

# *In Situ* ATR-FTIR Observation about Surfactant/Hydrogen-Terminated Si(111) Interface in Solution

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## Abstract

Development of novel functional devices has been expected by modification for Si surface. This study investigated immobilization and roles of the Si surface with flowing surfactant by *in situ* ATR-FTIR method. This result suggested that the surfactant prevented oxidation of the hydrogen-terminated Si surface from the higher concentration in aqueous solution. These would guard the Si surface against H<sub>2</sub>O molecules.

## Keywords

ATR-FTIR, Si, Hydrogen Termination, Surfactant

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## 1. Introduction

Recently, functional surfaces have been noticed on metal, semiconductor or other materials for general devices [1] [2]. Especially, Si semiconductor surface immobilized various molecules controllably is expected as a functional substrate and electrode for noble devices. Otherwise, a functional biological membrane consists of phosphatide, which has various properties by a part of hydrophobic and hydrophilic [3]-[6]. By its mimetic structure, this study has tried to immobilize surfactant molecules on a single crystal Si to inhibit the surface oxidation in solution toward applying electrochemical electrode. The Si surface is modified to atomically flat and hydrogen termination with etching by HF and NH<sub>4</sub>F solution [7]-[9]. Self-assembled monolayer (SAM) formation is expected on Si surface by the use of the surfactant molecules, which is a part of hydrophobia, and will be assembled on the hydrogen terminated Si surface. Hence, the SAM formation processes and inhibition of oxidation on Si surface were observed by *in-situ* ATR-FTIR in aqueous solution.

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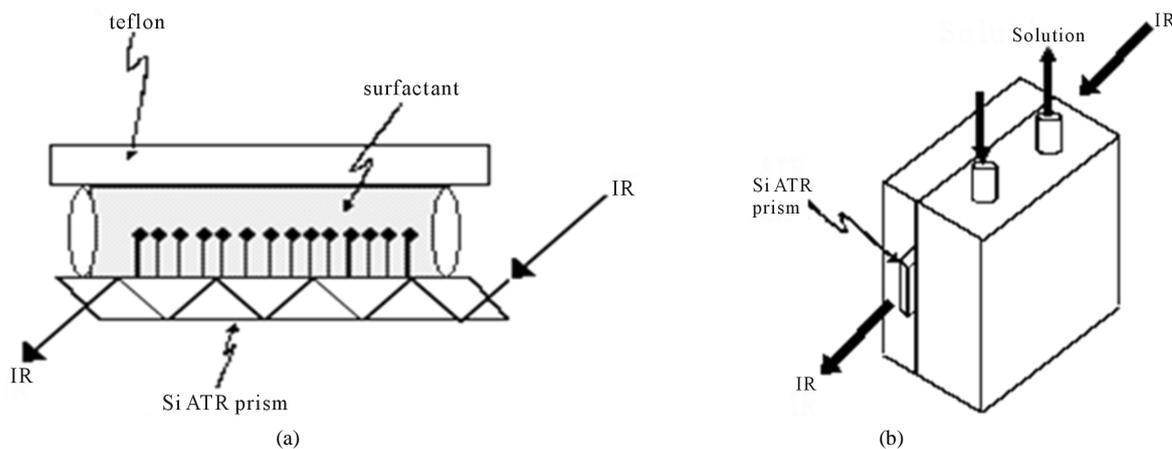
## 2. Experimental

Silicon wafers used Si(111) with mirror polishing both faces at 0.5 mm thickness, which was also applied as an ATR prism by cutting its both ends at 45 degrees. The Si(111) substrate was washed with RCA clean by boiling up solution of conc.  $\text{H}_2\text{SO}_4$  and 30%  $\text{H}_2\text{O}_2$  mixed solution immersing at 10 min, and 5% HF,  $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{O}_2$  mixed  $80^\circ\text{C}$  solution at 10 min, and washed pure water. Finally, the substrate was immersed in boiling up with solution of conc.  $\text{H}_2\text{SO}_4$  and 30%  $\text{H}_2\text{O}_2$  solution at 10 min to form  $\text{SiO}_2$  thin film on the silicon wafers.

