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# Formation of hexafluorosilicate on Si surface treated in $\text{NH}_4\text{F}$ investigated by photoemission and surface infrared spectroscopy

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The chemical nature of Si surfaces treated with ammonium fluoride ( $\text{NH}_4\text{F}$ ) has been investigated using photoemission and surface infrared spectroscopy. On the surface after treatment in  $\text{NH}_4\text{F}$  solution, there remain ammonium compounds such as  $\text{NH}_4\text{F}$  and  $\text{NH}_4\text{F}\cdot\text{HF}$ . Photoemission data demonstrate that under the atmospheric environment, the ammonium compounds remaining on the  $\text{NH}_4\text{F}$ -treated Si surface react with the Si substrate to generate the hexafluorosilicate salt,  $(\text{NH}_4)_2\text{SiF}_6$ . We propose that the formation of  $(\text{NH}_4)_2\text{SiF}_6$  or  $\text{SiF}_6^{2-}$  ions is the dominant reaction pathway in the  $\text{NH}_4\text{F}$  etching of Si crystals.

It is well established that treatment of Si in dilute hydrofluoric acid (HF) solution produces a hydrogen-terminated, chemically stable surface.<sup>1-4</sup> The resulting surface, however, has been reported to be rather rough when pure HF solutions are used.<sup>5,6</sup> Recently, Higashi *et al.*<sup>7,8</sup> have demonstrated that treatment in basic solutions, e.g., HF buffered with ammonium fluoride  $\text{NH}_4\text{F}$  (BHF), produces an atomically flat Si(111) surface which is dominantly covered with the monohydride Si(Si-H) oriented normal to the surface and displays the  $(1\times 1)$  periodic surface structure. This treatment therefore is a promising technique for the fabrication of high-density metal-oxide-semiconductor (MOS) devices, where preparing a microscopically flat Si wafer surface is desirable. For practical usage in the industry, however, more information about the chemistry of Si surfaces treated in basic solutions is needed. In particular, it would be quite important to elucidate the mechanism of the etching of Si crystals in basic solutions. Burrows and Yota<sup>9,10</sup> have recently investigated the chemistry of Si and Ge surfaces treated in BHF solution using surface infrared spectroscopy, and suggested that the hexafluorometallate compounds [ $(\text{NH}_4)_2\text{SiF}_6$  and  $(\text{NH}_4)_2\text{GeF}_6$ ] are generated on the surface after the treatment. It should be noted that, as they have pointed out, the formation of these compounds is thermodynamically favorable due to its large negative formation enthalpy and free energy compared to those of other Si compounds. Also noteworthy is that these compounds are very soluble in water. These facts suggest that the hexafluorometallate compounds may participate in the etching of Si and Ge crystals in BHF solutions.

The main purpose of the present study is to use photoemission and surface infrared spectroscopy to investigate the chemical nature of Si surfaces prepared in a saturated solution of  $\text{NH}_4\text{F}$  (pH $\sim$ 8). We confirm with infrared measurements that ammonium compounds such as  $\text{NH}_4\text{F}$  and  $\text{NH}_4\text{F}\cdot\text{HF}$  are present on the surface after treatment in  $\text{NH}_4\text{F}$ . Photoemission data demonstrate that the hexafluorosilicate salt  $(\text{NH}_4)_2\text{SiF}_6$  is generated through the interaction of the Si substrate with the ammonium compounds. We propose that the formation of  $(\text{NH}_4)_2\text{SiF}_6$

or  $\text{SiF}_6^{2-}$  ions plays an essential role in the etching of Si crystal in basic solutions.

Samples used were prepared from P-doped *n*-type Si(111) wafers with a resistivity of approximately 100  $\Omega$  cm. The procedure for sample surface treatment was as follows. First, the samples were chemically oxidized after the traditional RCA cleaning and subsequent deionized (DI) water rinse. The chemical oxidation was carried out by immersing the samples into a 1:1 boiled solution of  $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2$  for 5 min. The infrared reflection spectra measured for the samples thus oxidized were used as the background reference spectra. After chemical oxidation the samples were rinsed in DI water and then dipped into a saturated solution of  $\text{NH}_4\text{F}$  for oxide removal and hydrogen-termination of the surface. The samples after  $\text{NH}_4\text{F}$  treatment were placed into a dry  $\text{N}_2$  environment to record infrared absorption spectra, or transferred into an ultrahigh vacuum chamber with facilities for photoemission spectroscopy to measure photoemission spectra. In the present treatment, no DI water rinse was performed after the last etching step in  $\text{NH}_4\text{F}$  solution. Infrared absorption measurements were performed in the multiple internal reflection mode.<sup>11</sup> The sample used for the measurements was  $0.38\times 5\times 40$  mm<sup>3</sup> with 45° bevels on each of the short edges. 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 100 times, then exits through the other bevel to be focused onto a liquid-nitrogen-cooled HgCdTe detector. The resolution of the interferometer was set at 4 cm<sup>-1</sup>. Photoemission measurements were performed at the Synchrotron Radiation Laboratory of the Institute for Solid State Physics, the University of Tokyo. SR emitted from a 0.4 GeV electron storage ring was used as a light source. Photoelectrons were detected by a double-pass cylindrical mirror analyzer. Photoemission spectra of the valence-band and Si 2*p* core-level regions were measured at photon energies of 90 and 125 eV, respectively.

