Hydrogen interaction with a Si(113)-3 \times 2 surface* 

Kohei Mamiya, Masamichi Yoshimura,† and Kazuyuki Ueda  
Nano High-Tech Research Center, Toyota Technological Institute, 
2-12-1 Hisakata, Tempaku-ku, Nagoya 468-8511, Japan  
(Received 14 October 2005; Accepted 26 October 2005; Published 31 October 2005) 

We report ultrahigh vacuum scanning tunneling microscopy (UHV-STM) study of the atomic hydrogen adsorption onto a clean Si(113)-3 \times 2 surface on an atomic scale. Even after hydrogen exposure of 4 L, STM images reveal clearly that some adatoms are invisible and some pentamers change their image contrast, probably due to hydrogen adsorption at the surface dangling bonds of the corresponding sites. Based on the results of STM together with low-energy electron diffraction (LEED), we discuss the initial adsorption processes of atomic hydrogen on Si(113)-3 \times 2 and the transition from 3 \times 2 to 3 \times 1. [DOI: 10.1380/ejssnt.2005.263] 

Keywords: Si(113); STM; Hydrogen; Adsorption; Pentamer

I. INTRODUCTION

Recently, quantum devices such as quantum dots and quantum wires have been focused, where so called bottom-up techniques are often used as a fabrication method. In such fabrication, it is essential to utilize appropriate substrates for the quantum structures. Since a Si(113) surface structure has a one-dimensional character as like as Si(110) [1], and low surface energy comparable to Si(111) or Si(001) [2], it is expected to a suitable substrate for the low-dimensional structure. It was demonstrated that Ge nanowires were grown in the Si(113) surface [3]. As is the case for low-index Si surfaces, the clean Si(113) surface reconstructs into a 3 \times 2 superstructure at room temperature [4]. Since many dangling bonds exist in this surface, hydrogen termination might be effective to lower surface energy.

Figure 1 shows the structure model of a clean Si(113)-3 \times 2 surface, as was proposed by Dabrowski et al [5]. The solid rectangle shows a unit cell of 3 \times 2. The Si(113)-3 \times 2 surface consists of adatoms and two kinds of pentamers, one with interstitial Si atom (E) (referred to as ‘i-pentamer’ hereafter), and the other without it (‘n-pentamer’). The interstitial Si atom (E) is located below the tetramer (Fig. 1(b): Si atoms (A), (B) and (C)), and raises a pentamer to the vacuum side [5].

There have been several studies on the hydrogen adsorption on the Si(113) surface. Jacobi et al. reported by high resolution electron energy loss spectroscopy (HR-EELS) and LEED that atomic hydrogen forms a monohydride by saturation dangling bonds of a Si(113)-3 \times 2 surface at low exposures, while at higher exposures a dihydride phase is formed, and that these changes were clearly distinguishable in HR-EELS. Moreover, they showed that the structural phase changed from 3 \times 2 into 3 \times 1 at low exposures. Based on these results, they suggested that the structural change from 3 \times 2 into 3 \times 1-adsorbate proceeded without lateral Si transport [6]. Unfortunately, their pioneering work was done before the proposal of the structural model by Dabrowski, then detailed adsorption processes were not understood fully. To the best of our knowledge, there has been no real space study on the H/Si(113) system.

Here, we report on scanning tunneling microscopy (STM) study of the initial adsorption processes of hydrogen on the Si(113)-3 \times 2 surface. It was found by high-resolution STM images that atomic hydrogen reacts with adatoms and pentamers without breaking surface frameworks formed by 3 \times 2 reconstruction, which explains well the observed 3 \times 1 structure. The emission of interstitial atoms was not identified in the exposure range investigated in this study.

II. EXPERIMENTAL

The STM experiment was carried out at room temperature in ultrahigh vacuum (UHV) below 2.0 \times 10^{-8} \text{ Pa}. The specimen was cut from Si(113) wafer into the size of 7 \text{ mm} \times 1 \text{ mm} \times 0.5 \text{ mm}. After buffered HF treatment followed by dipping in H2O2 and H2SO4 solution, the specimen was introduced into the vacuum chamber. Then the sample was cleaned by degassing at 600°C for 10 h and

---

*This paper is presented at International Symposium on Surface Science and Nanotechnology (ISSS-4), Saitama, Japan, 14-17 November, 2005.
†Corresponding author: yoshi@toyota-ti.ac.jp

---

FIG. 1: (a) The structure model of a Si(113)-3 \times 2 surface proposed by Dabrowski. The surface consists of adatoms, i-pentamers and n-pentamers. The solid line indicates a 3 \times 2 unit cell. (b) Side view of a 3 \times 2 unit cell.
flashing at $\sim 1100^\circ C$ followed by annealing at 600$^\circ C$ for 10 min. This treatment results in a clean and well-ordered Si(113)-3 $\times$ 2 surface. The clean Si(113) surface was exposed at room temperature to atomic hydrogen produced by cracking hydrogen molecules using a hot tungsten filament at 1700$^\circ C$. Here, we express the amount of exposure of a hydrogen molecule with the unit of Langmuir (1 L =1.33 $\times$ 10$^{-4}$ Pa·sec). Tungsten tip was used as a probe, which was electrochemically etched in 2.5 N-KOH solution.

