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Real-time, *in situ* infrared study of etching of Si(100) and (111) surfaces in dilute hydrofluoric acid solution

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The chemical nature of Si(100) and (111) surfaces during immersion in dilute hydrofluoric acid (HF) solution was investigated “*in situ*” and in real time using infrared absorption spectroscopy in the multiple internal reflection geometry. In dilute HF solution, the Si surface is not completely terminated with hydrogen, but may be covered in part with hydrogen-associated Si fluorides, such as SiH₂(SiF) and SiH₂F₂. It is found that the hydrogen coverage of the surface depends on the HF concentration of the solution. At HF concentrations above 1%, the surface concentration of Si hydrides is reduced while that of Si fluorides is enhanced. We confirm that rinsing in water following HF immersion leads to complete hydrogen termination of the surface. Based on the present experimental results, we suggest that in dilute HF the Si surface is in chemical equilibrium with the solution to allow the coexistence of Si hydrides and Si fluorides on the surface. © 1996 American Institute of Physics. [S0021-8979(96)00406-9]

I. INTRODUCTION

In the fabrication of integrated circuits, preparing chemically clean silicon surfaces is quite important. One of the widely used cleaning techniques is chemical oxidation in peroxide solution followed by oxide removal in hydrofluoric acid (HF) solution.^{1,2} The surfaces thus produced are hydrophobic and quite stable for chemical attacks. Initially, the chemical stability of HF-treated Si surfaces was interpreted as being due to surface termination by fluorine.^{3,4} Later, it was revealed that hydrogen termination is responsible for the chemical stability of the surfaces.^{5–10}

Recently, Higashi *et al.*¹¹ have demonstrated that treatment with high-*pH* buffered HF (BHF) solution provides an atomically flat Si(111) surface. Interestingly, simple rinsing in boiled de-ionized (DI) water also leads to the production of a flat Si(111) surface.¹² In contrast, a microscopically smooth Si(100) surface cannot be produced by treatment with *pH*-enhanced solutions.^{10,13} It seems that the etching rate of Si crystals by a *pH*-enhanced solution is lower for the Si(111) crystal plane than for the Si(100) one. In fact, a long-term immersion into high-*pH* solutions such as NH₄F solution (*pH*~8) produces Si(111) microfacets on the Si(100) surface, as was confirmed with infrared studies.^{11,13,14}

A number of investigations on the etching mechanism of Si surfaces so far have been carried out theoretically and experimentally. Raghavachari *et al.*^{15,16} have investigated the mechanism leading to hydrogen termination of silicon surfaces using first-principles quantum chemical techniques. They proposed a model in which the initial removal of oxide by solvated HF leads to F termination of the surface dangling bonds and then the polarized Si—Si backbonds are readily attacked by HF to produce the final H-terminated Si surface. According to the model, fluorine-substituted silane species such as SiH₂(SiF) are populated on the surface in the course

of etching, and complete hydrogen termination of Si surfaces should be completed in dilute HF solution. On the other hand, it has been proposed by Jacob *et al.*¹⁷ that OH[−] ions present in *pH*-enhanced etching solutions play an essential role in etching the Si(111) surface. They suggested that oxidation of the surface Si—H species by OH[−] ions is an important (and probably rate limiting) step in the HF etching process of silicon. However, the mechanism responsible for the production of hydrogen-terminated Si surfaces seems very complex and has not yet been fully elucidated. To unravel the detailed mechanism leading to hydrogen termination, we need a better understanding of the surface chemistry and atomic process during etching in HF solutions. In particular, it is of importance to monitor “*in situ*” and in real time the chemical state of Si surfaces in etching environments.

In a previous study,¹⁸ we have carried out an *in situ* investigation of the chemical state of Si(100) surfaces while immersed in HF solution and in DI water using infrared absorption spectroscopy (IRAS). We demonstrated that the surface in dilute HF solution is not completely terminated by hydrogen, and that water rinsing is crucial to the complete hydrogen termination of the surface. The main issues we address in this study are to elucidate how Si(100) and (111) surfaces undergo chemical changes during immersion in dilute HF solution and in water, and to examine how the chemical state of Si surfaces in dilute HF solution changes as the HF concentration of the solution is varied.