Figure 1 shows typical infrared absorption spectra of Si(111) surfaces immersed in 40%  $\text{NH}_4\text{F}$  solution for approximately 15 min, measured before and after transfer into the vacuum chamber. In the spectrum of Fig. 1(a)

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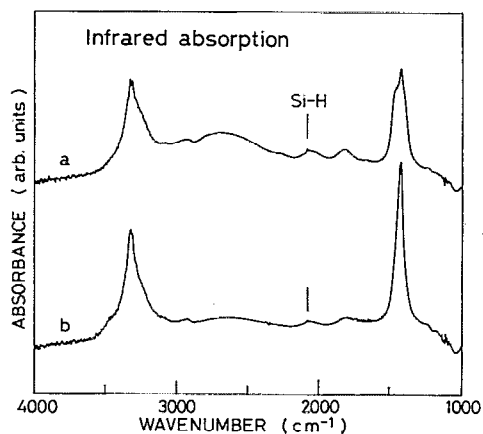


FIG. 1. Infrared absorption spectra of the  $\text{NH}_4\text{F}$ -treated Si(111) surfaces (a) before and (b) after transfer into the vacuum chamber.

there appear two strong peaks in the region of 1400–1600 and 3000–3400  $\text{cm}^{-1}$ , which correspond to the  $\text{NH}_4^+$  asymmetric bending and stretching vibrations, respectively. Besides these peaks, we can identify relatively weak, broad peaks at 1800, 2000, and 2700  $\text{cm}^{-1}$ . Remember that in the present surface treatment, no DI water rinse was carried out after immersing into  $\text{NH}_4\text{F}$  solution. In such a case, ammonium fluorides most probably remain on the surface after the treatment, as has previously been demonstrated by Yota and Burrows.<sup>9,10</sup> We therefore attribute the broad peaks to the ammonium fluorides that remain on the surface after  $\text{NH}_4\text{F}$  treatment. A very weak, sharp peak observed at 2080  $\text{cm}^{-1}$  is due to the surface Si—H bond oriented normal to the surface.<sup>7</sup> It can be seen from Fig. 1(b) that the peaks at 1800, 2000, and 2700  $\text{cm}^{-1}$  are reduced in intensity after transfer into the vacuum chamber. The strong absorption peaks, on the other hand, display an increase in intensity and decrease in peak width. Similar spectral changes were observed when the surface after  $\text{NH}_4\text{F}$  treatment was exposed to the air. These observations suggest that the ammonium compounds on Si readily dissociate and/or sublimate.

Figure 2 shows Si 2*p* core-level spectra of the Si(111) surfaces treated in  $\text{NH}_4\text{F}$  taken for different exposures to air. In each spectrum, an intense peak is due to photoemission from the bulk Si crystal. Core-level energies are given with respect to the energy of this peak. When the sample is transferred into the vacuum chamber immediately after  $\text{NH}_4\text{F}$  treatment, no chemical shifts of the Si 2*p* core-level energy are observed, as shown in Fig. 2(a). This indicates the absence of chemical bondings of Si with extrinsic atoms such as oxygen and fluorine. Figure 2(b) shows the spectrum measured for another  $\text{NH}_4\text{F}$ -treated surface that has been exposed to the air for about 30 min before it was transferred into the vacuum chamber. In this spectrum, a broad peak can be identified at approximately 6 eV higher than the bulk Si peak. Previous photoemission studies<sup>1,12–14</sup> have revealed that the Si 2*p* core-level chemical shift per oxygen or fluorine atom bonded to a silicon atom is approximately 1 eV. On the basis of the 6-eV chemical shift, we assign the peak of interest to the hexafluorosilicate com-

