PHYSICAL REVIEW B, VOLUME 64, 153406

Formation of a Si(100)$c(8\times2)$ surface phase using H-induced self-organization and H extraction

O. Kubo,* T. Kobayashi, and N. Yamaoka
Department of Electronic Engineering, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

A. A. Saranin and A. V. Zotov
Department of Electronic Engineering, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan
and Institute of Automation and Control Processes, 5 Radio Street, 690041 Vladivostok, Russia

H. Ohnishi
Research Center for Ultra-High Voltage Electron Microscopy, Osaka University, Ibaraki, Osaka 567-0047, Japan

M. Katayama and K. Oura
Department of Electronic Engineering, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

(Received 15 June 2001; published 18 September 2001)

A Si(100)$c(8\times2)$ surface phase has been fabricated using atomic-hydrogen-induced self-organization followed by hydrogen extraction by the tip of scanning tunneling microscope. Similar to a conventional Si(100)2×1 surface, the new phase is built of Si dimer rows, but with every second dimer row being missing. The second-layer Si atoms in the troughs between dimer rows are also dimerized. The second-layer Si dimers at the opposite sides of a top Si dimer row demonstrate a tendency to be out of phase. This configuration induces buckling of the top Si dimer with a $c(8\times2)$ periodicity.

DOI: 10.1103/PhysRevB.64.153406 PACS number(s): 68.35.Bs, 68.35.Ja, 68.37.Ef, 81.16.Rf

Nanoscale fabrication and control techniques have recently been used on various surfaces for realizing atomic-scale devices with new or advanced functions. Among them, the most actively used techniques are atom manipulation[1] and self-organized formation of nanostructures.[2] In particular, the deliberate use of hydrogen on semiconductor surfaces is highly attractive for the formation of nanostructures from the viewpoint of both atom manipulation[3–10] and self-organized formation.[11–14]

Since Lyding *et al.* reported the local desorption of hydrogen atoms from the Si(100)2×1 monohydride (MH) surface induced by the tip of a scanning tunneling microscope (STM),[3] nanostructure formation on Si surfaces terminated by hydrogen (H-terminated Si surfaces) has been intensively investigated both experimentally and theoretically.[3–10] Bearing in mind the significant difference in the chemical reactivity of H-terminated versus hydrogen-free Si surface regions, the patterned surface produced by selective hydrogen desorption can be used for selective deposition of atoms or molecules.[3,9,10] However, previous investigations have been performed only on the conventional H-terminated Si surface phases [2×1-H, 3×1-H on Si(100); 1×1-H on Si(111)], resulting in the conventional Si surface structures [Si(100)2×1; Si(111)2×1] on the H-extracted area without any peculiarity.

As concerns the self-organized formation of surface nanostructures, atomic hydrogen interaction with the adsorbate-induced Si surface phase has recently received considerable attention.[11–14] For example, when the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface phase is exposed to atomic hydrogen at 200 °C, hydrogen adsorption induces self-organization from a two-dimensional (2D) metal layer into 3D clusters of nanometer size.[11,12] Such a self-organization process is caused by the substitution of hydrogen for metal atoms. As a result, the bare Si area from which metal atoms have been expelled is terminated by hydrogen atoms. Sometimes, this area exhibits an unusual structure which is different from that of the conventional H-terminated Si surfaces [1×1-H, 2×1-H, 3×1-H on Si(100); 1×1-H, $\delta7\times7$-H on Si(111)].[15,16] For example, in the particular case of the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag, the H-terminated Si layer formed after the removal of Ag atoms shows up as an array of zig-zag rows with a local 2×1 periodicity.[11,12] Such a surface structure formed upon exposure to atomic hydrogen depends on the original superstructure; when the substrate Si atoms under the metal layer have been reconstructed in the original superstructure, an unusual H-terminated surface is often formed. Ag/Si(111)-H and In/Si(111)-H furnish examples of such a behavior.[11–13] However, these unusual H-terminated surfaces revert to the original metal-induced surface phases after hydrogen desorption upon annealing above 500 °C. Thus, these unusual surface Si structures remain stable only due to H termination and are lost when hydrogen is gone. Therefore, no peculiar adsorbate-free Si surface structures have been reported so far.

In this paper, we report the fabrication of a peculiar adsorbate-free Si reconstruction by the combined method of atomic-hydrogen-induced self-organization and hydrogen extraction for the first time. Hydrogen atoms were extracted by an STM tip from the unusual Si(100)4×1-H surface prepared by exposure of the Si(100)4×3-In surface to atomic hydrogen. As a result, a local adsorbate-free Si(100) surface phase with $c(8\times2)$ periodicity was formed. The formation mechanism of this peculiar surface phase is discussed below.