II. EXPERIMENT

Samples used here were prepared from *n*-type P-doped Si(100) and (111) wafers. The sample size was 0.5×10×40 mm³ with 45° bevels on each of the short edges. The samples were initially cleaned with the RCA method and then placed in a Teflon™ cylindrical cell, as is schematically illustrated in Fig. 1. The cell, through which dilute HF solution or DI water flowed upwards at a flow rate of approximately 4 cc/min, was sealed with a pair of Teflon rubber O-rings. Each of the long edges of the sample wafer was shaped like a knife

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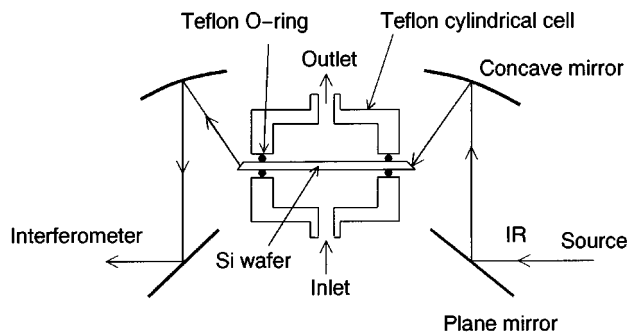


FIG. 1. Schematic of the experimental setup.

edge and the wafer was sandwiched between the two Teflon O-rings. The volume of the cell was approximately 5 cc. The details of the experimental setup will be described elsewhere.

The chemical state of Si surfaces during immersion in a flow of dilute HF solution or DI water was monitored by IRAS in the multiple internal reflection (MIR) geometry.^{19,20} As is illustrated in Fig. 1, infrared light which emerged from a globar lamp was focused at normal incidence onto one of the two bevels of the sample, and propagated through the Si wafer, internally reflecting about 80 times. The light that exited the sample through the other bevel, was focused onto a liquid-N₂-cooled HgCdTe detector through an interferometer (BOMEM MB-100). The resolution of the interferometer was set at 4 cm⁻¹. Infrared internal reflection spectra of Si surfaces taken during immersion in HF solution or in DI water exhibited strong absorption bands due to the solution. The infrared spectra measured for the chemically oxidized Si surface during immersion in DI water, therefore, were used as the background reference spectra. The chemical oxidation was performed by immersing the samples into a 1:1 boiled solution of H₂SO₄:H₂O₂ for 5 min.

In the present experimental setup, all of the internal reflections were not active reflections, because the entire Si wafer surface was not in contact with the solution. Considering the structure of the cell used, we estimated that about 80% of the surface was in contact with the etching solution. However, we could not determine an accurate number of the active reflections and correspondingly we could not obtain an absolute value of reflectance. So, the samples were carefully mounted on the Teflon cell so that the active area of the wafer surface was the same for all the samples. Additionally, the starting surface was a chemically oxidized surface. For each of the Si(100) and (111) surfaces, therefore, the vertical scale is the same for all the figures containing infrared spectra which we will show in the following.

III. RESULT AND DISCUSSION

A. Si(100)

Figure 2 shows a series of Si-H stretch vibration spectra of the Si(100) surface during immersion in a flow of 5% HF solution, collected for different immersion times. A broad peak at 2100 cm⁻¹ and a weak peak at 2080 cm⁻¹ can be attributed to the dihydride Si (SiH₂) and monohydride Si (SiH), respectively. We see that the SiH₂ peak increases in

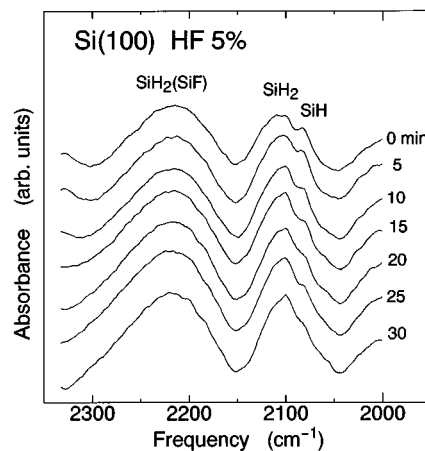


FIG. 2. Si-H stretch vibration spectra of the Si(100) surface during immersion in 5% HF. The figure attached to each spectrum indicates the immersion time in min.

