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Silicon-Monohydride Termination of Silicon-(111) Surface Formed by Boiling Water

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Aqueous HF etching of silicon surface removes surface oxide, leaving a silicon surface terminated inhomogeneously by silicon mono-, di, and trihydrides. We studied the effect of the immersion in water, following the HF etching, on the surface hydride structure on Si(111), by measuring Si-H stretching vibration using infrared absorption spectroscopy. Immersion in boiling water (100℃) for 600 s produces a surface homogeneously terminated with silicon monohydride normal to the surface and free of oxidation. We concluded that water can remove silicon dihydride and trihydride, and leave a silicon surface terminated with monohydride. The homogeneous surface has a low defect density of less than 0.5%.

Etching the surface oxide using an aqueous HF solution (HF in H_2O) is important to obtain a contamination-free and chemically stable silicon surface in device manufacture. The surface is mainly covered with atomic hydrogen just after HF treatment and fluorine remains as a minor spices.[1-3] Several researchers have found that the stability against oxidation disappears when the surface hydrogen desertion is achieved by heating the surface over 500℃[4-6] or by using electron beam bombardment.[7] They explain chemical stability in terms of the hydrogen termination of silicon dangling bonds. Chabal *et al.*[8] conclude that the HF treated silicon surface is inhomogeneous and atomically rough, based on observation of surface silicon hydride structures such as -SiH, -SiH_2, -SiH_3 as indicated by polarized attenuated-total-reflection (ATR) spectroscopy in the infrared region. This suggests that the surface must be studied to determine the microscopic surface reaction regarding such factor. This inhomogeneity has made it ambiguous to interpret experimental result in a view point from reaction of gas molecule with surface silicon hydrides. One possible solution is obtaining a homogeneous surface covered with a hydride structure.

Higashi *et al.*[9] have obtained an atomically flat Si(111) surface covered with silicon monohydride (-SiH) oriented normal to the surface using a basic solution (pH=9-10), a mixture of HF, NH_4F, and NH_4OH solutions. In this letter, we study the homogeneity of the hydrogen-terminated Si(111) surface during water immersion using a polarized ATR, and propose a new way to get a homogeneous, an atomically flat hydrogen-terminated silicon surface using the conventional HF solution and boiling water.

The experiment was carried out on 0.5 x 15 x 50 mm^3 nondoped Si(111) sample with 45-degree bevels on each of the short sides, cut from a 4-inch wafer. In our geometry, infrared radiation exiting the interferometer in a FTIR (Fourier transform infrared) spectrometer was internally reflected 100 times in the sample. The sample was cleaned by NH_4OH:H_2O_2 solution, rinsed in deionized water for 5 min, and dipped in 0.5% HF solution for 30 s to remove the thin native oxide formed during the previous cleaning procedure. The sample was placed in a dry nitrogen-purged environment and the spectrum was recorded. The same sample was then immersed in deionized water (>18 MW) and the reflection spectrum, R, recorded. This was done several times to obtain the spectrum as a function of the immersion time. The background reference spectrum, R_{ref}, was obtained from the chemically oxidized hydrogen-terminated surface using a boiling 50% HNO_3 solution at about 160℃. Because the surface state density for the chemically oxidized surface is negligible and no absorption occurs due to silicon hydride stretching vibrations in the spectrum.

After immersion in 1.5% HF solution (HF:H_2O=1.5:98.5), reflection spectrum, R, was recorded in wavenumbers from 4500 to 1500 cm^{-1}. The absorption was observed only from 2200 to 2000 cm^{-1}, in the region for Si-H