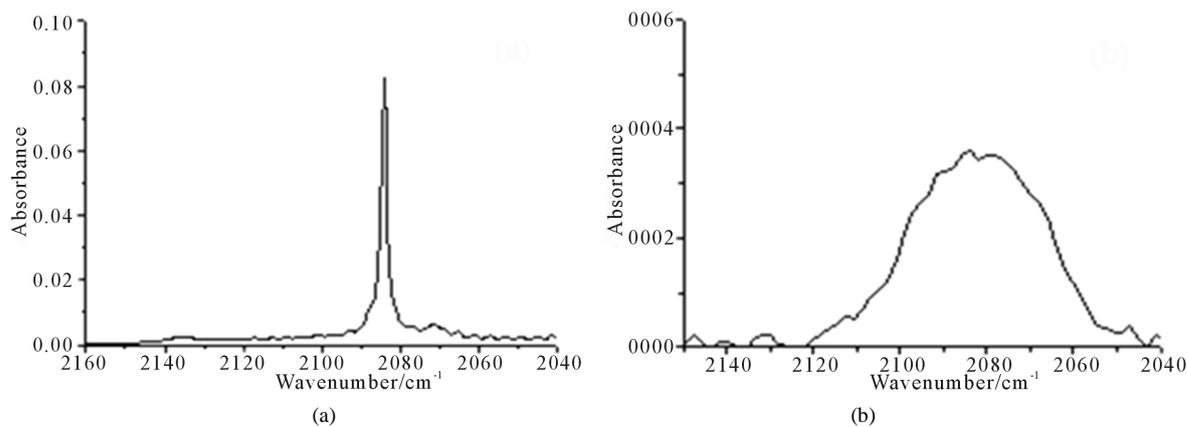
*In situ* ATR-FTIR was measured by IR incidence at 45 degrees to Si ATR prism with flowing pure water in **Figure 1(a)**, and the Si surface is modified to atomically flat and hydrogen termination by flowing 5% HF for 10 min and 40%  $\text{NH}_4\text{F}$  for 7 min. *In situ* measurement was carried out with flowing pure water or surfactant to a cell in **Figure 1(b)**. The measurement was from  $4000\text{ cm}^{-1}$  to  $1500\text{ cm}^{-1}$  and cumulative number of fifty.

## 3. Results and Discussion

First, hydrogen terminated Si(111) surface was observed by *ex situ* ATR-FTIR in **Figure 2(a)**. A sharp spectrum was at  $2083\text{ cm}^{-1}$  assigned to Si-H stretching vibration on the terrace surface, otherwise a broad spectrum of half-width  $30\text{ cm}^{-1}$  was observed *in situ* in **Figure 2(b)**. The broadness would cause the wide vibration energy by  $\text{H}_2\text{O}$  adsorption on the Si surface in flowing pure water [10]-[12]. Di-2-ethylhexyl sulfosuccinate sodium salt (aerosol OT) as surfactant is  $\text{C}_8\text{H}_{17}\text{COOCH}_2\text{CH}(\text{COOC}_8\text{H}_{17})\text{SO}_3\text{Na}$ , which the spectrum is assigned to  $3467\text{ cm}^{-1}$  (O-H stretching vibration),  $2957\text{ cm}^{-1}$  ( $\text{CH}_3$  asymmetry),  $2926\text{ cm}^{-1}$  ( $\text{CH}_2$  asymmetry),  $2858\text{ cm}^{-1}$  ( $\text{CH}_2$  symmetry),  $1735\text{ cm}^{-1}$  (C=O stretching vibration),  $1459\text{ cm}^{-1}$  ( $\text{CH}_2$  bending vibration),  $1212\text{ cm}^{-1}$  (C-C(=O)-O stretching vibration) in **Figure 3**.