intensity as the immersion time is increased, which clearly indicates that in dilute HF solution the chemical oxide on the Si substrate surface is etched away and the surface Si-H bond is increasingly populated, i.e., the dangling bonds on the surface become hydrogen terminated. On the other hand, the SiH peak intensity decreased with increasing immersion time. The appearance of the SiH peak and its decrease in intensity with an increase of immersion time can be rationalized as follows: Initially, the Si substrate surface was covered with chemical oxide, with the interface between the oxide and Si crystal surface being atomically rough. This is consistent with the results of Jacob *et al.*²¹ that chemical oxides have a rather rough SiO₂/Si interface compared to thermal oxides. When the oxide was etched away by HF, the substrate surface came up which was rough on an atomic scale. Such a surface should exhibit the monohydride vibration mode, because the monohydride mode is characteristic of a rough, hydrogen-terminated Si(100) surface with a number of steps and kinks.¹³ This is why at early stages of HF etching the surface exhibited the monohydride vibration peak, as shown in the top spectrum of Fig. 2. For further immersing in HF solution, the Si substrate surface was etched by HF although the etching rate could be rather low as compared to that for chemical oxide. We interpret that defect sites such as steps and kinks were favorably etched away to produce a flat Si(100) surface. This would lead to a decrease in the Si-H peak intensity. However, it should be pointed out that in dilute HF the Si(100) surface does not become atomically smooth, as has been demonstrated by previous works.^{10,14}

We can identify an intense, broad peak around 2230 cm⁻¹ in the spectra of Fig. 2. We shall briefly consider the origin of this peak below. We observed Si-H stretch vibration peaks due to the hydrogen-associated intermediate oxidation species, SiH₂(O₂) and SiH(O₃), on partially oxidized, hydrogen-terminated surfaces.²²⁻²⁴ Those oxidation species exhibited different Si-H stretch vibration frequencies, depending on the number of oxygen atoms around the central Si atom: SiH₂(O₂) and SiH(O₃) are observed at 2200 and 2250 cm⁻¹, respectively. The broad peak of concern is posi-

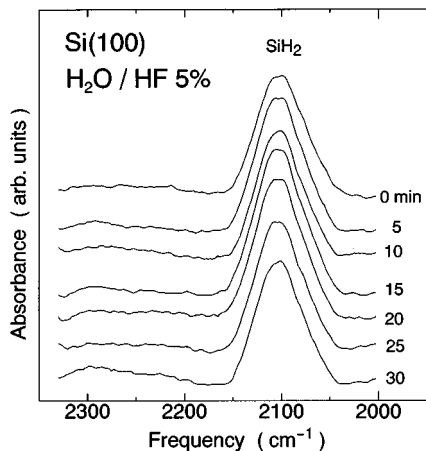


FIG. 3. Si–H stretch vibration spectra of the Si(100) surface immersed in DI water following immersion in 5% HF, taken for different immersion times in water. The figure attached to each spectrum indicates the immersion time in min. The vertical scale is the same as in Fig. 2.

tioned close to these peaks. However, it is unlikely that silicon oxide is formed on the Si surface during storage in dilute HF solution. A more plausible candidate for the origin of the 2230 cm^{-1} peak is hydrogen-associated Si fluorides. It is reported²⁵ that the Si–H vibration frequencies for fluorine-substituted silane molecules SiH_3F , SiH_2F_2 , and SiHF_3 are 2206 , 2245 , and 2314 cm^{-1} , respectively. These positions are close to that of the 2230 cm^{-1} peak. Lucovsky derived the semiempirical formula for calculating the Si–H stretch vibration frequency for various kinds of substituted silane molecules.^{25,26} Using the formula, we calculated a Si–H vibration frequency for the atomic configuration $\text{SiH}(\text{SiF}_2)$ of 2230 cm^{-1} , which coincides with the position of the peak of interest too. Thus, we assign the 2230 cm^{-1} peak to the hydrogen-associated Si fluorides: SiH_3F , SiH_2F_2 , SiHF_3 , and $\text{SiH}(\text{SiF}_2)$. SiH_2F_2 is a molecule and therefore is not chemically bound to the Si atoms on the surface. We understand this molecule is dissolved in the solution, staying in the vicinity of the surface. Considering the peak position, we speculate that both SiH_2F_2 and $\text{SiH}(\text{SiF}_2)$, in which two fluorine atoms are bonded to the central Si atom, are the dominant species. For convenience, we hereafter refer to the 2230 cm^{-1} peak as SiH_2SiF .

