

In situ infrared study of chemical state of Si surface in etching solution

著者	庭野 道夫
journal or publication title	Applied Physics Letters
volume	65
number	13
page range	1692-1694
year	1994
URL	http://hdl.handle.net/10097/47687

doi: 10.1063/1.112888

In situ infrared study of chemical state of Si surface in etching solution

Michio Niwano, Yasuo Kimura,^{a)} and Nobuo Miyamoto

Research Institute of Electrical Communication, Tohoku University, Sendai 980, Japan

(Received 3 May 1994; accepted for publication 18 July 1994)

We have “*in situ*” investigated the chemistry of Si(100) surfaces during immersion in hydrofluoric acid (HF) solution, using infrared spectroscopy in the multiple internal reflection geometry. During immersion in dilute HF solution, hydrogen termination is not completed and hydrogen-associated Si fluorides may be generated on the surface. We demonstrate that water rinse following treatment with HF solution leads to the complete hydrogen termination of Si surfaces.

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} However, the chemistry of Si surfaces during immersion in HF solution, in particular the mechanism leading to hydrogen termination of Si surfaces, has not been fully elucidated.

In this study, we have carried out an “*in situ*” investigation of the chemical state of Si surfaces during immersion in HF solution or water using infrared spectroscopy. The main purpose of this study was to find out at which stage of the cleaning process the hydrogen termination of Si surfaces is completed. This study would be the first in which the chemical state of Si surfaces during immersion in etching solution has been demonstrated.

Samples used here were prepared from *n*-type P-doped Si(100) wafers. The sample size was $0.5 \times 10 \times 40 \text{ mm}^3$ with 45° bevels on each of the short edges. The samples were initially cleaned with the traditional RCA method and then placed in a Teflon cylindrical cell, as is depicted in Fig. 1. The cell, through which dilute HF solution or de-ionized (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 edge and the wafer was sandwiched between the two O rings. The volume of the cell was approximately 5 cc.

The chemical state of Si surfaces during immersion in a flow of dilute HF solution or DI water was monitored by infrared spectroscopy in the multiple internal reflection geometry.¹¹ As 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 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.

Figure 2 shows Si-H stretch vibration spectra of the Si(100) surfaces collected during immersion in a flow of DI water and in a flow of dilute HF solution with two different HF concentrations. The surface which was immersed in DI water flow after etching in a flow of dilute HF solution with different HF concentrations, exhibited similar Si-H stretch vibration spectra, irrespective of HF concentration. As shown in Fig. 2, the spectrum collected in water is characterized by an intense, broad peak at 2100 cm^{-1} , which can be attributed to the dihydride Si (Si-H₂). The dihydride peak intensity was almost the same as that of the spectra collected for the HF-treated Si(100) surface in dry N₂ ambient.^{12,13} This implies that hydrogen termination of the HF-treated Si surface persists during immersion in DI water. However, Si(100) surfaces during immersion in a flow of dilute HF solution, showed Si-H vibration spectra quite different from those collected during immersion in DI water flow. As can be seen from Fig. 2, with immersion into a flow of HF solution the Si-H₂ peak is decreased in intensity, clearly indicating that the surface during immersion in HF solution is not completely terminated by hydrogen. Further, we can see that the Si-H₂ peak intensity decreases with HF concentration. For 5% HF, the peak intensity is only about 30% of that for DI water, which implies that the hydride coverage of the surface

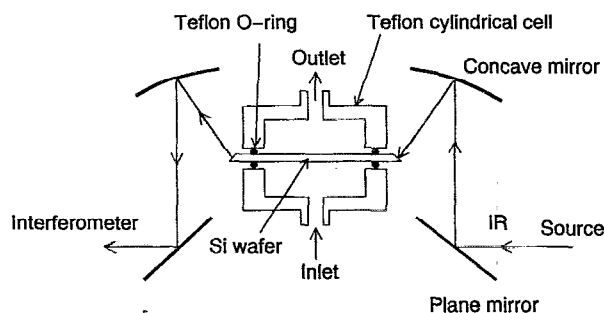


FIG. 1. Schematic of the experimental setup.

^{a)}Present address: Department of Electronic Engineering, University of Tokyo, Hongo 7-3-1, Tokyo 113, Japan.

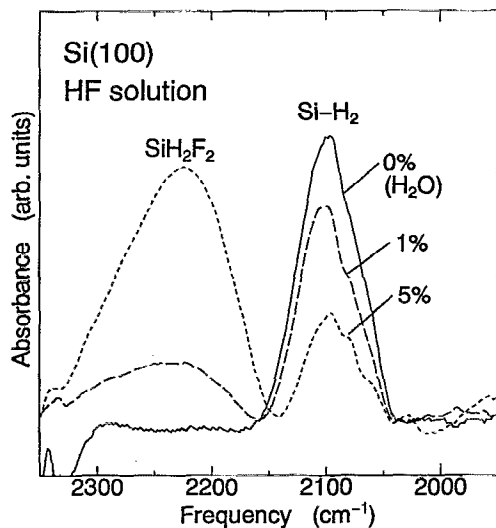


FIG. 2. Si-H stretch vibration spectra of the Si(100) surface during immersion in water and dilute HF solution with different HF concentrations: 1% and 5%.

is approximately 0.3. We speculate that the remaining part of the surface could be terminated by other Si complexes. For 5% HF, an intense, broad peak emerges around 2230 cm^{-1} . This peak, although its intensity is relatively weak, is also visible on the surface during immersion in 1% HF flow. We will discuss the origin of this peak below.

