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D. H. Huang

NTT R&D Center, dehaun@loki.stanford.edu

Y. Yamamoto

Stanford University

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HYDROGEN ATOM EXTRACTION AND REDEPOSITION ON HYDROGEN-TERMINATED SILICON SURFACE WITH SCANNING TUNNELING MICROSCOPE AT ROOM TEMPERATURE

D.H. Huang^{1,*} and Y. Yamamoto^{1,2}

¹ERATO Quantum Fluctuation Proj., JRDC, NTT R&D Center, 3-9-11 Midoricho, Musashino, Tokyo 180, Japan

²E.L. Ginzton Laboratory, Stanford University, Stanford, CA 94305, U.S.A.

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Abstract

We have previously demonstrated that hydrogen atoms on the hydrogen-terminated Si(100)-2x1:H surface can be extracted by applying either positive or negative voltage pulses between an STM tip and the sample surface with a certain tunneling current. This phenomenon suggests that electron excitation and field evaporation both play a role in atom transfer. Under our experimental conditions, hydrogen atoms are extracted in pairs from either a single dimer or from two adjacent dimers in neighboring rows. Hydrogen atoms can also be redeposited onto the Si(100)-2x1:H surface from a tungsten tip, which has picked up hydrogen from the sample surface through the application of prior voltage pulses, to fill out surface silicon dangling bonds preferably with negative sample voltage pulses.

Key Words: Hydrogen extraction and deposition, field-induced evaporation, electron excitation, hydrogen-terminated silicon surface, scanning tunneling microscope.

Introduction

The scanning tunneling microscope (STM) is a promising tool for manipulating atoms one by one [4, 10, 13, 19, 23], allowing the possibility of exploring electronic/photonic devices on an atomic scale [5, 14]. Based on the techniques of single atom manipulation, we have used an ultra-high vacuum (UHV) STM to fabricate atomic-scale devices. We are especially interested, for example, in fabricating atom chains with metal, semiconductor and insulator phases on an atomically flat insulating surface. In a previous paper [26], we obtained the following results by tight binding calculation: (1) an Si atomic chain, Si₂ molecular chain and two-dimensional (2D) Si atomic array are always metallic; (2) an Mg atomic chain is always an insulator; and (3) a 2D Mg atomic array features a metal-insulator phase transition at a certain lattice constant.

In this paper, we investigate the Si(100)-2x1 surface and its hydrogen termination, which may be used both as a substrate and an insulator for the fabrication of atom chains of the type previously studied theoretically [26]. We demonstrate that individual hydrogen atoms on the Si(100)-2x1:H surface can be extracted by applying appropriate voltage pulses with an STM tip. Hydrogen atoms, already on the tip, can be diffused to the apex of the tip with an appropriate positive sample bias, where they can then be redeposited onto the surface by the negative sample pulses. This technique of hydrogen atom manipulation holds promise for fabricating a grounding wire for atomic-scale devices on the hydrogen-terminated Si surface.

Experimental Apparatus

Experiments were performed using a JSTM-4500 XT UHV STM (JEOL, Akishima, Tokyo, Japan). Base pressure in the chamber was 2×10^{-8} Pa. The sample was an Sb-doped ($0.4 \sim 0.6 \Omega\text{cm}$) n-type Si(100) wafer which was outgassed at 550°C for over ten hours prior to removal of the surface oxide. A clean Si(100)-2x1 surface was then prepared by repeated flash heating

*Contact for Correspondence:

Dehuan Huang, address as above.

Telephone number: +81 (422) 36-2594

FAX number: +81 (422) 36-1867

E-Mail: dehuan@yqfp.jst-c.go.jp; or
dehaun@loki.stanford.edu

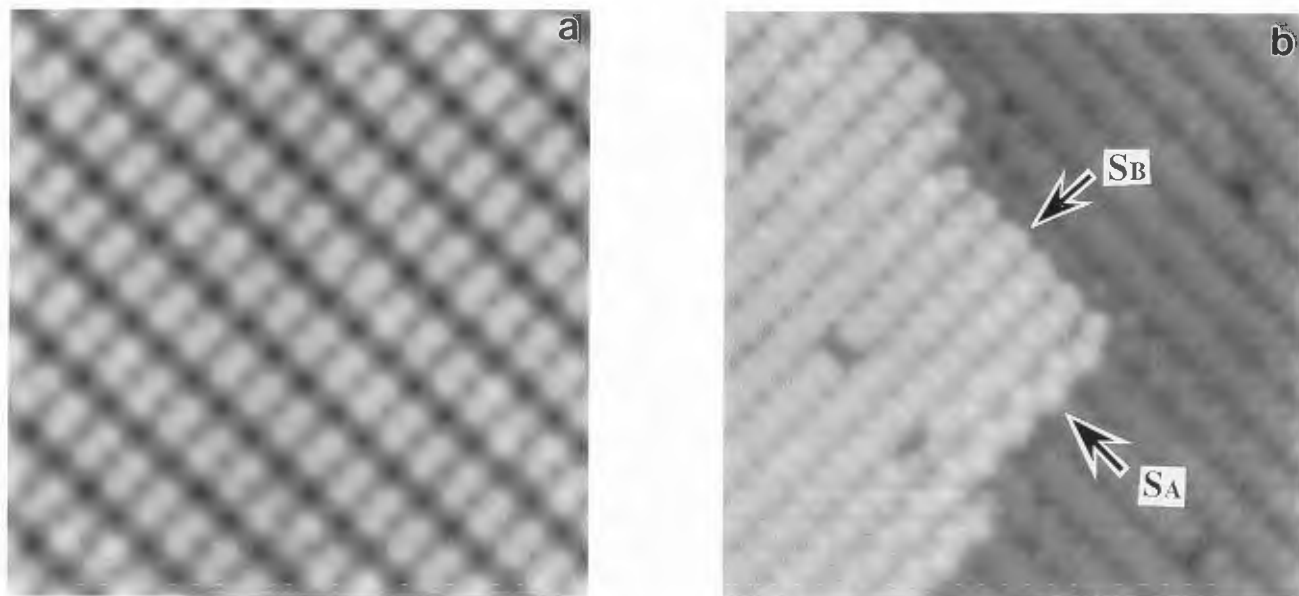


Figure 1. Clean Si(100)-2x1 surfaces recorded at sample bias of -2 V and tunneling current of 0.6 nA. (a) An STM image (6.0 nm x 6.0 nm) having defect densities of less than 1% in which the 2x1 Si dimers can be clearly seen; (b) an STM image (10.6 nm x 10.6 nm) with S_A and S_B steps.

