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MOLECULAR DYNAMICS SIMULATIONS OF SINGLE Si ADATOM DIFFUSION ON THE Si(001) SURFACE AND ACROSS SINGLE-LAYER Si(001) STEPS

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By using the Stillinger–Weber atomic interactional potential, we have carried out molecular dynamics simulations of single Si adatom diffusing on the Si(001) surface and single-layer Si(001) steps at temperatures ranging from 1000 K to 1300 K. We have presented one new diffusion pathway of a single Si adatom diffusing on the Si(001) along the direction perpendicular to dimer rows, that can weaken the diffusion anisotropy. We have investigated the process of the single Si adatom diffusing across single-layer Si(001) steps as well and given adatom diffusion pathways of step-flow and transformation of single-layer into double-layer steps. Our results show that the exchange between an adatom and a surface atom plays an important role in the adatom diffusion process above 1000 K.

Keywords: Surface diffusion; molecular dynamics simulation; step; Si(001); Stillinger–Weber potential.

1. Introduction

Different aspects of the Si(001) surface and monatomic steps on it have been intensively studied theoretically and experimentally due to their high interest value in basic research as well as in technology. In particular, the elementary processes involved in the homo-epitaxial growth of Si films are important for the production of good quality crystals. It is therefore interesting to understand what the diffusion

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mechanisms of the atoms on Si(001) and steps are, as they play an essential role in the understanding of crystal growth.

When a silicon crystal is cut along the (001) plane, the atoms at the surface are each left with two dangling bonds. The atoms on and near the surface rearrange into a lower energy "reconstructed" structure. The primary feature of this surface that is generally accepted is the presence of rows of dimers, created when neighboring surface atoms bond together. Atomic and electronic structures of the Si(001) surface have been studied extensively. There are $p(2\times2)$ and $c(4\times2)$ bulked reconstructions at low temperature and $p(2\times1)$ and $c(2\times2)$ ones at high temperature on the Si(001) surface.[1,2] Because there are dimer rows and channels between the rows, adatoms may diffuse rapidly along some directions and move more slowly along other directions. Many theoretical[3,4,17] and experimental[5,6,19] work have confirmed that adatom's diffusion on Si(001) is anisotropic, i.e. adatoms diffusing rapidly along the dimer row orient and move more slowly through the orient perpendicular to the dimer row.

However, an actual substrate usually is a Si(001) vicinal face with many single-layer steps which can increase the adatom's diffusion velocity, restrain irregular nucleation and improve growth quality of films. Because of the stress anisotropy, the surface is expected to break up into two degenerate stress domains with monatomic steps as their boundaries. The dimer rows rotate 90° from one terrace domain to the next owing to the diamond structure of Si, thus two types of monatomic steps coexit. Following the notations of Chadi,[7] the S_A step is parallel to the upper-terrace dimer rows and the S_B step is perpendicular to the upper-terrace dimer rows. There are two types of S_B steps: those with and without rebonded atoms on the lower edge. In spite of a number of theoretical[7,11–15] and experimental[8–10] works about atoms diffusing near the monatomic steps, very little is known about the dynamical effect.

The most systematic and unambiguous way to study dynamic effects of atom's diffusion is to perform long-time-scale molecular dynamics (MD) simulations. Finite temperature molecular dynamics (MD) simulations are very helpful when used to search for low energy barrier diffusion pathways of adatoms. We performed long-time-scale MD simulations of Si adatom diffusion on a Si(001) surface and near monatomic steps from the temperature of 1000 to 1300 K. Describing the Si–Si interaction using the empirical Stillinger–Weber (SW) potential.[16] We concentrated on the dynamical aspects. In this paper, we will report new diffusion pathways of an adatom diffusing on the Si(001) surface and across monatomic steps. We found that the exchange between adatoms and surface atoms did occur and played an important role above 1000 K.

2. Method of Calculation

We applied the empirical SW potential, which consists of two- and three-body terms, to our long-time-scale MD simulations. The Si(001) surface was modeled

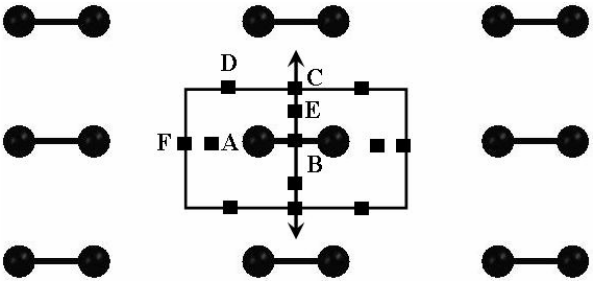

Fig. 1. Binding sites of the Si adatom on an Si(001) surface. Black circles and squares represent surface atoms and binding sites respectively. F is the most stable binding site. Arrows represent diffusion pathways parallel to the dimer row.

