Surface Structure and NH₄F-Etching Kinetics of Si (112) and (113)

Ken FUJITA and Norio HIRASHITA

VLSI Research and Development Center, Oki Electric Industry Co.,Ltd. Higashi-asakawa, Hachioji, Tokyo 193, Japan

Surface structures on stepped Si surfaces, with crystallographic orientation such as (112) and (113), treated in NH4F acid and buffered-HF solution were investigated using infrared light absorption spectroscopy and reflection high energy electron diffraction. It has been found that bilayer step edges with the dihydride on stepped surfaces fluctuate during NH4F etching and that the amplitude of the fluctuation is on an order of one row width of Si-H oscillators. It was inferred that stepped Si surfaces consist not only of {111} facets but also of {110} facets when the surfaces atomically roughen after buffered-HF etching.

I Introduction

Si surfaces treated in NH4F acid or buffered-HF (BHF) solution have been intensively studied because the surfaces are atomically flat¹) and hardly oxidized.²),³) Several investigators have studied the etching kinetics of Si with BHF using polarized infrared (IR) spectroscopy.⁴),⁵) However, their investigations have been restricted to the etching of on-axis or vicinal Si (111) surfaces. In order to refine the understanding of the etching process, it is desirable to study the etching of Si surfaces except for the vicinal (111), because the removal of Si atoms at step edges and kink sites on the surface is essential to atomically control surface flatness.

In the present study, we investigated surface structures on NH_4F - and BHF-treated Si (112) and (113) surfaces using IR absorption spectroscopy and reflective high energy electron diffraction (RHEED). It has been found that the NH_4F -treated surfaces consist of Si-H

rows which extend along the [110] and bilayer step edges whose fluctuation is comparable to the width of one row of Si-H oscillators on (111) terraces. The fraction of fluctuated step edges has been estimated by analyzing the absorption spectra. It has been inferred that Si (112) and (113) surfaces treated in BHF with pH of 6.4 become rough and consist not only of {111} facets but also of {110} facets.

II Experimental

All samples used were chemically oxidized in boiling HNO₃ prior to the etching with NH4F (pH=7.7) or BHF (pH=6.4) solutions. Here, the pH value of BHF was controlled by adding NH₄OH solution into NH₄F:HF (9:1 pH~5) solution. After the NH₄F- or BHF-treatment, the samples were loaded into the measuring instruments within 20 min. Surface morphology was checked by observing RHEED patterns from the [110] azimuth. Surface structures were investigated by

measuring IR absorption due to Si-H_x vibrations on the surface. Measurements were made by a conventional Fourier transform infrared (FTIR) spectrometer, purging optical paths with purified nitrogen at room temperature. The resolution was set to be 2 cm⁻¹. The sample surface was attached on a Ge attenuated total reflection prism. A polarizer was set before the Ge crystal. All absorption spectra were obtained by the light with electric field parallel to the incident plane because Si-H_x vibrating perpendicular to the surface is sensitively detected in this setup.

III Experimental results and discussion

Figure 1 shows the absorption spectra of Si (112) (a) and (113) (b) surfaces etched with NH4F solution for 4 min. In these spectra, the absorption lines labeled M', M, D and T are ascribed to the monohydride on Si (111) terraces, the monohydride at kinks of step edges, the dihydride on (001) facets and trihydride, respectively. Here, 'ss' represents the symmetric stretching mode and 'as' the antisymmetric stretching mode. The C mode is associated with the strained vertical dihydride species which has a strong repulsive interaction with the adjoining monohydride species at step edges.⁴⁾ The spectrum feature in Fig. 1(a), where the M' and C modes are dominant, shows that the bilayer step edges on the NH4F-treated Si (112) are almost straight without step bunching, resulting in a flat surface. The surface flatness was confirmed by observing the RHEED pattern shown in Fig. 2(a).

On the other hand, the D mode is conspicuous in Fig. 1(b), which indicates the presence of {001} facets on the NH4F-treated (113). On an ideal H-terminated Si (113) surface, bilayer step edges separate Si-H oscillators on (111) terraces into one row parallel to the step edges. Such a surface gives only the C mode absorption, because all Si-H oscillators are coupled with the adjacent

dihydride species of step edges. Thus neither M', M nor D mode should not appear for an ideally H-terminated (113). The origin of the $\{001\}$ facet can be explained by taking account of the fluctuation of step edges during etching as follows: It is known that Si atoms at kinks are preferentially removed during NH₄F etching rather than Si atoms at step edges.^{4),5)} However, Si atoms at step edges can be also removed because the ratio of the etching rate of Si atoms at kinks to the rate at step edges is not ideally infinite. This finite etching preference leads to the fluctuation of step edges during etching and inevitably gives rise to the step bunching, i. e., (001) facets on the (113). Thus the D mode absorption appears. The M' mode absorption seen in Fig. 1(b) is also due to the step fluctuation, because two rows of Si-H oscillators are neighboring at the fluctuated step.