of the sample to 1250°C for 20 seconds. During this procedure, the chamber pressure remained below 5×10^{-8} Pa. The STM tip was a 0.3 mm tungsten wire, sharpened by electrolytic etching using a 1 N solution of KOH. This tip was mounted on a tip holder in the STM and cleaned by electron-bombardment heating to above 1200°C in the UHV chamber. Although this step of tip cleaning was indispensable for our purpose, the tip was still contaminated at the atomic level and therefore not good enough for well-controlled atomic-scale processing. By applying an appropriate voltage pulse repeatedly between the tip and sample, however, residual contamination was removed, probably due to field evaporation, and a stable mini-tip was produced, as had been suggested by actual atom manipulation experiments [13].

The Si(100)-2x1 surface is made up of dimer rows. The distance between adjacent dimers in a row is 3.84 Å, and the spacing between adjacent dimer rows is 7.68 Å. In STM studies of the Si(100)-2x1 surface, defect densities ranging from about 3% to 10% have been observed [8, 20]. However, using the surface preparation method mentioned above, we successfully obtained the high-resolution Si(100)-2x1 surface images with defect densities less than 1% as shown in Figure 1, the 2x1 Si dimers and dimer rows are clearly resolved in these images.

The adsorption and desorption of hydrogen from silicon surfaces play important roles in many key technological processes. Recently, several groups have suc-

cessfully prepared high-quality Si(111) and Si(100) surfaces with ideal hydrogen termination using the wet chemical method [9, 21] and the dry etching process [3, 18], respectively. In this study, the hydrogen-terminated Si(100)-2x1 surface was prepared using the dry etching process. Atomic hydrogen was produced by decomposition of molecular hydrogen (purity 99.9999%) on a tungsten filament heated to 1500°C and placed ~5 cm from the sample surface. During this procedure, the UHV chamber was back-filled with about 10^{-4} Pa of hydrogen for 6 minutes. A monohydride surface was obtained by saturation exposure to atomic hydrogen at approximately 360°C. Under these conditions, dimer bonds remain intact and hydrogen reacts with surface dangling bonds to yield 2x1:H structures.

As shown in a recent STM study, there is a tendency for Si dimers to be doubly occupied during hydrogen termination of the Si(100) surface [2]. If the π -bond interaction between dangling bonds is stronger than the repulsive interaction between two hydrogen atoms on the same dimer, then a pairwise occupation of dimers becomes energetically favorable relative to singly occupied dimers. The 2x1 structure of the Si(100)-2x1:H surface looks similar to that of a clean Si(100)-2x1 surface. But, the Si(100)-2x1:H surface has a noticeably lower density of states in the band gap region [24, 25]. Our work (to be published) shows that tunneling resistivities on the Si(100)-2x1:H surface are about 1.5 and 5.5 times larger than those on a clean Si(100)-2x1 surface at -2.0 and +2.0 V, respectively.

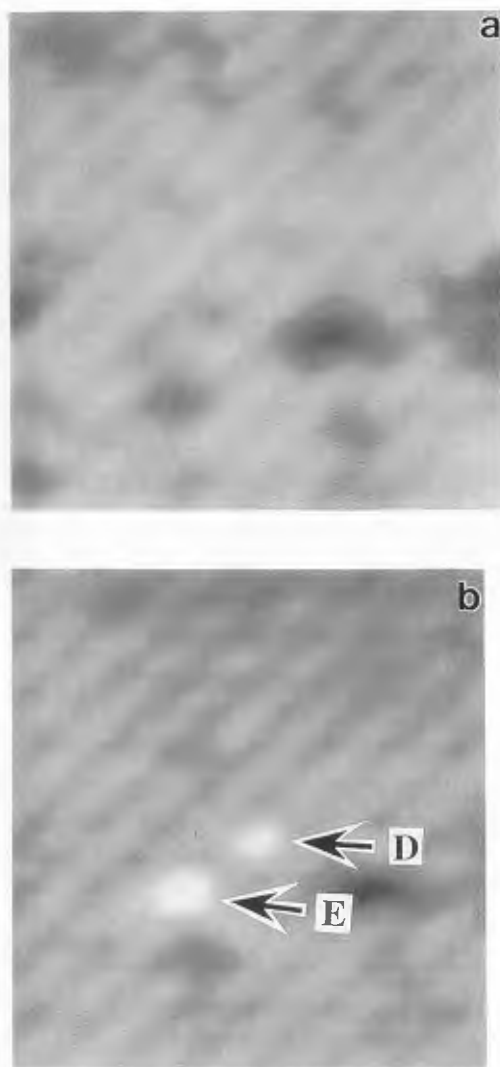


Figure 2. Individual hydrogen atom extraction from the Si(100)-2x1:H surface using a tungsten tip by the application of sample negative pulses. (a, b) STM images of the same area before and after applying voltage pulses of -8 V for 300 ms to the sample. A constant tunneling current of 10 nA was maintained during these voltage pulses. Each bright spot, indicated by D and E in (b), was created with 3 such pulses. Bright spot D may correspond to one Si dimer of the Si(100)-2x1:H surface and E to two dimers of two adjacent dimer rows as indicated by the paired open circles C in Figure 4. STM images (7.7 nm x 8.2 nm) were taken at a sample voltage of -2 V and tunneling current of 0.3 nA.

