

How to fabricate a defect free Si(001) surface

K. Hata, T. Kimura, S. Ozawa, and H. Shigekawa^{a)}

*Institute of Applied Physics and CREST, Japan Science and Technology Corporation (JST),
University of Tsukuba, Tsukuba 305-8573, Japan*

(Received 26 October 1999; accepted 20 March 2000)

We demonstrate the successful fabrication of an almost defect free Si(001) surface by refining the standard annealing and flashing surface preparation method. On any desired samples, we can routinely fabricate a surface with defect densities lower than 0.1%, significantly reducing the defect density compared to surfaces fabricated by standard methodology. © 2000 American Vacuum Society. [S0734-2101(00)12004-4]

I. INTRODUCTION

Even though a great deal of effort has been put forth to fabricate a defect free Si(001) surface, the Si(001) surface is believed to inevitably have a significant concentration of defects. Defects on the Si(001) surface influence, in some cases determine, the surface morphology of the surface.¹⁻¹² Numerous important processes such as crystal growth, site of adsorption, and oxidation are reported to be influenced by the defects, in most cases in a negative and undesired fashion.¹³⁻¹⁷ What makes the situation worse is the fact that the concentration and types of defects observed on the surface strongly depend on the preparation methods and samples, making comparison of research from different groups difficult. In order to diminish the influence of defects and make the intrinsic characteristics of the Si(001) surface clear, a method of fabricating a surface free from defects is urgently demanded and has been pursued by several different approaches. If realized, a defect free Si(001) surface would serve as a standard template for future surface science work. The method of fabricating a defect free surface is required to be as conventional as possible and be able to be applied to any desired sample. Many different surface preparation methods to obtain clean Si(001) surfaces have been proposed so far, for example, pre-chemical treatments, and passivation. As the scanning tunneling microscope (STM) has developed into the standard detector to check the cleanliness of the surface at an unprecedented resolution, many preparation methods, including the use of ion bombardment, have been discarded, and the simple annealing and flashing procedure has become established as the method of choice for surface preparation.¹⁸

The standard process of annealing and flashing widely employed in surface science work nowadays was guided by Swartzentruber *et al.*¹⁹ They have provided a procedure of pre-baking and flashing which is believed to optimum the cleanliness of Si(001). Ukraintsev, Dohnalek, and Yates studied the influence of metal impurities, stressing the importance of the material of the sample holders, and presented procedures to clean the sample holders.²⁰ However, the best published STM images of the Si(001) surface utilizing these

techniques show defects with a density around several percent (1%~).

In this article, we report on the success of fabricating an almost defect free Si(001) surface. On any desired sample, we can routinely fabricate a surface with defect densities lower than 0.1%, significantly reducing the defects compared to surfaces fabricated by standard methodology. Two important findings led us to the success of fabricating the defect free Si(001) surface: (1) split off dimers and missing dimer row defects can be eliminated by a simple combination of annealing at high temperatures (at a temperature range which was believed to lead to surface roughening) and a conventional flashing; (2) the density of the A, B, and C defects increases with the increase of vacuum pressure during flashing, and if the vacuum pressure during flashing is kept extremely low, it is possible to fabricate a surface which has almost no A, B, and C defects. The techniques used to fabricate the defect free Si(001) surface are very simple and should be applicable to many ultrahigh vacuum (UHV) systems and on every desired sample.

II. RESULTS AND DISCUSSION

The Si samples were clamped to a Ta holder by Mo clips and direct contact to stainless steel was avoided. No thermocouple was used as they are reported to contaminate the Si(001) surface,²⁰ and the temperature was measured by a pyrometer. N-type Si samples phosphorus doped with a conductivity of 0.1 Ω cm were used, though similar results were obtained with different doping levels and dopants. During preparation, great care was taken not to contact the Si samples with metals. The base pressure of the vacuum chamber was 3×10^{-9} Pa. After ultrasonic cleaning for 10 min in acetone, the Si(001) sample was loaded into vacuum and pre-baked at ~ 600 °C for 12 h with a vacuum pressure below -1.0×10^{-7} Pa. After pre-baking, the sample was once flashed to 1150 °C for 30 s to remove the oxidized layers. By this procedure, a clean Si(001) surface that shows a typical concentration of defects (several percent) is fabricated.^{19,20} We further reduce the density of defects by two extra processes described in the following and fabricate a defect free Si(001) surface.