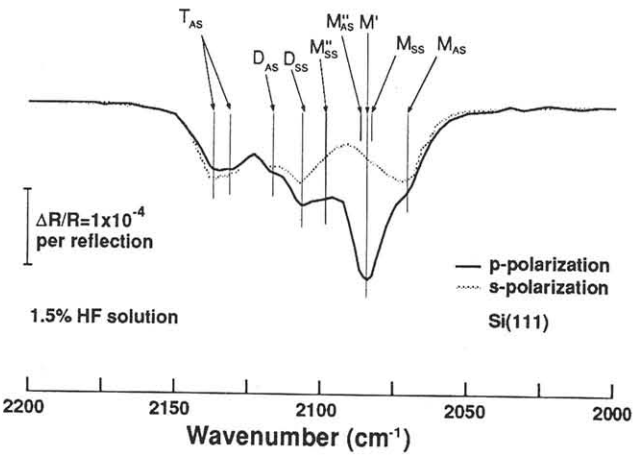

Fig. 1. Polarized infrared spectra of silicon-hydrogen stretching vibrations just after 1.5% HF treatment. We assigned these absorptions as a coupled -SiH on a double-layer step (M), a -SiH terminating dangling bond in [111] direction (M'), a coupled -SiH on a (100) step (M''), a coupled -SiH_2 on a (100) step(D), and a coupled -SiH_3 terminating dangling bond in [111] direction (T). SS and AS distinguish the symmetry and asymmetry mode of coupled vibrations. The resolution is 4 cm^{-1}.

stretching vibration. The reflectivity, $\Delta R/R_{ref}$, where $\Delta R=R-R_{ref}$, for p- and s-polarization condition are shown in Fig. 1. Several polarization-dependent absorptions appear. We also carried out an experimental for 1.5% (H:D)F solution for several isotope ratios of deuterium and hydrogen using heavy water. This experiment made it possible to decouple the interaction between neighbor hydrides and assign complex absorptions. Considering the polarization characteristics, the direction of surface silicon dangling bonds, and the model calculation for the coupled hydrides[8], we assigned these absorption as a coupled -SiH on a double-layer step (M), a -SiH terminating dangling bond in [111] direction (M'), a coupled -SiH on a (100) step (M"), a coupled $-SiH_2$ on a (100) steps (D), and a coupled $-SiH_3$ terminating dangling bond in [111] direction (T). This assignment is consistent with that reported previously[8], except for a slight shift of M' and a slight but distinguishable frequency splitting of T. These difference are discussed later in connection with remaining fluorine atoms. At this stage, we can confirm that the Si(111) surface after the HF treatment is atomically rough and inhomogeneouly covered with several silicon hydrides.

Following the 1.5% HF treatment, the sample was immersed in deionized water at 21℃. The dependence of the reflectivity on the immersion time is shown in Figs. 2(a) and (b). Both p-and s-polarized spectra clearly show the M' mode shift to a lower wavenumber of 2.8 cm^{-1} while remaining the spectrum shape for 5 s of immersion, and two T modes combine for 600 s of immersion. The wavenumbers for the other modes were unchanged. Immersion exceeding 600 s no longer changes spectra.

Our XPS (X-ray photoelectron spectroscopy) study of the HF-treated silicon surface clarified that very rapid removal of fluorine by water immersion. We found fluorine to be reduced from 12% ML to less than 5% ML after even 5 s of immersion.[10] This result suggests that the shift is related to the fluorine removal. The chemical state of the fluorine atom after HF treatment is discussed in detail elsewhere.[10]

With immersion time from 5 s to 1800 s, the M' mode is clearly strengthened but other modes, especially D, M", and M, decrease in p-polarization. These changes also observed in s-polarization as a decrease of the absorption area.

To clarify the etching effect on water temperature we immersed the sample into boiling deionized water (100℃) after 1.5% HF treatment. The spectrum changed drastically with the immersion time as shown in Fig. 3. It is clear that , even 30 s of immersion, silicon dihydiride, D, is removed completely. On the other hand, trihydride, T, is gradually done in the boiling water and 600 s is needed for complete removal. From the polarized spectra in Fig. 4, it was found that, after 600 s of immersion, it contained only M' mode at 2082.5 cm^{-1}, whose hydrogen atoms terminated dangling bonds perpendicular to the surface. It should be noticed that the boiling water removes even silicon trihydrides on the (111) terrace, T, which cannot be removed by water at 21℃

For the boiled surface, we did not observe any silicon oxide as shown in Fig. 5. From the detection limit of ATR and XPS, the amount was estimated to be less than 1 %ML. Furthermore, ATR spectrum for the boiled surface followed by 1.5% HF dipping confirmed the amount of the monohydride unchanged, compared with that before the HF dipping. These results means a full surface layer coverage by silicon monohydrides. We conclude that the immersion removes silicon hydrides at steps and converts them to silicon monohydride.

