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著者	庭野 道夫
journal or publication title	Journal of Applied Physics
volume	71
number	11
page range	5646-5649
year	1992
URL	<a href="http://hdl.handle.net/10097/47810">http://hdl.handle.net/10097/47810</a>

doi: 10.1063/1.350497

# Morphology of hydrofluoric acid and ammonium fluoride-treated silicon surfaces studied by surface infrared spectroscopy

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(Received 3 December 1991; accepted for publication 13 February 1992)

Morphologies of Si surfaces treated with aqueous solutions of hydrofluoric acid (HF) and ammonium fluoride ( $\text{NH}_4\text{F}$ ) have been investigated using surface infrared spectroscopy. We confirm that HF-treated Si(111) surfaces are terminated with a monohydride (Si—H), dihydride (Si— $\text{H}_2$ ), and trihydride (Si— $\text{H}_3$ ), whereas  $\text{NH}_4\text{F}$ -treated Si(111) surfaces are dominantly terminated with Si—H. For Si(100), treatment in  $\text{NH}_4\text{F}$  produces a surface for which the dihydride mode is enhanced compared to HF treatment, suggesting that surface Si—Si bonds on Si(100) are readily cleaved in a  $\text{NH}_4\text{F}$  solution to generate a dihydride Si. The effect of varying the HF concentration on the morphology of HF-treated Si(100) surfaces is investigated. It is demonstrated that 5% HF treatment produces Si(100) surfaces which have a larger density of surface Si—Si bonds than 50% HF or 0.5% HF treatment.

## I. INTRODUCTION

In order to perform successfully the oxidation or epitaxial growth of silicon in the fabrication of metal-oxide-semiconductor (MOS) devices, it is very important to prepare a clean Si surface which is free from impurities and also chemically stable. The treatment of Si wafers with a dilute hydrofluoric acid (HF) solution has so far been utilized as a method of removing native oxide from the surface and forming a chemically passive surface.<sup>1,2</sup> In fact, it has been recently reported that the HF-treated Si surface is dominantly terminated with Si—H bonds instead of Si—F bonds, and that this hydrogen-terminated surface is chemically stable.<sup>3-5</sup> In accordance with the development of ultra-large-scale integration (ULSI) circuits, however, the microscopic morphology of Si wafer surfaces prior to the oxidation or epitaxial growth has become crucial to device performance.

Recently, Higashi *et al.*<sup>6,7</sup> have revealed on the basis of infrared spectroscopic and scanning tunneling microscopic measurements that highly basic solutions (pH = 9–10) produce an ideally hydrogen-terminated Si(111) surface which is microscopically smooth and has the (1×1) periodic structure. On this surface, the unsaturated dangling bond of each of the surface Si atoms is terminated with hydrogen to produce the monohydride Si(Si—H) oriented normal to the surface. On the other hand, it has been demonstrated<sup>6,8,9</sup> that treatment of Si(111) wafers using standard HF solutions does not produce an atomically flat surface but a rather rough surface. More recently, however, it has been reported by Watanabe *et al.*<sup>10</sup> that immersion of HF-treated Si(111) surfaces in a boiling deionized (DI) water results in a smooth Si(111) surface. The morphology of HF-treated surfaces therefore possibly depends on the surface cleaning conditions. Another problem that we must address ourselves to is the effect of crystallographic orientation on the morphology of Si surfaces treated in aqueous solutions. Even if Si(111) and (100) surfaces were treated with the same etching solution, they would exhibit quite different morphologies because of the difference in the sur-

face bond topology. In fact, Higashi *et al.*<sup>6</sup> showed that treatment of Si surfaces in highly basic solutions, which is effective for producing an atomically flat Si(111) surface, does not result in a flat Si(100) surface but a rather rough surface with small (111) facets.

In this study, we investigate morphologies of the Si(111) and (100) surfaces that are treated in aqueous solutions of HF and ammonium fluoride ( $\text{NH}_4\text{F}$ ), using surface infrared spectroscopy. Note that a saturated solution of  $\text{NH}_4\text{F}$  is basic (pH ~ 8). We focus on the crystallographic orientation dependence of the morphology of Si wafer surfaces treated using these solutions. We also examine the effect of varying the HF concentration on the morphology of HF-treated Si(100) surfaces.