An example of an almost defect free Si(001) surface at 80 K is shown in the STM image of Fig. 1. Completely ordered

^{a)}Electronic mail: hidemi@ims.tsukuba.ac.jp; http://dora.ims.tsukuba.ac.jp

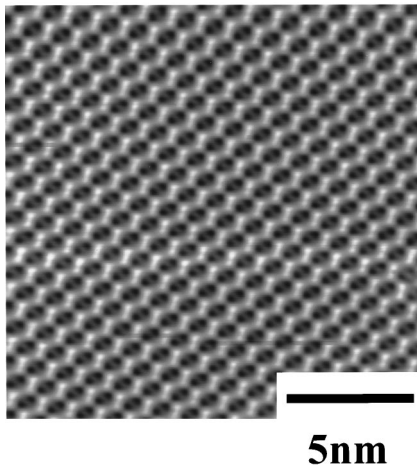


FIG. 1. STM image of the defect free Si(001) surface at 80 K. Tunneling conditions $V_s = +0.6$ V, $I = 1$ nA.

buckled dimers with no defects are observed.

Actually, defects are rarely observed on this surface. Note that Fig. 1 is an STM image of the empty states taken at a low surface bias (+0.6 V), a tunneling condition in which the defects are highlighted most (most of the defects appear as bright protrusions). This is important because there are some defects which are invisible at typical filled state STM images taken at a surface bias as high as -2 V. The defect density is lower than 0.1%, far lower than that achieved by standard surface preparation methods.

A flow chart of the complete procedure to fabricate a defect free surface is shown in Fig. 2. Process (*2) represents the conventional pre-baking and flashing described above while processes (*3) and (*4) are implemented to reduce the defect density further. Process (*3) removes the split off dimer and missing dimer row defects while process (*4) removes the A, B, and C defects. Process (*1) is necessary to make (*4) possible.

The first extra process (*3) eliminates the split off dimer and missing dimer row defects from the surface. Split off

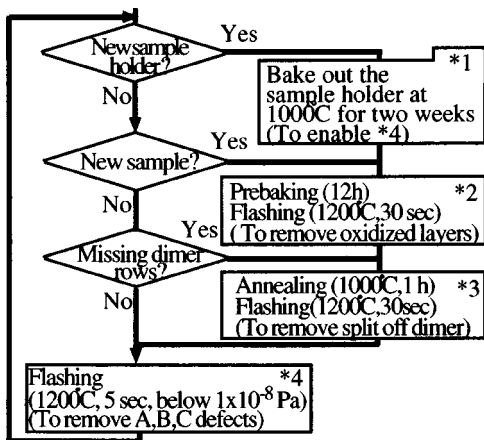


FIG. 2. Flow chart showing the procedure to fabricate a defect free Si(001) surface.

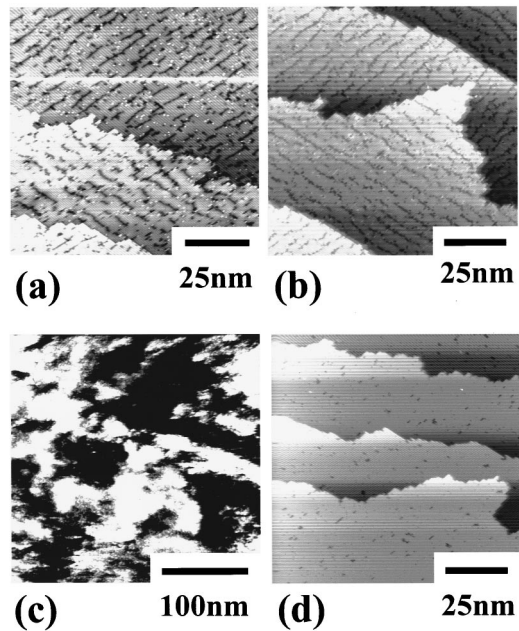


FIG. 3. (a) Empty ($V_s = +0.6$ V, $I = 1$ nA) and (b) filled state ($V_s = -1.5$ V, $I = 1$ nA) STM image of missing dimer rows formed by repeated flashing. (c) STM image ($V_s = -2.0$ V, $I = 1$ nA) of the surface after annealing at 950 °C. (d) After flashing at 1150 °C for 30 s ($V_s = -1.5$ V, $I = 1$ nA).

dimer defects are imaged by STM as two neighboring dark dimer sites, a neighbor bright dimer site, and a neighbor dark site.²⁰⁻²² Within typical experimental conditions, the split off dimer defects increase with repeated flashing and annealing and eventually they organize themselves with other vacancies producing the missing dimer rows having a $(2 \times n)$ overlayer.²⁰ The increase rate of the defects with flashing strongly depends on the condition of the holders and samples. No method has been reported to remove these defects, and once the missing dimer rows cover the surface, the sample is considered to have reached its lifetime and is replaced by a new sample.

