

Initial Process of Si Homoepitaxial Growth on Si(001)

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Initial growth processes of Si on the Si(001) surface are investigated by studying the stability of various ad-Si clusters and calculating energy barriers for some fundamental processes by using a first-principles method. An ad-Si perpendicular dimer on top of a substrate dimer row is formed easily and is the most stable among dimers, consistent with experiment. The dimer can be a diffusing unit at high temperatures but cannot be a nucleus for dimer row growth at lower temperatures. On the other hand, a quasistable parallel dimer in a trough attracts monomers and can be the nucleus of a diluted-dimer row.

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As the Si(001) surface is one of the most important solid surfaces from both scientific and technological points of view, experimental and theoretical studies have been done very intensively and many aspects of surface phenomena associated with this particular surface have been clarified. Nevertheless, there remain some important aspects which have not been well understood yet. One of them is the elementary processes in the homoepitaxial growth. It is well known that by using molecular beam epitaxy, one-dimensional dense-dimer rows, which are perpendicular to the substrate dimer rows, grow into long strings when the substrate temperature is around 500 K [1,2]. This seems to be a natural growth mode in the sense that covering the whole substrate with such dense-dimer rows leads smoothly to the formation of a new Si(001) surface. As this growth mode looks so natural, one may expect that the related fundamental processes will be rather simple. Contrary to such an expectation, no clear-cut idea has been available about them despite a huge accumulation of experimental [1–7] and theoretical [8–18] works. Even the stable ad-dimer configuration is still in controversy [10,15]. Moreover, there are observations about the existence of a metastable diluted-dimer row structure [3,5] at lower temperatures, which disappears at higher temperatures ($>350^\circ\text{C}$). The growth of diluted-dimer rows does not lead to the formation of a new Si surface in the homoepitaxial Si growth.

The aim of the present work is to resolve the difficulty in understanding the Si growth mechanism. We have performed a structural optimization for several different clusters composed of one to four ad-Si atoms and estimated the energy barriers for some possible growth processes. Based on these calculations, we will propose detailed atomic processes for the Si growth on the Si(001) surface.

The present calculations are based on first-principles molecular dynamics [19,20]. The Wigner interpolation formula is used as an exchange-correlation energy and potential [21]. The surface unit cell size is 4×4 with an

exception of 4×6 for diluted-dimer row configurations. A unit cell contains a slab of ten Si(001) layers and a vacuum region of the same thickness. The clean surface has $c(4 \times 2)$ symmetry. Additional Si atoms are placed on both sides of the slab to maintain inversion symmetry for convenience. The criterion for the force convergence is 0.5×10^{-3} Hartree/a.u. Two sampling k points are taken in the two-dimensional irreducible Brillouin zone. The cutoff energy for the expansion of wave functions is 9.0 Ry. In order to estimate the energy barrier, we performed the following two-step optimization process: First, we optimize the structure and calculate the total energy under the constraint that the center of mass of specified atoms is confined in a given plane perpendicular to the direction in which the specified atoms are supposed to move; second, the center of mass is shifted in the assumed direction by a small distance (0.1–0.2 a.u.).

Figure 1 shows our optimized configurations and their energies defined as

$$E_{n,i} = \{E[\text{surface} + (n \text{ ad-Si's})_i] - E[\text{clean surface}]\}/n, \quad (1)$$

with $E[A]$ the total energy for system A and (n, i) specifying the configuration i among clusters with n Si adatoms. The most stable position for the ad-Si atom is the M site in the trough between dimer rows (Fig. 1, configuration 1a), consistent with the result by Brocks, Kelly, and Car [14].

