Study of H:Si(113)\(2\times 2\) Structure by Scanning Tunneling Microscopy and \textit{Ab Initio} Calculation*  

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The H:Si(113) structure has been studied by scanning tunneling microscopy and \textit{ab initio} calculation. After exposing hydrogen atoms on a clean Si(113) surface, \(2\times n:H\) (\(n = 2,3\)) structures form. High-resolution STM images reveal that these structures show three types of protrusions. Islands growing one-dimensionally are observed on the local surface area. We performed an \textit{ab initio} calculation for several possible structural models of the \(2\times 2:H\) structure. Comparison of observed STM images and simulated images obtained by \textit{ab initio} calculation clarifies that the structural model composed of a pentamer without an interstitial atom and two three-coordinated site atoms is most favorable. Energy analysis indicates that this structural model is most stable. Based on these results, a structural model of the \(2\times 3:H\) structure is also proposed. The \(2\times n:H\) structures are expected to have anisotropic surface strain. [DOI: 10.1380/ejssnt.2010.261]

Keywords: Scanning tunneling microscopy; \textit{ab initio} quantum chemical methods and calculations; Surface relaxation and reconstruction; Hydrogen atom; Silicon

I. INTRODUCTION

The high-index Si(113) surface is one of the stable silicon surfaces, comparable to the Si(111) and (001) surfaces [1-3]. This surface has the potential for application as the substrate material for Si integrated circuits because a high-quality oxide layer can be produced [4]. Furthermore, the effect of the substrate anisotropy characteristic of high-index surfaces often appears during epitaxial growth. In addition, one-dimensional structures called nanowires are formed as a result of the adsorption of metal atoms on a Si(113) surface [5-13]. Therefore, the Si(113) surface has also attracted increasing interest due to possible application as the substrate in nanostructure fabrication, and the adsorption structure of metal atoms and gas molecules on this surface has been studied [14-16]. To perform epitaxial growth on the Si surface, hydrogen atoms play an important role in removal of contamination and oxide layers on the surface, i.e., wet and dry cleaning [17,18]. The hydrogen atoms are often terminated on the surface after this treatment. Thus, it is important to clarify the hydrogen-terminated structure on Si(113) for fundamental and industrial research. The formation of \(3\times 1\) and \(2\times n\) structures has been reported as the hydrogen adsorption structure on the Si(113) surface [19-22]. The \(3\times 1\) structure is formed at low substrate temperature, and its atomic structure is believed to be changed slightly from that of the clean Si(113) surface based on scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) results [19-21]. By contrast, the \(2\times n\) structures are formed at a temperature of about 400°C [19,22]. Some structural models have been proposed, but its atomic structure is not determined. In this work, we have studied H:Si(113)\(2\times n\) structures by STM and \textit{ab initio} calculation and discussed the atomic structure.

II. EXPERIMENTAL AND CALCULATION METHODS

The STM studies were performed in an ultrahigh-vacuum (UHV) system. The base pressure was 2.0×10\(^{-8}\) Pa. A 1×7 mm\(^2\) piece of the Si(113) substrate (boron doped, 10 Ω·cm) was cut from the wafer. The substrate temperature was controlled by a DC current passing through the sample. After outgassing at 600°C for 24 hours in UHV, the Si(113) surface was cleaned by flashing to 1200°C several times, followed by slow cooling below 750°C. After confirmation of a clean surface by STM observation, H atoms cracked by W-filament heating at about 1500°C were exposed to the Si(113) surface at 400°C. The STM observations were carried out at room temperature using a chemically etched W tip.

First-principles total energy calculation was performed using the Vienna \textit{Ab initio} Simulation Package (VASP) code based on density functional theory [23-26]. The wave functions were expanded by plane waves with the cutoff energy \(|k + G|^2 \leq 250\) eV, and a 4×4 mesh was used for Brillouin zone integration. Ions were represented by ultrasoft pseudopotentials, and the generalized gra-
gradient approximation (GGA) was used for the exchange-correlation potential [27-29]. The residual minimization method/direct inversion in the iterative subspace (RMM-DIIS) and conjugate gradient method algorithms were used for wave-function optimization and ionic relaxation, respectively [30,31]. The Si(113) surface was simulated by a repeated slab geometry, where one hydrogen layer on eight Si layers with hydrogen atoms passivating the Si atoms at the bottom of the slab and a vacuum layer of 15 Å spacing were included. The H and Si atoms on the top 1 + 7 layers of the slab were allowed to relax, while Si + H layers in the bottom were kept fixed to simulate bulk-like termination.

The STM simulation images were calculated based on the Tersoff-Hamann method [32], where constant-current images are approximated by an isosurface of the local density of state, integrated between the Fermi energy ($E_F$) and the tip bias voltage ($E_t + V_s$).

