

Rocking curves of reflection high-energy positron diffraction from hydrogen-terminated Si(111) surfaces

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Reflection high-energy positron diffraction experiments have been performed for Si(111) surfaces terminated with atomic hydrogen. From the rocking curve for the specular beam, the first to the fifth Bragg peaks were observed. The curve also showed an unanticipated dip in the total reflection region ($\theta < 1.4^\circ$), not found in the numerical analysis for the ideally hydrogen-terminated flat surface. This difference is attributed to the scattering of positrons by roughness and/or SiH₃ molecules on the surface, as confirmed in further numerical analysis.

INTRODUCTION

Reflection high-energy positron diffraction (RHEPD) is thought to hold potential in the surface study.¹⁻³ In particular, the change in the surface potential can be detected using the total reflection of a high-energy positron at a glancing angle of incidence.¹ Recently, we succeeded in obtaining clear RHEPD patterns using a hydrogen-terminated Si(111) surface.⁴ The appearances of the total reflection and the primary Bragg peak of positrons, which are not observed in reflection high-energy electron-diffraction (RHEED) experiment, were also confirmed from the rocking-curve analysis. Since positrons have a tendency to survey shallower layers as compared to electrons, the RHEPD intensity is more sensitive to the atomic arrangement at the topmost surface than the RHEED intensity. Thus the rocking curve analysis in RHEPD experiments is more simplified and less ambiguous than that in the RHEED experiments due to the suppressed contribution from a deeper layer. In this study, we investigated the structure of hydrogen-terminated Si(111) surfaces prepared by wet chemical methods using the RHEPD analysis in more detail.

Silicon (Si) surfaces terminated with atomic hydrogen are known to be stable against oxidation and impurity contamination even in air due to the passivation of surface dangling bonds. The hydrogen termination of Si surfaces by the wet chemical methods (e.g., HF acid etching) is one of the most important processes to obtain clean and inactive surfaces during device fabrication.⁵ Hydrogen-terminated Si surfaces are also useful as a substrate for molecular-beam epitaxial growth.

To reveal the structure of hydrogen-terminated Si surfaces, many extensive works have been performed with various approaches. Infrared absorption studies indicate that Si(111) surfaces, after etching by dilute HF solution, are terminated not only by monohydride ($\equiv\text{SiH}$) but also by dihydride ($=\text{SiH}_2$) and trihydride ($-\text{SiH}_3$).^{6,7} It was also found that Si(111) surfaces etched this way in dilute HF solution are well-ordered but microscopically rough.⁶⁻⁸ The flat terraces of the HF-prepared surfaces were reported to be termi-

nated mostly by trihydride. In fact, through the scanning tunneling microscope (STM) observations, the presence of the trihydride phase on the flat part of HF-prepared Si(111) surfaces was confirmed and a detailed structural model was proposed.⁹⁻¹¹ The existence of the trihydride phase on Si(111) surfaces was also indicated in RHEED and ultraviolet photoelectron spectroscopy (UPS) studies after exposing clean Si(111)- 7×7 surfaces to atomic hydrogen in an ultrahigh vacuum.^{12,13} A quite sharp infrared absorption peak at 2084 cm^{-1} , which was attributed to monohydride, was found using Si(111) surfaces treated by pH-controlled buffered HF solutions and boiled in ultrapure water after HF dipping.^{14,15} It was suggested that near ideally hydrogen-terminated Si(111) surfaces with few defects can be obtained by these methods. Indeed, the STM observation for Si(111) surfaces treated in this way confirmed the existence of monohydride.¹⁶ Morita *et al.* investigated the morphology of Si(111) surfaces finished either with NH₄F solution and pH-modified buffered HF solutions.^{17,18} Their results show that the Si(111) surfaces dipped in these solutions after repeating a cycle of oxidation by HNO₃ and its stripping by HF were atomically flat with terrace sizes of 20–60 nm. It was also shown that the defect density on terraces in the case of NH₄F dipping was much suppressed compared to the case of pH-modified HF dipping.

It is important to study the well-characterized hydrogen-terminated Si(111) surface to examine the capabilities of RHEPD experiment. We therefore performed RHEPD measurements using Si(111) surfaces finished by NH₄F. The first to fifth Bragg peaks with the total reflection region were observed. We also found a distinct structure in the total reflection region, which indicates the change in the surface potential by hydrogen-termination treatment.