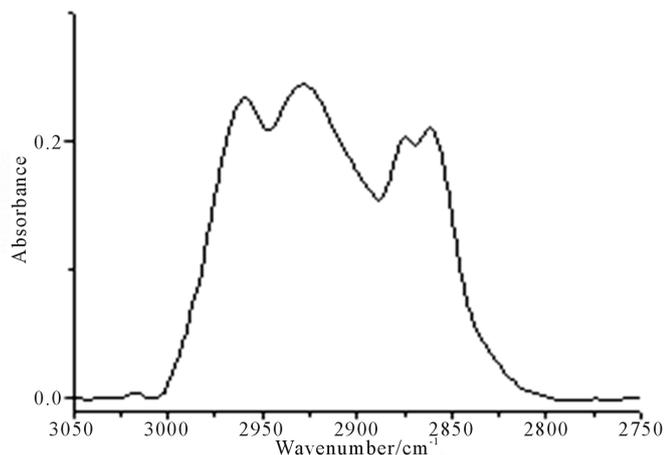


**Figure 1.** *In situ* ATR-FTIR cell system at about (a) a cross section of the cell; (b) a general view of them.

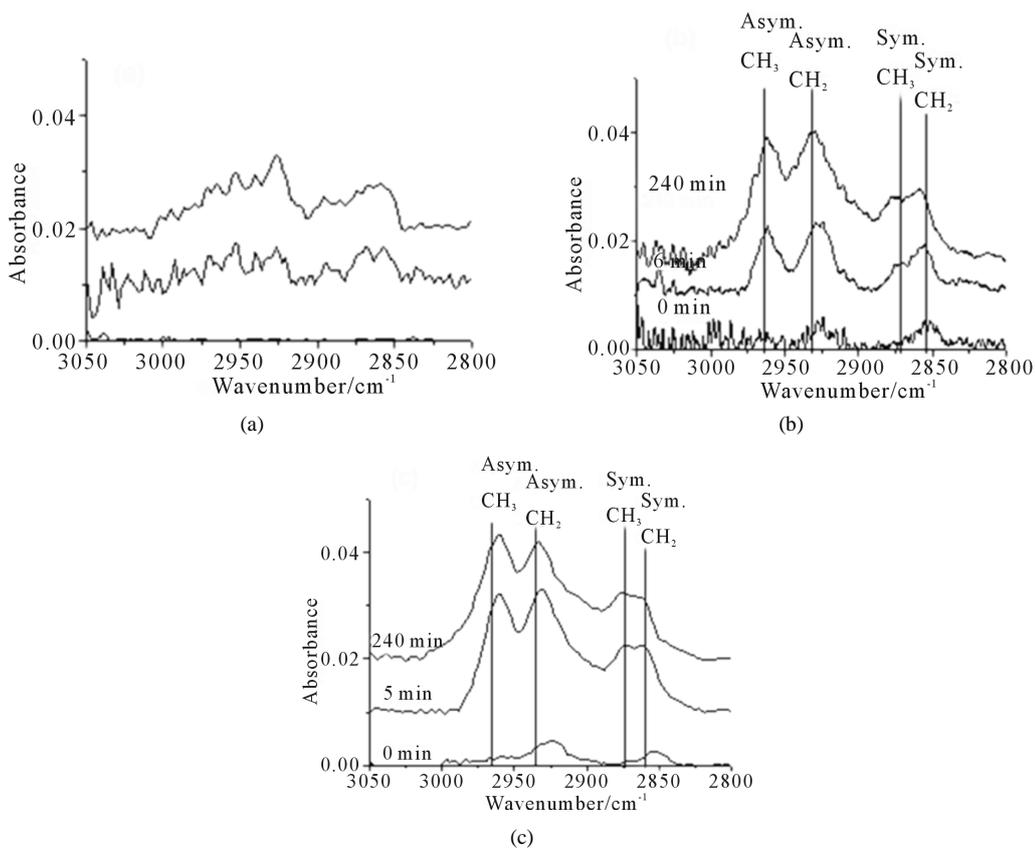


**Figure 2.** ATR-FTIR spectra of hydrogen-terminated Si(111) surface of (a) *ex situ*; (b) *in situ* in aqueous solution.

Spectra of Si-CH<sub>x</sub> on the Si surface was obtained at the aerosol OT concentration of  $1 \times 10^{-4}$  M,  $1 \times 10^{-3}$  M,  $1 \times 10^{-2}$  M *in situ* in **Figure 4**. The spectra showed CH<sub>x</sub> stretching vibration, and the peak intensity was increased with the flowing time. These results would indicate that the aerosol OT adsorbed on the Si surface by interaction between hydrophobic hydrogen-terminated Si surface and alkyl base of the aerosol OT. Furthermore, the methyl base at the extremity of the aerosol OT would selectively adsorbed on the Si surface by indicating the intense peaks based on the CH<sub>3</sub> relatively compared with the CH<sub>2</sub> peaks, nevertheless, the methyl base is less than the methylene base. **Figure 5** showed peak area of CH<sub>x</sub> *in situ* in the flowing aerosol OT, which saturation time of