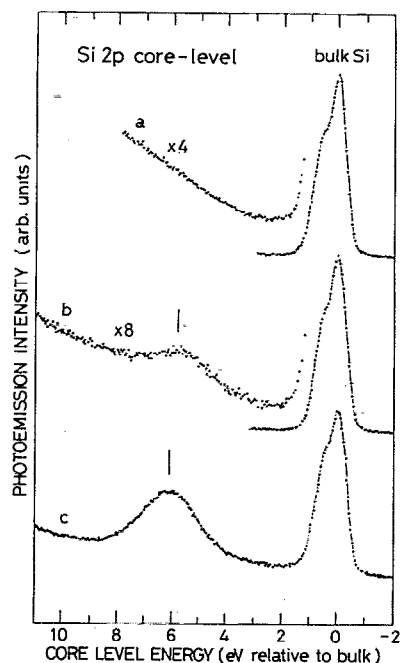


FIG. 2. Si 2*p* core-level spectra of the  $\text{NH}_4\text{F}$ -treated Si(111) surfaces (a) without exposure to the air, and with (b) 30 min, and (c) 4 h exposure to the air. Vertical lines indicate locations of photoemission from  $(\text{NH}_4)_2\text{SiF}_6$ .

pound, in which six fluorine atoms are bonded to the Si atom. Figure 2(c) shows that the 6 eV shifted peak significantly increases in intensity when the surface is further exposed to the air. We thus conclude that the ammonium hexafluorosilicate  $(\text{NH}_4)_2\text{SiF}_6$  is generated through the interaction of ammonium fluoride compounds with the Si substrate when the surface after  $\text{NH}_4\text{F}$  treatment is exposed to the air. We plot in Fig. 3 valence-band photoemission spectra of the same surfaces as in Fig. 2. In the spectrum of Fig. 3(a), four peaks, labeled A–D, can be identified. Peaks A and D can be ascribed to the bulk Si crystal, and peaks B and C mainly arise from the surface Si—H bond.<sup>15</sup> No other distinct peaks can be identified. The spectra of Figs. 3(b) and 3(c), on the other hand, exhibit two distinct peaks at 10 and 33 eV binding energy. From its energy position, the peak at 33 eV can be attributed to photoemission from the F 2*s* shallow core level, giving further evidence for the formation of  $(\text{NH}_4)_2\text{SiF}_6$ . Since the peak at 10 eV increases in intensity as the intensity of the 33 eV peak rises, we can also attribute it to  $(\text{NH}_4)_2\text{SiF}_6$ .

The results presented above demonstrate that under the atmospheric environment the ammonium hexafluorosilicate is generated on the Si surface after  $\text{NH}_4\text{F}$  treatment. Indeed, Yota and Burrows<sup>10</sup> have shown that the formation of  $(\text{NH}_4)_2\text{SiF}_6$  is thermodynamically favorable due to its large negative formation enthalpy and free energy compared to those of other Si compounds. Furthermore, it should be noted that  $(\text{NH}_4)_2\text{SiF}_6$  is very soluble in water. These facts suggest that the formation of hexafluorosilicate salts or ions may be crucial to the etching of Si crystals in  $\text{NH}_4\text{F}$  solution. The important point

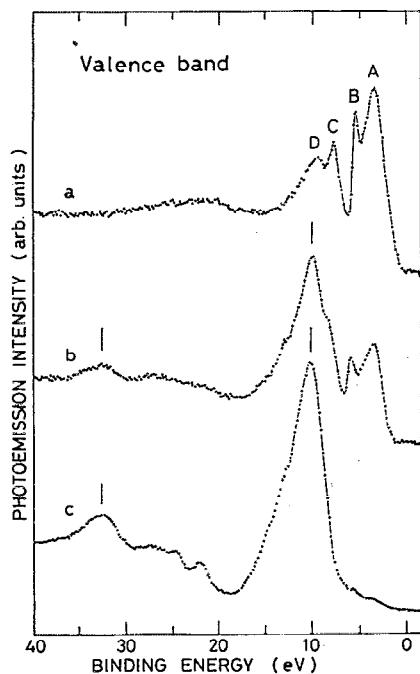


FIG. 3. Valence-band photoemission spectra of the same surfaces as in Fig. 2. Vertical lines mark locations of photoemission from  $(\text{NH}_4)_2\text{SiF}_6$ .

