Preparation and Characterization of Ultraclean H:Si(111)-(1×1) Surfaces Studied by HREELS, AFM and STM-STS*

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We review a wet chemical process to prepare the high quality hydrogen-terminated Si(111)-(1×1) surface and show that the two key issues for the high reproducibility are the etching time and the oxygen in the etching solution. We add ammonium sulfite to remove the oxygen according to the previous report [Appl. Surf. Sci. 130, 146 (1998)]. To elucidate the optimal etching time, the vibrational properties and the 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 NH4F etching process of Si(111) and indicate the high controllability of steps and terraces with atomic scale. The surface cleanliness and morphology strongly depend on the etching time. At the etching time of 10 min, we obtain an ultra-clean and atomically ordered surface with wide terraces of 36 ± 7 nm step distance. It is confirmed by AFM and STM that the 1.0% ammonium sulfite is useful to remove dissolved oxygen in the 40% NH4F etching solution and to prepare a high quality HSi(111)-(1×1) surface with low density of etch pits. The measurement of scanning tunneling spectroscopy (STS) shows the Schottky diode character of the surface. This surface is well applied to the initial stages of the nano-particle and film growth of Ag atoms and Pentacene molecules. [DOI: 10.1380/ejssnt.2009.557]

Keywords: Silicon; Hydrogen termination; HREELS; Atomic force microscopy; Scanning tunneling microscopy

I. INTRODUCTION

A simple reproducible process for contamination free, flat, and well-ordered semiconductor surface is important for fundamental surface science as well as many technological processes. Since the silicon surface is attractive for surface science and nanotechnology, a further improved preparation is expected to promote the development of fundamental and advanced research. Silicon is a basic substance for manufacturing electronic devices. Silicon surfaces with controlled steps and terraces will be the good template for epitaxial overgrowth. The hydrogen-terminated Si(111)-(1×1) [H:Si(111)-(1×1)] surface is one of the candidates for broad applications.

A wet chemical method by 40% NH4F solution is the well-known hydrogen-termination technique for Si(111) surfaces. From early 1990s [1], the studies about the high quality surface has been carried out intensively, and now the technique have been established. The obtained surface has (1×1) structure and typical passivated properties to some extent. However, the surface cleanliness and reproducibility are not enough to realize a wide range of application.

We have carefully read the previous reports, and find five key points in preparing a high-quality H:Si(111)-(1×1) substrate; the cleanliness of initial Si(111) wafer [2, 3], the initial situation of the silicon oxide layer [4, 5], the preferable etchant as NH4F, not as HF [6–9], the evolution of the cleanliness and surface morphology on H:Si(111)-(1×1) during etching [4, 10–13], and the influence of dissolved O2 in etchant solution [12, 14–18]. Especially, the time evolution of etching nature and the infection by the dissolved O2 in etching solution are still unclear. As approaches to removal of the dissolved O2, two methods have been reported. One is argon gas sparging by Wade and Chidsey [14], and the other is adding 0.5% (NH4)2SO3 to 40% NH4F by Fukidome and Matsumura [15]. The latter is easier than former, because the method is made by just solution preparation and don’t need any equipments.

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Nevertheless, the method should be improved. There are some visible contaminants and etching pits on surfaces in AFM observations.

To evaluate the prepared surface, both informations of surface contaminants and morphology are necessary. It is inadequate by depending on either-or information. The surface contamination can be estimated by surface vibrational spectroscopy. There are two methods for vibrational spectroscopy, such as infrared absorption spectroscopy (IRAS) and high resolution electron energy loss spectroscopy (HREELS). The former has advantages for ultra high energy resolution but has drawback for surface sensitivity. Hence, the IRAS measurements are usually done under multi-internal-reflection configuration [1, 4, 7]. The absorption of multi-reflected infrared light by Si bulk phonons make the signal-to-noise ratio decreasing except Si-H stretching mode at ~280 meV [19]. Recently single-pass transmission type of IRAS become to be able to use, and spectrum indicating peak of Si-H bending mode have been reported [20, 21]. But the case is limited, and the direct evaluation about contamination is generally still difficult. The characterization of oxygen related contamination by IRAS is mainly done by measuring the side bands of the Si-H stretching mode which arise from the oxidation [22–24]. On the other hand, HREELS has disadvantage for energy resolution, but has strong sensitivity for surface vibration. The actual HREELS performance of energy resolution is under several meV at present, which is difficult to observe the spectra with perfectly separated peaks, but enough to identify each vibrational mode on H:Si(111)-(1×1) surface. The strong sensitivity enables us to detect the small amount of surface contaminants. Therefore, it can be a more suitable tool to analyze the high-quality surface.