We have previously observed Si-H stretch vibration peaks due to the hydrogen-associated intermediate oxidation species, $\text{SiH}_2(\text{O}_2)$ and $\text{SiH}(\text{O}_3)$, on the hydrogen-terminated surfaces that were partially oxidized by exposure to air.¹³ Those oxidation species exhibited different Si-H stretch vibration frequencies, depending on the number of oxygen atoms around the central Si atom: $\text{SiH}_2(\text{O}_2)$ and $\text{SiH}(\text{O}_3)$ were observed at 2200 and 2250 cm^{-1} , respectively. The broad peak mentioned above is positioned close to these two peaks. However, it is unlikely that silicon oxide is formed on the Si surface during immersion in HF solution. We therefore determine that the peak of interest is not due to the intermediate oxidation species mentioned above. A more plausible candidate for the origin of the peak would be hydrogen-associated Si fluorides. It can be anticipated that such fluorides show higher Si-H vibration frequencies than the dihydride Si, with the shifts depending on the number of fluorine atoms around the central Si atom. In fact, it is reported¹⁴ that the Si-H stretch vibration frequencies for fluorine-substituted silane molecules SiH_3F , SiH_2F_2 , and SiHF_3 are 2206 , 2245 , and 2314 cm^{-1} , respectively. These values are close to the position of the peak of interest. Lucovsky derived the semiempirical formula for calculating the Si-H stretch vibration frequency for various kinds of substituted silane molecules.^{14,15} On the basis of the formula, we calculated a Si-H vibration frequency for the atomic configuration $\text{SiH}(\text{SiF}_2)$ of 2230 cm^{-1} . This value also coincides with the position of the peak of interest. Thus, we tentatively assign the broad peak observed at 2230 cm^{-1} to hydrogen-associated Si fluorides: SiH_3F , SiH_2F_2 , SiHF_3 , and $\text{SiH}(\text{SiF}_2)$. Unfortunately, we

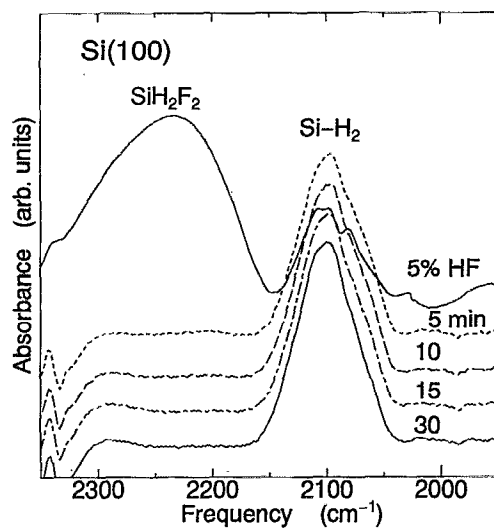


FIG. 3. Si-H stretch vibration spectra of the Si(100) surface immersed in DI water flow following immersion in 5% HF solution, taken for different immersion times in water.

cannot definitely determine which component dominates. Considering that the peak is positioned at 2230 cm^{-1} , however, we speculate that SiH_2F_2 and $\text{SiH}(\text{SiF}_2)$, in which two fluorine atoms are bonded to the central Si atom, could be the dominant species. For convenience, we refer to the broad peak as SiH_2F_2 in the following.

We have followed changes in the surface chemical state caused by water rinse following immersion in HF solution. The results are shown in Fig. 3. It is clear from Fig. 3 that when the surface initially was immersed in 5% HF solution and then immersed into a flow of DI water, the SiH_2F_2 peak vanished in a few minutes and the dihydride peak gradually increased with immersion time in water. This clearly indicates that the surface which is partially terminated by hydrogen while immersed in HF solution, becomes almost completely covered with hydrogen by a rinse in water. Interestingly, we observed that this change of surface state is reversible; that is, when the solution in which the Si wafer is immersed is changed from DI water to 5% HF solution, the dihydride peak is decreased in intensity, and the SiH_2F_2 peak increases instead. This suggests that the condition of equilibrium for the chemical reaction which takes place on the Si wafer surface while immersed in a solution strongly depends on whether the solution is water or HF solution. Also noteworthy about Fig. 3 is that a shoulder observed around 2080 cm^{-1} , which is most probably due to the monohydride Si (Si-H), is decreased in intensity with increasing immersion time in water. We have previously investigated the effect of HF concentration on the morphology of HF-treated Si(100) surfaces, and demonstrated that the monohydride peak intensity is lower for 0.5% HF than for 5% HF.¹² This is consistent with the present result. The monohydride on the hydrogen-terminated Si(100) surface is most probably due to the dimer site where two adjacent surface Si atoms are bonded with each having the Si-H bond.¹² We therefore sug-

gest that the water molecule plays a role in breaking the surface Si—Si bond.

