposition processes.

It is well known that the diffusion on the dimerized surface becomes anisotropic due to the difference of the activation energy parallel and perpendicular to the dimer rows [14]. Above room temperature the adatoms will move exclusively along the dimer rows. When the diffused adatoms encounter the (single or double) steps, they will have a chance to form bonds at the step edge. It has been speculated that the atomic growth on a Si (001) surface may be initiated near the step edge. With this argument the vicinal Si (001) surface with a miscut angle of approximately 8° in the (110) direction has been utilized primarily in the growth process [2,15].

In order to resolve this speculation, we added four atoms to the surface. Two atoms are placed about 3 Å above the rebonded atoms (r_1 and r_2) whereas the other two are placed near the dimer d_3 at the lower terrace. We performed microcanonical molecular dynamics with the 2500 time steps of 5τ (1.2×10^{-16} sec). The temperature increases from $T = 0$ K. The adatoms will be moved by the forces of the neighbors on the surface. At the same time the atoms at the surface also feel the additional forces from the adatoms, thus obtaining the thermal energy. The temperature increases but stabilizes at about 400 K after about 500 time steps. Figure 2 illustrates the evolution of the system at intervals of 500 time steps. Figure 2(a) is the initial configuration at $t = 0$. The four adatoms are far from the stable positions and thus two atoms at the step edge are repelled because of the undesired forces as shown in Fig. 2(b). As the adatoms near the step edge try to bond with the rebonded atoms (r_1 and r_2) and the neighbors at the upper terrace, the rebonded atoms recover the bond angle distortions and move to the right, as shown in Fig. 2(c). The adatoms are still very unstable due to the unsaturated dangling bonds. The two adatoms near the step edge are not completely bonded to the bottom atoms yet. The other two adatoms above the lower terrace dimer try to break the dimer bond while at the same time these two adatoms feel the forces from recovered rebonded atoms (r_1 and r_2) at the step edge. It is relatively easy for dimer d_3 which is close to the step edge to break over the regular dimer, as explained above. This bond breaking is also enhanced by the unstable (recovered) rebonded atoms at the step edge. In Fig. 2(d) the bonds between the top adatoms and the bottom atoms of the upper terrace become stronger and stronger, and at the same time the adatoms at the lower terrace keep moving to stable positions. In Fig. 2(e) the two adatoms at the step edge make a dimer while the rebonded atoms (r_1 and r_2) move to the right to rebond with the other two adatoms at the lower terrace. When the rebonded atoms (r_1 and r_2) lose their bonds with the upper terrace atoms, they try to rebond to the lower terrace atoms because of the unpaired electrons. Once the new bonds with the lower adatoms are formed, the rest of the atoms are immediately stabilized. Thus in Fig. 2(f) one can see very stable structures although they fluctuate by the thermal motion at about 400 K. Two adatoms at the step edge form a new dimer ($d_2^{'}$) by removing the rebonded steps whereas the other two adatoms at the lower terrace form new rebondings ($r_1^{'}$ and $r_2^{'}$) to the neighbors by breaking the dimer at the lower terrace. Thus a new, rebonded step is generated. The growth will continue in the $(1\bar{1}0)$ direction as the new adatoms are deposited. This clearly demonstrates that the good quality of atomic growth can indeed be accelerated on a vicinal Si (001) surface with a large miscut angle. It should be noted that the rebonded step edge plays a key role in this process. This can be expected since the formation energy of the rebonded atoms is about half that of the dimer. This process can be utilized in molecular beam epitaxial growth of a Si or Si/Ge superlattice.

