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Preparation of an Ultraclean and Atomically Controlled Hydrogen-Terminated Si(111)-(1×1) Surface Revealed by High Resolution Electron Energy Loss Spectroscopy, Atomic Force Microscopy, and Scanning Tunneling Microscopy: Aqueous NH_4F Etching Process of Si(111)

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We propose an improved *wet chemical* process for preparing a high-quality hydrogen-terminated Si(111)-(1×1) surface and show an atomically ordered and ultraclean surface without carbon and oxygen contamination. The vibrational properties and surface morphology are investigated by high-resolution electron energy loss spectroscopy (HREELS), atomic force microscopy (AFM), and scanning tunneling microscopy (STM). The HREELS spectra and images of AFM and STM reveal the precise aqueous NH_4F etching process of Si(111) and indicate the high controllability of steps and terraces at the atomic scale. The surface cleanliness and morphology strongly depend on the etching time. At the etching time of 10 min, we obtain an ultraclean and atomically ordered surface with wide terraces of 36 ± 7 nm step distance. It is confirmed by AFM and STM that 1.0% ammonium sulfite is useful for removing dissolved oxygen in the 40% NH_4F etching solution and for preparing a high-quality H:Si(111)-(1×1) surface with a low density of etch pits. The onset of tunneling current and the gap of 1.39 eV are measured by scanning tunneling spectroscopy. There is no peak at -1.3 eV in comparison with the previous report [Phys. Rev. Lett. **65** (1990) 1917]. [DOI: 10.1143/JJAP.46.5701]

KEYWORDS: silicon, hydrogen termination, HREELS, AFM, STM

1. Introduction

A clean and ordered surface is a prerequisite for basic surface studies as well as many technological processes. Furthermore, the control of steps and terraces is necessary for good epitaxial overgrowth. Methods for the low-temperature preparation of clean surfaces are required to fully enable low-temperature fabrication processes on silicon. The hydrogen-terminated Si(111)-(1×1) [H:Si(111)-(1×1)] surface is one of the candidates. In 1990, Higashi *et al.* successfully produced the H:Si(111)-(1×1) by *wet chemical* process.[1] After this report, the H:Si(111)-(1×1) surface became a prototype of the passivated surface for many experimental and theoretical studies. However, there had been few systematic investigations of both the vibrational properties and surface morphology of H:Si(111)-(1×1) for practical use.

According to previous reports, there are five important issues in preparing a high-quality H:Si(111)-(1×1) substrate. First, the initial Si(111) wafer must be clean without any organic contamination to form a uniform oxide layer.[2,3] Second, the structure of the H-passivated surface strongly depends on the nature of the initial silicon oxide layer.[4,5] Third, the etchant of NH_4F is better than HF for atomically flat and smooth surfaces.[6–9] Fourth, the aqueous NH_4F etching process of Si(111) surface strongly influences the cleanliness and surface morphology of H:Si(111)-(1×1).[4,10–13] Finally, it is important to remove the dissolved O_2 from the NH_4F etching solution.[12,14–18]

There are two ways to investigate the H:Si(111)-(1×1) surface: one is vibrational study by infrared absorption spectroscopy (IRAS), and the other is morphological study by scanning tunneling microscopy (STM) or atomic force microscopy (AFM). The above-mentioned works were independently performed by IRAS[1,4,7] and STM/AFM[3,6,8–10,13–17] and it is hard to obtain a good H:Si(111)-(1×1) substrate with a fragmentary knowledge of each process. For example, Jakob *et al.* reported that the etching for 5 min in the 40% NH_4F etchant is optimal for the production of a highly homogeneous H:Si(111)-(1×1) surface. This result was estimated by a narrow IR absorption linewidth of 0.71 cm^{-1} of the Si–H stretching mode at 2084 cm^{-1} [4] and, up to now, the etching time is still believed to be an optimal etching time.[12] There should be morphological information for use in the study of epitaxial overgrowth as well as many technological processes. We need a precise recipe for a reproducible and high-quality H:Si(111)-(1×1) substrate.

