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# Structural evolution of the Si(113) surface: *Ab initio* and tight-binding molecular dynamics calculations

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The structural evolution of the Si(113) surface is investigated by *ab initio* calculations and by tight-binding molecular dynamics calculations using the environment-dependent tight-binding Si potential. In this study, it is found that $3\times 2$ and $3\times 1$ phases have interstitial structures and the transition from $3\times 2$ to $3\times 1$ phase results from the increasing of interstitial atoms. The existence of the interstitial structures is proved by the analysis of scanning tunneling microscopy (STM) images and the calculation of surface core level shifts using final state pseudopotential theory. The study of adsorption energy clarified that the phase transition from the $3\times 2$ to $3\times 1$ interstitial surface plays an important role in the behavior of the {113} facet in the selective epitaxial growth of Si(001). It is also found that the domain boundary observed frequently in the filled state STM images of Si(113) is formed by the local $3\times 1$ interstitial structure on the $3\times 2$ interstitial surface.

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Si surfaces have been intensively studied for decades. While Si(001) and Si(111) surfaces have clearly revealed their fundamental structures by experiments and theoretical calculations, the Si(113) surface has given rise to a lot of debate because of its fundamental structure.[1–4] Recently, a detailed understanding for the atomic structure of the Si(113) surface has become more important because of its potential application to the Ge nanowire[5] and its existence in the selective epitaxial growth (SEG) of Si(001).[6] Many studies have shown that the Si(113) surface at room temperature reconstructs to a $3\times 2$ phase using low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM) measurements.[7–9] The $3\times 2$ surface is observed to transform easily to a $3\times 1$ surface at about 600 °C.[4,8] The phase transition has created a lot of interest, since it resembles the transition from $c(4\times 2)$ or $p(2\times 2)$ to $2\times 1$ phase in the Si(001) structure. Ranke suggested a dimer model for the $3\times 1$ phase of the Si(113) surface.[1] On the basis of the dimer model, the oppositely puckered (OP) model [see Fig. 1(a)] of the $3\times 2$ phase was suggested to explain that the phase transition is similar to that induced by the dimer buckling on the Si(001) surface.[3] The OP model was supported by some experiments.[4,10] On the theoretical side, Dabrowski *et al.*[2] proposed the $3\times 2$ interstitial structure [see Fig. 1(b)] for the $3\times 2$ phase using an *ab initio* method and they also showed the similarity between their theoretical STM images and experiment. However, the real structure of the $3\times 1$ phase was not clearly addressed in their literature.

On the other hand, the {113} facet has been frequently observed during homoepitaxial and heteroepitaxial growth on Si(001).[11,12] Especially, in the initial stage of SEG of Si(001), it is found that, once the {113} facet is formed, the epitaxial layer scarcely grows in the [113] direction, as compared to the growth of the (001) surface in [001] direction, until the {113} facet is expanded and changed into the {111} facet.[13,14] Theoretical calculations have tried to explain the formation process of the {113} facet.[15,16] Those energetics gave a clue for the formation of the {113} facet in the very initial stage. However, those could not provide a detailed understanding of the process, because the surface structure of the {113} facet was assumed to be the successive bunching of *Db* rebonded steps (SDS), as shown in Fig. 1(c). Moreover, the energetics for adatoms and addimers on the SDS surface was not sufficiently described.

In this Brief Report, we present a detailed description of the structure and evolution process of the Si(113) surface and suggest an answer to the long-standing question of the phase transition on the Si(113) surface. In this calculation, we perform *ab initio* total energy calculations and a tight-binding molecular dynamics simulation. In calculating the adsorption