We found that it is possible to eliminate the split off dimer and missing dimer row defects by annealing the substrate for a long time (1 h~) at high temperatures ($950-1000$ °C) followed by conventional flashing. Annealing Si(100) surfaces to high temperature is usually avoided because it is reported to result in surface roughening.²³ Figures 3(a) and 3(b) show the filled and empty state STM images of a surface covered with a certain ratio of missing dimer row defects which were formed by repeated flashing treatments (this is a case of heavy and intentional contamination taken for demonstration purposes). Annealing this surface at 950 °C for 1 h resulted in surface roughening as shown in Fig. 3(c). We found that it is possible to clean the surface with subsequent flashing at 1150 °C for 30 s (required time depends on the degree of roughening) as shown in Fig. 3(d). It is striking to observe that the missing dimer rows have been eliminated by this process. Once the split off dimers and missing dimer row defects are eliminated, the sample remains clean and free from these defects after subsequent

flashing, provided the sample holder contains no stainless steel and is thoroughly outgassed by process (*1). In usual experimental conditions (no intentional contamination), we can reduce the density of the split off dimer defects almost to zero by this process (we have noticed that this process does not always work, the reason is not known at this stage).

At this stage we cannot present a complete explanation for the elimination of the split off dimers and missing dimer rows. Many researchers have reported that the split off dimer and missing dimer row defects are induced by heavy metal contamination, particularly Ni.^{20–22} For the case of Si(111), Yoshimura, Shinabe, and Yao have shown the dissipation of the superstructures associated with deposited Ni metals and the recovery of the clean 7×7 structure of Si(111) by annealing at 1000 °C for a long time.²⁴ The difference between Si(001) and Si(111) is that it is necessary to combine the high temperature annealing (950 °C~, 1 h~) and subsequent flashing to eliminate the missing dimer rows of Si(001). It might be that the heavy metals in the sample and sample holder accumulate in the vicinity of the surface during annealing and are removed by subsequent flashing.

The second extra process (*4) eliminates the A, B, and C defects from the surface. After the sample and sample holder are completely cooled down, an additional flashing is carried out at 1150 °C for a very short time (~5 s). What is critical here is to keep the increase of vacuum pressure (outgas from the sample holder) during flashing as minimum as possible. For the case of the surface shown in Fig. 1, the worst vacuum pressure during flashing at 1150 °C was 7×10^{-9} Pa. The increase of vacuum pressure during flashing is minimized by pre-baking the sample holder and the surroundings at high temperatures for a couple of weeks in UHV with a dummy Si sample [process (*1)]. This thorough outgassing of the sample holder is required once provided the sample holder is not contaminated accidentally. In our system, if the vacuum pressure during flashing is kept below 1×10^{-8} Pa, we can obtain a surface with extremely low defect density on any desired substrate, while if the vacuum pressure exceeds 1×10^{-7} Pa during flashing, the surface is covered with numerous defects. If the vacuum pressure during flashing is kept below 1×10^{-8} Pa, the slow cooling down process conventionally employed to reduce the defects is not necessary, though it would decrease the defect density in other cases.

Dependence of the density of the C defects on vacuum pressure during flashing has also been previously reported by Ukraintsev and co-workers, though their clean surface shows a defect density of several percent.²⁵ The concentration of the C defect shows the strongest dependence on vacuum pressure during flashing and is most easy to reduce. What is surprising here is that the concentration of the A and B defects can be reduced almost to zero in an extremely clean fabrication condition, giving counter evidence to the suggestion that the A and B defects might be a feature of the ground state of the Si(100) surface.²⁶

Realization of the defect free Si(100) surface has several important implications for future studies. The defect free