**Figure 3.** Absorption spectra of the aerosol OT about CH<sub>x</sub> peaks.

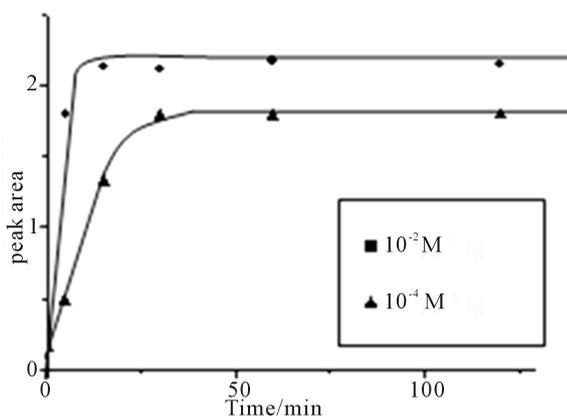


**Figure 4.** *In situ* ATR-FTIR spectra of the Si surface under the flowing aerosol OT at the concentration of (a)  $1 \times 10^{-4}$  M; (b)  $1 \times 10^{-3}$  M and (c)  $1 \times 10^{-2}$  M.

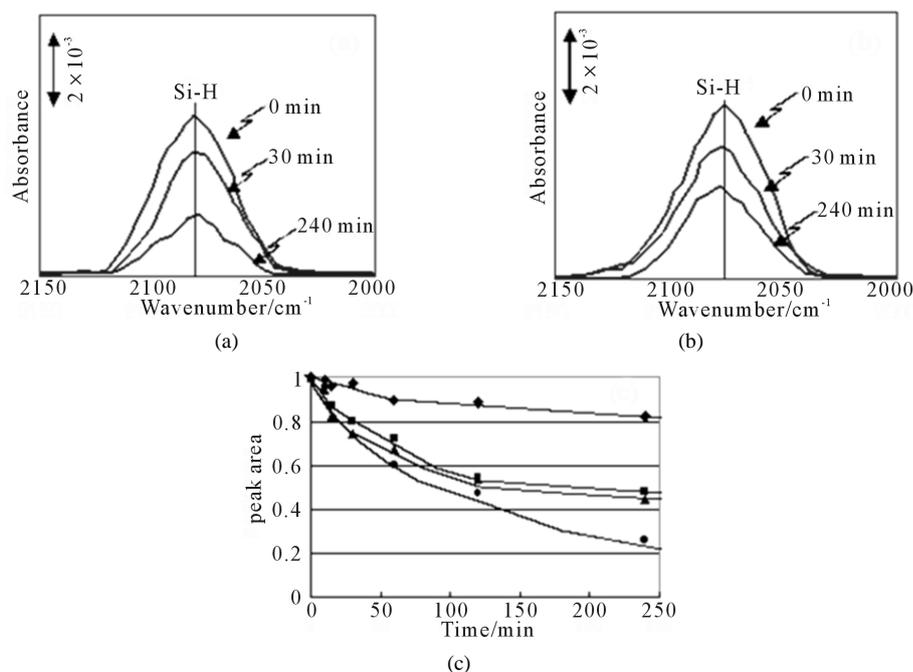
the peak area was shorter with higher concentration to be adsorbed on Si surface by diffusion rapidly.

In the same way, spectrum of Si-H was obtained in the flowing pure water in **Figure 6(a)**, which indicated decrease with the flowing time. This result would show oxidation on the Si surface. On the other hand, the spectrum under the flowing aerosol OT obtained the gradual decrease in **Figure 6(b)**. The tendency indicated dependence on the aerosol OT concentration remarkably, which was indicated by plotting normalized peak areas to flowing time in **Figure 6(c)**. These results will suggest that the aerosol OT prevented the oxidation on the Si surface by guarding against from H<sub>2</sub>O molecules.