EXPERIMENT

The specimens used in this study were cut from a Si(111) wafer ($15\times 15\times 0.5\text{ mm}$, $10\ \Omega\text{ cm}$, n -type). After degreasing and stripping the native oxide by 1% HF solution, they were subjected to the hydrogen-termination treatment. First, the

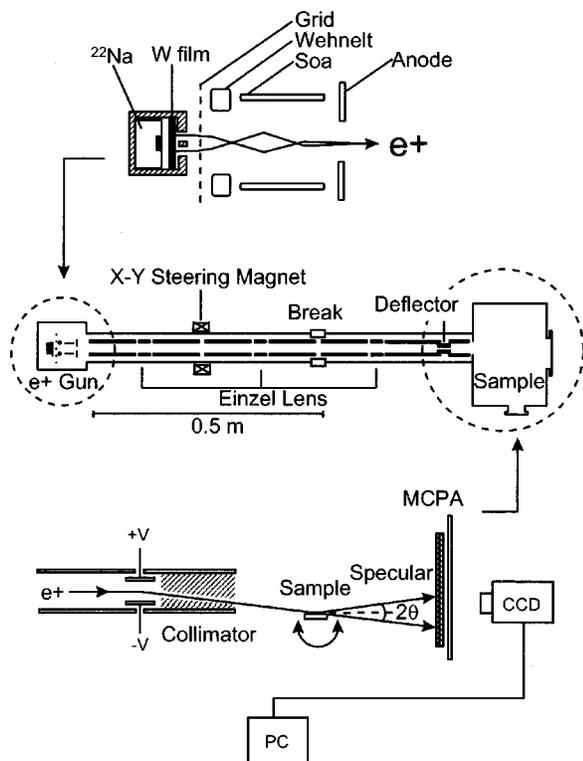


FIG. 1. Schematic drawing of the slow positron beam apparatus used in the reflection high-energy positron diffraction experiments.

specimens were boiled in concentrated HNO_3 to grow an oxide layer and subsequently the oxide layer was removed in 1% HF. After repeating this process three times, the specimens were finished by dipping in 40% NH_4F (0°C) for 20 min. The above procedure was proposed by Morita *et al.* to make a flat Si(111) surface terminated by monohydride.¹⁸ To confirm that the surface was actually terminated by atomic hydrogen, infrared absorption measurements were performed. The results showed that the absorption peak at 2084 cm^{-1} related to the local vibration of Si-H was fairly strong and those from SiH_2 and SiH_3 were not clearly observed. The atomic force microscopy (AFM) observation was also made to check the flatness of the surface. The mean roughness was determined to be less than a few \AA in terraces.

After the etching treatment, specimens were set in the vacuum chamber with a base pressure of 7×10^{-10} Torr. Reflection high-energy positron diffraction experiments were carried out using a 20-keV positron beam for the $[11\bar{2}]$ and $[1\bar{1}0]$ incidences. It is reported that diffraction spots disappeared in the one-beam condition (7.5° off from the $[11\bar{2}]$ direction) and therefore the vertical atomic displacement of the topmost surface could be determined from the rocking curve.^{19,20} We thus also made RHEPD experiments in this mode. Figure 1 schematically shows the positron beam apparatus used in this study. Fast positrons emitted from a ^{22}Na (~ 10 MBq) source are moderated at a tungsten film with a thickness of 5000 \AA . The slow positrons were electrostatically accelerated and transported using three Einzel lenses. After the electrostatic deflection, the beam was ultimately collimated to below 1-mm diameter using a 140-mm length stainless collimator. The final beam flux of the beam was approximately 3000 positrons/sec. The glancing angle θ was