Mechanism of Hydrogen Manipulation

Hydrogen can be extracted locally from hydrogen-terminated silicon surfaces by scanning an STM tip over the surface while applying a continuous bias of several volts [18] or by applying pulses of several volts [11]

between the STM tip and surface. Nanometer scale patterns [18] and atomic-scale structures [11] have been achieved by these processes, respectively. Shen *et al.* [22] proposed two mechanisms for this process on the Si(100)-2x1:H surface: direct electronic excitation of the Si-H bond at high bias (>6.5 V) and multiple vibrational excitation by tunneling electrons at low bias (about 2 to 5 V). These mechanisms correspond to a tunneling current effect, and only occur when tunneling electrons run into the sample surface produced by a positive sample bias [18]. In this case, hydrogen extraction is achieved by exciting and breaking chemical bonds at the Si(100)-2x1:H surface with incoming electrons. Our experiments show that under appropriate tunneling current conditions, hydrogen atoms on the Si(100)-2x1:H surface can also be extracted with negative sample bias [11, 12], indicating this process may also have a field-induced mechanism, namely, a manipulation process having an electric field effect [1, 6]. Single hydrogen atoms can also be redeposited onto the Si(100)-2x1:H surface from an STM tip that has already picked up hydrogen atoms from the surface through the application of prior voltage pulses, to fill out surface Si dangling bonds preferably with negative sample voltage pulses. This phenomenon is similar to single Si atom deposition on the Si(111)-7x7 surface through field evaporation [15].

Extraction of Individual Hydrogen Atoms

We can extract individual hydrogen atoms from a predetermined atomic position on a Si(100)-2x1:H surface by placing an STM tip just above the position and applying a positive or negative voltage pulse between the tip and sample surface at room temperature. This voltage pulse is typically $\pm 8-9$ V and lasts for 50-300 ms. The STM current feedback loop maintains a constant current of 2 nA for positive sample voltage pulses or 10 nA for negative ones while the extraction voltage pulse is applied. We found that hydrogen atom extraction can be achieved with a sample voltage pulse in both polarities, but redeposition is more likely to occur at the negative pulse.

An example of single hydrogen extraction from the Si(100)-2x1:H surface using a tungsten tip by the application of negative sample pulses is shown in Figure 2. Figures 2a and 2b show STM images of the same area before and after applying voltage pulses of -8 V for 300 ms to the sample. A constant tunneling current of 10 nA was maintained during these pulses. Each bright spot (indicated by D and E in Figure 2b) was created with three successive such voltage pulses. The hydrogen-desorbed sites appear brighter because hydrogen extraction restores a clean silicon π -bond state, and increases the efficiency of electron transfer between tip and sample.

Figure 3 (at right). STM image (13.0 nm x 13.0 nm) of a chain (68.7 Å long) of Si dimers with equal separation (17.2 Å) created on the monohydride Si(100)-2x1:H surface with a tungsten tip (taken at a sample voltage of -2 V and tunneling current of 0.3 nA). Each bright spot corresponds to a single Si dimer of this surface, created by removal of two adsorbed hydrogen atoms from each Si dimer through 3 pulses of +8 V for 50 ms applied to the sample under constant current (2 nA) conditions.

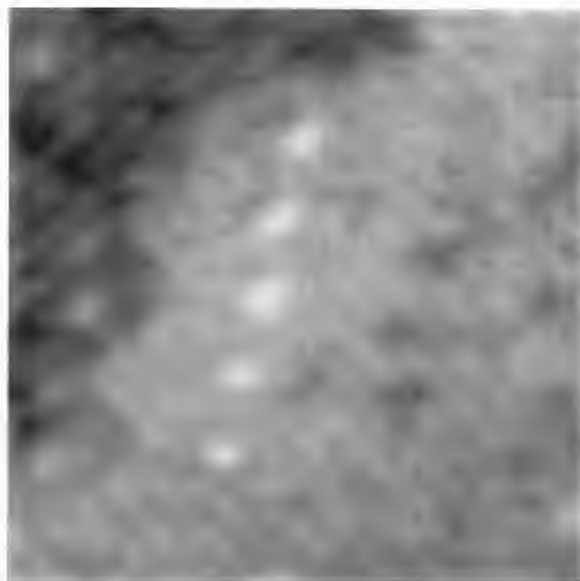
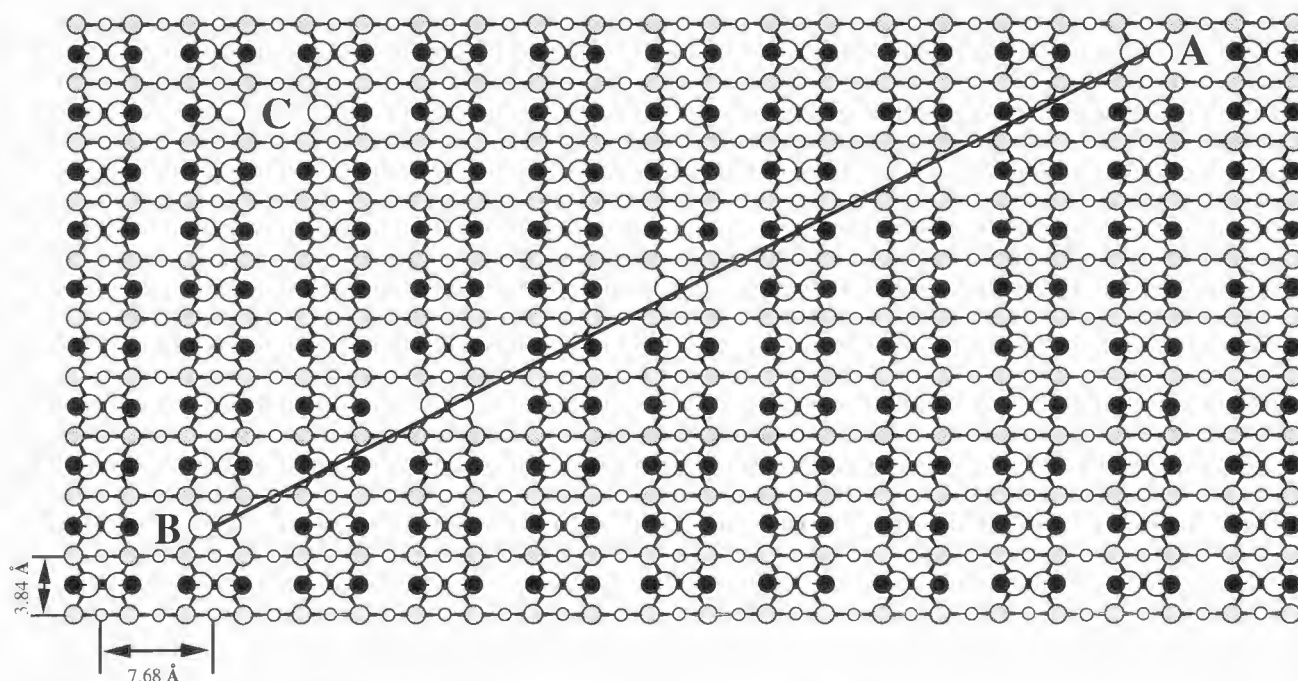