## II. EXPERIMENT

Samples used were prepared from *n*-type Si(111) and Si(100) wafers with resistivities varying from 50 to 120  $\Omega$  cm. The sample was  $0.5 \times 5 \times 40$  mm<sup>3</sup> with 45° bevels on each of the short edges. Infrared absorption measurements were performed in the same internal reflection geometry as Chabal *et al.*<sup>11</sup> The infrared radiation exiting an interferometer (BOMEM MB-100) is focused at normal incidence onto one of the two bevels, propagates through the wafer, internally reflecting about 80 times, then exits through the other bevel to be focused onto a liquid-N<sub>2</sub>-cooled HgCdTe detector. The spectral resolution of the interferometer was set at 4 cm<sup>-1</sup>.

Samples were prepared as follows. First, the samples were chemically oxidized after the traditional RCA cleaning. The chemical oxidation was performed by immersing the samples into a 1:1:1 boiled solution of H<sub>2</sub>O:HC1:H<sub>2</sub>O<sub>2</sub> for 5 min. The reflection spectra measured for the sample surfaces thus oxidized were used as the background reference spectra,  $R_{\text{ref}}$ . After chemical oxidation the samples were dipped into the solution of interest for oxide removal and hydrogen termination of the surface. They were then placed into a dry N<sub>2</sub> environment, and reflection spectra,  $R$ , were recorded.

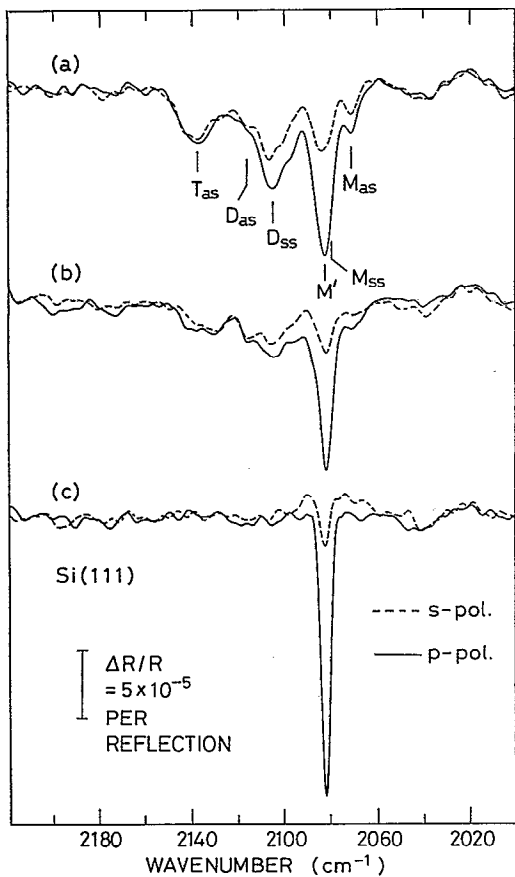


FIG. 1. Polarized infrared spectra of silicon—hydrogen stretching vibrations for different surface treatments for Si(111); (a) 5% HF, (b) 5% HF treatment followed by DI water rinse, and (c) 40%  $\text{NH}_4\text{F}$ .

### III. RESULTS AND DISCUSSION

#### A. Si(111)

As mentioned previously, the morphology of Si(111) surfaces treated using highly basic or dilute HF solution has been investigated by Chabal and co-workers using surface infrared spectroscopy.<sup>6–9</sup> They demonstrated that treatment in highly basic solutions produces an ideally hydrogen-terminated Si(111) surface for which the unsaturated dangling bond of each of the surface Si atoms is terminated with hydrogen to generate the monohydride Si (Si—H) oriented normal to the surface. On the contrary, treatment in a dilute HF solution has been shown to produce a rather rough surface on which defect modes, i.e., dihydride Si (Si—H<sub>2</sub>) and trihydride Si (Si—H<sub>3</sub>) exist, besides monohydride Si.<sup>8,9</sup> However, recent infrared spectroscopic studies<sup>10</sup> have clearly demonstrated that immersing HF-treated Si(111) surfaces into a boiling DI water results in an atomically flat surface. We thus reexamined morphologies of Si(111) surfaces treated with dilute HF and  $\text{NH}_4\text{F}$  solutions with the thought that the surface cleaning conditions could strongly affect the morphology of the resultant Si surfaces.