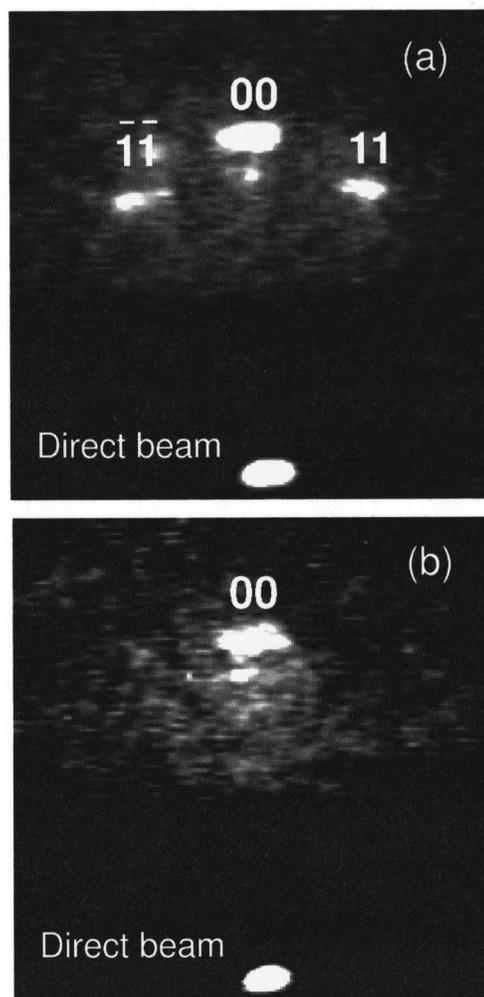


FIG. 2. RHEPD patterns from the Si(111) surface prepared by dipping in 40% NH_4F solution (0°C) after repeating a cycle of oxidation by boiling in HNO_3 and stripping the oxide layer by dipping 1% HF solution for three times for (a) the $[11\bar{2}]$ incidence and (b) one-beam condition (7.5° off from $[11\bar{2}]$). The glancing angle was fixed at $\theta = 4^\circ$.

changed by a mechanical rotator with an angular resolution of $\pm 0.1^\circ$. The reflected positrons were collected using a Hamamatsu F2226-24 type microchannel plate assembly with a phosphor screen. The phosphor screen images were observed by a charge-coupled device (CCD) camera connected to a personal computer. Rocking curves for specular beams were determined by measuring the beam intensity as a function of glancing angle.

RESULTS AND DISCUSSION

Figure 2 shows the RHEPD patterns obtained for the $[11\bar{2}]$ incidence and one-beam condition at $\theta = 4^\circ$. For the $[11\bar{2}]$ incidence, the (11) and $(\bar{1}\bar{1})$ spots with a specular spot were clearly observed. Since fractional order spots are not observed in the patterns, the Si(111) surface prepared by NH_4F solution maintains a 1×1 structure. This result is consistent with the previous work and also the low-energy electron-diffraction experiment.^{4,8} For the one-beam condi-

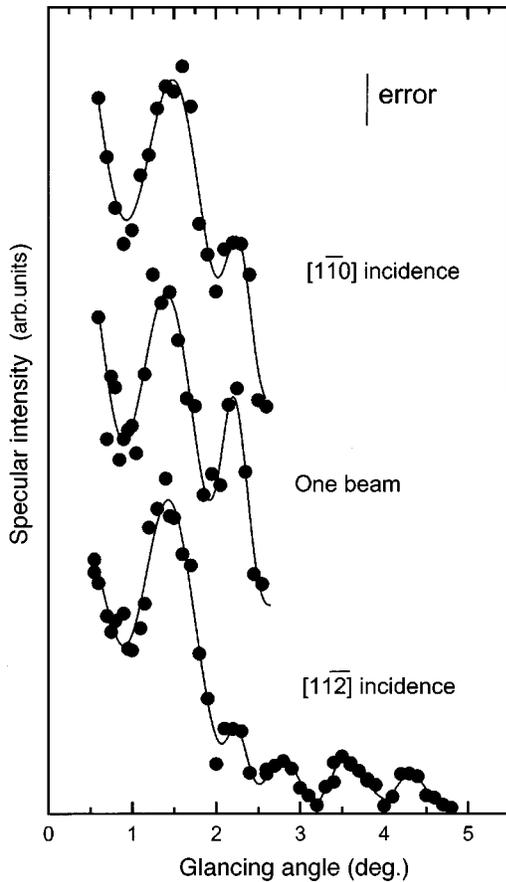


FIG. 3. RHEPD rocking curves from the Si(111) surface terminated by atomic hydrogen for the $[11\bar{2}]$ and $[1\bar{1}0]$ incidence and one-beam condition (7.5° off from $[11\bar{2}]$). The specimen was prepared by dipping in 40% NH_4F solution (0°C) after repeating a cycle of oxidation by boiling in HNO_3 and stripping the oxide layer by dipping 1% HF solution three times.