All experiments were carried out in an ultrahigh vacuum (UHV) chamber equipped with STM and low-energy electron diffraction facilities. The base pressure was typically 8×10^{-11} Torr. The STM tips were fabricated by electro-

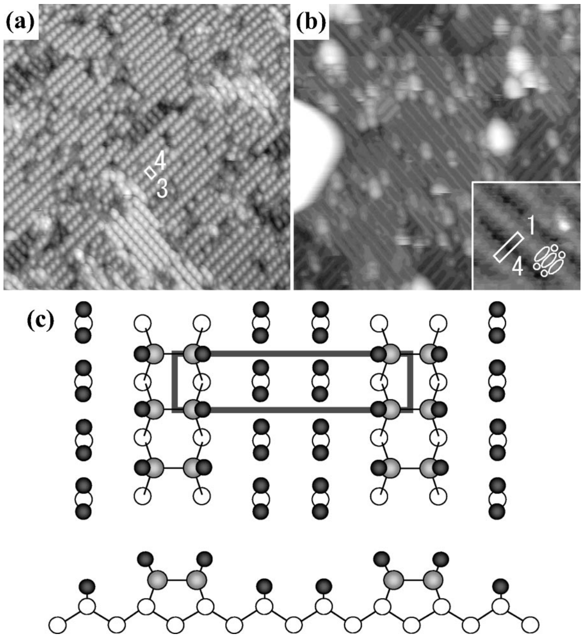

FIG. 1. (a) 500×500 Å^2 STM image of Si(100)4×3-In surface formed by deposition of about 0.6 ML of In onto Si(100)2×1 surface at 400 °C. (b) 500×500 Å^2 STM image of Si(100)4×1-H surface with an In cluster (large semicircle on the extreme left) formed by exposure of Si(100)4×3-In surface shown in (a) to 500 L of hydrogen at 300 °C. Tunneling conditions (a) −1.9 V, 0.2 nA and (b) −2.0 V, 0.2 nA. (c) Structural model of Si(100)4×1-H. Black, gray, and white circles indicate hydrogen atoms, top-layer Si atoms, and second (and third)-layer Si atoms, respectively.

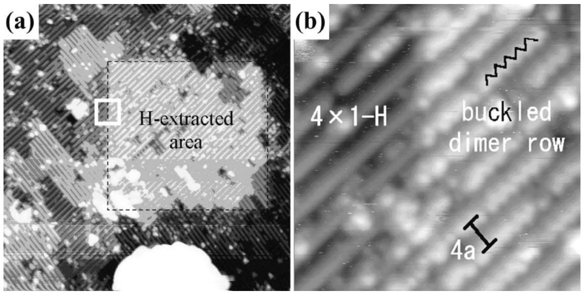

FIG. 2. (a) 1000×1000 Å^2 STM image of the Si(100)4×1-H surface from which hydrogen atoms were extracted by scanning STM tip under the following conditions: $Vs=+6.0$ V, $It=0.20$ nA, scanning speed = 100 nm/s, interval of scanning lines = 0.125 nm/scan, scanned area = 500×500 Å^2. (b) Magnified image (150×150 Å^2) of (a), in which buckled dimer rows with intervals of $4a$ periodicity were observed. The image was taken at a sample bias of −1.7 V and tunneling current of 0.2 nA.

chemical etching of a W wire (ϕ 0.3 mm) and then cleaned by *in situ* annealing. Si(100) samples ($2\times13\,\mathrm{mm}^2$) were cut from *n*-type Si wafers (0.05 Ω cm) and placed into the UHV chamber. After degassing at 600 °C for more than 12 h, the samples were cleaned by repeated heating at 1200 °C in UHV of less than 5×10^{-10} Torr to obtain a 2×1 surface. Indium (In) was deposited from a tantalum foil tube by direct-current heating. For atomic hydrogen exposure, H_2 gas was admitted into the chamber and dissociated into atomic hydrogen with an 1800 °C tungsten filament, 7 cm from the Si surface. Since the arrival rate of atomic hydrogen is unknown, the dose of molecular hydrogen is specified and expressed in units of Langmuir ($1\ \mathrm{L}=1\times10^{-6}$ Torr s). In our case, to form a completely H-terminated Si(100)2×1-H surface, a clean Si(100)2×1 surface was exposed to 500 L of hydrogen at 300 °C. All STM observations and manipulations were carried out at room temperature (RT).