To estimate the cleanliness of H:Si(111)-(1×1), we used high-resolution electron energy loss spectroscopy (HREELS) instead of IRAS. Over the past two decades, the IRAS has been used as a preeminent technique for studying semiconductor surface and interface passivation and resolves the key issues to prepare a high-quality H:Si(111)-(1×1).[1,4,5,7] In the case of silicon, the sensitivity is very low below 1500 cm^{-1} due to the multiphonon absorption bands.[19,20] The major contaminant of H:Si(111)-(1×1) is oxygen. Authentic infrared spectra of SiO_2 exhibit peaks at approximately 1100, 800, and 400 cm^{-1}, which are assigned to Si–O–Si asymmetric stretching mode, symmetric stretching mode and bending (rocking) mode, respectively.[21] Up to now, the oxidation of H:Si(111)-(1×1) is studied

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by the side bands of the Si–H stretching mode at 2084 cm^{-1} [22–24] and IR is unable to detect the three main oxygen related peaks. HREELS has a wide spectral range and high sensitivity for the vibrational excitations at surfaces.[25] It is easy for HREELS to detect the oxygen-related peaks and other contaminant peaks.

For the high potential applicability of HREELS for H:Si(111)-(1×1) study, Dumas and Chabal,[26,27] and Stuhlmann *et al.*[28] observed the H:Si(111)-(1×1) prepared using the same recipe.[1,4,6,7] They clearly showed the Si–O–Si asymmetric and symmetric stretching modes. Recently, Yamada *et al.* measured the HREELS spectra of H:Si(111)-(1×1) but still present a clear peak of the Si–O–Si symmetric stretching mode.[18] Until now, no one has succeeded in removing the oxygen-related peaks from the HREELS spectra of H:Si(111)-(1×1) surface.

In this report, first, we reconsider the preparation process of H:Si(111)-(1×1) and propose the improved recipe. Second, we measure the HREELS spectra of H:Si(111)-(1×1) to estimate the cleanliness. The spectra indicate that the surface is ultraclean without carbon and oxygen contamination. Third, we observe the surface morphology by AFM and STM to investigate the aqueous NH_4F etching process and to control the steps and terraces. This observation reveals the atomically controlled ordered surface of H:Si(111)-(1×1). Finally, the surface electronic density of states is measured by scanning tunneling spectroscopy (STS).

2. Experimental Procedure

The vibrational spectra were measured by HREELS (Δ0.5, Specs) in ultra high vacuum (UHV).[29] The surface morphology in a large scale of 10 μm was observed by the contact mode of AFM (NanoScope IIIa, Digital Instruments) in air, and the atomic-scale morphology by the constant-current mode of STM (VT-STM, Omicron) in UHV. A liquid nitrogen-cooled sorption pump and a turbo-molecular pump were used for the evacuation of the load-lock chamber. The sorption pump is useful for removing oil vapor from a mechanical pump and we always turned off the ion gauge to avoid contamination from the ionized residual gas.

The samples were cut to $10 \times 8\,mm^2$ in size from a 0.6-mm-thick commercial n-type Si(111) wafer (P doped, 3–8 Ω cm, Shinetsu Handotai). The H:Si(111)-(1×1) surfaces were prepared by an improved version of wet chemical treatment reported by Yamada *et al.*[18] It includes three processes. First, the surface was cleaned by successive washings with trichloroethylene and acetone in an ultrasonic bath for 10 min. Then, we put the sample in the boiled ultrapure water (Millipore Mili-Q) for 20 min. Second, a uniform sacrifice oxide layer was formed at the Si(111) surface in a SPM solution (sulfuric acid and hydrogen peroxide mixture; three parts of concentrated H_2SO_4 and one part of 30% H_2O_2 heated at 120 °C) for 10 min. SiO_2 thickness of 10 nm was formed with this process. We rinsed the Si(111) surface thoroughly in running ultrapure water and dried by N_2 gas after the formation of the oxide layer. Third, the SiO_2 film was etched at room temperature using 40% w/w NH_4F (Morita Chemical, Japan). The purity of NH_4F was necessary for eliminating hydrocarbon contamination. Furthermore, we added 1.0% w/w of $(NH_4)_2SO_3$ to the solution to reduce O_2 dissolved from the atmosphere.[15,16] The etching period was varied from 0 to 30 min to investigate the time evolution of the surface morphology and vibrational properties. The surface was strongly hydrophobic after 5 min of etching and was stable in air for at least some hours. No further sample treatment was necessary even in UHV to achieve the best sample quality for HREELS and STM. All of the measurements were carried out at room temperature.