As methods for observing the surface morphology, there are two methods such as atomic force microscopy (AFM) and scanning tunneling microscopy (STM). The former has a capability for large scale monitoring and the latter has a quite well atomic resolution. Therefore AFM-STM combined observation show clearly the nature of surface for large scale and local morphology. Up to now, the previous reports have relied on IRAS [1, 4, 7] and STM/AFM [3, 6, 8–10, 13–17], independently.

On the above point of view, we have done the developments of preparation method for H:Si(111)-(1×1) surface by adjusting the time of etching and solution components. The quality of obtained surfaces has been verified by vibrational measurements using HREELS, and by morphological observation using AFM and STM also.

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 optimal etching time and efficiency of adding 1% (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}. 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\textsubscript{4}F etching process. The observed images reveal the atomically controlled ordered surface of H:Si(111)-(1×1). Finally, the tunnleing property is measured by scanning tunneling spectroscopy (STS). The STS spectrum shows the Schotky diode character.

II. EXPERIMENTAL

The details of apparatus and sample treatment have been explained in our previous reports [25, 26]. HREELS (Δ0.5, Specs) measurements have done in ultra high vacuum (UHV) situation. The large scale morphology observation is performed by the contact mode of AFM (NanoScope IIIa, Digital Instruments) at atmosphere, and the atomic-scale morphology by the constant current mode of STM (VT-STM, Omicron) in UHV. The UHV chambers were equipped with oil-free load-lock sample introduction systems to transfer specimen from the atmosphere to UHV without contamination. The first stage of each load-lock system is evacuated by liquid-N\textsubscript{2} sorption pump and turbomolecular pump. After evacuation from the atmospheric pressure, the pumping device is switched into a turbomolecular pump running at the top speed. We always turned off an ion gauge in load-lock systems to avoid contamination from the ionized residual gas.

The sample were cut from 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]. Firstly, the sample was degreased in a sequential ultrasonic bath of trichloroethylene and acetone for 10 min, and boiled in the ultrapure water (Millipore Mili-Q) for 20 min. Second, an 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\textsubscript{2}SO\textsubscript{4} and one part of 30% H\textsubscript{2}O\textsubscript{2} heated at 120°C) for 10 min. Then the sample was rinsed thoroughly in running ultrapure water and dried by N\textsubscript{2} gas blower. Finally, the SiO\textsubscript{2} film was etched at room temperature using 40% w/w of NH\textsubscript{4}F (Morita Chemical, Japan) with 1.0% w/w of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}. The various concentration of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} was checked and we optimised from the previous value, i.e., 0.5%, reported by Fukidome and Matsumura [15].

No further sample treatment was necessary even in UHV to achieve the best sample quality for HREELS and STM with the above-mentioned sample introduction systems.

The etching time was varied from 0 to 30 min for bringing out the etching time evolution, and we used 40% w/w NH\textsubscript{4}F as etching solution also for elucidating the efficacy of 1.0% w/w of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} for removing the O\textsubscript{2} dissolved from the atmosphere [15, 16].

III. RESULTS AND DISCUSSION

Figure 1 shows HREELS spectra of the H:Si(111)-(1×1) surface prepared with different etching time. The primary energy of the incoming electrons was set at 5.2 eV. The spectra were recorded in specular configuration to observe almost all of the surface vibrational modes through the dipolar scattering [27]. Peaks were 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).

The peaks at 78.1 and 258.5 meV are associated with the H-Si bending mode and stretching mode respectively, as previously assigned [28–30]. Each mode has been also
hydrocarbon contaminants corresponding to CH...

symmetric stretching mode and bending mode, respectively. The assignment of the peak at 97.3 meV had argument until now. The discussion about it is given later.

The weak signal at 364 meV in spectrum (a) comes from hydrocarbon contaminants corresponding to CH₄ (z = 1, 2, 3) stretching mode. Other relatively weak peaks at 23.8 and 62.8 meV in (d), (e), and (f) are considered to be surface phonon modes when we refer to the result of phonon measurement by Stuhlmann et al. [30] and by Kato et al. [26].

These spectroscopic results indicate the changeover of the surface structure. The spectrum shown in Fig. 1(a), which has the Si-O-Si bending asymmetric stretching modes and CH₄ stretching mode, represents the Si oxide layer with some hydrocarbon contaminants. After the etching time of 1 or 2 min, the SiO₂ islands and the clean H:Si(111)-(1x1) surface coexist, including the carbon contamination. After 5 min, the clean H:Si(111)-(1x1) 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. After 5 min of etching in 40% NH₄F solution, corresponding to the previous best time condition [4], the SiO₂ layer is almost removed and a highly homogeneous surface, but with oxygen contamination, is formed. Finally, an ultraclean H:Si(111)-(1x1) surface was obtained at 10 min of etching.