We now discuss whether other types of stepped surfaces such as S_A, S_B, and D_A can be utilized in the growth process. The anisotropic diffusion on a dimerized Si (001) surface becomes dominant at temperatures above T_D where the diffusion length becomes greater than the step length l. The diffusion parallel to the dimer row is predominant over the one normal to the dimer row above T_D. In the case of S_B, the dimer row at the lower terrace is parallel to the step edge. Hence the number of atoms supplied to the step edge by the anisotropic diffusion is limited. The atoms from the upper terrace are uniformly supplied since the dimer row at the upper terrace is normal to the step edge although they may be hindered by a step potential barrier. Once the atoms are nucleated at any step site, a kink is formed. The kink becomes longer and longer because more atoms from the lower terrace can be nucleated while the growth of steps nearby is suppressed due to relatively smaller supplies. Thus the grown step edge becomes rough. This argument can be similarly applied to the D_A step. The growth rate is lower at D_A than at S_B because fewer adatoms are supplied from the upper terrace in the case of the D_A step (the dimer row is parallel to the step edge). In the case of S_A, in contrast, adatoms can be uniformly supplied to the step edge from the lower terrace because the dimer row is normal to the step edge, while the diffusion to the step edge from the upper terrace is limited because the dimer row at the upper terrace is parallel to the step edge. Therefore, the growth of the steps becomes uniform. This explanation is confirmed by experiment [6]. A uniform growth rate is required for a vicinal surface because the step length is short. The surface with step S_A has an advantage over the one with step S_B in this sense but there are no rebonded atoms in S_A. Furthermore, the adatoms supplied from the upper terrace in S_A are relatively small compared to those in S_B. As the dimer rows of both upper and lower terraces of the step D_B are normal to the step edge, enough adatoms can be supplied uniformly from both terraces and these are easily nucleated at the rebonded step edge. Therefore one can say that the vicinal stepped Si (001) surface of D_B type is the most suitable surface for the growth process.

In summary, we have obtained a fully relaxed Si (001) stepped surface with a misorientation angle of 9° in the (110) direction. The rebonding energy at the step edge is approximately 0.7 eV/bond, or half a dimer bond energy (1.6 eV/bond). We clearly demonstrate that the atomic growth process can indeed be initiated from the rebonded atomic sites at the step edge. It should be noted that the rebonded step edge plays a key role in the growth process. The vicinal stepped Si (001) surface (D_B type) with large misorientation angle is the most suitable surface for the growth process.

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[12] H. S. Lim, K. C. Low, and C. K. Ong, Phys. Rev. B**48**, 1595 (1993). This is related to the fact that our previous tight binding calculation of the diamond (001) surface does not show the asymmetric dimers. Because the electrons of carbon atoms are strongly localized, the dimer has fewer interactions with its neighboring dimers and hence the dimer becomes symmetric. This issue will be discussed in a separate paper.

[13] The dimer energy is calculated by constructing pure Si (001) surface slabs with the same number of layers as a vicinal surface. The energy gain of the rebonded atom is then obtained by subtracting the total energy of the fully relaxed vicinal surface from that of an ideal one. The effect of the relaxation of neighboring atoms near the step edge is neglected. However, the bond distances between the rebonded atoms (r_1 and r_2) and the neighboring bottom atoms are 2.33 and 2.35 Å, which is close to an ideal one of 2.35 Å. Hence the rebonded energy per bond is a reasonable value.

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FIG. 1. (a) The triclinic supercell of an ideal (unreconstructed) Si (001) stepped surface with the bottom Si layer saturated by H atoms. Each surface atom has two unpaired electrons. (b) The fully relaxed surface. Large and small spheres indicate Si and H atoms, respectively. Two Si layers from the bottom and the H layer are fixed during the relaxation. The dimers are formed. The atoms near the step edge are rebonded to the upper terrace atoms.

FIG. 2. Snapshots of *ab initio* MD trajectories approximately every 500 time steps. New steps are generated in the $(1\bar{1}0)$ direction. See text for details.

TABLE I. Surface bonding configuration of a fully relaxed vicinal Si (001) surface. The bond numbers correspond to Fig. 1. The parameter Δz is the asymmetry along the surface. All units are in Å. All dimer bond lengths are contracted whereas the bond lengths of the rebonded atoms are enlarged.

species	Δz	dimer bond length
d_1	0.52	2.33
d_2	0.35	2.30
d_3	0.23	2.27
r_1		2.45
r_2		2.43