Si(100) surface readily manifests its importance in STM studies of the clean surface of Si(100).²⁷ Even though numerous STM studies have been carried out on the Si(100) surface, most of them have concentrated on the filled state STM images taken at relative high surface biases as -2 V. Only recently it was realized that probing the surface of Si(100) with various biases is important, particularly through research of adsorbed atoms which revealed that some adsorbed atoms are invisible in the filled state STM images taken at conventional surface biases (-2 V).^{27–31} In addition, recently it has been pointed out that the dangling-bond orbitals are roughly localized in the range of $\sim\pm 1$ V from the Fermi level, and in a typical STM image taken at the surface bias of -2 V, a significant part of the tunneling current must come from other states than the dangling bond orbitals.^{27,32} Defects are the major reason why most of the previous STM studies mainly concentrated on the filled state images taken at a relatively high bias (-2 V). At -2 V, most of the defects on the surface are observed as dark sites or vacancies or are even invisible, thus scanning at -2 V provides the most apparent clean STM image of the surface. When one attempts to lower the bias, defects become very bright because many of them are metallic,^{1,14,16} making it difficult to observe the dimers clearly. This aspect is demonstrated in the STM images of Figs. 4(a) and 4(b) taken at room temperature. We switched the surface bias to various values during scanning of a surface that had a typical density of defects. It is easy to realize that the defects become very bright at low biases and in the empty state images. Particularly, at -0.5 V, defects are highly contrasted and seriously disturb the scanning, making it difficult to observe the dimers. However, in some particular locations (indicated by the arrows and surrounded by the circles), a new feature is readily observable. There, each of the two atoms of the dimers are clearly resolved as round protrusions, giving a filled state STM image of the dimers similar to the empty state STM images. This aspect becomes clear in a STM image taken on a defect free surface at a surface bias of -0.6 V as shown in Fig. 4(c). On a defect free surface, we are no longer bothered by the defects and the surface can be probed at any desired surface bias except those in the band gap. Again, in Fig. 4(c), each of the two atoms of the dimers is clearly resolved. We interpret the new feature observed in the filled states at low biases as the following: (1) at low biases (-0.5 V), STM observes the dangling bond orbital. (2) At high biases (-2 V), tunneling from other states starts to participate in which are localized between the Si–Si dimer bond, and as a result, the dimer is observed as a single oval. A detailed discussion is given elsewhere.²⁷ Furthermore, Qin and Lagally have observed some new features in the empty state STM images of the dimers taken at low biases, and have given a similar interpretation.³² These results suggest that it is important to image the surface with a lower surface bias than before, a task much easily fulfilled on a defect free surface.

III. CONCLUSION

In conclusion, we have succeeded in fabricating a clean Si(001) surface with an extremely low concentration of de-

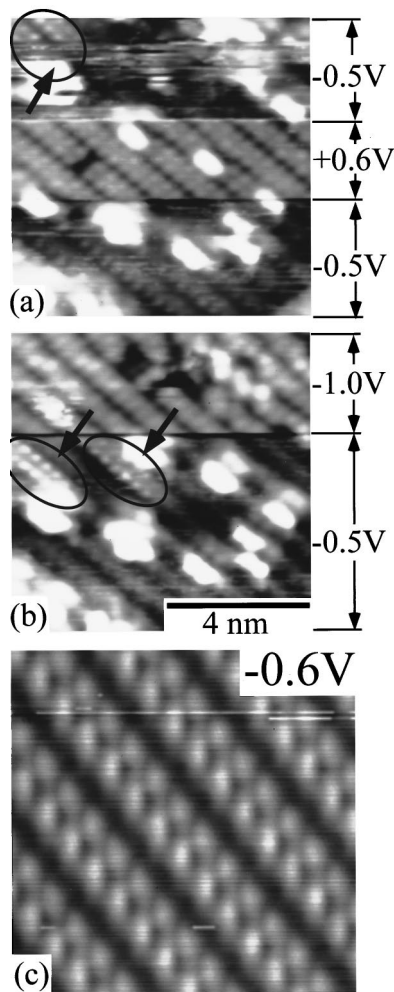


FIG. 4. (a), (b) STM images of a surface that showed a typical density of defects probed with various surface biases indicated in the right of the figures. (c) A STM image of defect free Si(100) surface taken at -0.6 V. Tunneling current 1 nA.

fects by refining the standard annealing and flashing surface preparation method. The key point in fabricating a defect free surface is twofold: (1) eliminating the split off dimer and missing dimer row defects by a combination of annealing at high temperature ($950^{\circ}\text{C}\sim$) for a long time (1 h \sim) and flashing at 1150°C (2) and to keep the increase of the vacuum pressure during flashing as minimum as possible which eliminates the A, B, and C defects. Realization of the defect free Si(001) surface should revolutionize some fields of surface science work on Si(001) such as studies of adsorption, since some adsorbates are imaged similar to the defects by STM. What is more important, the defect free Si(00) surface should serve as a standard template for future surface science work.

ACKNOWLEDGMENTS

This work was supported by the Shigekawa Project of TARA, University of Tsukuba. The support of a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan is also acknowledged.