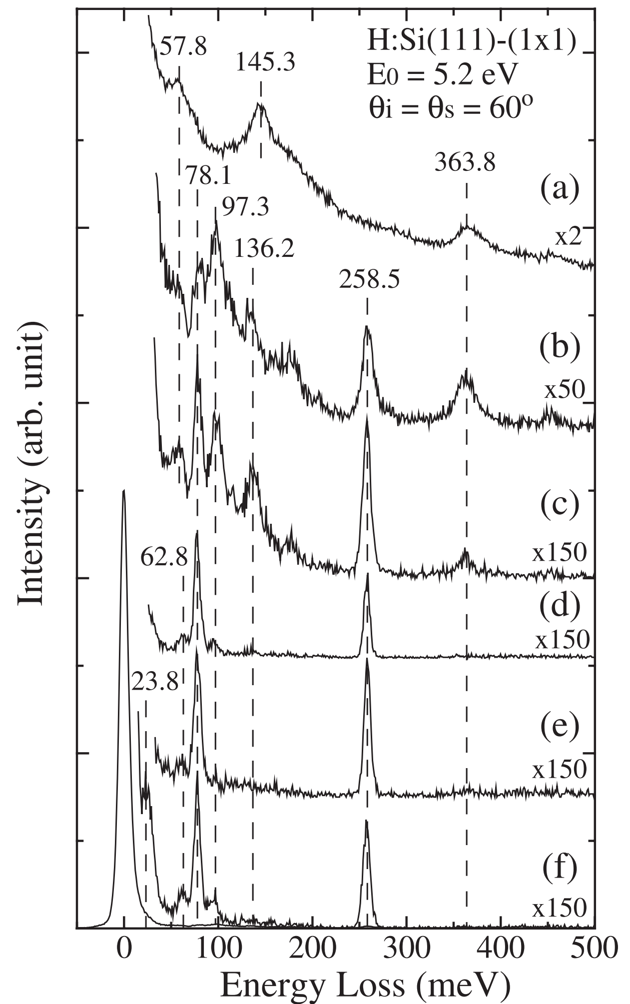

Fig. 1. HREELS spectra of H:Si(111)-(1×1) with specular reflection geometry ($\theta_i = \theta_s = 60°$). The etching time is 0 min (sacrifice oxide layer) (a), 1 min (b), 2 min (c), 5 min (d), 10 min (e), and 15 min (f). The incident energy of the electron beam is 5.2 eV and the FWHM of the elastic peak is 21 meV for (a), 13.0 meV for (b), and 7.3 meV for (c) to (f). The FWHM's of the loss peaks are the same as those of elastic peaks without the 363.8 meV peak in (b).

3. Results and Discussion

3.1 *HREELS spectra of H:Si(111)-(1×1)*

Figure 1 shows HREELS spectra of the H:Si(111)-(1×1) surface prepared by the procedures mentioned above with different etching time. The primary energy of the incident electron beam (E_0) was 5.2 eV, and the incident angle (θ_i) and the scattering angle (θ_s) of the electron beam were 60°. The angles are measured from the surface normal and the dipole scattering is dominant in this specular configuration.[25] These spectra encompass the peaks associated with

all of the adsorbed species on the specimen, including the impurities. Peaks are clearly resolved at 57.8, 78.1, 97.3, 136.2, 145.3, 258.5, and 363.8 meV in (a)–(c), and at 23.8, 62.8, 78.1, 97.3, 136.2, and 258.5 meV in (d)–(f). These energy losses are assigned to the terminating H species, residual oxide film, and other impurities by referring to previous findings.