We interpret the present experimental results as follows: The Si surface during immersion in dilute HF solution is not completely terminated by hydrogen and is partially covered with Si hydrides such as SiH_2F_2 and $\text{SiH}(\text{SiF}_2)$. SiH_2F_2 is a gas-phase species. Such a gas-phase species may stay in the vicinity of the surface like a stagnant layer. H_2F_2 or HF_2^- present in dilute HF solution could be involved in the formation of the Si fluorides. It is also most likely that the surface during immersion in HF is partially terminated by Si fluorides in which no hydrogen atoms are bonded to the central Si atoms: SiF , SiF_2 , and SiF_3 , although those fluorides do not exhibit any vibration bands in the frequency region investigated in this study. When the surface is rinsed in water after immersion in HF solution, its chemical state drastically changes; the hydrogen-associated Si fluorides are thoroughly removed and the surface Si—F bonds are converted to the Si—H bond through the interaction with water, leading to the complete hydrogen termination of the surface. However, it should be pointed out that, as a number of studies have demonstrated, minimal fluorine is left behind on Si surfaces without water rinse following HF treatment. We also confirmed with photoemission measurements that fluorine-associated peaks are quite weak in intensity on the unrinsed Si surfaces. It seems that the simple removal of Si surfaces from dilute HF solution results in the removal of most fluorides. We speculate that while the surface removed from HF solution is dried, most fluorides are removed as a gas-phase species such as SiH_2F_2 , HF, and H_2F_2 , and most surface Si—F bonds react with water remaining on the surface to be converted to the Si—H bond. For this case, however, fluorine will not be completely removed from the surface, as has been previously demonstrated by Watanabe and Shigeno.¹⁶

In summary, *in situ* investigation of the chemical state of

Si(100) surfaces while immersed in dilute HF solution has been carried out using infrared spectroscopy in the multiple internal reflection geometry. We observed the incomplete hydrogen termination of the surface during immersion in HF solution, and suggested the formation of hydrogen-associated Si fluorides such as $\text{SiH}_2(\text{F}_2)$ and $\text{SiH}(\text{SiF}_2)$ on the surface. We also clearly demonstrated that water rinse leads to the complete hydrogen termination of Si surfaces. The present experimental results would give a clue to the elucidation of the mechanism of etching in HF solution.

The authors wish to thank Koji Kinashi and Jun-ichi Sawahata for their help on the measurements. This work was supported by a Grant-in-Aid for Developmental Scientific Research (Grant No. 0555109) from the Ministry of Education, Science and Culture of Japan.

- ¹W. Kern, *J. Electrochem. Soc.* **137**, 1887 (1990).
- ²T. Buck and F. S. McKim, *J. Electrochem. Soc.* **105**, 709 (1958).
- ³S. I. Raider, R. Flitsch, and M. J. Palmer, *J. Electrochem. Soc.* **122**, 413 (1975).
- ⁴B. R. Weinberger, G. G. Peterson, T. C. Eschrich, and H. A. Krasinski, *J. Appl. Phys.* **60**, 3232 (1986).
- ⁵H. Ubara, T. Imura, and A. Hiraki, *Solid State Commun.* **50**, 673 (1984).
- ⁶E. Yablonovitch, D. L. Allara, C. C. Chang, T. Gmitter, and T. B. Bright, *Phys. Rev. Lett.* **57**, 249 (1986).
- ⁷F. J. Grunthaner and P. J. Grunthaner, *Mater. Sci. Rep.* **1**, 69 (1986).
- ⁸M. Grundner and H. Jacob, *Appl. Phys. A* **39**, 73 (1986).
- ⁹V. A. Burrows, Y. J. Chabal, G. S. Higashi, K. Raghavachari, and S. B. Christma, *Appl. Phys. Lett.* **53**, 998 (1988).
- ¹⁰Y. J. Chabal, G. S. Higashi, K. Raghavachari, and V. A. Burrows, *J. Vac. Sci. Technol. A* **7**, 2104 (1989).
- ¹¹Y. J. Chabal, *Surf. Sci. Rep.* **8**, 211 (1988).
- ¹²M. Niwano, Y. Takeda, Y. Ishibashi, K. Kurita, and N. Miyamoto, *J. Appl. Phys.* **71**, 5646 (1992).
- ¹³M. Niwano, J. Kageyama, K. Kinashi, J. Sawahata, and N. Miyamoto, *Surf. Sci. Lett.* **301**, L245 (1994).
- ¹⁴G. Lucovsky, *Solid State Commun.* **29**, 571 (1979).
- ¹⁵G. Lucovsky, *J. Vac. Sci. Technol.* **16**, 1225 (1979).
- ¹⁶S. Watanabe and M. Shigeno, *Jpn. J. Appl. Phys.* **31**, 1702 (1992).

Published without author corrections