The most stable dimer configuration is shown in Fig. 1 as 2a and the ad-Si dimer buckles like the buckled dimers on a clean surface. A parallel dimer configuration on top of the substrate dimer row (Fig. 1, configuration 2b) is the second most stable configuration. The energy difference between these two configurations is 0.073 eV/ad-dimer. (Note that the energy in Fig. 1 is per one adsorbed Si atom.) In contrast with our result, Brocks, Kelly, and Car [15] found configuration 2b the most stable, more stable than configuration 2a [22]. Experimentally,

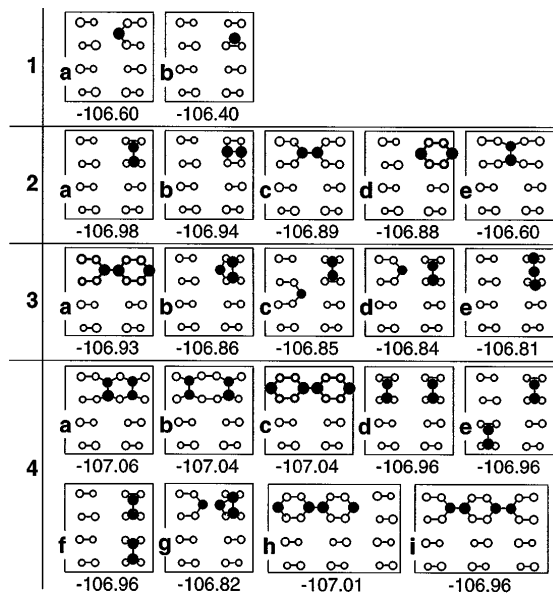


FIG. 1. Optimized configurations and their energies (in eV) defined by Eq. (1) in the text. Black circles and open circles represent ad-silicon atoms and the substrate 1st layer silicon atoms, respectively. Numbers in the left column denote the number of adatoms. Each configuration is specified in the text with a combination of the number and an alphabetical character on the frame like, for example, configuration 3d.

configuration 2a is an order of magnitude more populated than that of 2b [5,10]. The population difference between them leads to an experimental estimation of the energy difference of 0.06 ± 0.01 eV/ad-dimer [10], very close to our estimation. Anyway the important feature common to the two calculations is that the dimers on top of the dimer row are more stable than those in the trough and it is in clear contrast with the theoretical prediction [10] based on the Stillinger-Weber potential. We will come back to this point later.

We calculated the energy barrier for forming the most stable dimer (Fig. 1, configuration 2a) from monomers and found that no additional activation energy to the diffusion barrier of a monomer is required to form the dimer (Fig. 2). The monomers can diffuse easily and whenever two of them meet together, they form the stable dimer. The energy barrier to dissociate the dimer is estimated to be 1.33 eV.

We then studied the dimer diffusion processes. By using two step optimization, we estimated the energy barriers of two diffusion processes along and across the substrate dimer rows. Figure 3 shows the energy variation along the diffusion path parallel to the substrate dimer row. The energy barrier in this case is 1.45 eV [24], only slightly larger than the dissociation barrier mentioned above. On the other hand, the diffusion barrier across the dimer rows is 1.8 eV. These results suggest that dimers can diffuse along the dimer row at certain high temperatures. Dijkkamp, van Loenen, and Elswijk

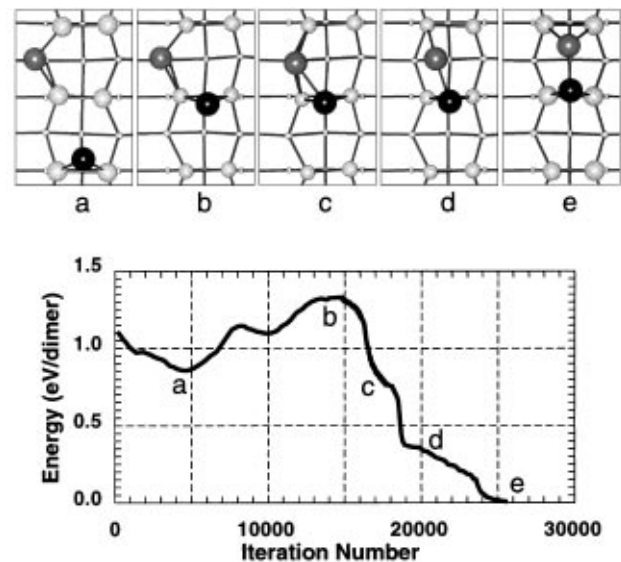


FIG. 2. Energy variation against the configuration change in the dimer formation process. "a, b, ... and e" in the energy curve denotes the configurations shown in the upper panel.