Figure 4 (below). Schematic diagram of a hydrogen-terminated Si(100)-2x1:H surface. Filled circles represent hydrogen atoms in the top layer of the Si(100)-2x1:H surface, while larger open circles represent Si adatoms in the second layer that are exposed-only after the removal of hydrogen. Shaded and smaller open circles represent Si atoms in the third and fourth layers, respectively. The dimer at A corresponds to the bright spot D in Figure 2b created by hydrogen extraction. The dimers indicated by paired open circles between A and B correspond to the pattern created in Figure 3. The paired open circles at C represent possible formation E in Figure 2b.



We also continuously extracted individual hydrogen atoms from the Si(100)-2x1:H surface to fabricate a chain, as shown in Figure 3. The length of the chain between the centers of the two bright spots at the end, as indicated by the line from the paired open circles A to B in Figure 4, is 68.7 Å, with equal separation of 17.2 Å between the centers of each of the two neighboring bright spots. This chain was created by applying three pulses of 8 V each for 50 ms to the selected Si

dimers, with a tunnel current of 2 nA. Each bright spot in Figure 3 corresponds to one Si dimer of the Si(100)-2x1:H surface, as illustrated by the paired open circles between A and B in Figure 4.

These results show that under our experimental conditions, hydrogen extraction on the saturated monohydride surface occurs in pairwise fashion from Si dimers. This pairing phenomenon has also been observed during thermal desorption from the Si(100)-2x1:H surface at

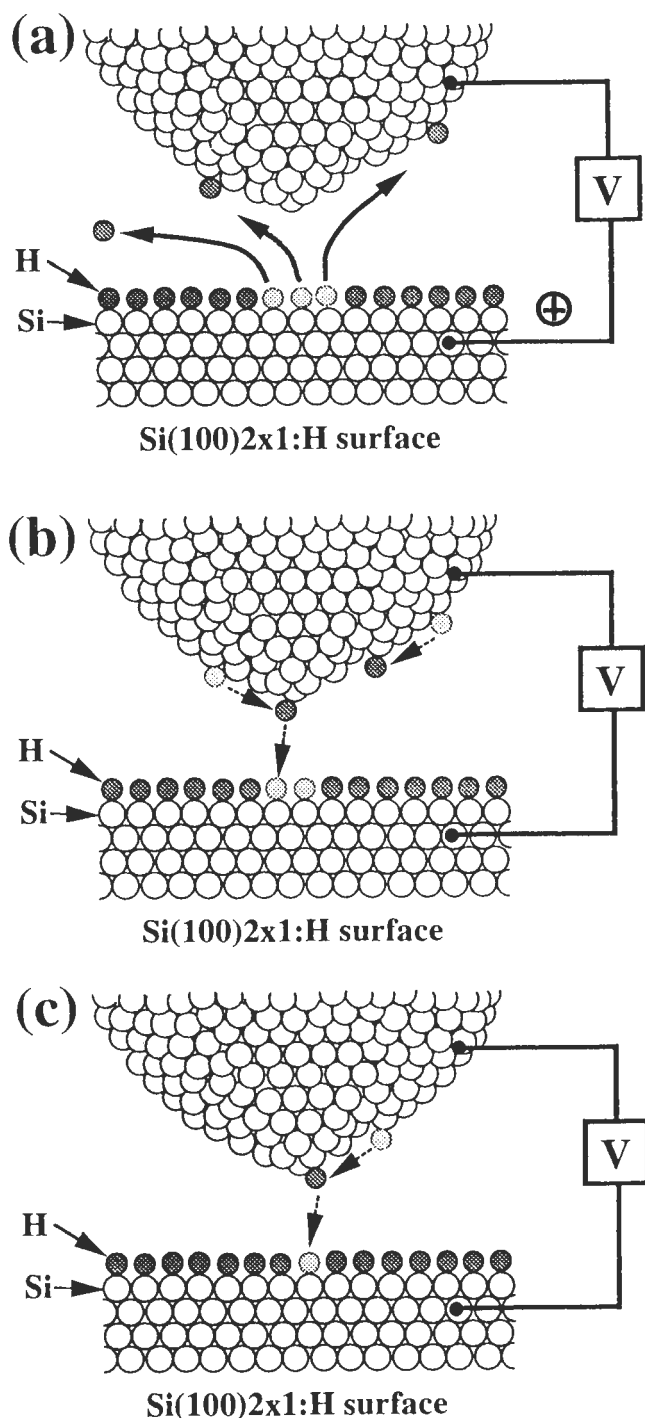


Figure 5. The sequence of hydrogen atom diffusion to the tip apex and followed to be deposited onto the surface. (a) Hydrogen atoms stick on the tip due to hydrogen extraction from the monohydride surface with positive sample voltage pulses. (b) The field-gradient-induced diffusion of hydrogen atoms to the tip apex is controlled by the application of a +3.5 V sample bias. (c) Hydrogen atom deposition occurs by the subsequent application of sample voltage pulses of -8.5 V for 300 ms at a constant current of 10 nA.