In a practical surface cleaning process of silicon, silicon wafers are rinsed with DI water following HF dipping. The effect of water rinsing has been reported to remove fluorine contaminations left behind on the Si surface after HF treatment.^{27,28} However, the change in the surface chemical state caused by water rinsing has not yet been investigated in detail. Figure 3 shows a series of Si–H stretch vibration spectra of the Si(100) surface which was immersed into a flow of DI water following HF dipping. These spectra have been collected for different water immersion times. We can see from comparison of Figs. 2 and 3 that the SiH_2 peak intensity is enhanced by immersing the surface in DI water. The SiH_2 intensity measured for the surface during storage in DI water was nearly equal to that measured for the surface which was dried by purging the cell with dry N_2 after water rinsing. Additionally, it is well established that the HF-

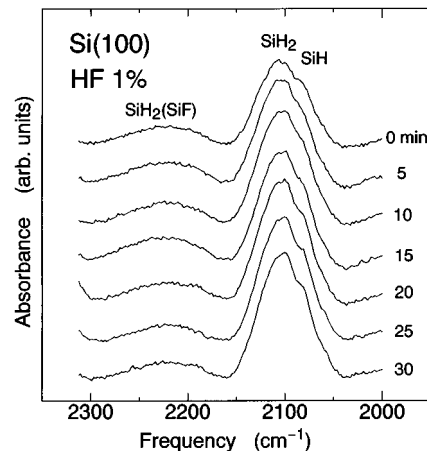


FIG. 4. Si–H stretch vibration spectra of the Si(100) surface during immersion in 1% HF. The figure attached to each spectrum indicates the immersion time in min.

treated Si(100) surface is hydrogen terminated with negligibly small amounts of fluorine.^{27–29} We thus determine that the Si surface during storage in water is almost completely terminated with hydrogen. Comparison of Figs. 2 and 3 indicates that the SiH_2 peak intensity in 5% HF is approximately half of that in DI water. This suggests that the hydrogen coverage of the surface during storage in 5% HF is only about 0.5. We speculate that the rest of the surface may be terminated with hydrogen-substituted Si fluorides, such as SiH_2F_2 and $\text{SiH}(\text{SiF}_2)$.

Figure 4 shows a series of Si–H stretch vibration spectra of the Si(100) surface collected during immersion in 1% HF for different immersion times. The SiH_2 peak intensity increased with increasing immersion time, which is the same trend as observed for 5% HF. However, there is a marked difference between the cases of 5% HF and 1% HF: The SiH_2 peak intensity for 1% HF is larger than that for 5% HF. In contrast, the $\text{SiH}_2(\text{SiF})$ peak intensity for 1% HF is much smaller than that for 5% HF. These findings suggest that the chemical state of the Si(100) surface during storage in dilute HF strongly depends on the HF concentration. As shown in Fig. 5, due to water rinsing the $\text{SiH}_2(\text{SiF})$ peak almost completely vanished whereas the SiH_2 intensity was slightly increased. We notice that an increase in the SiH_2 intensity caused by water rinsing is much smaller for 1% HF than for 5% HF. This suggests that the hydrogen coverage for 1% HF solution is higher than for 5% HF.