Figure 1 shows the internal reflection spectra of the Si—H stretch mode obtained for the Si(111) surfaces under different treatments. In this figure, the reflectivity  $\Delta R/R$

$R_{\text{ref}}$  where  $\Delta R = R - R_{\text{ref}}$ , are shown for  $p$  polarization (electric field in the plane of incidence) and  $s$  polarization (electric field perpendicular to the plane of incidence) conditions. Several absorption bands can be identified. We see that an absorption band at  $2083 \text{ cm}^{-1}$  shows a strong polarization dependence; it is very weak in the  $s$  polarized spectra. Considering the polarization characteristics and the model calculations by Chabal *et al.*,<sup>9</sup> we assign these absorption bands as the coupled monohydride ( $M_{\text{ss}}$ ,  $M_{\text{as}}$ ), the isolated monohydride ( $M'$ ) oriented normal to the Si(111) surface, the dihydride ( $D_{\text{ss}}$ ,  $D_{\text{as}}$ ), and the trihydride ( $T_{\text{as}}$ ), as shown in Fig. 1. Subscripts  $\text{ss}$  and  $\text{as}$  denote the symmetric and asymmetric modes of the coupled Si—H stretching vibrations, respectively. As can be seen from Fig. 1(a), the Si(111) surface after 5% HF treatment for 5 min is characterized by a large density of defect modes (coupled monohydride, dihydride, and trihydride), indicating that the surface is rather rough with hydrogen adsorbed at step and defect sites. Fig. 1(b) shows the spectrum of the surface treated with 5% HF and subsequently rinsed in DI water for 1 min. Comparison of Figs. 1(a) and 1(b) demonstrates that due to DI water rinse the coupled monohydride, dihydride, and trihydride modes are reduced considerably, but the isolated monohydride mode ( $M'$ ) remains, which implies that the HF-treated surface becomes smooth when subsequently rinsed in DI water. These observations are consistent with the results of Higashi *et al.*<sup>6,7</sup> and Watanabe *et al.*<sup>10</sup> However, it should be noticed that upon DI water rinse the defect modes do not completely vanish. This indicates that HF-treated Si(111) surfaces are rather rough in the atomic level.

In contrast to HF treatment,  $\text{NH}_4\text{F}$  treatment was found to produce an atomically flat Si(111) surface, as will be shown below. Figure 1(c) shows the SiH stretch spectrum of the Si(111) surface treated with a saturated (40%) solution of  $\text{NH}_4\text{F}$  for 7 min. The defect modes disappear and only the isolated Si—H mode ( $M'$ ) is visible. This implies that the surface is dominantly terminated with the monohydride perpendicular to the (111) surface and is atomically flat accordingly. Although not shown in the figure, we observed no remarkable change in the SiH stretch spectra with subsequent DI water rinse. It appears that immersion in water does not alter the morphology of the atomically flat, hydrogen-terminated Si(111) surface. In other words, the monohydride oriented normal to the (111) surface seems to be very stable in water. Quite recently, we have performed photoemission measurements on the  $\text{NH}_4\text{F}$ -treated Si(111) surface, and obtained a preliminary result which shows that no silicon oxides are present on this surface.<sup>12</sup> This contrasts with the case of HF treatment, where a small amount of native silicon oxide has been identified on the surface.<sup>12</sup> Hence,  $\text{NH}_4\text{F}$  treatment appears to produce Si(111) surfaces quite different from those prepared using a dilute HF solution.

#### B. Si(100)

Since the ideal, flat Si(100) surface is characterized by a surface Si atom which has two unsaturated dangling bonds, hydrogen-termination of the surface is expected to

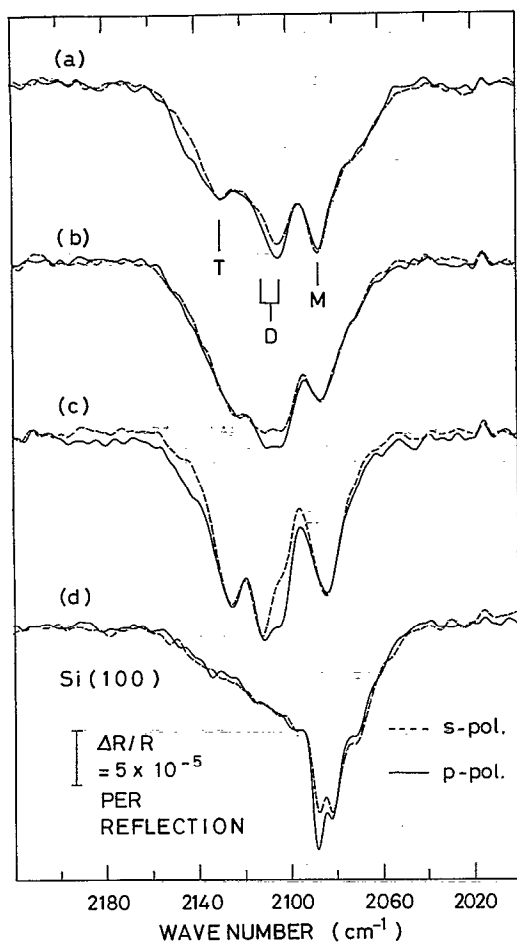


FIG. 2. Polarized infrared spectra of silicon-hydrogen stretching vibrations for different surface treatments for Si(100); (a) 5% HF, (b) 5% HF treatment followed by DI water rinse, (c) 40%  $\text{NH}_4\text{F}$  for 7 min, and (d) 40%  $\text{NH}_4\text{F}$  for 14 min.