tion, diffraction spots disappear and only a specular beam is seen. This result certainly indicates that the transverse symmetry on an atomic plane vanishes in the one-beam condition. That is, the real atomic planes on which atoms discretely distribute may be considered as a virtual atomic plane on which atoms continuously distribute.^{19,20}

Figure 3 shows the RHEPD rocking curves for the $[11\bar{2}]$ and $[1\bar{1}0]$ incidences and also the one-beam condition. From the result for $[11\bar{2}]$ incidence, a series of peaks are seen at around 1.5° , 2.2° , 2.8° , 3.6° , and 4.3° . The Bragg condition is given by

$$E_0 \sin^2 \theta = 37.5n^2/d^2 + eV_0. \quad (1)$$

Here, E_0 is the energy of the positron, n is the integer, d is the atomic plane spacing, and eV_0 is the crystal inner potential.¹⁴ Taking E_0 , d , and V_0 to be 20 keV, 3.14 Å, and 12 eV, respectively, the first to the fifth Bragg peaks are expected to appear at 1.61° , 2.11° , 2.76° , 3.46° , and 4.20° from Eq. (1). The observed peak positions agree well with the calculated Bragg peak positions for the 111, 222, 333, 444, and 555 reflections. Although only the primary Bragg peak was observed in the previous work,⁴ the above result shows the appearance of the higher-order Bragg peaks. This

is due to the improvement of the angular resolution from $\pm 0.5^\circ$ to $\pm 0.1^\circ$. It is also indicated that the Bragg peak position itself may approximately conform to the Bragg equation. The primary Bragg reflection for Si(111) surfaces is a unique feature in the position diffraction experiments and not observed in the electron-diffraction experiment due to the refraction effect. The 222 reflection is forbidden in the kinematic theory due to the extinction rule. The appearance of the 222 reflection is explained as a dynamical effect.

The critical angle for the total reflection is given by

$$\sin \theta_C = \sqrt{eV_0/E_0}. \quad (2)$$

From this equation, θ_C is estimated to be 1.4° . Thus, when the rocking curve is taken below 1.4° , it should reflect the topmost surface state. In the total reflection region, a certain ‘‘dip’’ structure is found at around 1° . It seems that the structure in the total reflection region does not change with the incident direction. The similar structures in the total reflection region for the different azimuth imply that the specular beam intensity is not sensitive to the horizontal and vertical atomic positions on the top layer since most positrons are reflected on the top layer. The observed structure in the total reflection region cannot be explained by considering the specimen surface as completely flat.¹ A flat Si(111) surface would have an almost steplike surface potential. It is therefore inferred that the surface potential is changed from that of a flat Si(111) surface due to the hydrogen termination so that an interference effect occurs for reflected positron waves as discussed later.

To analyze the rocking curves in detail, the dynamical calculation was performed by the multislice method including five beams.²¹ In the selection of the surface structures for the calculation, the following experimental results and findings reported previously are taken into account.

For the present specimen, the infrared absorption peak related to Si-H vibration was strong and that related to SiH_3 vibration could not be clearly observed. It is therefore expected that the present Si(111) surface is flat on an atomic scale and the terraces are terminated mainly by monohydride. This conclusion is consistent with the reports that the Si(111) surfaces prepared by NH_4F solution contain one or two monolayer height steps and the typical terrace width is approximately 100 nm.^{17,18} Since the coherent length of the positron beam is 10–20 nm and hence much shorter than the terrace width, the effect of steps on the rocking curve should be weak. Considering the fact that the surface roughness is a few Å in the AFM observation, however, irregularities might exist on terraces and they affect the positron reflection intensity. Although trihydride may be a minority phase on the present specimen surface from the infrared absorption measurements, several reports show that it is a stable phase on the flat terraces by the wet hydrogen-termination treatment.^{9–11} The UPS study suggested that the trihydride phase becomes predominant in place of the monohydride phase during the etching of the Si(111) surface by atomic hydrogen in a vacuum.¹³