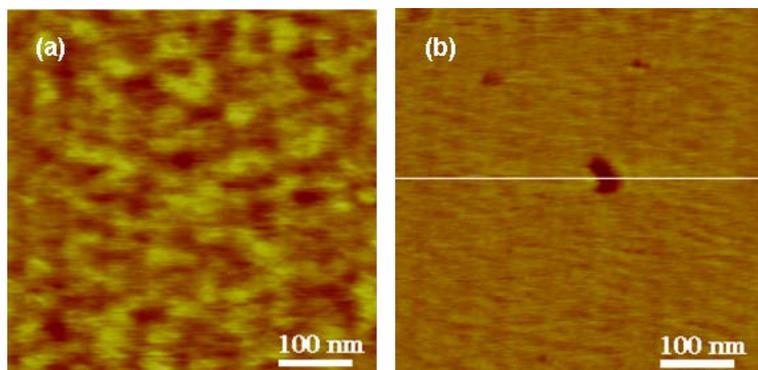
**Figure 7** shows AFM images on the Si(111) surface after measuring *in situ* ATR-AFM with flowing (a):  $1 \times 10^{-4}$  M and (b):  $1 \times 10^{-2}$  M aerosol OT for 90 min. The surface was rough in the concentration of  $1 \times 10^{-4}$  M, and was smooth in that of  $1 \times 10^{-2}$  M. These results will indicate difference of amounts of adsorption, and will adsorb densely and orientationally in the case of flowing the  $1 \times 10^{-2}$  M aerosol OT. Hence, the hydrogen-terminated Si(111) surface would prevented the oxidation from attacking the H<sub>2</sub>O molecules by adsorption the aerosol OT, which will be efficient with the higher concentration to larger coverage as shown in **Figure 8**.



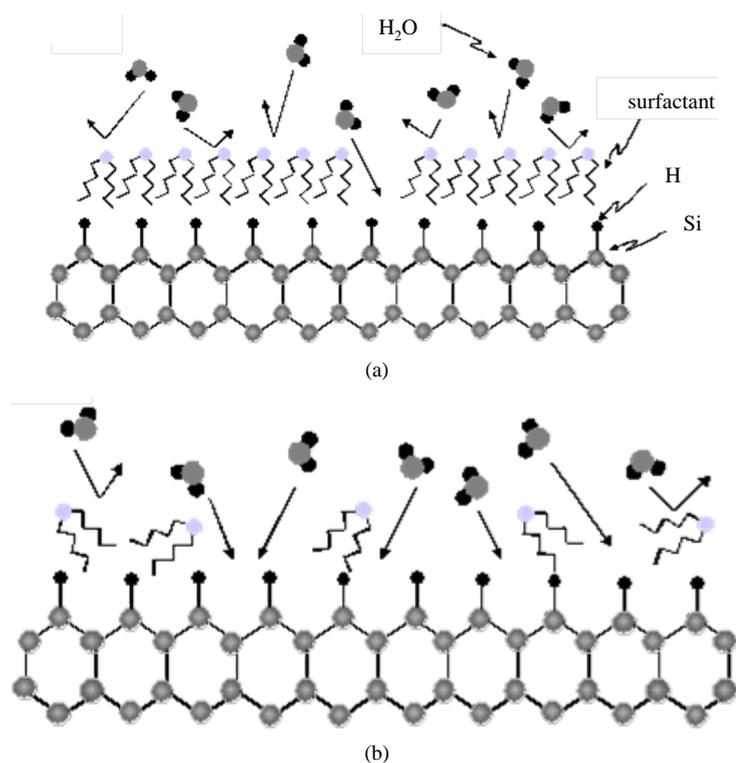
**Figure 5.** Time course of the CH<sub>x</sub> peaks area in **Figure 4**.



**Figure 6.** *In situ* ATR-FTIR spectra of the Si-H peaks on the hydrogen-terminated Si(111) under the flowing (a) aqueous solution and (b) aerosol OT. Time course of normalized peak area is in (c) at the concentration of  $\blacklozenge$ ;  $1 \times 10^{-2}$  M,  $\blacksquare$ ;  $1 \times 10^{-3}$  M,  $\blacktriangle$ ;  $1 \times 10^{-4}$  M and  $\bullet$ ; 0 M.



**Figure 7.** AFM images after the measuring samples in the aerosol OT at the concentration of (a)  $1 \times 10^{-4}$  M and (b)  $1 \times 10^{-2}$  M.



**Figure 8.** Mechanism of preventing the oxidation by interaction between surfactant and  $\text{H}_2\text{O}$  molecules on the hydrogen-terminated Si(111) surface at (a)  $1 \times 10^{-2}$  M and (b)  $1 \times 10^{-4}$  M.

## 4. Conclusion

This study was investigated about surfactant/hydrogen-terminated Si(111) interface with *in situ*. Area of Si-H peak by *in situ* ATR-FTIR measurement does not have much change with the higher aerosol OT concentration. This result will suggest that the aerosol OT guard the oxidation against  $\text{H}_2\text{O}$  molecules by adsorption to the Si surface, and AFM images will support them.