The fluctuation amplitude can be discussed based on the spectrum of the NH₄F-treated (112). If the step edges fluctuate over the width of two rows of Si-H oscillators, the D mode should be conspicuous in Fig. 1(a) because the monohydride species is separated into only two rows by step edges on the (112). In fact, almost no D mode is observed in Fig. 1(a), which indicates that the fluctuation amplitude of step edges is restricted to within the width of one row of Si-H oscillators. The fraction x of bunching step edges per unit step length on the (113) can be estimated by comparing the intensities of the M' and C mode absorption in Fig. 1. The ratio of the M' mode oscillators to the C_i (i=1,2 and 3) mode oscillators on the (112) or (113) can be expressed by

$$N_{M'}^{(112)} / N_{C_{i}}^{(112)} = 2$$
(1)
and
$$N_{M'}^{(113)} / N_{C_{i}}^{(113)} = x / 1-x,$$
(2)

where N is the density of each oscillator. Herein, the effect of the step bunching is taken into account only for the (113), because the effect is expressed by x^2 for the (112). The absorption intensities I of the M' and C_i mode on the (112) and (113) have a relationship with the densities of Si-H oscillators as

$$\frac{I_{M'}^{(112)}I_{C_{i}}^{(113)}}{I_{C_{i}}^{(112)}I_{M'}^{(113)}} = \frac{\cos^{2}\theta_{M'}^{(112)}\cos^{2}\theta_{C_{i}}^{(113)}}{\cos^{2}\theta_{C_{i}}^{(112)}\cos^{2}\theta_{M'}^{(113)}} \frac{N_{M'}^{(112)}}{N_{C_{i}}^{(112)}} \frac{N_{C_{i}}^{(113)}}{N_{M'}^{(113)}},$$
(3)

where θ is the vibrating angle of the oscillators⁵). In order to obtain integrated intensity of each mode absorption, the spectra in Fig. 1 were decomposed by the least-square method. The peak energies of distinguished absorption components agree with previous report⁵) except for the C₂ mode.⁶) From eqs.(1) - (3) and obtained integrated absorption intensities, the fraction x was estimated to be 0.27, 0.23 and 0.17 from the C₁, C₂ and C₃ mode, respectively. These values are fairly close to each other, indicating that the fluctuation of step edges remains during NH₄F etching.

It is known that the morphology of stepped surfaces is atomically rough after etching in BHF solution with low pH values. However, detailed structures of the rough surface have not been well understood. To study



Fig. 1. Absorption spectra of Si (112) (a) and (113) (b) surfaces treated with NH4F acid. The absorption lines labeled M', M and D are associated with the vibrations of the monohydride on (111) terraces, the monohydride at kinks and the dihydride of straight step edges, respectively. Here, 'ss' represents the symmetric stretching mode and 'as' represents the antisymmetric stretching mode. The absorption peaks denoted by C are ascribed to the monohydride and the dihydride coupling at step edges.



Fig. 2. RHEED patterns of Si (112) surfaces treated in a NH4F acid (a) and buffered-HF (BHF) solution with a pH of 6.4.

the rough surface, (112) and (113) surfaces were treated in the BHF solution with a pH value of 6.4 for 4 min. Figure 2(b) shows the RHEED pattern of the (112) surface, which indicates that the surface is atomically rough. Figure 3(a) and (b) show the absorption spectra of the rough (112) and (113) surfaces, respectively. In the spectra, the M_{SS} mode absorption is most remarkable at 2088 cm⁻¹ and the M' mode absorption is also conspicuous at 2082 cm⁻¹. The latter absorption is associated with {111} terraces and/or facets. Although the former one is attributed to the step edges or kinks on {111} facets, the absorption is so intense that it is not likely to be attributed to only {111} facets, suggesting other kind of facets. The {112}, {113} facets and other facets, tilted from $\{111\}$ toward <112>, are ruled out for the candidate. This is because the spectrum feature similar to Fig. 1 should remain in Fig. 3 if these surfaces are stable in the BHF solution. The most plausible facet is the $\{110\}$, which can be terminated with only monohydride species, because the monohydride remains more than the dihydride and the trihydride during BHF etching.4),5)

Figure 3(c) shows the absorption spectrum of the (110) surface treated in the BHF solution (pH=6.4). Evidently only one absorption is noticeable at 2088 cm⁻¹ in this spectrum. This absorption can be attributed to the M_{ss} mode by considering Si-H bonding configurations on the (110) surface. If the (110) surface is atomically flat after BHF-treatment, the surface can be terminated with only monohydride species forming buckling structures which are similar to step edges with monohydride species on vicinal Si (111) tilted toward

[112]. On this surface, the symmetric stretching mode of the monohydride vibrates perpendicular to the (110) surface, while the antisymmetric stretching mode vibrates parallel to the surface. The observed absorption can be ascribed to the symmetric vibrations, because our optical







FIG. 4. RHEED pattern of the Si (110) surface treated in the BHF solution (pH=6.4).

setup sensitively detects only vibrations perpendicular to the surface. This assignment is supported by the fact that the absorption is observed at 2088 cm⁻¹ where the Mss mode is also observed for vicinal Si (111). Thus the sharp absorption in Fig. 3(c) implies that smooth (110) surfaces are formed during BHF-treatment. To confirm the surface flatness, a RHEED pattern was observed for the (110) surface treated in the BHF solution. In the obtained pattern, shown in Fig. 4, bright spots are on a concentric circle, which exhibits that the (110) surface is smoothly etched in the solution. These results indicate that H-terminated (110) surfaces are stable during BHF treatment and cause IR absorption at 2088 cm⁻¹. Therefore, it can be inferred that stepped surfaces such as the (112) and (113) are also covered not only with {111} facets but also with {110} facets after BHF-treatment.

IV Conclusions

In conclusion, we have investigated the surface structures on Si (112) and (113) surfaces etched in NH4F (pH=7.7) and BHF (pH=6.4) solutions using IR absorption spectroscopy and RHEED pattern observation It has been found that the step edges with the dihydride species fluctuate in the width of one Si-H row though NH4F acid provides almost straight step edges. It was inferred that stepped Si surfaces consist not only of $\{111\}$ facets but also of $\{110\}$ facets when the surfaces atomically roughen after BHF etching.

References

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