- ¹R. J. Hamers and U. K. Kohler, *J. Vac. Sci. Technol. A* **7**, 2854 (1989).
- ²K. Hata, M. Ishida, K. Miyake, and H. Shigekawa, *Appl. Phys. Lett.* **73**, 40 (1998).
- ³M. Uchikawa, M. Ishida, K. Miyake, K. Hata, R. Yoshizaki, and H. Shigekawa, *Surf. Sci.* **357/358**, 469 (1996).
- ⁴R. A. Wolkow, *Phys. Rev. Lett.* **68**, 2636 (1992).
- ⁵H. Tochiyama, T. Amakusa, and M. Iwatsuki, *Phys. Rev. B* **50**, 12262 (1994).
- ⁶K. Hata, T. Kimura, Y. Sainoo, K. Miyake, R. Morita, M. Yamashita, and H. Shigekawa, *Jpn. J. Appl. Phys., Part 1* **38**, 2904 (1999).
- ⁷T. Yokoyama and K. Takayanagi, *Phys. Rev. B* **56**, 10483 (1997).
- ⁸T. Yokoyama and K. Takayanagi, *Phys. Rev. B* **57**, 4226 (1998).
- ⁹A. R. Smith, F. K. Men, K.-J. Chao, and C. K. Shih, *J. Vac. Sci. Technol. B* **14**, 914 (1996).
- ¹⁰H. Shigekawa, K. Miyake, M. Ishida, K. Hata, H. Oigawa, Y. Nannichi, R. Yoshizaki, A. Kawazu, T. Abe, T. Ozawa, and T. Nagamura, *Jpn. J. Appl. Phys., Part 2* **35**, L1081 (1996).
- ¹¹H. Shigekawa, K. Hata, K. Miyake, M. Ishida, and S. Ozawa, *Phys. Rev. B* **55**, 15448 (1997).
- ¹²H. Shigekawa, K. Miyake, M. Ishida, and K. Hata, *Jpn. J. Appl. Phys., Part 1* **36**, L294 (1997).
- ¹³Ph. Avouris and D. Cahill, *Ultramicroscopy* **42–44**, 838 (1992).
- ¹⁴K. Hata, S. Ozawa, and H. Shigekawa, *Surf. Sci.* **441**, 140 (1999).
- ¹⁵K. Hata, R. Morita, M. Yamashita, and H. Shigekawa, *Jpn. J. Appl. Phys., Part 1* **38**, 3837 (1999).
- ¹⁶K. Hata, S. Ozawa, Y. Sainoo, K. Miyake, and H. Shigekawa, *Surf. Sci.* **447**, 156 (2000).
- ¹⁷M. W. Rowe, H. Liu, G. P. Williams, and R. T. Williams, *Phys. Rev. B* **47**, 2048 (1993).
- ¹⁸J. T. Yates, Jr., *Experimental Innovations in Surface Science* (Springer, Berlin, 1997), p. 790.
- ¹⁹B. S. Swartzentruber, Y.-W. Mo, M. B. Webb, and M. G. Lagally, *J. Vac. Sci. Technol. A* **7**, 2901 (1989).
- ²⁰V. A. Ukraintsev, Z. Dohnalek, and J. T. Yates, Jr., *Surf. Sci.* **388**, 132 (1997).
- ²¹H. Niehus, U. K. Kohler, M. Copel, and J. E. Demuth, *J. Microsc.* **152**, 735 (1988).
- ²²F. K. Men, A. R. Smith, K. J. Chao, Z. Zhang, and C. K. Shih, *Phys. Rev. B* **52**, 8650 (1995).
- ²³R. J. Hamer, R. M. Tromp, and J. E. Demuth, *Phys. Rev. B* **34**, 5343 (1986).
- ²⁴M. Yoshimura, S. Shinabe, and T. Yao, *Surf. Sci.* **357**, 917 (1996).
- ²⁵V. A. Ukraintsev and J. T. Yates, Jr., *Surf. Sci.* **346**, 31 (1996).
- ²⁶N. Roberts and R. J. Needs, *Surf. Sci.* **236**, 112 (1990).
- ²⁷K. Hata, S. Yasuda, and H. Shigekawa, *Phys. Rev. B* **60**, 8164 (1999).
- ²⁸B. S. Swartzentruber, *Phys. Rev. B* **55**, 1322 (1997).
- ²⁹J. van Wingerden, A. van Dam, M. J. Haye, P. M. L. O. Scholte, and T. Tuinstra, *Phys. Rev. B* **55**, 9352 (1997).
- ³⁰P. J. Bedrossian, *Phys. Rev. Lett.* **74**, 3648 (1995).
- ³¹X. R. Qin and M. G. Lagally, *Science* **278**, 1444 (1997).
- ³²X. R. Qin and M. G. Lagally, *Phys. Rev. B* **59**, 7293 (1999).