A very small amount of silicon monohydride at the (111) step, M, is explained by the 0.5° misorientation introduced during wafer slicing and polishing. The structure defect density can be determined from the area under the s-polarized spectrum because only modes at defects have vibrational components parallel to the surface. We obtained a value of 0.5%. The homogeneity or flatness is at the same level as performed by Higashi *et al.*[9]

The morphology shown in Fig. 3 was obtained when we immersed the sample in water at 21℃ for 1800 s between the HF treatment and the boiling water immersion. Our XPS study showed few fluorine of less than 1 %ML remaining after 1800 s of immersion in water. This result means the existence of fluorine at the surface is not necessary to produce the homogeneous and flat surface. We can conclude that the process in which hydrogen terminated silicon surface is immersed in water is essential to obtain the homogeneous surface.

We tried to explain the observation on the structure-selective etching of the hydrides and conversion to

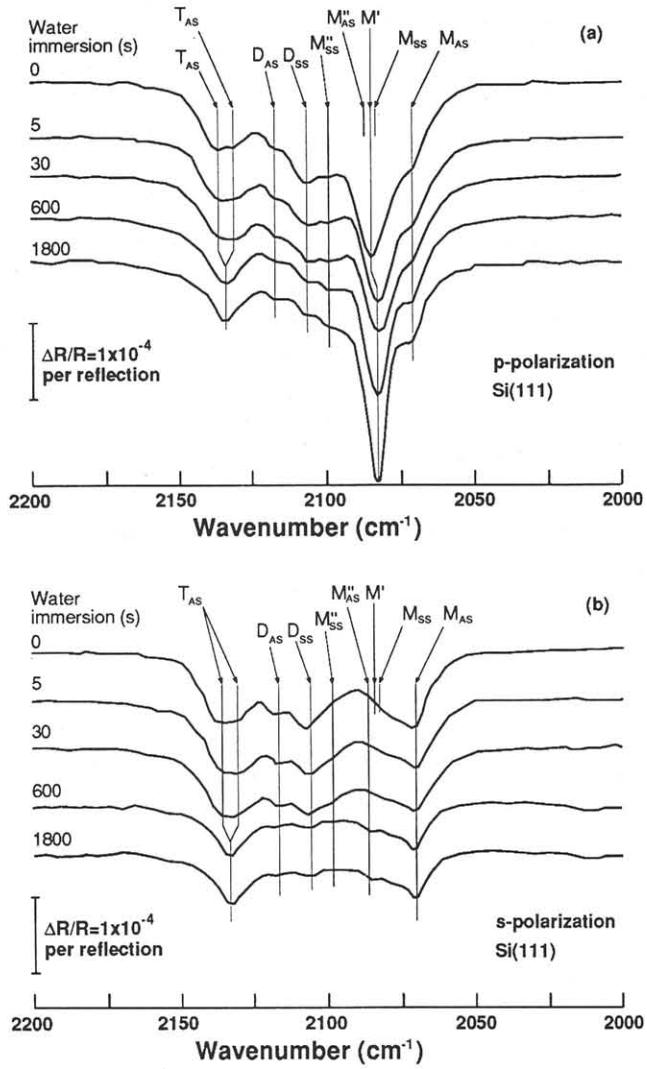

Fig. 2(a) and (b) Effect of immersion in water at 21℃ following 1.5% HF treatment, in spectra for the silicon-hydrogen stretching vibration. Spectra were recorded (a) p-polarized and (b) s-polarized.

monohydride termination by water. It is pointed out for HF treated (100) and porous silicon that, in the initial stage of oxidation by oxygen, insertion of oxygen atom into Si-Si backbonds occurs selectively.[11,12] We also detected stretching vibration corresponding to -SiOH and HSi-O-Si- structure on HF treated Si(100) surface followed by water immersion. These facts suggest the model in which water attack the backbond for hydrogen-terminated Si(111) surface, as is the case for Si(100) surface. Phenomenally, water seems to react with silicon di- and tri-hydrides and remove them from the surface, leaving hydrogen termination to the new surface. Using this model the temperature characteristics of trihydride etching by water can be understood quantitatively, when we introduce so-called steric hindrance of trihydride against water molecule. However detailed chemistry is still unknown. Theoretical calculation may be needed to explain the phenomenon in molecule level.