[7] observed diffusion of clusters, although the character of the clusters was not identified. They tentatively estimated the diffusion barrier to be about 1 eV, which may depend on the assumed frequency factor. Based on our simulation, we believe that the diffusing cluster observed by Dijkkamp, van Loenen, and Elswijk [7] may be the ad-dimer of 2a because it is so easily formed and very stable.

Among the clusters composed of four ad-Si atoms, the most stable one can be regarded as the unit of the dense-dimer row configuration (Fig. 1, configuration 4a). With the results mentioned so far, one may speculate that the dimer (Fig. 1, configuration 2a) will be a basic building unit for constructing a dense-dimer row. Two dimers may come close to each other as shown in configuration 4d and transform into stable configuration 4a. As an intermediate state between configurations of 4d and 4a, we have found a fairly stable configuration 4b which is obtained by rebonding in the substrate. This rebonding process requires 1.3 eV as an energy barrier (Fig. 4). From configuration 4b to that of 4a, we considered a

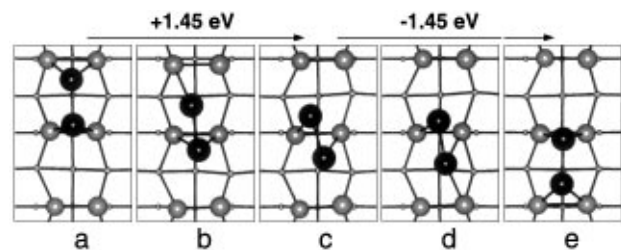


FIG. 3. Configuration change in the process of dimer diffusion along the substrate dimer row.

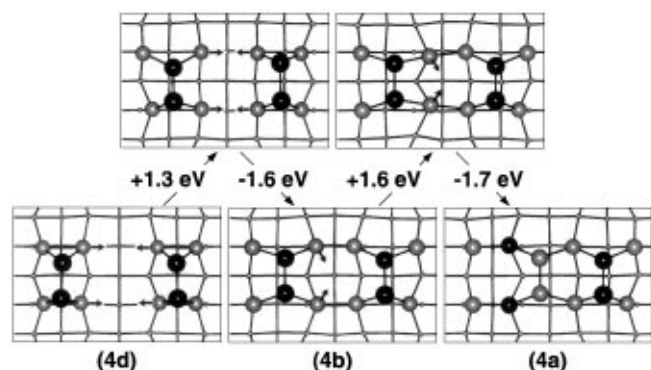


FIG. 4. Formation process of the shortest dense-dimer row configuration of 4a from configuration of 4d. Open circles with arrows are the substrate atoms under control. From 4d, we moved four substrate atoms to rebond as shown in 4b. From 4b to 4a, we pulled two substrate atoms up to the vacuum as an ad-dimer sinks into the substrate.

process of exchanging atoms between the ad-Si dimer and the substrate as shown in Fig. 4. The energy barrier of this process is 1.6 eV. Therefore, the maximum energy barrier in the process from configuration 4d to that of 4a is slightly larger than the diffusion barrier of the dimer along the dimer row. However, the energy barrier for configuration 4b to transform back to that of 4d is also 1.6 eV, the same as the energy barrier from 4b to 4a. In this sense, once configuration 4d changes to that of 4b, it eventually ends up with configuration 4a in most cases. Therefore, the critical process for the formation of dense-dimer rows from stable ad-dimers is the one from the 4d to 4b configurations with an energy barrier of 1.3 eV. We point out here the possible existing experimental support for configuration 4b. For a low coverage regime at 475 K, islands formed by two ad-dimers across the neighboring substrate dimer rows are clearly observed [1]. This type of island will probably correspond to configuration 4b. Another related example can also be seen at the edge of the dense-dimer rows (see the upper-right panel of Fig. 2 of Ref. [4]). Ad-Si monomers whose diffusion barrier is 0.6–0.7 eV cannot be detected by scanning tunneling microscopy (STM) at room temperature because of their rapid movement. Considering this feature of monomers, we expect that processes associated with stable ad-Si dimers mentioned above, whose energy barriers range from 1.3 to 1.45 eV, can occur frequently above 500 K to contribute to the formation of one-dimensional dense-dimer rows.