## References

- [1] Aoki, H., Hasegawa, K., Tohda, K. and Umezawa, Y. (2003) Voltammetric Detection of Inorganic Phosphate Using Ion-Channel Sensing with Self-Assembled Monolayers of a Hydrogen Bond-Forming Receptor. *Biosensors and Bioelectronics*, **18**, 261-267. [http://dx.doi.org/10.1016/S0956-5663\(02\)00177-X](http://dx.doi.org/10.1016/S0956-5663(02)00177-X)

- [2] Xiao, K.P., Bühlmann, P. and Umezawa, Y. (1999) Ion-Channel-Mimetic Sensing of Hydrophilic Anions Based on Monolayers of a Hydrogen Bond-Forming Receptor. *Analytical Chemistry*, **71**, 1183-1187. <http://dx.doi.org/10.1021/ac9809635>
- [3] Tang, Z., Jing, W. and Wang, E. (2000) Self-Assembled Monolayer Growth of Phospholipids on Hydrophobic Surface toward Mimetic Biomembranes: Scanning Probe Microscopy Study. *Langmuir*, **16**, 1696-1702. <http://dx.doi.org/10.1021/la981491s>
- [4] Yang, Z. and Yu, H. (1999) Biomembrane Mimetic Surfaces by Phospholipid Self-Assembled Monolayers on Silica Substrates. *Langmuir*, **15**, 1731-1737. <http://dx.doi.org/10.1021/la980839g>
- [5] Rossi, S., Karlsson, G., Ristori, S., Martini, G. and Edwards, K. (2001) Aggregate Structures in a Dilute Aqueous Dispersion of a Fluorinated/Hydrogenated Surfactant System. A Cryo-Transmission Electron Microscopy Study. *Langmuir*, **17**, 2340-2345. <http://dx.doi.org/10.1021/la001444b>
- [6] Yang, W.Y. and Youn-Sik, L. (2002) Surface Modification of Porous Vesicles via Hydrolysis. *Langmuir*, **18**, 6071-6074. <http://dx.doi.org/10.1021/la0203077>
- [7] Dumas, P., Chabal, Y.J. and Jakob, P. (1992) Morphology of Hydrogen-Terminated Si(111) and Si(100) Surfaces upon Etching in HF and Buffered-HF Solutions. *Surface Science*, **269-270**, 867-878. [http://dx.doi.org/10.1016/0039-6028\(92\)91363-G](http://dx.doi.org/10.1016/0039-6028(92)91363-G)
- [8] Jakob, P. and Chabal, Y.J. (1991) Chemical Etching of Vicinal Si(111): Dependence of the Surface Structure and the Hydrogen Termination on the pH of the Etching Solutions. *The Journal of Chemical Physics*, **95**, 2897-2909. <http://dx.doi.org/10.1063/1.460892>
- [9] Jakob, P., Chabal, Y.J., Raghavachari, K., Becker, R.S. and Becker, A.J. (1992) Kinetic Model of the Chemical Etching of Si(111) Surfaces by Buffered HF Solutions. *Surface Science*, **275**, 407-413. [http://dx.doi.org/10.1016/0039-6028\(92\)90813-L](http://dx.doi.org/10.1016/0039-6028(92)90813-L)
- [10] Kimura, Y., Kondo, Y. and Niwano, M. (2001) Initial Stages of Porous Si Formation on Si Surfaces Investigated by Infrared Spectroscopy. *Applied Surface Science*, **175-176**, 157-162. [http://dx.doi.org/10.1016/S0169-4332\(01\)00029-0](http://dx.doi.org/10.1016/S0169-4332(01)00029-0)
- [11] Niwano, M., Miura, T., Tajima, R. and Miyamoto, N. (1996) Infrared Study of Chemistry of Si Surfaces in Etching Solution. *Applied Surface Science*, **100-101**, 607-611. [http://dx.doi.org/10.1016/0169-4332\(96\)00348-0](http://dx.doi.org/10.1016/0169-4332(96)00348-0)
- [12] Niwano, M., Kondo, Y. and Kimura Y. (2000) *In Situ* Infrared Observation of Etching and Oxidation Processes on Si Surfaces in NH<sub>4</sub>F Solution. *Journal of the Electrochemical Society*, **147**, 1555-1559. <http://dx.doi.org/10.1149/1.1393393>