It is therefore natural to assume that the surface is basically terminated by monohydride but containing roughness. Then, we examined the following structural models in the calculation: (a) a Si(111) surface terminated only by monohydride (ideally hydrogen-terminated surface), (b) a Si(111)

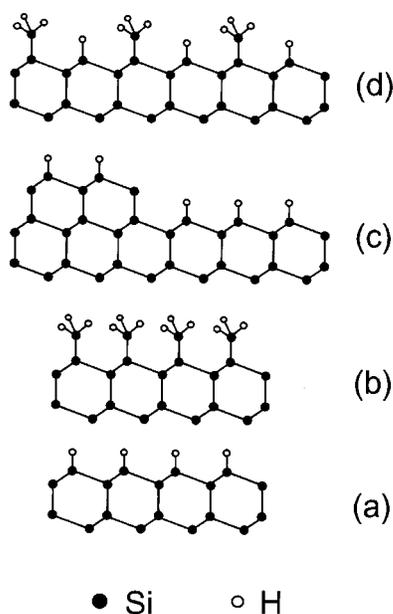


FIG. 4. $[1\bar{1}0]$ side view of atomic arrangement of (a) a Si(111) surface terminated only by monohydride, (b) a Si(111) surface terminated by trihydride, (c) a Si(111) surface terminated by monohydride containing bilayer roughness, and (d) a Si(111) surface terminated by monohydride with the adsorption of trihydride on the top layer assumed in the dynamical calculation. The fractions of SiH and SiH₃ of models (c) and (d) on the top layers are assumed to be 0.4 and 0.2, respectively, in the calculation. Si-Si and Si-H bond lengths are assumed to be 2.35 and 1.2 Å, respectively.

surface terminated only by trihydride (missing top layer), (c) a Si(111) surface terminated by monohydride containing bilayer roughness, and (d) a Si(111) surface terminated by monohydride with the adsorption of SiH₃ on the top layer. These structural models are schematically shown in Fig. 4. In the calculations, Si-Si and Si-H bond lengths were assumed to be 2.35 and 1.2 Å, respectively. No relaxations of interlayer distance were taken into account. Figures 5(a)–5(d) show the results of the computation based on the above models for the $[11\bar{2}]$ incidence with the experimental result. In models (c) and (d), the total fractions of SiH and SiH₃ on the top surfaces are set to be 0.4 and 0.2, respectively.

In each curve, the five peaks at around 1.4° – 1.5° , 2.0° – 2.1° , 2.6° – 2.8° , 3.4° , and 4.1° are commonly found. These correspond to the first to fifth Bragg peaks. The 444-reflection intensity is stronger than 333- and 555-reflection intensities. This effect is also evident in the kinematical calculation. The experimental curve shows that the 444-reflection intensity is slightly stronger than 333 and 555 reflections. However, the peak width of the 444-reflection width is somewhat broader than that of the calculated peak. The reason for the discrepancy of the 444-peak width between experiment and calculations is not obvious at present. To elucidate this point, it is necessary to evaluate the lattice relaxations and the effect of adsorption of positrons (i.e., inelastic processes) in detail. It is noted from the calculation that the specular intensity at $\theta > 3^{\circ}$ does not change significantly in the above surface models. On the contrary, the specular intensity at $\theta < 2^{\circ}$ strongly depends on the surface structure as discussed below.