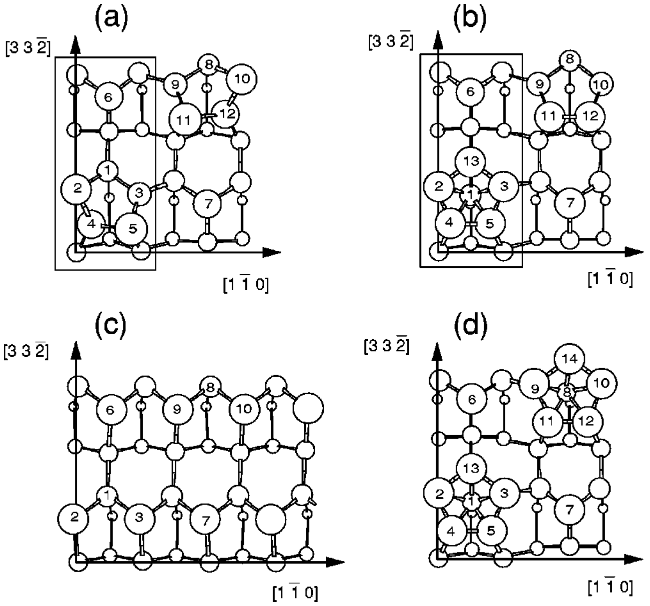

FIG. 1. Top views of several optimized structures of Si(113). (a) OP surface, (b) $3\times 2$ interstitial surface, (c) SDS surface, (d) $3\times 1$ interstitial surface. The size of cells is $3\times 2$ with the exception of $4\times 2$ for the SDS surface. Large circles indicate topmost atoms. Squares by solid lines correspond to cells in Fig. 3. Note numbers on some atoms to realize differences among surface structures.

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energy, because a comprehensive search for adsorbates on various surfaces of Si(113) and Si(001) is very expensive using *ab initio* methods, we have employed tight-binding molecular dynamics calculations and selected plausible candidates for study by more accurate *ab initio* calculations. Tight-binding calculations are performed using the recently developed environment-dependent Si tight-binding model. The model is very accurate and describes the surface property as well as the bulk and electronic properties of Si. It has also been successfully applied to describe the Si cluster, the Si(001) and Si(111) surface, and Si diffusion.[17] *Ab initio* total energy calculations are carried out in the local density approximation with the Ceperley-Alder[18] form of the exchange-correlation energy parametrized by Perdew and Zunger.[19] The surface unit cell size for Si(113) is $3\times2$ with the exception of $4\times2$ for the SDS surface[20] and for the Si(001) $c(4\times2)$ surface it is $4\times4$. A unit cell contains a vacuum region of 12 Å and a slab of 9 double layers for Si(113) or 12 layers for Si(001). Adsorbates are placed on both sides of the slab to maintain inversion symmetry. Periodic boundary conditions are applied to the directions parallel to the surface. Five **k** points for Si(113) and two **k** points for Si(001) are selected avoiding the $\Gamma$ point in the two-dimensional irreducible Brillouin zone. The basis set contains plane waves up to an energy cutoff of 10 Ry. Structural relaxations are performed until the force on each atom is less than 0.02 eV/Å.

First, we calculate the surface energies for various structures using the *ab initio* method. It is found that the OP structure is lower in the surface energy than Ranke $3\times1$ structure by 0.7 meV/Å$^2$, which is very similar to the result (0.8 mev/Å$^2$) in a previous calculation.[3] The change from the OP to the $3\times2$ interstitial structure by the insertion of an interstitial Si atom [atom "1" in Fig. 1(b)] induces a surface energy decrease of 3.9 meV/Å$^2$. The $3\times1$ interstitial structure [see Fig. 1(d)] is higher in the surface energy than the $3\times2$ interstitial structure by 1.6 meV/Å$^2$. While Dabrowski *et al.*[2] reported that the surface energy of the $3\times1$ interstitial structure is the same as that of the Ranke's $3\times1$ structure, the present calculation reveals that the $3\times1$ interstitial structure is lower in the surface energy than Ranke's $3\times1$ structure by 3.0 meV/Å$^2$.[21] The SDS surface is much higher (15.0 meV/Å$^2$) in the surface energy than the $3\times2$ interstitial structure. From these results, it appears that the SDS surface is relatively unstable, and even if it is formed, it can easily change into a structure of lower surface energy. Thus, from the point of view of the surface energy, the $3\times2$ interstitial structure is preferred in the Si(113) surface. Then, we question the real structure of the $3\times1$ phase observed in the experiment. We consider that it is the $3\times1$ interstitial structure since it is very close to the $3\times2$ interstitial in the structure and the surface energy. We will come back to this point later.