To prepare an unusual H-terminated Si surface, the Si(100)4×3-In surface phase was formed [Fig. 1(a)] by the deposition of about 0.6 ML In onto the Si(100)2×1 surface at 400 °C.[17] Each 4×3 unit cell is associated with a round protrusion as indicated in Fig. 1(a). As for the structure of the Si(100)4×3-In surface, 0.5 ML Si atoms were found to be reconstructed under the In layer.[17] When this surface was exposed to 500 L of atomic hydrogen at 300 °C, In atoms were expelled from their original positions and agglomerated into 3D clusters, as shown in Fig. 1(b). On the bare Si substrate area, an unusual 4×1-H surface phase was observed as shown in the inset of Fig. 1(b). This 4×1-H surface consists of Si and hydrogen atoms, and does not incorporate In atoms. A plausible structural model of this surface is shown in Fig. 1(c), in which top Si dimers are terminated by hydrogen in the form of MH dimers, whereas second-layer Si atoms form dihydride (DH) species. However, at higher sample temperatures during hydrogen exposure, MH dimers are formed both in top and second layer.[17] The specific structure of the Si(100)4×1-H surface with every second dimer row missing is inherited from a Si substrate reconstruction in the original Si(100)4×3-In phase which is known to have a top Si atom density of 0.5 ML.[17]

Next, local hydrogen extraction was performed from the surface shown in Fig. 1(b) by the STM tip scanning in the constant current feedback mode at a scanning speed of 100 nm/s, interval of scanning lines of 0.125 nm/scan, sample bias voltage of +6.0 V, and tunnel current of 0.20 nA. After scanning a 500×500 Å^2 area, a bright square could be observed in the STM image, as shown in Fig. 2(a), indicating that hydrogen atoms were extracted and Si dangling bonds appeared on the scanned area. Figure 2(b) shows a magnified image of the area at the boundary of the scanned region indicated by the white square in Fig. 2(a). In the right half of Fig. 2(b), which shows the H-extracted area, zig-zag rows at intervals of $4a$ [where a is the lattice constant of the Si(100) bulk crystal] are observed, while the area outside the scanned region (left half) shows straight rows at the same intervals of $4a$. This result indicates that the Si atoms in the Si(100)4×1-H surface had maintained their original arrangement after hydrogen extraction. Namely, STM-induced hydrogen extraction converts rows of symmetric MH dimers into the rows of buckled Si dimers shown in Fig. 2(b) as zig-zag chains.[18] Thus, the peculiar structure of Si dimer rows with $4a$ spacing is formed, in agreement with the proposed 4×1-H structural model shown in Fig. 1(c). To our knowledge, this is the first report of a peculiar adsorbate-free Si surface phase on a Si(100) substrate, which cannot be formed using conventional preparation techniques.

The buckled dimer rows were often arranged with $c(8\times2)$ periodicity, as shown in Fig. 3(a). Sometimes a non-

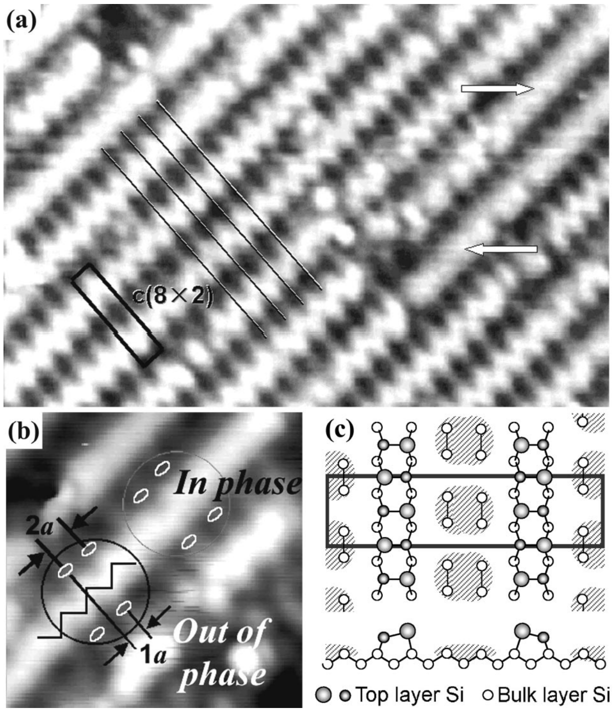

FIG. 3. (a) 180×120 Å^2 STM image of the H-extracted area, most of which showed $c(8\times2)$ periodicity. (b) Magnified image of (a), in which the second-layer Si dimers were resolved. These images were taken at a sample bias of -1.7 V and tunneling current of 0.2 nA. (c) Schematic illustration of the proposed structural model of the H-extracted area, in which gray circles, white circles, and the striped area show Si atoms in the top layer, those in the second (and third) layer, and dark protrusions observed in (b), respectively.