preferentially produce the dihydride Si,  $\text{Si-H}_2$ . First, we show in Figs. 2(a) and 2(b) the SiH stretch spectra of the 5% HF-treated surfaces with and without subsequent DI water rinse, respectively. Both spectra exhibit spectral features quite different from the corresponding spectra for Si(111) as shown in Figs. 1(a) and 1(b). We see from Fig. 2(a) that as expected, the dihydride mode is significantly enhanced compared with the corresponding spectra for Si(111). A more interesting point about the spectra of Fig. 2(a) is that the monohydride mode is comparable to the dihydride mode. The monohydride Si on Si(100) is considered to correspond to the atomic bonding configuration in which one of the two unsaturated dangling bonds of a surface Si atom is bonded to a neighboring Si atom to form a surface Si—Si bond, and the other is bonded to hydrogen, that is,  $\text{H-Si-Si-H}$ .<sup>6</sup> The presence of the monohydride mode therefore suggests that there exist a relatively large number of unbroken Si—Si bonds on the Si(100) surface treated with 5% HF solution. The spectra of Fig. 2(b) demonstrate that subsequent DI water rinse results in the reduction in the amount of monohydride and enhancement of the dihydride mode. This can be explained as follows. If

the Si—Si bond of a  $\text{H-Si-Si-H}$  complex on Si(100) were cleaved, an additional unsaturated dangling bond would be generated on each of the two Si atoms. When those Si dangling bonds are attacked by hydrogen in water,  $\text{Si-H}_2$  will be generated, leading to the enhancement in the amount of dihydride Si. Of course, we cannot exclude the possibility that the Si dangling bonds are attacked by a hydroxyl radical to form Si—OH groups. Although we could not identify distinct absorption bands corresponding to the stretching vibrations of Si—OH, which would appear around  $3300\text{ cm}^{-1}$ , our recent photoemission studies<sup>12</sup> have demonstrated that spectral features corresponding to surface Si—OH bonds show up in the valence-band photoemission spectra measured for the Si(100) surface of interest. It is, therefore, most likely that due to DI water rinse Si—OH groups as well as Si—H groups are formed. When a water molecule is dissociatively adsorbed at the active dangling bonds generated by the cleavage of surface Si—Si bonds,  $\text{Si-H}_2$  and  $\text{H-Si-OH}$  will be produced. This also results in the increase in the amount of dihydride Si in compensation for the loss of monohydride Si, which is consistent with the experimental results.

Figures 2(c) and 2(d) show the SiH stretch spectra of the Si(100) surface prepared using a 40%  $\text{NH}_4\text{F}$  solution, taken for different durations of immersion. We can see from Fig. 2(c) that a short-term  $\text{NH}_4\text{F}$  treatment produces a Si(100) surface for which the dihydride mode is enhanced. This indicates that surface Si—Si bonds are readily broken to produce the dihydride, which is the same trend as observed for the surface treated with dilute HF and subsequently rinsed in DI water. However, as is shown in Fig. 2(d), further immersion in  $\text{NH}_4\text{F}$  results in the increase of the monohydride mode and decrease of other modes (dihydride and trihydride). Also noteworthy is that there appears the absorption line at  $2083\text{ cm}^{-1}$ , which, as mentioned earlier, is characteristic of the ideally H-terminated (111) surface. These facts strongly suggest the generation of small (111) facets. Considering this faceting and the results obtained for the  $\text{NH}_4\text{F}$ -treated Si(111) surface, we can conclude that an aqueous solution of  $\text{NH}_4\text{F}$  has a lower etching rate for Si(111) than for Si(100). This, in turn, suggests that an etching solution effective to the production of an atomically flat Si(111) surface is not necessarily suitable for preparing a flat Si(100) surface.