It is easily recognized that the eminent peaks at 78.1 and 258.5 meV are associated with the H–Si bending mode and the H–Si stretching mode, respectively, as the energy loss previously assigned by Dumas and Chabal[26,27] and Stuhlmann *et al.*[28] Similar frequencies for H–Si stretching mode are given in early works by infrared reflection spectroscopy[1,30] and H–Si bending mode using the recently developed IR spectrometer.[20]

Another major peak on Si is that of silicon oxide. The peaks at 136.2 (145.3), 97.3, and 57.8 meV in Figs. 1(a)–1(c) correspond to the Si–O–Si asymmetric stretching mode, symmetric stretching mode and bending mode, respectively.[21] Hydrocarbon contaminants exhibit C–H stretching vibrations around 2950 cm^{-1}, associated with the 363.8 meV peak in the spectra. Other relatively weak peaks in Figs. 1(d)–1(f) peaked at 23.8 and 62.8 meV are considered to be surface phonon modes when we refer to the result of phonon measurements by Stuhlmann *et al.*[28] and by Kato *et al.*[29]

These spectroscopic results indicate the evolution of the surface structure. The spectrum of a sacrifice oxide layer shows the Si–O–Si rocking, asymmetric stretching modes and CH_x stretching mode. After the etching time of 1 or 2 min, the SiO_2 islands and the clean H:Si(111)-(1×1) surface coexist, including the carbon contamination. After 5 min, the clean H:Si(111)-(1×1) surface is already formed but there is still the Si–O–Si symmetric stretching mode at 97.3 meV. The oxygen-related peak disappears at 10 min and reappears at 15 min. The loss intensity of 258.5 meV is the strongest at 10 min. The carbon impurities were on the surface of the oxide layer and disappeared simultaneously with the removal of the oxide layer.

The results indicate that the initial stages of SiO_2 etching are the same as that reported by Jakob *et al.*[4] After 5 min of etching in 40% NH_4F solution, the SiO_2 layer is almost removed and a highly homogeneous H:Si(111)-(1×1) surface is formed. However, the HREELS spectra show that the surface still has oxygen contamination and that we obtained an ultraclean H:Si(111)-(1×1) surface at 10 min of etching.