with a slab containing 21 layers of 128 atoms each. To model single-layer steps, we removed half of the upmost surface atoms. We chose the x-axis to be along the [110] direction, the y-axis along the [−110] direction, and z-axis along the [001] direction. Periodic boundary conditions were imposed in the x- and y-directions. In order to eliminate the interaction between the upmost surface and the downmost one, a vacuum space corresponding to forty silicon layers, which is about 54 Å in the present work, had been used to separate them. The simulations were done at several temperatures ranging from 1000 to 1300 K. At the beginning of the simulations, we set the temperature of the system. To control the temperature, the velocity scale constant temperature scheme was applied. For the numerical integration, the Verlet algorithm was applied to integrate Newton's 3N equations with a timestep of 0.5 fs. Before starting the MD simulations, the geometry of the systems applied by the simulations were optimized, in order to start from the ordered $p(2 \times 1)$ reconstructed surface. The downmost two layers atoms were fixed. The simulations were performed for 300 ps.

3. Results and Discussion

3.1. *Si adatom diffusion on Si(001)*

We have studied Si adatom diffusion at several temperatures ranging from 1000 to 1300 K. We found that the diffusion behaviors at the different temperatures from 1000 to 1300 K are similar. Hence, we choose the diffusion behavior at 1100 K to describe. Before describing our results, we illuminate different binding sites of adatoms on Si(001). Figure 1 shows the different binding sites of adatoms on Si(001). Sites B, C, D and F are the top of a dimer, the top of the dimer row, the side of the dimer row and the trough between the dimer rows respectively. Sites A and E are two saddles.[17]

We performed the simulation for 300 ps with the adatom initially in configuration B [Fig. 2(a)]. During most of the simulation time, the adatom diffused along the direction parallel to the dimer row, on the top of dimer row or in the trough

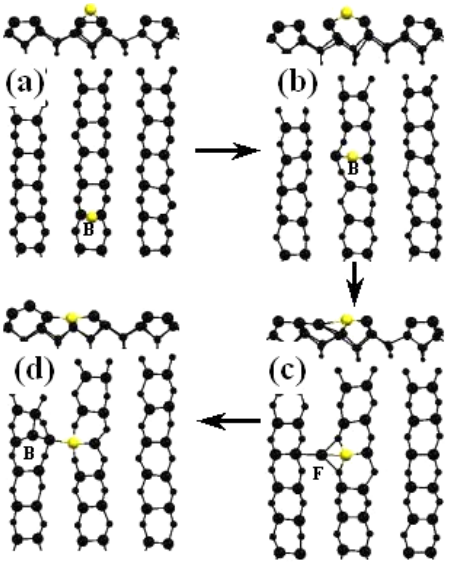

Fig. 2. The Si adatom diffusion pathway perpendicular to the dimer row on Si(001). The top of each of picture is the side view and the bottom is the top view. The grey circle represents the adatom. Black circles represent the surface atoms. The following figures are presented in the same way.

between the dimer rows. The pathway is similar to the pathway that Zhang[17] had reported, which only involved the leapfrog mechanism.

In this paper, we will report a new pathway that the Si adatom diffuses along the direction perpendicular to the dimer row from the top of the dimer row to the trough between the dimer rows and then to the top of the adjacent dimer row (Fig. 2), which involves the exchange between the adatom and the surface atoms. The Si adatom landing on the B site on the top of a dimer can hop to site A, and then hop to site F perpendicular to the direction of the dimer row, across the dimer directly through breaking the two bonds between the adatom and the two surface atoms, which are just under the adatom. It is so difficult to break the covalent bond between adatom and the surface atom that the adatom is less likely to diffuse along the pathway. At higher temperatures, however, the exchange between the adatom and the surface atom might reduce the energy barrier of diffusion.[18]

Figure 2(c) shows the exchange between the adatom and the surface atom. The adatom diffusing on the top of the dimer row pushed one atom of the dimer to the F site in the trough between the dimer rows. The pushed atom diffused in the trough and then climbed up to the neighboring dimer row through exchanging with the surface atom [Fig. 2(d)].