In Fig. 6 we show the evolution of the SiH_2 peak intensity while dipped in a flow of dilute HF solution with five different HF concentrations and DI water. Here the term “peak intensity” denotes the peak height. It is obvious from the left-hand panel of Fig. 6 that in dilute HF the SiH_2 peak intensity increases with increasing immersion time. This trend has been observed for all the HF concentrations. As already mentioned, this indicates that in dilute HF chemical oxide on the Si substrate the surface is etched away by HF and subsequently hydrogen termination of the substrate surface increasingly proceeds. The SiH_2 intensity reached equilibrium at immersion times around 20 min. The immersion

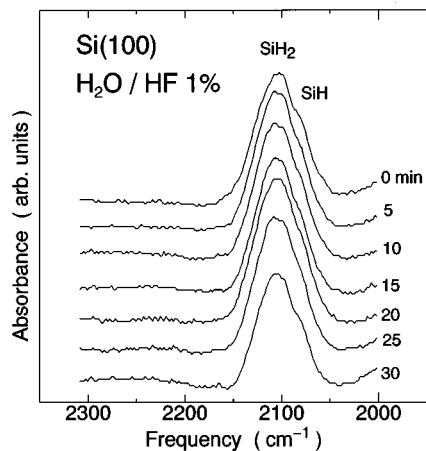


FIG. 5. Si-H stretch vibration spectra of the Si(100) surface immersed in DI water flow following immersion in 5% HF, taken for different immersion times in water. The figure attached to each spectrum indicates the immersion time in min. The vertical scale is the same as in Fig. 4.

time required for the SiH₂ intensity to reach equilibrium probably depends on the flow rate of HF solution in the cell. If the flow rate were varied, the immersion time needed for equilibrium would change. An important point to note is that the SiH₂ intensity at equilibrium was dependent on the HF concentration; it was smaller for higher HF concentrations. This point will be discussed later.

As shown in the right-hand panel of Fig. 6, when the Si surface was dipped into water, the SiH₂ intensity increased. Additionally, the SiH₂ intensity in water was almost independent of the HF concentration. These findings suggest that water rinsing produces a completely hydrogen-terminated surface. However, this does not mean that fluorine content on the surface after water rinsing is independent of the HF concentration. An IRAS technique utilized in this study is not surface sensitive enough for detecting extremely small amounts of fluorine on the HF-treated surface. We also see from Fig. 6 that when the water immersion time exceeds 20 min, the SiH₂ intensity slightly decreases. The hydrogen-

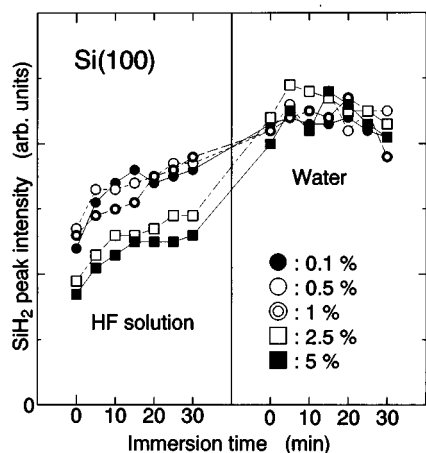


FIG. 6. SiH₂ and SiH₂(SiF) peak intensities as a function of immersion time. The left-hand panel is for immersion in dilute HF solution and the right-hand panel is for immersion in water.

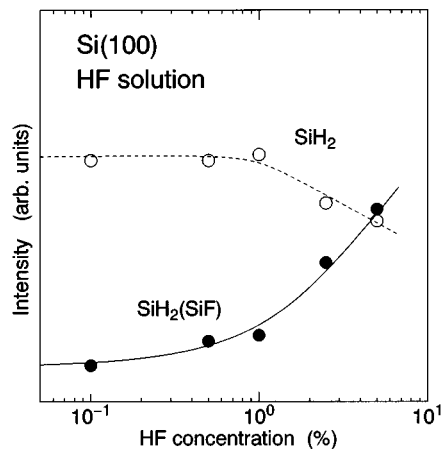


FIG. 7. SiH₂ and SiH₂(SiF) peak intensities in dilute HF solution as a function of HF concentration.

terminated Si surface in water is attacked by a number of water molecules as well as small amounts of oxygen molecules dissolved in water. This most probably induces oxidation of the surface. When the surface is oxidized, the surface Si-H bond is replaced by the Si-OH or Si-O-Si bridging bond, leading to the decrease in the SiH₂ peak intensity. We will report elsewhere the details of the oxidation of hydrogen-terminated Si surfaces during storage in DI water.