The efficacy of added 1% (NH₄)₂SO₃ is shown in figure 2. Figs. 2(a) and (b) correspond to spectra of surface etched by 40% NH₄F with and without 1% (NH₄)₂SO₃, respectively. Figs. 2(a) is the same as the spectrum as shown in Fig. 1(e). Figs. 2(c) and 2(d) is spectra taken from previous reports by Dumas et al. [28] and Stuhlmann et al. [30], in which the original way of etching by 40% NH₄F without 1% (NH₄)₂SO₃ was used [4]. Each etching time is 10 min for Fig. 2(c) and 2(d). And, each primary energy of the incident electron beam (E₀) was 5.2, 5.1, 5, and 6 eV, for Figs. 2(a)-2(d) respectively. The difference of each values of E₀ often causes cross-section to change drastically, but it is not so significant in this incident energy range (i.e., 4-6 eV) [29].

Previous reported HREELS spectra about H:Si(111)-(1x1) surfaces are usually the same as shown in Fig. 2(c) and 2(d) [28–30]. Our data, shown in Fig. 2(b), obtained for H:Si(111)-(1x1) surface prepared by 10 min of etching using 40% NH₄F, obviously duplicates these spectra.

It is the peak at 97.3 meV that makes distinct difference

FIG. 1: HREELS spectra of H:Si(111)-(1x1) with specular geometry (θᵢ = θₛ = 60°) from Ref. [25]. Each spectrum corresponds to the etching time of 0 min (a), 1 min (b), 2 min (c), 5 min (d), 10 min (e), and 15 min (f). The energy of incident electron is 5.2 eV.

FIG. 2: HREELS spectra of H:Si(111)-(1x1) prepared by etching for (a) 10 min in 40% NH₄F with 1% (NH₄)₂SO₃ added; (b) 5 min in 40% NH₄F; (c) and (d) 6.5 min in 40% NH₄F from Ref. [28, 30]. The incident energies of electron beam are (a) 5.2 eV; (b) 5.1 eV; (c) 5 eV; and (d) 6 eV. The spectra were recorded in the specular reflection geometry of θᵢ = θₛ = 60° for (a)-(c) and θᵢ = θₛ = 65.8° for (d).
FIG. 3: AFM images of H:Si(111)-(1×1) from Ref. [25]. 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), respectively. The area is 1×1 µm².

between spectrum of Fig. 2(a) and others. This difference should come from differences of surface preparation about the etching time and the etching solution component. In spite of difference of the etching times, the surface prepared by traditional NH₄F solution reveal the same vibrational spectra, shown in Figs. 2(b)-2(d). Therefore, it is obvious that added 1% (NH₄)₂SO₃ to 40% NH₄F work well to remove the dissolved O₂ from etching solution and enable to eliminate the 97.3 meV-peak.

In the past time, since the 97.3 meV-peak had shown clear shape and the cross section seemingly has correlated intensity to Si-H bending mode of 78.1 meV, the origin of this peak was ambiguous. There are some reports which referred the probability of the intrinsic mode on the clean surfaces arised from Fermi resonant vibration [28, 29] and contamination mode originated from hydrogen oxides [30]. We observed that the spectrum without any clear peaks at 97.3 meV independent from the intensity of the Si-H bending mode peak as shown in Fig. 2(a). It also shows that the spectra indicate no signals at the energy range from 400 to 500 meV, where the OH stretching mode should be. We conclude an origin of the vibrational mode at 97.3 meV is silicon oxide species.

From consideration about reducing ability of (NH₄)₂SO₃ as well as vibrational frequency matching, we assign the peak to the Si-O-Si symmetric stretching mode.

The comparison of these spectra indictsates an effect of (NH₄)₂SO₃ directly. The SO₃⁻⁻ ions in the etching solution react with the dissolved oxygen from atmosphere, and, on the prepared surfaces, the HREELS spectra show three peaks of hydrogen terminated surface origins.

Figure 3 shows AFM images for the different etching
times. The results show the real nature of surface indicated in HREELS spectra. The Figs. 3(a) and 3(b) show the etching process for removal of the SiO$_2$ film. The oxide film was removed perfectly until 3 min of etching. After 3 min, the surface morphology changes with increasing etching time. At 3 min, the surface is covered with zig-zag steps. To etching time of 7 min, as shown in Figs. 3(b)-3(d), the zig-zag shapes transform to straight. At 10 and 11 min, we clearly see the parallel and straight steps of 36 ± 7 nm distance and visible triangular terraces (hillocks). The triangular terraces grow until 20 min in Fig. 3(g).