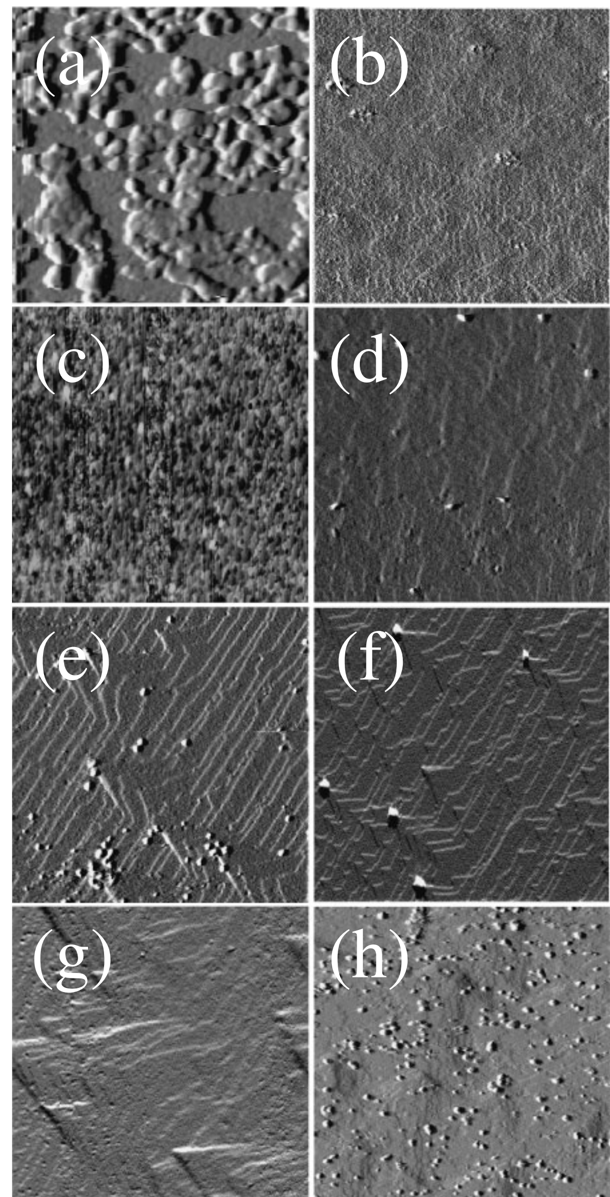

Fig. 2. AFM images of H:Si(111)-(1×1). The etching time is 1 min (a), 3 min (b), 5 min (c), 7 min (d), 10 min (e), 11 min (f), 20 min (g), and 30 min (h). The (a), (c), and (g) are topographic images and the others are differential images to intensify the step edges. The area is 1 × 1 μm^2. At 10 min in (e), we clearly see the atomically flat terraces separated by relatively straight steps and triangular terraces. Hines *et al.* named the triangular terraces as hillocks and the hillock growth in (g) is the hallmark of rapid kink etch at straight steps.[11]

3.2 *AFM and STM images of H:Si(111)-(1×1)*

AFM observation was performed on the H:Si(111)-(1×1) surface to correlate the surface morphology with the HREELS spectra. Figure 2 shows AFM images for the different etching times. We cut the samples close to each other from the Si(111) wafer and etched at the indicated times. At an etching time of 1 min, the oxide film is removed partially and small SiO_2 islands are observed, as shown Fig. 2(a). The heights of the islands are between 2 and 3 nm. At 3 min, the oxide layer is almost removed and the small zigzag steps appear partially in Fig. 2(b). The step is preferentially etched and the residual oxides are mainly at terraces and at the small dots. The surface morphology evolves with increasing etching time. At 5 min, the surface is uniformly etched and we find the parallel and zigzag steps in Fig. 2(c). The morphology is very similar to that shown in Fig. 1(c) of ref. 16. The distance between the steps is approximately 33 ± 8 nm along the left-up to right-down corner of Fig. 1(c). At 10 and 11 min, we clearly see the parallel and straight steps of 36 ± 7 nm distance and big triangular terraces (hillocks). The triangular terraces grow until 20 min in Fig. 2(g) and at 30 min, suddenly disappear. The surface is undulated and many small dots (pits) are shown in Fig. 2(h). Garcia *et al.* concluded that well-aligned step lines formed in NH_4F solution are always parallel to the $[11\bar{2}]$ direction.[12] According to the results, we estimate that the step lines seen in Fig. 2 are parallel to the $[11\bar{2}]$ direction.

By taking into account the development of the etch hillocks model proposed by Hines,[10–12] the AFM images of Figs. 2(e)–2(g) are clearly understood. The model assumes the flat terraces and triangular terraces, i.e., hillocks, as shown in Figs. 2(e) and 2(f). The kinks at the step are the etching sites. If the kink etch at straight steps is faster than that at one side of the triangular hillocks, the hillocks grow due to the retardation of flat terraces (straight steps) as shown in Fig. 2(g).

In contrast, the step lines in Figs. 2(c)–2(e) behave differently. The zigzag steps, i.e., smaller hillocks, decay and form straight step edges. There could be a two-step etching process from Figs. 2(c)–2(e) to 2(e)–2(g). It is observed that the wide smooth terraces are formed at 10 min of etching.

To investigate the atomic structure of this surface, we performed STM measurements of the H:Si(111)-(1×1) surface. Figure 3 shows the STM images of the H:Si(111)-(1×1) surface after 10 min of etching with three scales: $190 \times 190\,\text{nm}^2$ in (a), $9.0 \times 9.0\,\text{nm}^2$ in (b), and $20 \times 20\,\text{nm}^2$ in (c). The straight steps in Fig. 2(e) are resolved into the small etch morphology shown in Fig. 3(a). The average terrace width (step distance) is about 40 nm and the cross section shows that each height of the steps is a single Si atom step of 0.31 nm. We clearly observe the atomic image in Fig. 3(b). The observed lattice distance is 0.38 nm. It is very close to the crystallographic distance of 0.383 nm. We often find the dark areas on the terraces, in which 1×1 periodicity is reserved as shown in Fig. 3(c). They are not atomic voids but are considered to be due to electronic properties by impurities underneath.