We plot in Fig. 7 the SiH₂ intensity at equilibrium in dilute HF solution as a function of the HF concentration. For comparison, we also show the dependence of the SiH₂(SiF) intensity on the HF concentration. There is a correlation between the SiH₂ and SiH₂(SiF) intensities: When the HF concentration exceeds 1%, the SiH₂ intensity decreases, while the SiH₂(SiF) intensity increases. This suggests that as the HF concentration increases, the Si surface becomes partially hydrogen terminated and the concentration of hydrogen-substituted Si fluorides is increased correspondingly. Takahagi *et al.*²⁸ demonstrated with x-ray photoemission measurements that fluorine content on the HF-treated Si surface increases with an increase of HF concentration, which is the same trend as observed for the SiH₂(SiF) intensity. We therefore suggest that treatment with dilute HF solutions with HF concentrations below 1% produces Si surfaces with low fluorine content.

The experimental results presented above showed that the Si surface while immersed in dilute HF solution is *not completely* terminated with hydrogen but may be covered in part with Si fluorides, such as SiH₂F₂ and SiH(SiF₂). We could not confirm the existence of Si fluorides in which no hydrogen atoms are bonded to the central Si atom: SiF, SiF₂, and SiF₃, because those silicon fluorides do not exhibit any vibration bands in the measured frequency range. However, such fluorides likely exist on the surface during immersion in dilute HF solution, although their concentration could be quite small. An important point we want to emphasize here is that Si hydrides and Si fluorides most probably coexist on the Si surface in dilute HF solution. We speculate that the Si surface in dilute HF is in chemical equilibrium with the solution to allow the coexistence of the hydride and fluoride

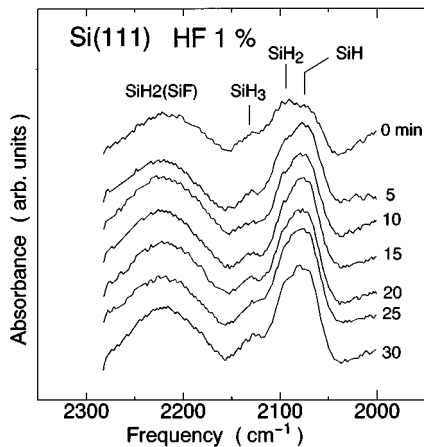


FIG. 8. Si-H stretch vibration spectra of the Si(111) surface during immersion in 1% HF solution. The figure attached to each spectrum indicates the immersion time in min.

species, and that the equilibrium constant, which determines the concentration of hydrides and fluorides, depends on the HF concentration.

B. Si(111)

Figure 8 shows a series of Si-H stretch vibration spectra of the Si(111) surface collected during immersion in a flow of 1% HF solution for different immersion times. An intense, broad peak at 2075 cm^{-1} can be attributed to the monohydride Si. A weak peak observed at 2130 cm^{-1} is due to the trihydride Si (SiH_3). Previous works show that the monohydride SiH peak is quite sharp on the hydrogen-terminated surface in dry N_2 ambient: The full width at half-maximum (FWHM) of SiH for the ideal hydrogen-terminated Si(111) surface is reported to be 1 cm^{-1} or less.¹¹ However, the SiH peak observed in the spectra of Fig. 8 has a FWHM of about 50 cm^{-1} . In addition, the SiH peak is slightly shifted to lower frequencies as compared to the previously reported position, 2083.7 cm^{-1} .¹¹ We attribute the broadening and shift of the SiH peak to the interaction of the surface S-H bond with water molecules surrounding it. Because of the peak broadening, we could not analyze the SiH peak intensity quantitatively. We therefore only concentrate on the changes in spectral profile caused by immersion into dilute HF and water.