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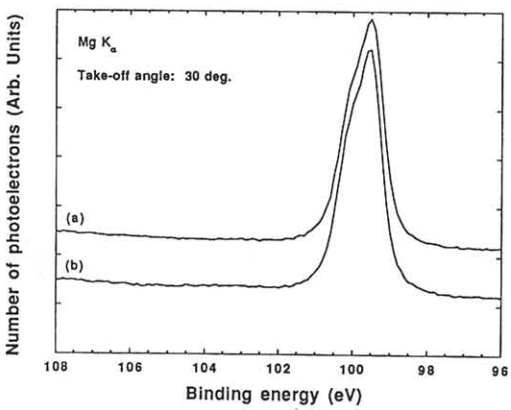

Fig. 5(a) and (b) Silicon 2p photoelectron spectra for (a) before and (b) after the sample was immersed in the boiling water for 600 s. There exists no silicon oxide peak in the both spectra.

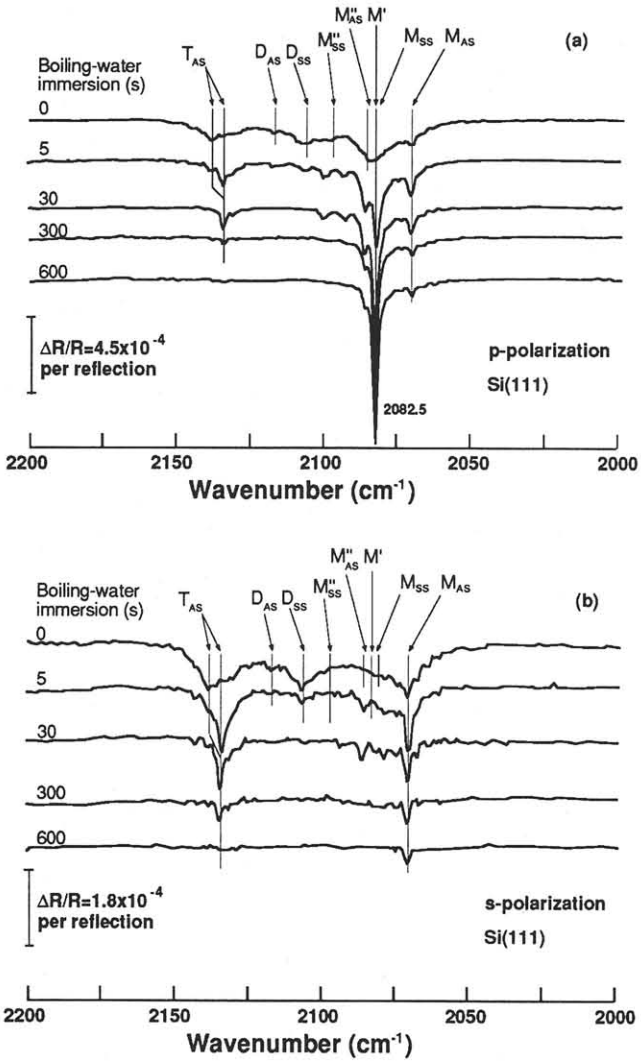

Fig. 3(a) and (b) Effect of immersion in water at 100℃ following 1.5% HF treatment Spectra were recorded (a) p-polarized and (b) s-polarized. The resolution is 0.5 cm^{-1}.

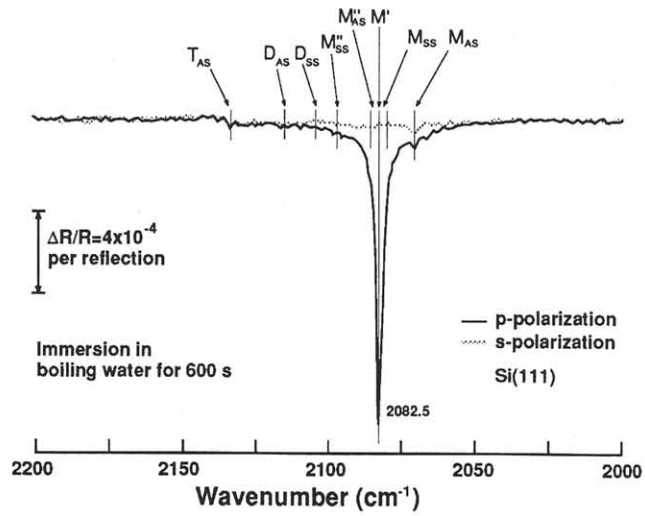

Fig. 4. Polarized infrared spectra for immersion in boiling water at 100℃ for 600 s, following dipping in the 1.5% HF solution. Resolution is 0.5 cm^{-1}.