III. RESULTS AND DISCUSSION

Figures 1(a) and (b) show filled- and empty-state STM images of the clean Si(113) surface. The T-shaped and jellyfish-shaped protrusions are observed in the 3×2 phase in the filled- and empty-state image, respectively. The structural model of the clean Si(113)3×2 surface proposed by Dabrowski et al. is composed of three-coordinated sites, like the adatoms in the Si(111) surface, and pentamers containing the dimers in the Si(001) surface [2]. One type of pentamer has an interstitial atom and the other does not (referred to as the i-pentamer and n-pentamer, respectively). In the filled-state image, the dimer of the i-pentamer and the adatoms are observed as protrusions, and the dimer atoms of the n-pentamer and the atoms of the i-pentamer are observed in the empty-state image [insets in Figs. 1(a) and (b)] [2,3].

Figure 2(a) shows the empty-state STM image after exposing atomic hydrogen on the clean Si(113) surface at 400°C for 220 L (1 L = 1.33×10−4 Pa). Well-ordered protrusions that are different from those on the clean surface are observed, though the arrangement of the protrusions is distorted in some areas. The surface structure is the 2×n (n = 2, 3) phase, which corresponds to previous research [19,22]. One-dimensional islands that grow toward the [1-10] direction are observed locally [black arrow in Fig. 2(a)]. A clear STM image of this surface in the filled state cannot be observed.

In Fig. 3(a), three types of protrusion (defined as α, β, and γ protrusions) are observed in the 2×2 phase (defined as 2×2:H structure). The α and γ protrusions are ball-shaped, and the interval is 0.38 nm toward the [1-10] direction. The β protrusion is elliptical, and the interval is 0.80 nm toward the [1-10] direction. This protrusion looks like slightly asymmetric in this figure. A trench occurs at the border of the unit cell phase (between the α and γ protrusions). On the other hand, Fig. 3(b) shows a high-resolution STM image of the surface structure in the 2×3 phase (defined as 2×3:H structure). The 2×3:H structure is composed of the protrusions of the 2×2:H structure (α, β, and γ) and additional protrusions (α′ and β′). The trench is also observed at the border of the phase.

To clarify the atomic structure of the 2×2:H surface

FIG. 1: (a) Filled- and (b) empty-state STM image of the clean Si(113) surface [(a) $V_s = -2.00$ V, $I_t = 0.20$ nA, (b) $V_s = +1.50$ V, $I_t = 0.20$ nA]. Insets show the model of Si(113)3×2 structure and the position of the protrusions observed with each bias voltage [2-3].

FIG. 2: Empty-state STM image after exposing hydrogen atoms on the clean Si(113) surface ($V_s = +3.00$ V, $I_t = 0.15$ nA)
structure, *ab initio* calculation is performed for some proposed structural models. Figures 4(a)-(d) show the structural models that converge as the result of the relaxation calculation. Model A, shown in Fig. 4(a), is composed of a three-coordinated site (i.e., an adatom, indicated by a black arrow) and a pentamer without an interstitial atom (i.e., an n-pentamer, indicated by a gray arrow) [19,22]. In Model B, shown in Fig. 4(b), an interstitial atom is added to the pentamer in Model A (i.e., it is composed of an i-pentamer, indicated by a gray arrow). Model C, shown in Fig. 4(c), is composed of an n-pentamer and two three-coordinated sites arranged at 0.38 nm intervals toward the [1-10] direction (indicated by a black arrow). The hydrogen atoms are adsorbed on the adatom and four atoms of the pentamer in all models. The structural model in which an interstitial atom is added to the pentamer in Model C is proposed as Model D, shown in Fig. 4(d). As the result of the relaxation calculation, only the pentamer in Model D is tilted by the presence of the interstitial atom.

Based on these results, simulated empty-state STM images of each model are calculated [shown in Figs. 5(a)-(d)]. Protrusions are observed at the site of the three-coordinated atom and four atoms in the pentamer in the simulated STM images of all structural models. The simulation images of Models A and B differ from the observed image in the interval distance of the protrusions corresponding to γ [Figs. 5(a) and (b)]. Because the protrusions corresponding to α and γ become imbalanced due to the tilted pentamer, the simulation image of Model D is also not consistent with the observed image in Fig. 3(a). Only the simulated STM image of Model C has the characteristic of the ball- (α and γ) and the ellipse-shaped (β) protrusions although not perfectly consistent with the observed STM image. The simulated STM images calculated by Tersoff-Hamann method cannot take account of the tip condition and it is difficult that the observation STM image is perfectly consistent with the simulated one.

http://www.sssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/)
On the basis that the profile shape of the protrusions of the observed and the simulated images is moderately consistent, we conclude that Model C is favorable as the 2×2:H structure. The similar structural model of the 2×2 surface structure that is formed by the adsorption of chlorine atom on Si(113) surface is reported [33,34]. Considering the high chemical reactivity of hydrogen and chlorine atoms, it is appropriate that the similar atomic structures are formed.