As shown in Fig. 8, the SiH peak increased in intensity as the immersion time was increased. This is the same trend as observed for the Si(100) surface, and indicates that in dilute HF solution chemical oxide on the Si(111) surface is etched by HF and the surface SiH bond is increasingly populated. Another interesting point about Fig. 8 is that at the initial stage of etching in HF the dihydride (SiH_2) peak can be clearly observed. In the top spectrum of Fig. 8, the SiH_2 peak is larger in intensity than the SiH peak. As previously demonstrated,¹¹ an ideal hydrogen-terminated Si(111) surface is characterized by a single monohydride peak. When the surface is atomically rough, all the hydride modes would appear because of the existence of defect sites, such as steps and kinks. The appearance of the SiH_2 peak therefore sug-

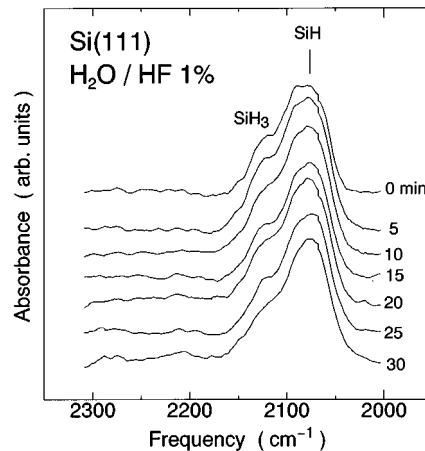


FIG. 9. Si-H stretch vibration spectra of the Si(111) surface immersed in DI water flow following immersion in 1% HF, taken for different immersion times in water. The figure attached to each spectrum indicates the immersion time in min. The vertical scale is the same as in Fig. 8.

gests that the surface is microscopically rough immediately after the oxide is etched away. With increasing immersion time, the SiH peak intensity increased while the SiH_2 peak intensity was reduced, an indication that the surface becomes flat through the preferential etching of defects sites. The $\text{SiH}_2(\text{SiF})$ peak can be identified on the Si(111) surface during immersion in HF solution. A close inspection of Fig. 8 indicates that the $\text{SiH}_2(\text{SiF})$ peak exhibits a gradual increase in intensity as the immersion time is increased. It appears that Si fluorides are increasingly populated on the surface at early stages of etching.

We plot in Fig. 9 a series of Si-H stretch vibration spectra of the Si(111) surface which was immersed into a flow of DI water after HF etching, collected for different immersion times. We see that as the immersion time increases, the SiH peak slightly increases while the SiH_3 peak intensity decreases. As mentioned above, the SiH_3 vibration mode indicates the presence of defect sites, such as steps and adatoms. The decrease in the SiH_3 intensity therefore suggests that such defects are etched by rinsing in water to produce a flat Si(111) surface. This is consistent with the previous results that the Si(111) surface becomes smooth when it is rinsed with water following HF treatment.^{11,12,14} It has been proposed by Jacob *et al.*¹⁷ that OH^- ions present in pH-enhanced etching solutions may play an essential role in etching the Si(111) surface. They suggested that oxidation of the surface Si-H species is an important (and probably rate limiting) step in the HF etching process of silicon. This would be the case for etching by water, because in water OH^- species are present due to the dissociation of H_2O . Then the surface Si-O species would be generated on the surface during storage in water. In this study, however, we could identify no distinct vibration peaks due to the surface Si-O species, such as $\text{SiH}_2(\text{O}_2)$ and $\text{SiH}(\text{O}_3)$, as is evident from Fig. 9. The reason for this would be twofold: First, the concentration of such oxidation species is extremely low. Second, the HF etching rate for such oxidation species is quite high.

IV. SUMMARY

Real-time, *in situ* investigation of the chemical state of Si(100) and (111) surfaces while immersed in dilute HF solution and in water has been carried out using infrared absorption spectroscopy in the multiple internal reflection geometry. We observed the *incomplete* hydrogen termination of the Si surfaces during immersion in HF solution, and suggested the formation of hydrogen-associated Si fluorides, such as $\text{SiH}_2(\text{F}_2)$ and $\text{SiH}_2(\text{SiF})$, on the surface. It was revealed that the concentrations of hydride and fluoride in dilute HF depend on the HF concentration. We also demonstrated that water rinse leads to the complete hydrogen termination of Si surfaces. On the basis of the present experimental results, we propose that in dilute HF solution the surface is in chemical equilibrium with the solution to allow the coexistence of Si hydrides and Si fluorides on the surface. The present experimental results would give a clue to the elucidation of the mechanism of etching in HF solution.

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