In order to give a quantitative analysis, we have calculated the local potential energy minima and the energy barriers between sites by fully relaxing the cordinates of the adatom and of all the substrate atoms. We found that the adatom

can move easily along the path B-E-C-D-E*-B* (A*, B*, C*, D*, E*, F* are the A, B, C, D, E, F equivalent sites in the adjacent cell, respectively) parallel to the dimer row, with the 0.35 eV energy barrier, which is extraordinarily close to that which Toh *et al.*[4] reported, 0.33 eV higher than that which Zhang *et al.*[17] reported, 0.288 eV, but is lower than that which Brocks *et al.*[3] reported, 0.6 eV. The adatom can also diffuse in the trough parallel to the dimer row with the 0.58 eV energy barrier. However, the adatom needs to conquer the 1.14 eV barrier along the line B-A-F-A*-B* and 1.25 eV barrier along the path C-D-D*-C*, along the direction perpendicular to dimer rows, which are lower than that which Lim *et al.*[19] reported, 1.4 eV. For adatom diffusion perpendicular to dimer rows, as we mentioned above, when exchanging with a surface atom, the adatom need only conquer 0.74 eV. As for that barrier, the exchange with a surface atom occurs only at a comparatively high temperature as we simulated. At those temperatures, which our simulations performed, for diffusion perpendicular to the dimer row, the exchange events occurred frequently, indicating that the diffusion constant in the direction perpendicular to the dimer row is affected by the exchange mechanism. The exchange played an important role in the diffusion perpendicular to the dimer row.

3.2. *Si adatom diffusion on the S_A step*

3.2.1. *Diffusion from the lower terrace to the upper one*

Our simulations show that the adatom landing on the lower terrace of a single-height step can climb up to the upper terrace through exchanging with the surface atom on the upper terrace. Since the dimer rows on the lower terrace are perpendicular to the S_A step, the adatom located on this terrace has no difficulty reaching the step, by moving rapidly on top of the dimer rows. Our potential energy calculations show that adatoms which located the trough in the lower terrace (Fig. 3.) can approach the S_A step in the trough easily with the 0.58 eV barrier. In the adatom diffusion process, it is trapped at the S site, because the S site is the local minimal potential energy site. The adatom trapped there needs to conquers a 1.16 eV barrier to climb up the upper terrace. The adatom located on the dimer row on the lower terrace can approach the S_A step along the dimer rows with a 0.35 eV barrier. Such an adatom denoted in grey in Fig. 3(a), reaches position C in Fig. 3(a) without difficulty, by moving on top of a dimer row. Once there, the adatom moves back onto the lower terrace with more difficulty due to unsaturated bonds on the upper terrace. Before hopping to site S [Fig. 3(b)], the adatom needs overcome an energy barrier of 1.48 eV to climb up the upper terrace. The adatom can also exchange energy with the neighboring atom on the upper terrace and push the atom up to the upper terrace as shown in Fig. 3(c). The lifted atom on top of the upper terrace diffuses parallel to the upper dimer rows more easily [Fig. 3(d)]. This exchange process must conquer a 1.05 eV barrier, which is extraordinary close to that which Zhang *et al.*[11] reported, 1.08 eV.

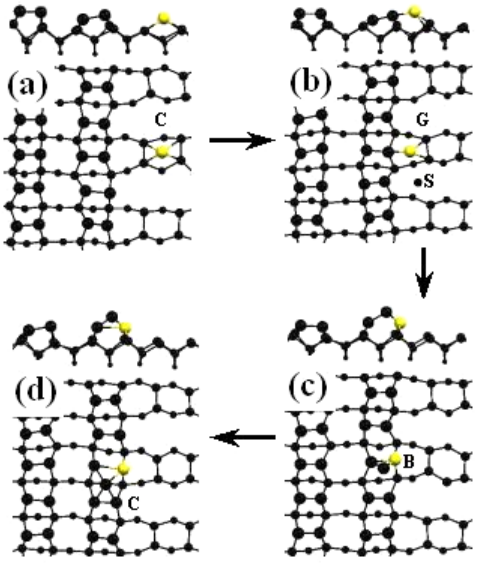

Fig. 3. The mechanism of an adatom diffusing across the monatomic step S_A from the lower terrace to the upper one.

3.2.2. *Diffusion from the upper terrace to the lower one*

Since dimer rows on top of the upper terrace of the S_A step are parallel to the direction of the S_A step, adatoms located on it are more likely to hop on top of one dimer row parallel to the step. The adatoms need to overcome a relatively higher barrier to move directly to the lower terrace due to bonds with the upper terrace atoms. Potential energy calculations show that the fastest pathway for moving across the S_A step from the upper terrace to the lower terrace is 1.27 eV. For the adatom, this barrier is too high to overcome to cross the S_A step. However, the exchange between the adatom and the surface can reduce the energy barrier.[18] We will present the exchange process in which the adatom hops to the lower terrace from the upper one. The adatom landing on site C [(Fig. 4(a)] on top of the upper terrace hops to position B along the dimer row more easily with the 0.35 energy barrier. Once the adatom hops to site B on top of the dimer, it can push one atom neighboring the step of the dimer down to the lower terrace and replace the surface atom as shown in Fig. 4(c). In Fig. 4(c), position S has a lower potential energy, so the atom being pushed down can hop to site S more easily and diffuse in the trough along the direction of dimer rows [Fig. 4(d)]. This exchange process must have a 1.15 eV energy barrier lower than the energy barrier, 1.27 eV, adatoms moving directly to the lower terrace. Compared to other relevant barriers (see what the paper is involved), this is rather high. Hence, these exchange processes occur in relatively high temperatures as we simulated.