In figure 3, the ellipse-shaped (β) protrusion looks like slightly asymmetric. There is possibility that an asymmetric dimer is formed in the pentamer [35]. The relaxation calculation for the structural model (Model C) with an asymmetric dimer is performed. As the result, the atoms of the Si dimer converge at the symmetric position. Considering the symmetric β protrusions are also observed in the other area, it is assumed that the distortion of the protrusion is caused by the tip condition.

The surface formation energy, which depends on the H chemical potential, is calculated to determine the relative stability of these structural models. At zero temperature, the formation energy \( \Omega \) was defined as [36,37],

\[
\Omega = E + E_0 - n_{Si} \mu_{Si} - n_{H} \mu_{H},
\]

where \( E \) is the total energy at zero temperature, which is calculated by ab initio calculation, \( E_0 \) the zero-point energy, and \( n_{Si} \) and \( n_{H} \) the numbers of Si and hydrogen atoms, respectively. The chemical potential of an Si atom, \( \mu_{Si} \), is approximated by that of bulk Si crystal. The zero-point energy arises from Si-H vibrational modes. Because the hydrogen is bonded to a single Si atom in these structural models, we assume that the zero-point energy is proportional to the number of H atoms: \( E_0 = n_{H} e_0 \). Here, \( e_0 \) is defined as 0.21 eV, which corresponds to the zero-point energy per H atom in SiH\(_4\) [36]. The calculated formation energies per 1×1 unit cell for the structural models of the 2×2:H structure are shown in Fig. 6 as a function of the chemical potential of the adsorption hydrogen atom, \( \mu_{H} \). The reference value of \( \mu_{H} \) is estimated using the total energy of SiH\(_4\) molecules:

\[
(E(\text{SiH}_4) + 4e_0 - \mu_{\text{Si}})/4 = -3.16 \text{ eV},
\]

which means that SiH\(_4\) can be formed at no energy cost [36]. To compare the structural models, the chemical potential of the adsorption H atoms (on the top layer) is varied from the point where the formation energies of the bare Si(113) surface and the structural models cross. The chemical potential of H atoms in the bottom layer is ignored because all structural models have the same structure in this layer. This figure shows that the formation energy of Model C is lower than that of the other models over the whole range. The several structural models that change the hydrogen adsorption sites are also calculated. These calculations result in the higher surface energy and the different simulation images from the observation one. The formation energy indicates stabilization of the system. Therefore, this result also suggests that Model C is the most favorable of the proposed structural models.

On the basis of the above results, the 2×3:H structural model shown in Fig. 7(a) is proposed. This structural model consists of two three-coordinated sites and two n-pentamers. An STM simulation image of this structural model is shown in Fig. 7(b). The character of the protrusions in the simulated image is similar to that of the observed image in Fig. 3(b). At a high substrate temperature, the 2×n reconstructed structures tend to be formed by adsorption of metal atoms and molecules of gas [5-15]. This surface structure often leads to formation of one-dimensional structures: nanowires and nanodots [5-12]. This is assumed to be caused by the anisotropic surface strain of the surface structure [12,13]. One-dimensional islands are observed locally on the H:Si(113)2×n structures (shown in Fig. 2), indicating that the 2×n:H structure also has anisotropic surface strain. This strain is assumed to play a role in forming specific islands during surface reconstruc-

![FIG. 6: Formation energy as a function of the chemical potential of the adsorption hydrogen atom for an ideal Si(113) surface and 2×2:H structural models [Models A-D shown in Figs. 4(a)-(d)]. The vertical dotted line at -3.14 eV indicates the chemical potential, at which the formation energy of SiH\(_4\) is equal to zero.](http://www.sssj.org/ejssnt)
IV. CONCLUSIONS

H:Si(113)\(2 \times n\) surface structures have been studied by STM and \textit{ab initio} calculation. By exposing hydrogen atoms on a clean Si(113) surface at 400°C, the \(2 \times 2: \text{H}\) and \(2 \times 3: \text{H}\) structures are observed. These structures are composed of ball- and the ellipse-shaped protrusions. Based on high-resolution STM images, structural models of the \(2 \times 2: \text{H}\) structure are proposed. A comparison of the observed STM image and a simulated image obtained by \textit{ab initio} calculation clarifies that the structural model composed of a pentamer and two three-coordinated atoms is most favorable. This result is also supported by an analysis of the surface formation energy. The simulated STM image of the \(2 \times 3: \text{H}\) structural model constructed on the basis of the above results is also similar to the observed image. The existence of one-dimensional islands on the local surface area suggests that \(2 \times n: \text{H}\) structures have anisotropic surface strain.

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