420–480°C [2], in which pairs of dangling bonds can be found localized on single Si dimers, suggesting that extraction involves the direct recombination of hydrogen atoms from the dimers of the monohydride surface. It was found that this paired structure of hydrogen extraction on the Si(100)-2x1:H surface may also exist on two dimers of two adjacent dimer rows, as indicated by E in Figure 2b, which may correspond to a paired open circles C in Figure 4.

Redeposition of Individual Hydrogen Atoms

In a previous study of time-resolved Si atom redeposition from a tungsten tip on a silicon surface at room temperature [7, 16, 17], we found that single Si atoms near the apex of the tip can be dislodged and diffused to the tip apex due to a bias after the pulse, and then redeposited onto the surface by the subsequent application of appropriate voltage pulses. Thus, the possibility of such atom deposition depends not only on the amplitude and duration of the applied voltage pulse, but also strongly on the bias conditions after the pulse. The polarity and amplitude of the bias after the pulse may control the direction of this field-gradient-induced diffusion and the diffusion speed of atoms to the tip apex, respectively. We successfully increased or suppressed Si atom redeposition by simply increasing and decreasing the applied bias after the pulse.

In this study of individual hydrogen atom redeposition, we used the same method to redeposit hydrogen atoms onto the hydrogen-terminated Si(100)-2x1:H surface from a tungsten tip to fill out surface Si dangling bonds preferably with negative sample voltage pulses. The sequence is illustrated schematically in Figure 5. Some of hydrogen atoms extracted from the Si(100)-2x1:H surface by the application of voltage pulses will stick to the tip, as illustrated in Figure 5a. After placing the tip on a new predetermined atomic position, we apply three sample voltage pulses of -8.5 V for 300 ms to deposit hydrogen atoms back to the surface, as illustrated in Figures 5b and 5c. During approximately 300 ms intervals of pulses, a sample bias of 3.5 V was applied for the purpose of diffusing hydrogen atoms to the tip apex, and a tunneling current of 10 nA is always maintained while a voltage pulse is being applied. Figure 6 shows an example of the hydrogen deposition. One of two bright spots (as indicated by F in Figure 6a) that may correspond to a pair of Si dangling bonds becomes doubly occupied following deposition of hydrogen atoms as shown in Figure 6b.

Conclusions

We have previously demonstrated that adsorbed hydrogen atoms on the hydrogen-terminated Si(100)-2x1:H

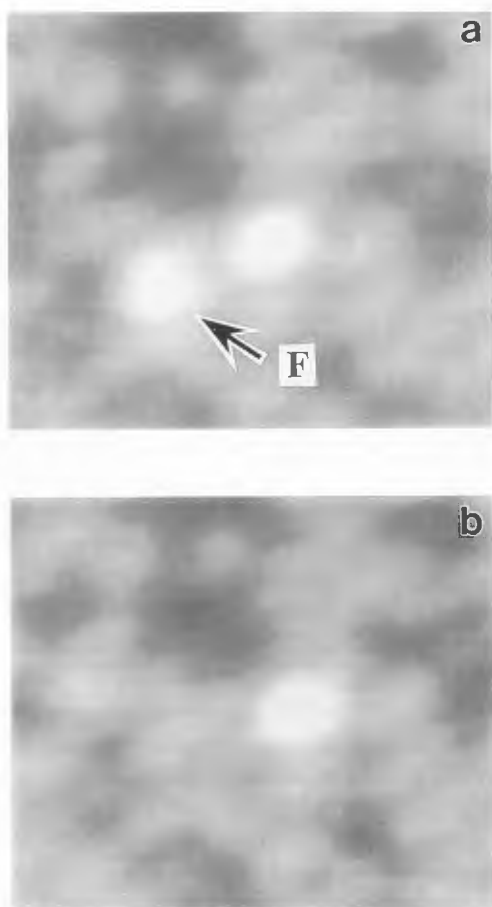


Figure 6. An example of hydrogen atom deposition on the Si(100)-2x1:H surface. One of two bright spots as indicated by F (a), corresponding to a pair of Si dangling bonds, "disappears" following deposition of hydrogen atoms (b). The deposition process is described in Figure 5. Hydrogen deposition from an STM tip is more likely achieved by the negative sample pulse. The STM image (6.6 nm x 5.6 nm) was taken at a sample voltage of -2 V and tunneling current of 0.3 nA.

surface can be extracted by applying both positive and negative voltage pulses between the tip and sample. This implies that the mechanism for manipulating hydrogen atoms on this surface is due to not only electron excitation but also field evaporation. Under our experimental conditions, there is a pairing effect that forces hydrogen atoms to leave the surface in pairs from individual dimers or from adjacent dimers of neighboring dimer rows. By controlling the bias conditions between the tip and the sample after hydrogen extraction, some of the hydrogen atoms transferred to the tip will diffuse back to the tip apex, where they can be redeposited on

the surface by subsequent voltage pulses. We found that hydrogen atom extraction can be achieved by a voltage pulse of either polarity, but redeposition is more likely with negative sample bias.