However, there are problems with the idea that the dimer (Fig. 1, configuration 2a) may be the dominant building unit for dense-dimer rows at low temperatures. In fact, it was clearly stated that the ad-dimers 2a do not aggregate directly into dense-dimer rows [5]. The most important point is that this dimer is a quite independent object and that it attracts neither monomers nor dimers. The energies for configurations of 3b, 3c, and 3d are

essentially nothing but the weighted average of the energies of configurations of 1a and 2a. The fact that all configurations of 4d, 4e, and 4f and that of 2a have almost the same energy implies that there is no energy gain by bringing the two dimers to the neighboring positions. Therefore, the probability of realizing configuration 4d will not be high, and the efficiency of the dimers of 2a to form the dense-dimer row will be fairly low at low temperatures.

On the other hand, we found a quasistable dimer in the trough (Fig. 1, configuration 2c) or configuration 2d attracts monomers strongly to the neighboring M sites to form a trimer as in Fig. 1, configuration 3a, because dimer 2c creates four active dangling bonds at the substrate dimers to which this dimer is bonded and configuration 2d has two active dangling bonds at the ad-Si's. Note that trimer 3a definitely has a lower energy than any combination of a monomer and dimer 2a. The process of diluted-dimer growth is exactly the same as what was proposed for Al adsorption on Si(001) surface by Brocks, Kelly, and Car [25]. The existence of this diluted-dimer row is actually supported by measurements of STM [1,5]. Here we would like to make a comment on the arguments about the dimer stability by Zhang *et al.* [10]. Based on their observation that the population of the ad-dimers in the trough increases as a result of annealing at higher temperatures, they claim that configurations 2c and 2e have lower energies than those of 2a and 2b. We propose here an alternative interpretation to their observation. If configurations 2c and 2e would be more stable than those of 2a and 2b, we expect that the former configurations would be observed even before annealing considering the fact that a stable monomer configuration is 1a. It would be more probable that some elements on the surface may diffuse into the region of the dimer by annealing and modify the local atomic configuration [26]. In order to check the unit-cell-size dependence of our calculation, we performed calculations by doubling the unit cell size for 2a and 2c configurations and found that the change in the energy difference is only 3%.

The energy difference between the dense-dimer row and the diluted-dimer row is 0.15 eV/ad-atom for infinite length rows. Once the dimer row becomes long, the energy difference between the diluted-dimer row and the dense one will become large. Therefore, a long diluted-dimer row has to transform into possibly some pieces of dense-dimer row by some thermal processes. It was observed that the diluted-dimer rows disappear at higher temperatures ($>350^{\circ}\text{C}$) [1]. If a long string of diluted-dimer rows exists, the probability of dimers and/or monomers striking the string will be high. By such a collision, the diluted-dimer row may change locally its configuration into a dense one.

We have studied the detailed atomic processes in the initial crystal growth of Si on the Si(001) surface. We have found that the most stable dimer can be easily

formed and that it can be a diffusing unit along the substrate dimer row at certain high temperatures. We have estimated the energy barrier for stable dimers to form dense-dimer rows and concluded that such a process will be important at high temperatures. However, as this dimer attracts neither monomers nor dimers and the energy barrier for diffusion of the dimer is high (1.45 eV), it cannot be a nucleus for the growth of a dense-dimer row at lower temperatures. On the other hand, a metastable dimer in the trough can be a nucleus for a diluted-dimer row at low temperatures, which, however, cannot grow into a very long string and may eventually transform into some pieces of the dense-dimer row.

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 [22] The present calculation uses a unit cell twice as large as that of Ref. [15]. If we take only the Γ point, which corresponds to two k points in the calculation of Ref. [15], the energy difference is reduced to 0.012 eV/ad-dimer. In addition to this, a different version of exchange-correlation energy and potential can produce the same order of difference. However, we found that the energy difference becomes 0.115 eV/ad-dimer with the generalized gradient approximation (GGA) [23]. In this GGA calculation, the correlation part of Ceperly and Alder's result [*Phys. Rev. Lett.* **45**, 566 (1980)] as parametrized by Perdew and Wang [*Phys. Rev. B* **45**, 13244, (1992)] was used.
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