The surface morphological evolution can be understood by site specific etching mechanism [10–12]. The morphology shown in Fig. 3(b) seems to reflect the initial interface between the substrate and oxide film. There should be many reactive defects and trihydride sites on the surface which can’t be detected by AFM resolution. The zig-zag shapes indicate that many kink sites exist in the step also. The defect and trihydride will turn to triangular etch pits through the following etching. These are found in Fig. 3(c). At the same time, the kink sites will be etched intensively, and the step turn to a crystallographically preferable shape which has straight parts and hillocks. Furthermore, when the step line moved by etching collied with etch pit, the step line will be straight.

Because a straight step is [112] step (step downside direction is alligned with [112]) and hillock step is [112] step, the etching rate of these steps are different from each other. These etching rate difference cause the hillock growth and the morphological changes into aggregated huge hillock. On the other hand, the hillock becomes smaller when the the [112] step or apex, so-called point site, of the hillock are etched. As shown in Figs. 3(e)-3(f), some hillocks have bright spots on the apices. In both AFM and STM measurements, we observed these spots repeatedly as nanometer-scale structures, with a typical height ranging 3–8 nm. From the etching process of removing the silicon oxide film as shown in Figs. 2(a) and 2(b), these spots seem to be residual SiO$_2$ islands. As a result, the hillock will be pinned at the SiO$_2$ point and more slowly decayed than other free hillocks. This hillock decay effect could cause the initial small hillocks desappearing as shown in Figs. 3(b)-3(e).

Finer morphology was obtained by STM measurements as shown in Fig. 4. Figs. 4(a) and (b) show the STM images of the H:Si(111)-(1×1) surface at 10 min of etching by NH$_4$F with 1% (NH$_4$)$_2$SO$_3$. On the other hand, Fig. 4(c) shows a STM image about the surface etched by NH$_4$F only.

Fig. 4(a) shows the microscopic step shape which is looked like a straight step in AFM observation. The average terrace width 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. The Fig. 4(b) is a result of atomic-scale observation. The observed a surface lattice constant is 0.38 nm, which corresponds to the 2D crystallographic lattice constant.

The difference between Fig. 4(a) and (c) clearly reveals the benefit of the added 1% (NH$_4$)$_2$SO$_3$ in the point of morphology. In Fig. 4(c), there are big etch pits and atomically flat terrace is hardly observed. The etching of the Si(111) surface in NH$_4$F solution containing dissolved O$_2$ loses the site specificity at step edges and the layer-by-layer etching process disappears; the etching of Si(111) surfaces in NH$_4$F solution containing dissolved O$_2$ occurs at step edges and terraces with an equal probability and forms a rather smooth but atomically rough surface [12].

The results of HREELS and STM indicate that the (NH$_4$)$_2$SO$_3$ is useful for preparing atomically ordered smooth surface without contamination.

We also measured a STS spectrum on H:Si(111)-(1×1) as shown in Fig. 5. This tunneling current-voltage (I-V) curve is well-known as Schottky diode character which was reported previously [33–35].

The hydrogen atoms bond with dangling bonds on the silicon surface, and there is no surface state which pins the Fermi level. This situation implies that the surface has a semiconductor Schottky barrier. The STM observation system mimics a Metal(tip)-Insulator(vacuum)-Semiconductor(silicon) [MIS] system corresponding to a Schottky diode. In our case, the wafer is n-type whose band bends upward near the physical surface, and the current from the tip to sample is diminished. The STS spectrum indicates that the surface is ideally terminated by hydrogen and the observed STM images of the surface is interpreted as the contrast of a diode current, not the direct wave function contour of hydrogen atoms.

**IV. CONCLUSION**

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. These results clearly show that two key issues, such as etching time and oxygen dissolved in the etching solution, are important to realize the reproducible sample preparation. The vibrational modes measured by HREELS reveal the precise etching process of Si(111) and show that the ultraclean surface of H:Si(111)-(1×1) is formed after 10 min of etching with 40% NH$_4$F added by 1% (NH$_4$)$_2$SO$_3$. 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 HREELS and STM that the 1.0% am-

http://www.sssj.org/ejsmnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejsmnt/)
monium sulfite is very useful for removing oxygen from the 40% NH₄F etching solution and 10 min is the optimal etching time for preparing a high quality H-Si(111)-(1×1) surface with a low density of etch pits. The tunneling current-voltage curve is measured by STS. The STS spectrum reflects the Schottky diode character which depends on doping type of semiconductor.

The ultraclean and atomically ordered H:Si(111)-(1×1) can be used for surface science study as well as technological processes. Up to now, this process has been applied for various film growth studies, such as Ag nanoparticles [36] and pentacene films [37–40].

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