Acknowledgments

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References

- [1] Aono M, Kobayashi A, Grey F, Uchida H, Huang DH (1993) Tip-sample interactions in the scanning tunneling microscope for atomic-scale structure fabrication. *Jpn J Appl Phys* **32**: 1470-1477.
- [2] Boland JJ (1991) Evidence of pairing and its role in the recombinative desorption of hydrogen from the Si(100)-2x1 surface. *Phys Rev Lett* **67**: 1539-1542.
- [3] Boland JJ (1991) The importance of structure and bonding in semiconductor surface chemistry: hydrogen on the Si(111)-7x7 surface. *Surf Sci* **244**: 1-14.
- [4] Eigler DM, Schweizer EK (1990) Positioning single atoms with a scanning tunneling microscope. *Nature* **344**: 524-526.
- [5] Eigler DM, Lutz CP, Ridge WE (1991) An atomic switch realized with the scanning tunneling microscope. *Nature* **352**: 600-603.
- [6] Grey F, Kobayashi A, Uchida H, Huang DH, Aono M (1993) Nanolithography and atomic manipulation on silicon surfaces by STM. In: *The Technology of Proximal Probe Lithography*. Marrian CRK (ed.). SPIE Optical Engineering Press, Bellingham, WA, USA. pp. 74-99.
- [7] Grey F, Huang DH, Aono M (1994) The sound of one atom hopping: atomic manipulation on silicon surfaces by STM. *Phil Mag* **70**: 711-720.
- [8] Hamers RJ, Koehler UK (1989) Determination of the local electronic structure of atomic-sized defects on Si(001) by tunneling spectroscopy. *J Vac Sci Technol A* **7**: 2854-2859.
- [9] Higashi GS, Chabal YJ, Trucks GS, Raghavachari K (1990) Ideal hydrogen termination of the Si(111) surface. *Appl Phys Lett* **56**: 656-658.
- [10] Hosoki S, Hosaka S, Hasegawa T (1992) Surface modification of MoS₂ using an STM. *Appl Surf Sci* **60/61**: 643-647.
- [11] Huang DH, Yamamoto Y (1996) Manipulating atoms one by one with a scanning tunneling microscope. *Surf Rev Lett* **3**: 1463-1472.
- [12] Huang DH, Yamamoto Y (1996) Si dimer

chain on Si(100)-2x1:H surface fabricated by scanning tunneling microscope. *Jpn J Appl Phys* **35**: 3734-3737.

[13] Huang DH, Uchida H, Aono M (1992) Fabrication of atomic-scale structures on the Si(111)-7x7 using a scanning tunneling microscope (STM). *Jpn J Appl Phys* **31**: 4501-4503.

[14] Huang DH, Uchida H, Aono M (1994) Scanning tunneling microscope fabrication of atomic-scale memory. *Jpn J Appl Phys* **33**: L190-L193.

[15] Huang DH, Uchida H, Aono M (1994) Deposition and subsequent removal of single Si atoms on the Si(111)-7x7 surface by a scanning tunneling microscope. *J Vac Sci Technol B* **12**: 2429-2433.

[16] Huang DH, Grey F, Aono M (1995) Role of diffusion in atomic manipulation on silicon by scanning tunneling microscope. *Jpn J Appl Phys* **34**: 3373-3375.

[17] Huang DH, Grey F, Aono M (1995) Atom-scale manipulation of Si(111)7x7 by STM: dependence on polarity and amplitude of voltage pulses. *Surf Sci* **331-333**: 365-369.

[18] Lyding JW, Shen T-C, Hubacek JS, Tucker JR, Abeln GC (1994) Nanoscale patterning and oxidation of H-passivated Si(100)-2x1 surfaces with an ultrahigh vacuum scanning tunneling microscope. *Appl Phys Lett* **64**: 2010-2012.

[19] Lyo I-W, Avouris Ph (1991) Field-induced nanometer- to atomic-scale manipulation of silicon with the STM. *Science* **253**: 173-176.

[20] Mo YW, Kariotis R, Swartzentruber BS, Webb MB, Lagally MG (1990) Scanning tunneling microscopy study of diffusion, growth, and coarsening of Si on Si(001). *J Vac Sci Technol A* **8**: 201-206.

[21] Morita Y, Miki K, Tokumoto H (1991) Direct observation of SiH₃ on a 1%-HF-treated Si(111) surface by scanning tunneling microscopy. *Appl Phys Lett* **59**: 1347-1349.

[22] Shen T-C, Wang C, Abeln GC, Tucker JR, Lyding JW, Avouris Ph, Walkup RE (1995) Atomic-scale desorption through electronic and vibrational excitation mechanisms. *Science* **268**: 1590-1592.

[23] Uchida H, Huang DH, Grey F, Aono M (1993) Site-specific measurement of adatom binding energy difference by atom extraction with the STM. *Phys Rev Lett* **70**: 2040-2043.

[24] Uchiyama T, Tsukada M (1993) Atomic and electronic structure of the Si(001) surface induced by hydrogen-adsorption. *Surf Sci Lett* **295**: L1037-L1042.

[25] Uchiyama T, Tsukada M (1994) Theory of scanning tunneling microscopy and spectroscopy on hydrogen-adsorbed Si(100) surface. *J Vac Sci Technol B* **12**: 2205-2208.

[26] Yamada T, Yamamoto Y, Harrison WA (1996) Energy band of manipulated atomic structures on an insulator substrate. *J Vac Sci Technol B* **14**: 1243-1249.

Discussion with Reviewers

H. Shigekawa: The quality of Figures 2, 3 and 6 is poor. For example, it is difficult to compare the structures of bright spots in them with the structural models in Figure 5. They must be replaced with better ones.

Authors: We are sorry; at this time, we cannot provide other better Figures 2, 3 and 6 because these are our best images for the first demonstration of individual hydrogen extraction and deposition on the Si(100)-2x1:H surface by the application of voltage pulses.

H. Iwasaki: Is there any reason why the STM images of hydrogen manipulated surfaces are not well resolved compared to the clean surface in Figure 1?

Authors: This may be due to slightly modification of the STM tip after atom manipulation that may result in the lower resolution of the STM images.