buckled dimer row could be found, as indicated by an arrow in Fig. 3(a), whereas buckled dimer rows with 4×2 periodicity were seldom observed. In the enlarged image shown in Fig. 3(b), dark protrusions with intervals of $2a$ are also seen at both sides of the buckled dimer rows. These protrusions are thought to correspond to two dimers in the second layer, which are probably hydrogen-free Si dimers. The structural model of the H-extracted area with $c(8\times2)$ periodicity is shown in Fig. 3(c).

Let us consider the mechanism of buckled dimer formation. Usually, buckled dimers are observed at S_A steps (where the dimer rows of the upper terrace are parallel to the step line),[18] near the C-type defects,[19] and at very low temperatures.[20] However, the buckled dimers observed in the present study could be found not only at step edges or defects but also throughout the entire H-extracted area even under RT observation. The mechanism of buckling in this study can be explained based on the model of buckled dimer formation at an S_A step edge.[18] The upper-edge Si atoms, aligned with the center of dimer rows on the lower terrace, receive upward stress, while the other upper-edge Si atoms receive downward stress, resulting in the buckled dimer row formation at the upper step edge. Accordingly, the arrangement of the second-layer Si dimers at the H-extracted surface dictates the buckling of the top Si dimers and can be described as follows.

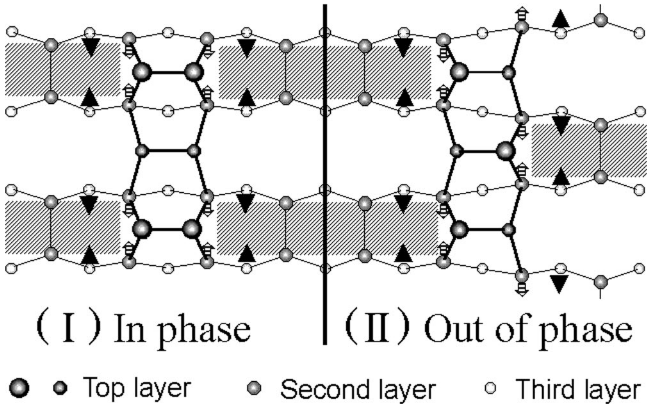

FIG. 4. Schematic illustration of two arrangements of the second-layer Si dimers between the top buckled dimer row. (I) Dimer rows on one side of the top buckled dimer row are at symmetrical sites with respect to those on the other side (in phase). (II) Dimer rows on one side of the top buckled dimer row are shifted by $1a$ with respect to those on the other side (out of phase).

Consider two possible arrangements of the second-layer Si dimers, as shown in Fig. 4. In the first case, the dimer rows at one side of the top buckled dimer row are at symmetrical sites with respect to those at the other side [(I) in phase]. In the second case, the dimer rows on one side of the top buckled dimer row are shifted by $1a$ with respect to those on the other side [(II) out of phase]. In the first case (I), the top dimers are not buckled because both atoms in each dimer are pushed up or pulled down. In the second case (II), the top dimer row shows buckling because one atom is pushed up while the other is pulled down within each dimer. In this study, we observed that the out of phase configuration of the second-layer Si dimers is preferable, as is shown inside the black circle in Fig. 3(b). Such areas mostly showed buckled dimer rows. Sometimes, we observed in-phase second-layer Si dimers. In this case, most of the top dimer rows between such second-layer Si dimers did not show buckling, as indicated by the gray circle in Fig. 3(b). Thus, the buckling mechanism described above can account for our results. It is most likely that when hydrogen atoms are extracted from the Si(100)4×1-H surface, the second-layer Si atoms (former DH species) tend to form out of phase dimers, resulting in the buckled dimer formation in the top Si layer throughout most of the H-extracted area. A similar behavior was reported by Bedrossian and Kaxiras for the monolayer-high single-dimer-row formation using Xe bombardment of the Si(100)2×1 surface followed by annealing.[21] According to their report, the positions of dimer rows on opposite sides of the single dimer row were mostly out of phase. They also calculated that the out of phase dimer rows are lower in energy than the in phase dimer rows, by 0.4 eV per dimer.