we want to emphasize is that the formation of  $\text{SiF}_6^{2-}$  complex ions would be enhanced under the presence of electron donors, since it requires two additional electrons around the Si atom that initially has four valence electrons in the  $sp^3$  hybridization orbitals. It should be noted that  $\text{NH}_3$  serves as an electron donor for the Si—H bond, that is,  $\text{Si—H} + \text{NH}_3 \rightarrow \text{Si}^- + \text{NH}_4^+$ . Also, as is well known,  $\text{NH}_3$  is generated through the dissociation of  $\text{NH}_4\text{F}$  in water,  $2\text{NH}_4\text{F} \rightarrow \text{NH}_4^+ + \text{HF}_2^- + \text{NH}_3$ . We therefore propose that Si crystal is readily etched in  $\text{NH}_4\text{F}$  solution through the formation of  $(\text{NH}_4)_2\text{SiF}_6$  or  $\text{SiF}_6^{2-}$ . As previously demonstrated,<sup>7,16</sup>  $\text{NH}_4\text{F}$  solution has a higher etching rate for Si(100) than for Si(111), which enables us to obtain an atomically flat Si(111) surface. We think this anisotropic etching also is closely related to the formation of  $\text{SiF}_6^{2-}$  ions. On the hydrogen-terminated Si(100) surface, a Si atom in the outermost layer has two Si—H bonds, whereas on the ideally hydrogen-terminated Si(111) surface the topmost Si atom has only one Si—H bond. We therefore naively interpret that the formation of  $\text{SiF}_6^{2-}$ , which requires the rupture of two Si—H bonds, is more favorable for Si(100) than for Si(111). Also noteworthy is that hy-

droxyl may also function as an electron donor for the surface Si—H bond. This implies that the etching of the Si(100) crystal surface may be promoted in basic solutions. Hence, we can explain the observation that an atomically flat Si(111) surface is produced in basic solutions. The proposed mechanism of the etching of Si in basic solutions, however, remains speculation. More elaborate studies are needed to obtain further evidence for the proposed mechanism.

In summary, we have investigated the chemical nature of Si surfaces after treatment in  $\text{NH}_4\text{F}$  solution using photoemission and surface infrared spectroscopy. It was demonstrated that the ammonium hexafluorosilicate  $(\text{NH}_4)_2\text{SiF}_6$  is generated on the  $\text{NH}_4\text{F}$ -treated Si surface. We proposed that the formation of  $(\text{NH}_4)_2\text{SiF}_6$  or  $\text{SiF}_6^{2-}$  complex ions is crucial to the etching of Si crystal in basic solutions.

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- <sup>1</sup>F. J. Grunthaner and P. J. Grunthaner, *Mater. Sci. Rep.* **1**, 69 (1986).
- <sup>2</sup>M. Grundner and H. Jacob, *Appl. Phys. A* **39**, 73 (1986).
- <sup>3</sup>H. Ubara, T. Imura, and A. Hiraki, *Solid State Commun.* **50**, 673 (1984).
- <sup>4</sup>E. Yablonovitch, D. L. Allara, C. C. Chang, T. Gmitter, and T. B. Bright, *Phys. Rev. Lett.* **57**, 249 (1986).
- <sup>5</sup>V. A. Burrows, Y. J. Chabal, G. S. Higashi, K. Raghavachari, and S. B. Christman, *Appl. Phys. Lett.* **53**, 998 (1988).
- <sup>6</sup>Y. J. Chabal, G. S. Higashi, K. Raghavachari, and V. A. Burrows, *J. Vac. Sci. Technol. A* **7**, 2104 (1989).
- <sup>7</sup>G. S. Higashi, Y. J. Chabal, G. W. Trucks, and K. Raghavachari, *Appl. Phys. Lett.* **56**, 656 (1990).
- <sup>8</sup>G. S. Higashi, R. S. Becker, Y. J. Chabal, and A. J. Becker, *Appl. Phys. Lett.* **58**, 1656 (1991).
- <sup>9</sup>V. A. Burrows and J. Yota, *Thin Solid Film* **193/194**, 371 (1990).
- <sup>10</sup>J. Yota and V. A. Burrows, *J. Appl. Phys.* **69**, 7369 (1991).
- <sup>11</sup>Y. J. Chabal, *Surf. Sci. Rep.* **8**, 211 (1988).
- <sup>12</sup>F. J. Himpsel, F. R. McFeely, A. Taleb-Ibrahimi, J. A. Yarmoff, and G. Hollinger, *Phys. Rev. B* **38**, 6084 (1988).
- <sup>13</sup>M. Niwano, H. Katakura, Y. Takeda, Y. Takakuwa, N. Miyamoto, A. Hiraiwa, and K. Yagi, *J. Vac. Sci. Technol. A* **9**, 195 (1991).
- <sup>14</sup>F. R. McFeely, J. F. Morar, N. D. Shinn, G. Landgren, and F. J. Himpsel, *Phys. Rev. B* **30**, 764 (1984).
- <sup>15</sup>M. Niwano, Y. Takeda, K. Kurita, and N. Miyamoto, *J. Appl. Phys.* **72**, 2488 (1992).
- <sup>16</sup>M. Niwano, Y. Takeda, Y. Ishibashi, K. Kurita, and N. Miyamoto, *J. Appl. Phys.* **71**, 5646 (1991).