M.G. Lagally: There is a lack of explanation of "field-induced mechanism" proposed, or term introduced there is vague, for the interpretation of why negative sample bias can also be used to extract H atoms from Si(100)-2x1:H surface.

H. Iwasaki: The conclusion that extraction of hydrogen atoms is "due to not only electron excitation but also field evaporation" seems to barely come from the observed facts that those atoms could be extracted by applying positive or negative voltage pulses between the STM tip and the sample surface.

Authors: As stated in **Mechanism of Hydrogen Manipulation**, the field-induced mechanism of atom extraction with an STM tip has already been demonstrated [1, 6]. When an appropriate negative sample bias is applied, the hydrogen atoms on the Si(100)-2x1:H surface can be extracted as positive ions through field evaporation.

M.G. Lagally: Why the feature E in Figure 2 is interpreted as hydrogen desorption from two dimers of two adjacent dimer rows (C in Figure 4)? Is it possible from two dimers of the same dimer row? Since it is in the vicinity of surface defects as observed from Figure 2a, is there any influence on the appearance because of the defects?

Authors: In order to answer the second part of this question, we have to do more experiments with careful analysis. At present, we do not know whether there is any influence on the appearance of hydrogen extraction because of surface defects. As for the first part of this question, from the images of Figure 2, the hydrogen-desorbed pattern (E in Figure 2) is located between two adjacent dimer rows, so we suppose there may be a possible formation of hydrogen desorption as C in Figure 4.

Reviewer IV: It seems there are two kinds of contrast in Figure 3.

Authors: This is because the image of the Si(100)-2x1:H surface in Figure 3 has a S_B step at the upper left area. Then there should be two kinds of contrast. It is the same as shown in Figure 1b.

J.R. Tucker: The experiments of Shen *et al.* [22] were performed by scanning an STM tip across the surface under constant DC current conditions at each voltage. Here we found that single H-atoms were often desorbed (not pair), the desorption occurred only for positive sample voltage (not for negative voltage), and plots of tip retraction versus applied voltage indicated a maximum electric field near ~ 5 -6 V in a regime where evidence for electron-stimulated desorption (not field emission) is most compelling. Do you think that large transient electric fields which are generated at the onset of the voltage pulses in the present work (before the feedback loop can respond) might account for the apparent disagreements between these two studies?

M.G. Lagally: People have demonstrated that both single H atom and paired H atoms extraction from a Si dimer can be realized with STM by applying positive bias to the monohydride sample surface [22]. Therefore, it is possible that only paired H desorption can occur under certain experimental conditions.

Authors: In a previous study of field-induced atom manipulation, we found that the field overshoot can be as much as 25% during the voltage pulse because the voltage rise time remains much faster than the tip retraction [28]. This may be one of the apparent disagreements between these two studies.

H. Iwasaki: The authors state that hydrogen deposition from an STM tip is achieved more preferably by the negative sample pulse. Could they explain as to how this is achieved?

Authors: According to our experiments, we can redeposit hydrogen back to the surface only by the application of the negative sample pulses after hydrogen is diffused to the tip apex. The physical mechanism of hydrogen deposition is electronic excitation [22] or electron bombardment. Single hydrogen atoms can be redeposited onto the Si(100)-2x1:H surface from an STM tip that has already picked up hydrogen atoms from the surface through the application of prior voltage pulses, to fill out surface Si dangling bonds preferably with negative sample voltage pulses. This phenomenon is similar to single Si atom deposition on the Si(111)-7x7 surface through field evaporation [15]. We have performed several experiments with different positive sample biases, as well as different tunneling currents, however, so far, we have not succeeded in depositing hydrogen atoms back to the

surface.

J. Shapter: A figure of the differing spectroscopy of the hydrogen-terminated and clean Si surface used to prove the adsorption of the H would add to the paper. I realize it is not new but I think it still adds to the paper.

Authors: The differing spectroscopy is arranged in another paper (under preparation). Here, we would only give a result "Our work shows that tunneling resistivities on the Si(100)-2x1:H surface are about 1.5 and 5.5 times larger than those on a clean Si(100)-2x1 surface at -2.0 and +2.0 V, respectively." at the end of **Experimental Apparatus**.

J. Shapter: The redeposited H could simply be from H adsorbed on the tungsten from the background gas in the system. The background gas in the UHV systems tends to be mostly H or H₂. Have the authors done any experiments to examine the origins of the redeposited H?

Authors: Kuramochi *et al.* [30] demonstrated that hydrogen atoms are supplied to a Pt tip through dissociative adsorption of gaseous H₂ and are deposited onto the Si(111)-7x7 surface by field evaporation. But this is not our experimental case, because we used a different UHV chamber for the preparation of surface hydrogen termination, namely, there is no background gas in the STM chamber, so the origin of the redeposited hydrogen is from the STM tip that has already picked up hydrogen atoms from the Si(100)-2x1:H surface through the application of prior voltage pulses.

J. Shapter: Why the use of differing tunneling currents at positive and negative sample biases?

Authors: This is because there are different thresholds of field, F , for hydrogen extraction at positive and negative sample biases. A tunneling current corresponds to the tip-sample separation, s , and field $F = V/s$. Therefore, differing tunneling currents at positive and negative sample biases have to be used for producing different thresholds of field [29].

Reviewer IV: Tunneling current should change when pulse voltage is applied to the tip!

Authors: In the first paragraph of **Extraction of Individual Hydrogen Atoms**, we state: "The STM current feedback loop maintains a constant current of 2 nA for positive sample voltage pulses or 10 nA for negative ones while the extraction voltage pulse is applied". These mean that when a voltage pulse is applied, the STM tip has to retract a certain distance to maintain the pre-set constant tunneling current due to a current feedback loop. But, at the leading and trailing edges of the pulse, since the feedback loop cannot respond as fast as

the applied pulse, a large transient current occurs.