We investigate the stability of adatoms on various structures by calculating adsorption energies. The adsorption energy per Si adatom is defined as

$$\begin{aligned}E_{\mathrm{ad}}=[&E_{\mathrm{tot}}(\text{adatoms}+\text{Si}(001\ \text{ or }\ 113))\\&-nE_{\mathrm{tot}}(\text{Si atom in vacuum})\\&-E_{\mathrm{tot}}(\text{Si}(001\ \text{ or }\ 113))]/n,\end{aligned}$$

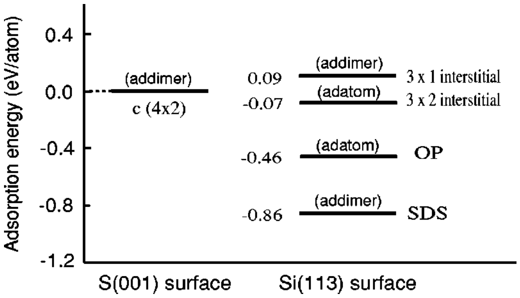

FIG. 2. Relative values of the lowest adsorption energy for adsorbates on various Si(113) surfaces to that on the Si(001) $c(4\times2)$ surface. Parentheses indicate the type of the adsorbate.

where $n$ is the number of adatoms, $E_{\mathrm{tot}}$(Si atom in vacuum) is the total energy of a Si atom in vacuum, and $E_{\mathrm{tot}}$(Si(001 or 113)) and $E_{\mathrm{tot}}$(adatoms+Si(001 or 113)) are the total energies of Si(001) or each Si(113) surface and the adsorbate system, respectively. Figure 2 shows the lowest adsorption energies for each system relative to that for adsorbates on the Si(001) $c(4\times2)$ surface. It is interesting to note that the adsorption energy of an adatom is quite low on the OP surface. In this system, an adatom is located nearby atom "1" in Fig. 1(a) and it pushes atom "1" down gradually during the relaxation resulting in a structural deformation. In fact, it leads the surface structure to the $3\times2$ interstitial without any energy barrier as shown in Fig. 3. As a result of the relaxation, atoms 2, 3, 4, 5, and the adatom

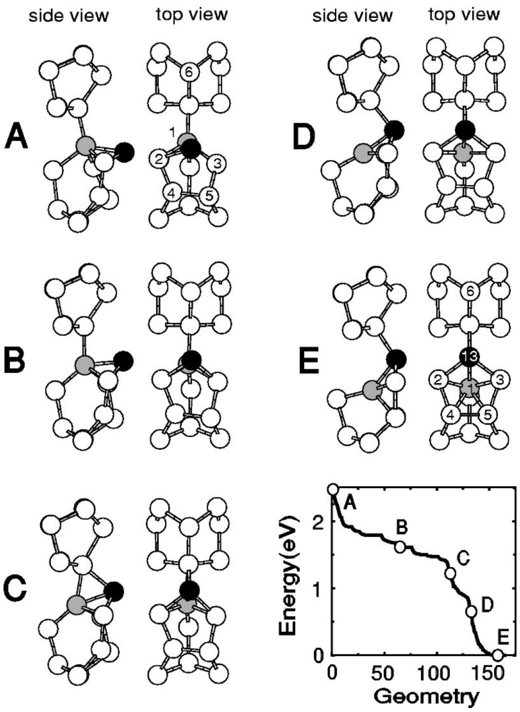

FIG. 3. Sequential configuration change and total energy variation by the structural relaxation of an adatom on the OP surface. Black and shaded circles denote adatoms and surface atoms pushed by adatoms, respectively. Numbers on some atoms match the numbers in Figs. 1(a), 1(b). Letters in the energy curve correspond to configurations.