As mentioned above, we observed that water or highly basic solutions play a crucial role for the etching of Si crystal surfaces. This suggests that the HF concentration most probably affects the morphology of Si surfaces treated in a dilute HF solution. Recently, Miyauchi *et al.*<sup>13</sup> have measured the density of impurities at the interface between HF-treated Si(100) substrates and Si films formed by low-temperature chemical vapor deposition, and demonstrated that impurities such as carbon, fluorine, and oxygen are present at the interface for Si(100) substrates treated with 49% HF and 0.05% HF solutions but those impurities are not detectable for 5% HF-treated Si(100) surfaces. They suggested that desorption of impurities is related to the chemical nature of HF-treated surfaces. We propose here that the surface chemical nature responsible for the ob-

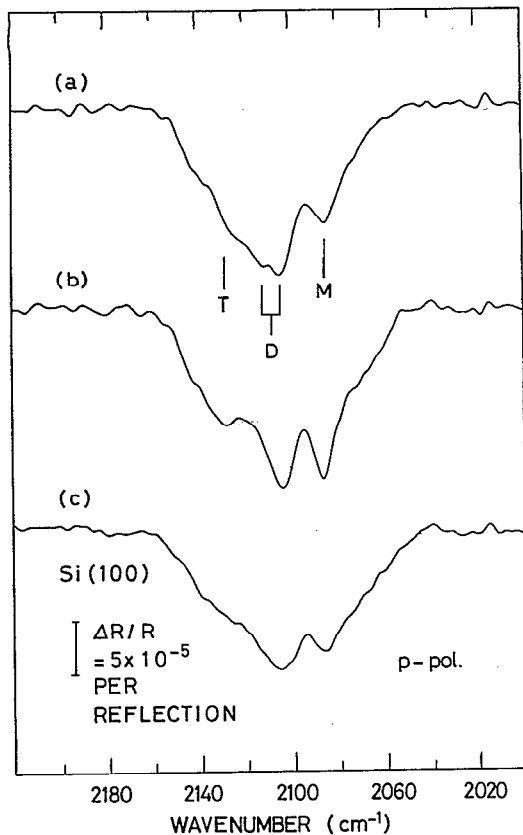


FIG. 3. Polarized infrared spectra of silicon—hydrogen stretching vibrations of the HF-treated Si(100) surface for different HF concentrations; (a) 0.5% HF, (b) 5% HF, and (c) 50% HF. Only the *p*-polarization spectra are shown.

served difference in the density of impurity is closely related to the morphology of HF-treated Si surfaces. For confirming this idea, we have examined the effect of the HF concentration on the morphology of HF-treated Si(100) surfaces. Figure 3 shows typical SiH stretch spectra of a series of Si(100) surfaces, treated in 0.5% HF, 5% HF, and 50% HF solutions for 5 min. Only the *p*-polarized spectra are shown, since no distinct polarization dependence was observed. Notice that for 5% HF treatment the monohydride mode is relatively enhanced, while for 0.5% HF and 50% HF treatments the dihydride is larger than the monohydride. As mentioned previously, the enhancement of the dihydride mode is most probably due to the cleavage of surface Si—Si bonds. We therefore interpret that 5% HF treatment yields a Si(100) surface which has a larger density of surface Si—Si bonds than 0.5% HF and 50% HF treatments. Furthermore, we consider a Si surface which has a large number of surface Si—Si bonds as the surface for which the density of the active Si dangling bonds protruding from the surface is low. For such a sur-

face, the probability that impurities are adsorbed instead of hydrogen would be low. Hence, we interpret that the 5% HF-treated surface has a low density of active Si dangling bonds protruding from the surface, thus leading to the suppression of adsorption of impurities. This is our qualitative explanation for the experimental results obtained by Miyauchi *et al.*<sup>13</sup>

As can be seen from Figs. 2 and 3, the SiH stretch spectrum of the 0.5% HF-treated Si(100) surface is quite similar to that of the surface treated in 5% HF and subsequently rinsed in DI water. In addition, we observed that a long-term DI water immersion after HF treatment yields SiH stretch spectra very much similar to those of the NH<sub>4</sub>F-treated surface shown in Fig. 2(c), irrespective of the HF concentration. These facts lead us to conclude that water plays a crucial role for the cleavage of surface Si—Si bonds on the Si(100) surface.

#### IV. CONCLUSIONS

The morphology of Si(111) and (100) surfaces treated with aqueous solutions of HF and NH<sub>4</sub>F has been investigated using surface infrared spectroscopy in the multiple internal reflection geometry. We found that NH<sub>4</sub>F treatment produces a Si(111) surface which is dominantly terminated with monohydride Si (Si—H). For Si(100), it was found that NH<sub>4</sub>F treatment or DI water rinse produces a surface for which the dihydride (Si—H<sub>2</sub>) mode is enhanced, suggesting that surface Si—Si bonds are readily broken in these solutions. It was also suggested that 5% HF treatment produces a Si(100) surface which has a larger density of surface Si—Si bonds than 0.5% HF and 50% HF treatments.

Another importance conclusion is that the treatment that is effective for preparing a clean, atomically flat Si(111) surface may not be suitable to the preparation of a flat Si(100) surface.

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