H. Iwasaki: In the case of redeposition of hydrogen, is there similar effect to the "pairing effect" in extraction observed? Is there any evidence that both of the two Si dangling bonds are filled by the deposition of hydrogen atoms in Figure 6.

H. Shigekawa: Is a pair of dangling bonds formed by the pairing effect filled by hydrogen atoms simultaneously in the redeposition process? If so, do you have any idea about the mechanism?

Authors: When we deposit hydrogen atoms back to the Si(100)-2x1:H surface, we found that one bright spot, corresponding to one paired Si dangling bonds, was always filled out. This phenomenon implies that there may be a pairing effect in the hydrogen deposition, although the exact origin is unclear at present.

Reviewer IX: How did the authors verify that a monohydride surface was formed? Is the recipe guaranteed not to produce di- and trihydride? I know this was a problem in some of Higashi's earlier work. The rationalization for single versus double hydrogen occupancy of the Si dimers following dry etching is not clear.

Authors: As indicated in the fourth paragraph of **Experimental Apparatus**, a monohydride Si(100)-2x1:H surface looks similar to that of a clean Si(100)-2x1 surface. The surface structures of dihydride surface (Si(100)-1x1:H) and alternating monohydride and dihydride surface (Si(100)-3x1:H) are different from the monohydride surface (Si(100)-2x1:H); it can easily be distinguished from the STM images. On the other hand, during the hydrogen termination of the Si(100)-2x1 surface by the dry etching process, described in the third paragraph of **Experimental Apparatus**, the monohydride Si(100)-2x1:H surface can be formed by a saturation exposure to atomic hydrogen at approximately 360°C, and the Si(100)-1x1:H surface and the Si(100)-3x1:H surface, then, at approximately 130°C and at room temperature, respectively [27]. Higashi's work related to the wet chemical method on the Si(111) surface [9] is different from ours. During the dry etching process, at room temperature, hydrogen atoms singly occupy the Si dimers while at higher temperature (approximately 360°C) these atoms tend to pair up [2]. This pairing phenomenon is due to a π -bonding interaction which favors pairing individual dangling bonds on the dimers.

Reviewer IV: Electron excitation mechanism is suggested at low voltage of less than 5 V. The experimental results shown here deal with high voltages of around 8 V. The author seems to be comparing quite different regime.

Authors: The electron excitation mechanism of hydrogen extraction from the Si(100)-2x1:H surface by the application of a positive sample bias proposed by Shen *et al.* [22] has two voltage ranges: (1) direct electronic excitation of the Si-H bond at high bias (> 6.5 V); and (2) multiple vibrational excitation by tunneling electrons at low bias (about 2 to 5 V). The experimental result shown in Figure 3 in this paper was obtained by the application of the positive sample voltage pulse of 8 V. This implies that the physical mechanism for this hydrogen extraction in Figure 3 is related to direct electronic excitation. For details, please see **Mechanism of Hydrogen Manipulation**.

M.G. Lagally: Authors state that "... each bright spot in Figure 3 corresponds to one Si dimer ...", and thus, hydrogen extraction in this study occurs in a pair-wise fashion. However, from Figure 3, all 5 "bright spots" apparently are not equal in size, and the resolution of the image is not adequate to establish the claim whether each bright spot corresponds to one dimer.

H. Iwasaki: Could the authors distinguish whether a pair of hydrogen atoms are vacant or single atom is vacant on the Si(100)-2x1:H surface?

H. Shigekawa: Do you have any idea for the observed pairing effect in the hydrogen extraction process?

Authors: We measured the sizes of the bright spots in Figure 3 and found that the sizes of each of the bright spot are approximately the same as the width of the dimer row, as well as the single dimer. Therefore, it is reasonable to consider that each bright spot corresponds to one Si dimer. Boland [2] has also observed this pairing phenomenon during thermal desorption from the Si(100)-2x1:H surface at 420-480°C.

J. Shapter: Is the electron bombardment of the tip necessary for some reason since the ultimate usefulness of the tip will be determined by the subsequent cleaning at the sample? The authors indicate that the electron-bombardment heating is indispensable. An explanation of why it is essential in this case may be appropriate.

Reviewer IX: How did the authors know there was atomic-scale contamination of the tip; specifically how was this contamination removed?

Authors: For single atom manipulation, one of the most important techniques is to prepare a clean and stable tip. In a previous study [13], we have demonstrated that the cleanliness and structure of the tip at atomic scale are of importance in extracting single atoms and proposed electron bombardment with field evaporation as a method such for preparing a tip suitable for single atom manipulation. Usually, after the electron bombardment, the tip is already good enough for imaging the surface, but it is still contaminated at the atomic

level and not good enough for well-controlled atomic-scale processing. When one uses such a tip only after electron bombardment to manipulate single atoms, one may find that in the beginning of the atom manipulation process by the application of a voltage pulse between the tip and sample, foreign contamination will be deposited from the tip onto the surface. This indicates that the tip is contaminated at the atomic scale. However, if an appropriate voltage pulse is repeatedly applied, one finds that the contamination deposited from the tip is rapidly reduced and finally a clean and stable tip is obtained.

Additional References

- [27] Boland JJ (1992) Role of bond-strain in the chemistry of hydrogen on the Si(100) surface. *Surf Sci* **261**: 17-28.
- [28] Grey F, Huang DH, Kobayashi A, Snyder EJ, Uchida H, Aono M (1994) Time-resolved atomic-scale modification of silicon with a scanning tunneling microscope. *J Vac Sci Technol B* **12**: 1901-1905.
- [29] Kobayashi A, Grey F, Williams RS, Aono M (1993) Formation of nanometer-scale grooves in silicon with a scanning tunneling microscope. *Science* **259**: 1724-1726.
- [30] Kuramochi H, Uchida H, Aono M (1994) Local hydride formation of the Si(111)-(7x7) surface by hydrogen atoms deposited from a scanning tunneling microscope tip. *Phys Rev Lett* **72**: 932-935.