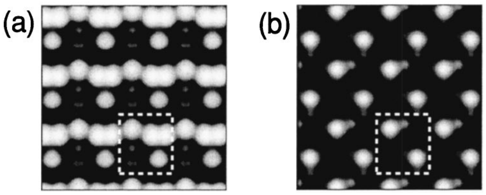

FIG. 4. Theoretical filled state STM images: (a) 3×2 interstitial structure with $V_s = -2$ eV and (b) 3×1 interstitial structure with $V_s = -1$ eV. Dashed squares indicate 3×2 cells corresponding to Figs. 1(b) and 1(d).

transform to a surface pentamer in the final geometry. The structural transformation induced by an adatom strongly support the fact that the OP surface is unstable. One may expect that an adatom nearby atom 8 in the 3×2 interstitial structure [see Fig. 1(b)] also leads to 3×1 interstitial structure without energy barrier. However, the reason why there is a small energy barrier (0.04 eV) is quite interesting. While there is enough space for atom 1 to be pushed down by an adatom in the structural change from the OP to the 3×2 interstitial structure, it is not the case in the structural change from the 3×2 interstitial to the 3×1 interstitial because of the compactness of the 3×2 interstitial structure.

It is noted in Fig. 2 that the SDS surface gives a very low adsorption energy for an addimer. The adsorption energy is much lower than that of adsorbates on the Si(001) surface, which means the adsorbates are strongly adsorbed and piled on the SDS surface. Hirayama *et al.*[6] suggested that the {113} facet forms an SDS structure during the SEG of Si(001), and Oshiyama[15] tried to explain it by *ab initio* calculation. The {113} facet of SDS structure might be formed in the very initial stage of the SEG. However, at long range order, the SDS structure could be changed since the adsorbates have a tendency to stay on the surface of SDS structure rather than on the Si(001) surface due to the difference of adsorption energies. This might be the reason why the 2×1 long range order with the SDS structure[6] is not observe in experiment.

We suggest that the 3×1 interstitial structure plays an important role in the behavior of the {113} facet in the SEG. The growth rate of the {113} facet is much lower than that of the Si(001) surface,[13] which indicates that most Si adsorbates on the {113} facet do not contribute to the growth of the {113} facet, but flow into the Si(001) surface. In order to satisfy such a growth condition, the adsorption energy of adsorbates on the {113} facet should be higher than that on the Si(001) surface. Figure 2 shows that the 3×1 interstitial structure is the unique structure of the {113} facet satisfying the growth condition. Hence, the 3×1 interstitial is considered to be the structure of the phase at the temperature range (600–700 °C) of SEG.

Theoretical calculations are used to explain the STM images.[22] We calculate filled state STM images of various Si(113) surfaces to compare with experiments. In this calculation, it is found that the theoretical STM image of the 3×2 interstitial structure [Fig. 4(a)] is in excellent agreement with experiment.[7] This is also very similar with the theoretical STM image of Dabrowski *et al.*[2] Experimental evidence for the existence of the 3×1 interstitial structure, even though its real structure was not recognized, is found in the STM images in the literature.[8] Our theoretical STM image of the 3×1 interstitial structure [Fig. 4(b)] reproduces plausibly the experimental STM image showing 3×1 periodicity at about 700 °C.[8] Theoretical STM images for other surface structures are not observed in experiments. From the analysis of the STM images shown in Fig. 4, the surface pentamers [in Figs. 1(b) and 1(d)] are concealed in the filled state STM images of 3×2 and 3×1 interstitial structure, whereas the dimer atoms [atoms 11 and 12 in Fig. 1(b)] and adatoms [atoms 6 and 7 in Figs. 1(b) and 1(d)] are expressed as bright spots. This analysis leads to an understanding of the surface domain boundary found frequently on the Si(113) surface, which has been a long-standing issue.[7,8] The filled state image in Fig. 5(a) is reconstructed on the basis of Figs. 4 and 5 in Ref. 7, and it shows the domain boundary dividing the surface into two areas of the 3×2 phase. On the basis of the present analysis of the STM images of the Si(113) surface, its real structure is visualized as in Fig. 5(b). Since dark images indicated by white-dashed circles in Fig. 5(a) originate from the surface pentamers, it is concluded that the reality of the domain boundary is the local 3×1 interstitial structure. The domain boundary is considered to be evidence of the phase transition from the 3×2 to the 3×1 interstitial structure.