III. RESULTS AND DISCUSSION

Figure 2 shows a filled-state STM image of the clean Si(113) surface obtained at the sample bias voltage of $-1.80$ V. The scanning area is 3.4 nm $\times$ 3.5 nm. The row of isolated spherical protrusions and the band structure along [110] are arranged alternately in the [332] direction. The spherical protrusion corresponds to an adatom shown in Fig. 1 and the band structure the dimer part of the n-pentamer (D atoms) and adatoms [5]. Figures 3 show empty-state STM images of Si(113)-3 $\times$ 2, where the position of i-pentamer as well as interstitial atoms E is indicated for eyes’ guide [5]. Figure 3(a) reveals a pentagonal shape corresponding to the i-pentamer, while in Fig. 3(b) the pentamers are hardly to recognize and jellyfish-like structure is clearly visible in place by the enhanced contrast at B atoms [5]. The head of jellyfish consists of B atoms and D atoms [5]. These two types of empty-state images are considered to come from different experimental conditions, especially from the atomic and electronic structure of the tip apex, because we see both structures even with the same bias voltage and tunneling current. Dabrowski et al. [5] reported both structures and Sakama et al. [7] observed jellyfish structure. Of great importance is that the atoms in i-pentamers are only accessible by empty-states STM images. After atomic hydrogen exposure, only jellyfish structure was obtained in this study, then we compare hydrogen adsorption structure with the jellyfish structure in the following section.

Figures 4 show a filled-state image (a) and an empty-state image (b) of the Si(113) surface after 2 L-hydrogen exposure. In Fig. 4(a), some of the spherical protrusions are invisible and the fragmentation of band structures is observed. This clearly indicates that atomic hydrogen bonds to Si adatoms. In empty-state STM images of Fig. 4(b), some i-pentamers (jellyfish) changed their images contrast, especially at the leg part of the jellyfish, namely, C atoms. It is noted here that the empty-state images can be observed brightly at bias voltages above 2.5 V, indicating the disappearance of surface empty-states near Fermi level by hydrogen adsorption. Thus, atomic hydrogen also reacts with the i-pentamers, although the detailed adsorption sites cannot be identified at this stage. Figures 5 show LEED patterns from a clean Si(113) surface (a) (Fig. 2 and Fig. 3) and 60 L-hydrogen exposed Si(113) surface (b) (similar to the surface shown in Fig. 4), showing 3$\times$2 and 3$\times$1 surface periodicity, respectively. The transition from 3$\times$2 to 3$\times$1 is consistent with the early study by Jacobi et al. where abrupt decrease in intensity of 3$\times$2 spot was observed by hydrogen adsorption [6]. The anomalous finding is that the hydrogen-reacted surface revealed by STM (Fig. 4) does not show large defect formation or clustering but slight change in the
FIG. 4: (a) Filled-state (−2.50 V, 0.27 nA, 7.0 × 7.5 nm²) and (b) empty-state (1.38 V, 0.27 nA, 7.0 × 7.5 nm²) STM images of Si(113) surface after 4 L-hydrogen exposure.

FIG. 5: LEED images from a clean Si(113)-3×2 surface (a) and a H/Si(113)-3×1 surface (60 L). The primary electron energy is 41 eV.

contrast. This imply that the hydrogen is likely to react with the dangling bonds of surface atoms in Si(113), and the framework due to pentamer formation is remained.

IV. CONCLUSION

Initial reaction of atomic hydrogen with Si(113)-3×2 surface has been investigated by STM and LEED. Upon hydrogen exposure, LEED pattern indicates the transition from 3×2 to 3×1. The STM images of hydrogen reacted surface reveal the change in image contrast at adatoms as well as pentamer atoms. The interesting finding is that the 3×2 unit is basically preserved, but the distinction between n-pentamers and i-pentamers becomes obscure by hydrogen adsorption, giving rise to 3×1 surface periodicity. This result is consistent with the report by Jacobi et al. where no bond breaking happens during the transition from 3×2 to 3×1.

[1] T. An, M. Yoshimura, I. Ono and, K. Ueda, Phys. Rev. B 61, 3006 (2000).
[2] J. M. Gibson, M. L. McDonald, and F. C. Unterwald, Phys. Rev. Lett. 55, 1765 (1985).
[3] Z. Zhang, X. Zhu, K. Sumitomo, H. Omi, T. Ogino, Surf. Interface Anal. 36, 114 (2004).
[4] U. Myler and K. Jacobi, Surf. Sci. 220, 353 (1989).
[5] J. Dabrowski, H.-J. Mussig, and G. Wolff, Phys. Rev. Lett. 73, 1660 (1994).
[6] K. Jacobi and U. Myler, Surf. Sci. 284, 223 (1993).
[7] H. Sakama, D. Kunimiatsu, M. Kageshima, and A. Kawazu, Phys. Rev. B 53, 6927 (1996).
[8] J. Dabrowski, H.-J. Mussig, and G. Wolff, J. Vac. Sci. Technol. B 13, 1597 (1995).