To confirm the effect of $(NH_4)_2SO_3$, we etched the sample in 40% NH_4F without 1.0% of $(NH_4)_2SO_3$. The STM image is shown in Fig. 4. Although the surface is rather flat and smooth, where the height difference is below 0.8 nm, there are big etch pits and we hardly observe the atomic structure. The etching of Si(111) surfaces in NH_4F solutions containing dissolved O_2 loses the site specific etching process at step edges and the layer-by-layer etching process disappears; the etching of Si(111) surfaces in NH_4F solution containing dissolved O_2 occurs at step edges and terraces with equal probability and forms a rather smooth but atomically rough surface.[12] These results indicate that the $(NH_4)_2SO_3$ is useful for preparing atomically ordered smooth surface.

Finally, we measured the density of states using STS as shown in Fig. 5. Although we need some discussion about the interpretation of normalized dI/dV and the gap,[31] we simply estimate the onset of tunneling current: the gap is 1.39 eV from the normalized dI/dV. This is slightly bigger than the indirect bulk silicon band gap between Γ and Δ points of 1.11 eV.[32]

Up to now, the STS spectra of the H:Si(111)-(1×1) surface was reported by Becker *et al.*[33] The surface images clearly show the many contaminations, and the STS spectrum has a peak at -1.3 V. We consider that the present spectra shows that of a clean H:Si(111)-(1×1) surface.

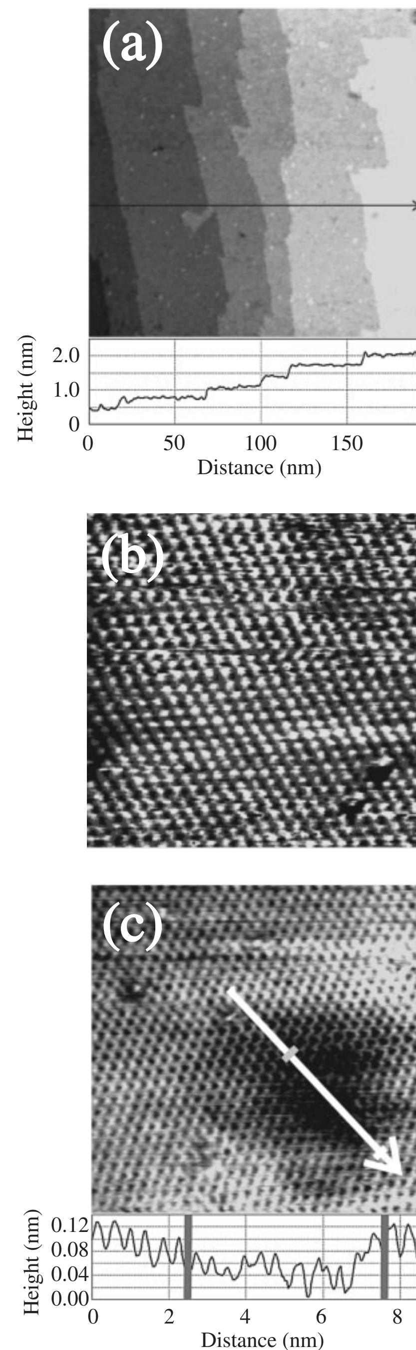

Fig. 3. STM images of H:Si(111)-(1×1) surface. The areas are $190 \times 190\,\text{nm}^2$ in (a), $9.0 \times 9.0\,\text{nm}^2$ in (b), and $20 \times 20\,\text{nm}^2$ in (c). $V = -2.14$ V and $I = 0.2$ nA in (a), $V = 2.67$ V and $I = 1.71$ nA in (b), and $V = -1.53$ V and $I = 0.56$ nA in (c). The cross sections indicated by arrows are shown.