As seen in Fig. 5(a), in the flat Si(111) surface terminated

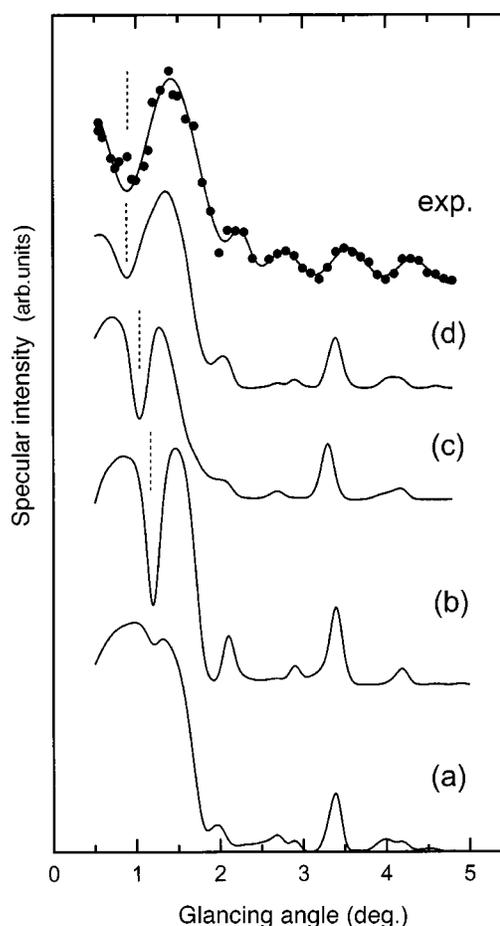


FIG. 5. Calculated RHEPD rocking curves for models (a)–(d) shown in Fig. 4 with the experimental result for the $[11\bar{2}]$ incidence. The dotted lines indicate the positions of dip as a guide for the eye.

with monohydride, no distinct structures appear in the total reflection region ($< 1.4^{\circ}$). The rocking curve is similar to that of the bulk Si(111) surface.¹ It is also known that the structure is insensitive to the azimuth from Fig. 5(a) and Ref. 1. Dynamical calculations for a system of potassium adsorbed on the Si(100)- 2×1 surface shows that a dip structure appearing in the total reflection region is due to a potential barrier by adsorbates.¹ However, the above calculation result suggests that the effect of adsorbed atomic hydrogen on the total reflection of positrons is negligible. The atomic scattering factor of a Si atom is about 5.3 Å and that of a H atom is about ten times smaller at $\sin \theta/\lambda = 0$.²² The above result is therefore qualitatively explained as the small potential barrier of adsorbed hydrogen atoms. Probably, the effect of hydrogen on the rocking curve is rather weak and appears at significantly small angles ($< 0.3^{\circ}$). Thus, the obtained rocking curves in the total reflection region are not expected for the ideally hydrogen-terminated flat Si(111) surface. It is found that the second model (terminated with trihydride) gives rise to a dip structure at around 1.2° despite the flat surface. Here, it was again revealed that hydrogen atoms on the top layer have almost no important contribution to the dip structure as well as model (a). The dip structure is resulting from the outermost Si layer. That is, the outermost Si layer provides a potential barrier in front of the step potential

of the bulk crystal just like an adsorbed layer. However, the agreement in the dip position and the line shape between the calculation and experiment is still inadequate in this model. In models (c) and (d), the dip positions shift toward smaller angle, i.e., they are located at around $\theta = 1^\circ$ and 0.9° , respectively. It is obvious from the result of model (c) that the dip appears at $\theta > 1^\circ$ if monolayer roughness is assumed. This was checked in the calculation. Taking the line shapes up to 2° into account, the agreement between the experiment and model (d) seems to be better. It is concluded that the present Si(111) surface prepared by NH_4F solution is mostly terminated with SiH but SiH_3 molecules remain. The origin of the roughness measured for terraces might be the adsorption of SH_3 molecules on the SiH surface

As shown in STM studies, the Si(111) surfaces treated by NH_4F solution are locally flat and monohydride is predominant.^{17,18} The above analysis based on the dynamical calculation, however, suggests that the surface may not be perfectly flat. Roughness resulting from irregularly hydrogen-terminated parts like SiH₃ is introduced to some

extent. The RHEPD rocking curves in the total reflection region show the presence of the irregularities on the surface.

SUMMARY

In summary, RHEPD experiments have been carried out using the hydrogen-terminated Si(111) surface prepared by NH_4F solution. The diffraction spots except the specular beam were found to vanish in the one-beam condition. This result coincides well with the theoretical prediction that the discrete atomic potential can be considered as an averaged potential in the one-beam condition. From the rocking curves for the specular beams, the first to the fifth Bragg peaks were confirmed to appear. Anomalous dip structures were observed in the total reflection region of the rocking curves. These structures could be explained by taking into account of surface roughness and / or adsorption of SiH_3 molecules on the SiH surface. From the comparison between experiment and calculations, it was shown that the rocking curve at low glancing angles is strongly altered depending on the surface structure.

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