In conclusion, local hydrogen extraction from the Si(100)4×1-H surface has been performed using the STM tip. After hydrogen extraction, a local adsorbate-free Si(100) surface phase with $c(8\times2)$ periodicity was observed. The monohydride dimer rows at intervals of $4a$ transformed into the buckled Si dimer rows after the hydrogen extraction. Hydrogen was also extracted from the second-layer dihydrides between the top buckled dimer rows and the dihydrides were also transformed into Si dimers. These second-layer Si dimers tended to be out of phase on opposite sides of the top Si dimer row, which induced buckling of the top Si dimers with $c(8\times2)$ periodicity. The present study demonstrates the possibility of the artificial formation of peculiar structures on Si(100) substrate.

We would like to thank Mr. T. Harada for his great help. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan. One of the authors (O. K.) acknowledges the Japan Society for the Promotion of Science for support.

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*Author to whom correspondence should be addressed. Electronic address: okubo@ele.eng.osaka-u.ac.jp

[1] For example, D. M. Eigler and E. K. Schweizer, Nature (London) **344**, 524 (1990).

[2] For example, G. M. Ribeiro, A. M. Bratkovski, T. I. Kamins, D. A. A. Ohlberg, and R. S. Williams, Science **279**, 353 (1998).

[3] J. W. Lyding, T.-C. Shen, J. S. Hubacek, J. R. Tucker, and G. C. Abeln, Appl. Phys. Lett. **64**, 2010 (1994).

[4] T.-C. Shen, C. Wang, G. C. Abeln, J. R. Tucker, J. W. Lyding, Ph. Avouris, and R. E. Walkup, Science **268**, 1590 (1995).

[5] Ph. Avouris, R. E. Walkup, A. R. Rossi, T.-C. Shen, G. C. Abeln, J. R. Tucker, and J. W. Lyding, Chem. Phys. Lett. **257**, 148 (1996).

[6] S. Watanabe, Y. A. Ono, T. Hashizume, and Y. Wada, Phys. Rev. B **54**, 17 308 (1996).

[7] C. Thirstrup, M. Sakurai, T. Nakayama, and M. Aono, Surf. Sci. **411**, 203 (1998).

[8] K. Stokbro, C. Thirstrup, M. Sakurai, U. Quaade, B. Y.-K. Hu, F. P. Murano, and F. Grey, Phys. Rev. Lett. **80**, 2618 (1998).

[9] T. Hashizume, S. Heike, M. I. Lutwyche, S. Watanabe, K. Nakajima, T. Nishi, and Y. Wada, Jpn. J. Appl. Phys. **35**, L1085 (1996).

[10] T.-C. Shen, C. Wang, and J. R. Tucker, Phys. Rev. Lett. **78**, 1271 (1997).

[11] H. Ohnishi, Y. Yamamoto, K. Oura, I. Katayama, and Y. Ohba, J. Vac. Sci. Technol. A **13**, 1438 (1995).

[12] K. Oura, H. Ohnishi, Y. Yamamoto, I. Katayama, and Y. Ohba, J. Vac. Sci. Technol. B **14**, 988 (1996).

[13] A. A. Saranin, E. A. Khramtsova, K. V. Ignatovich, V. G. Lifshits, T. Numata, O. Kubo, M. Katayama, and K. Oura, Phys. Rev. B **55**, 5353 (1997).

[14] K. Oura, V. G. Lifshits, A. A. Saranin, A. V. Zotov, and M. Katayama, Surf. Sci. Rep. **35**, 1 (1999).

[15] J. J. Boland, Phys. Rev. Lett. **65**, 3325 (1990).

[16] F. Owman and P. Martensson, Surf. Sci. **303**, L367 (1994).

[17] A. A. Saranin, A. V. Zotov, V. G. Lifshits, J.-T. Ryu, O. Kubo, H. Tani, T. Harada, M. Katayama, and K. Oura, Phys. Rev. B **60**, 14 372 (1999).

[18] R. J. Hamers, R. M. Tromp, and J. E. Demuth, Phys. Rev. B **34**, 5343 (1986).

[19] R. J. Hamers and U. K. Kohler, J. Vac. Sci. Technol. A **7**, 2854 (1989).

[20] H. Tochihara, T. Amakusa, and M. Iwatsuki, Phys. Rev. B **50**, 12 262 (1994).

[21] P. Bedrossian and E. Kaxiras, Phys. Rev. Lett. **70**, 2589 (1993).