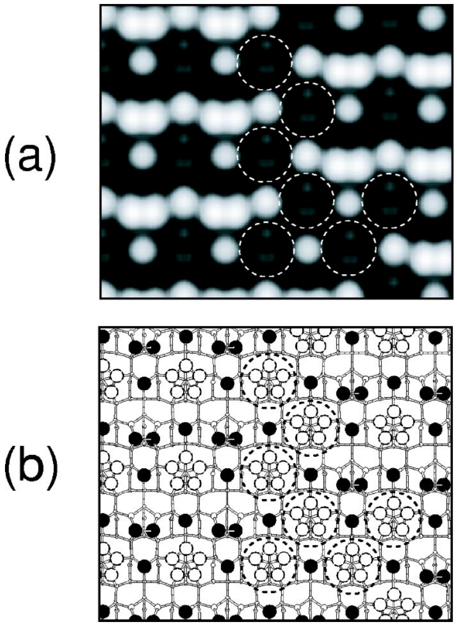

FIG. 5. STM image of a Si(113) surface including a domain boundary (a) and the suggested surface structure (b). Black circles in (b) indicate surface dimers and adatoms. White circles in (b) indicate surface pentamers. White-dashed circles in (a) correspond to black-dashed circles in (b).

Another evidence for the existence of the interstitial structures is obtained from surface 2*p* core level spectra of Si(113). Surface 2*p* core level spectra were presented by Hwang *et al.*[4] In their experiment, the core level spectra were considered to be originated from the OP surface. We calculate the surface 2*p* core level spectra using final state pseudopotential theory[23] and the results show that the lowest surface core level shift in the OP structure is $-0.230$ eV, which is at variance with the lowest core level spectra $S3$ ($-0.501$ eV) obtained by Hwang *et al*. The present calculation reveals that the lowest core level shifts in the $3\times2$ and the $3\times1$ interstitial structures are $-0.609$ eV and $-0.579$ eV, respectively, which are similar to $S3$, and they originate from interstitial atoms. The highest core level spectra $S1$ reported by Hwang *et al.*[4] are found to originate from atom 6 and 7 in Fig. 1. Therefore, the core level spectra $S3$ is an important evidence supporting the existence of interstitial structures. Details on adsorption energies, the structures of adsorbate systems, and surface core level shifts will be published elsewhere.[24]

In summary, we studied the structural evolution of Si(113) by *ab initio* calculations and by tight-binding molecular dynamics calculations. In our calculation, the OP and SDS surfaces are likely to be unstable from the point of view of the surface energy and the adsorption energy. It is found that the OP surface can be easily changed by an adatom to the $3\times2$ interstitial surface without any energy barrier. The existence of interstitial structures is supported by the analysis of STM images and the calculation of surface core level shifts using final state pseudopotential theory. The calculation of the adsorption energies clarified that the phase transition from the $3\times2$ to the $3\times1$ interstitial structure plays an important role in the behavior of the {113} facet in the SEG of Si(001). It appears that the domain boundary observed frequently in the filled state STM images is formed by the local $3\times1$ interstitial structures on the $3\times2$ interstitial surface.

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[21] The test of convergence is performed with 15 double Si layers of inversion symmetry and the change of energy difference is found to be less than 0.2 meV/Å$^2$. In the work of Dabrowski *et al.* (Ref. 2), they relaxed only three double layers and fixed two double layers to bulk sites in the slab of five double layers with hydrogen passivation.

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