4. Conclusions

We propose the improved preparation process of H:Si(111)-(1×1) by *wet chemical* method and characterized the vibrational properties and surface morphology by HREELS, AFM, and STM. The vibrational modes measured by HREELS reveal the precise aqueous NH_4F etching process of Si(111) and show that the ultraclean surface of H:Si(111)-(1×1) is formed after 10 min of etching. The AFM and STM images show that the surface is atomically ordered. The straight steps run parallel with the distance of 36 ± 7 nm. It is confirmed by AFM and STM that the 1.0% ammonium sulfite is very useful for removing oxygen from the 40% NH_4F etching solution and for preparing a high-quality H:Si(111)-(1×1) surface with low density of etch

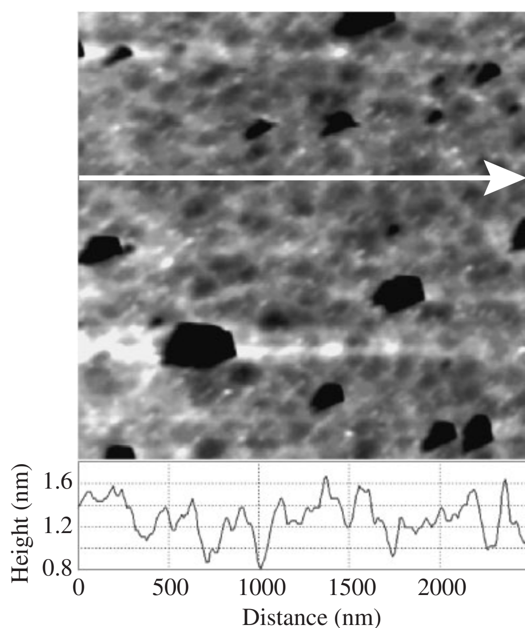

Fig. 4. STM image of H:Si(111)-(1×1) surface prepared by 40% NH_4F without 1.0% of $(NH_4)_2SO_3$. The area is $2.5 \times 2.5\,\mu m^2$. $V = 2.09$ V and $I = 0.19$ nA. The cross section indicated by the arrow is shown.

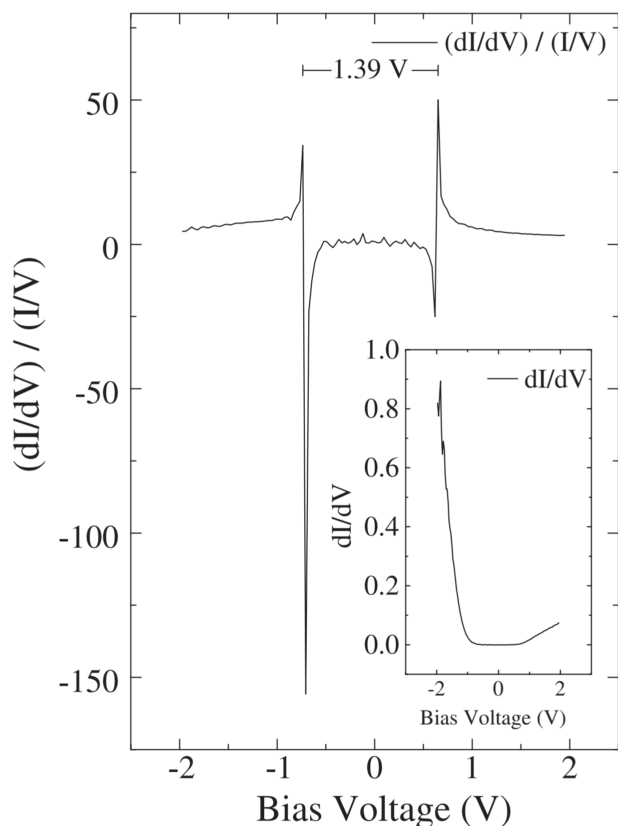

Fig. 5. STS spectrum of H:Si(111)-(1×1) surface: normalized dI/dV and the dI/dV curves. The spectrum is observed at a preset tunneling current of 0.50 nA and a gap voltage of −2.09 V.

pits. The onset of the tunneling current is measured by STS. The ultraclean and atomically ordered H:Si(111)-(1×1) can be used for surface science study as well as technological processes.

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