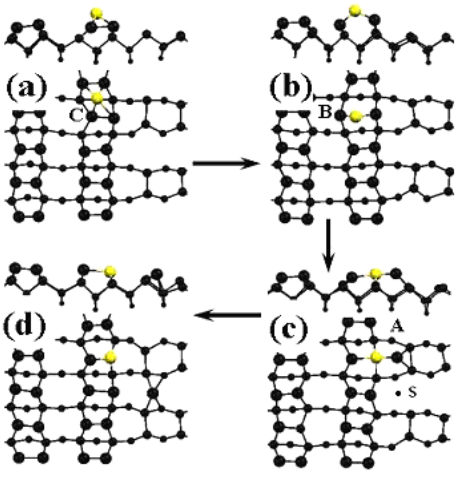

Fig. 4. The mechanism of an adatom diffusing across the monatomic step S_A from the upper terrace to the lower one.

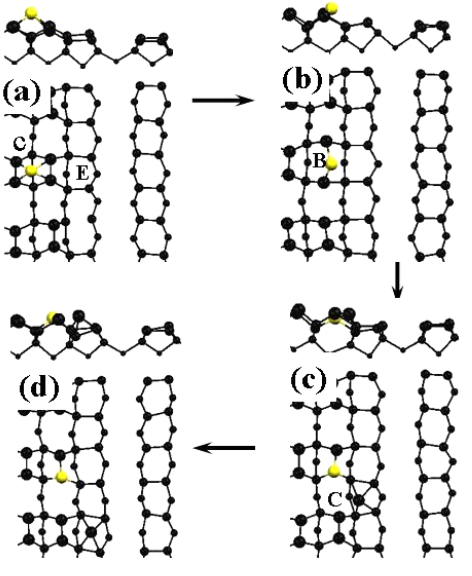

Fig. 5. The mechanism of an adatom diffusing across the monatomic rebounded step S_B from the upper terrace to the lower one.

3.3. *Si adatom diffusion on the rebonded S_B step from the upper terrace to the lower one*

Adatoms located on the upper terrace of the rebonded S_B step have no difficulty to move to the step more easily with a 0.42 eV barrier due to the dimer rows on it perpendicular to the step. Figure 5(a) shows that an adatom diffuses to position

C near the S_B step along the direction parallel to the dimer row. The atom must overcome a 0.98 eV barrier to move to the local potential mininal site E on the lower terrace. Zhang *et al.*[11] have discovered that the adatom can move down the S_B step aided by another adatom located at the site E through the two adatoms bonding to the dimer. Adatoms located in the trough on the upper terrace also need conquer an energy barrier of 1.42 eV to cross over the S_B to the lower terrace.

Now, we will report another new pathway by which the adatom on top of the upper terrace can move down to the lower terrace by exchanging with a substrate atom. When the adatom hops to site B shown in Fig. 5(b), it can push the surface atom under it to the lower terrace and replace the latter position. Since the dimer rows on the lower terrace are parallel to the S_B step, the atom being pushed down will move along the step and hop into the trough of the lower terrace occasionally. This exchange process needs only to overcome a barrier of 0.72 eV.

By the way, we have performed simulations and did not find any event that adatoms diffuse across the unrebouded S_B step from either the upper terrace or the lower one. Adatoms located on one of the terraces moved only on the same terrace and could not diffuse across the step to the other one.

4. Conclusion

In this paper, we have performed molecular dynamics simulations about adatoms diffusion on the Si(001) and across single-layer steps, by using the SW potential.

We presented an adatom diffused perpendicular to the dimer row by exchanging with the surface atom with an energy barrier of 0.74 eV. It might increase the diffusion constant perpendicular to the dimer row and weaken the anisotropy of Si adatom's diffusion on the Si(001).

Our results present that an adatom can climb up to the upper terrace from the lower one near the S_A step and move down to the lower terrace from the upper one near the rebonded S_B step. These help us understand the kinetic factors controlling the transformation of monatomic steps to bilayer steps.

In conclusion, the mechanism of adatoms diffusion is complex at higher temperatures, which involves not only simple leapfrog but also exchange with surface atoms. Indeed, the exchange with the surface atom plays important role in the adatom diffusion either on the Si(001) or across the monatomic step at higher temperatures.

Acknowledgment

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