

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 H₂O molecules.

Keywords

ATR-FTIR, Si, Hydrogen Termination, Surfactant

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 NH₄F 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. H_2SO_4 and 30% H_2O_2 mixed solution immersing at 10 min, and 5% HF, NH_4OH and H_2O_2 mixed 80°C solution at 10 min, and washed pure water. Finally, the substrate was immersed in boiling up with solution of conc. H_2SO_4 and 30% H_2O_2 solution at 10 min to form 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% NH_4F 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 cm^{-1} to 1500 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 cm^{-1} assigned to Si-H stretching vibration on the terrace surface, otherwise a broad spectrum of half-width 30 cm^{-1} was observed *in situ* in **Figure 2(b)**. The broadness would cause the wide vibration energy by H_2O 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 cm^{-1} (O-H stretching vibration), 2957 cm^{-1} (CH_3 asymmetry), 2926 cm^{-1} (CH_2 asymmetry), 2858 cm^{-1} (CH_2 symmetry), 1735 cm^{-1} (C=O stretching vibration), 1459 cm^{-1} (CH_2 bending vibration), 1212 cm^{-1} (C-C(=O)-O stretching vibration) in **Figure 3**.

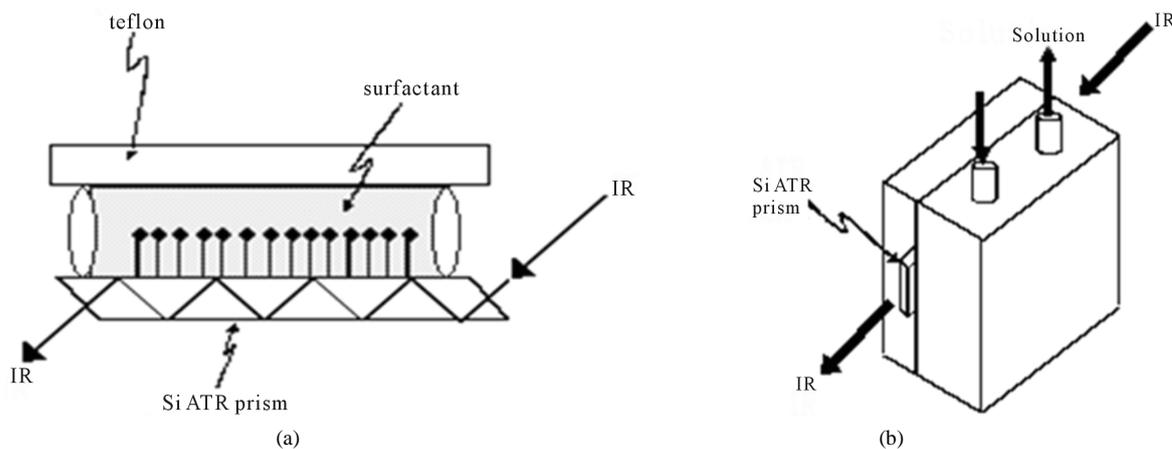


Figure 1. *In situ* ATR-FTIR cell system at about (a) a cross section of the cell; (b) a general view of them.

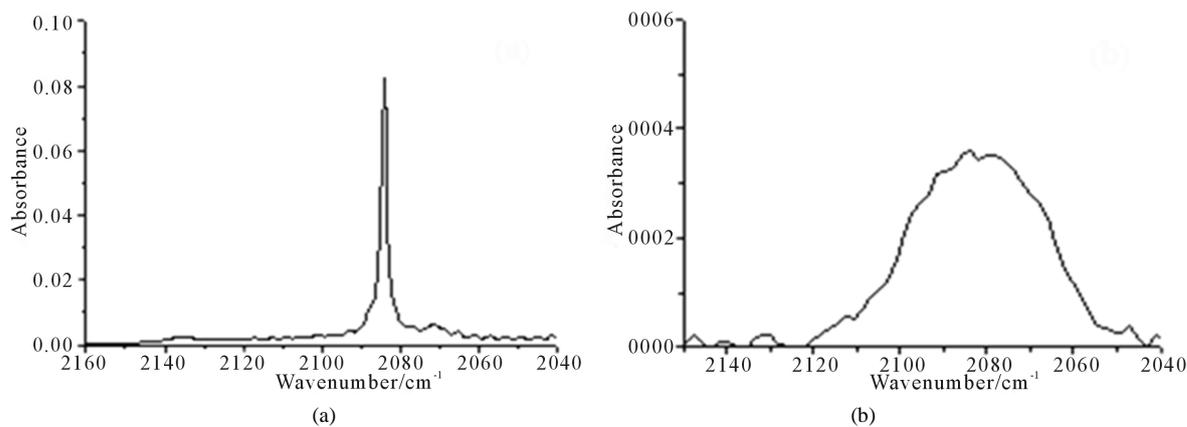


Figure 2. ATR-FTIR spectra of hydrogen-terminated Si(111) surface of (a) *ex situ*; (b) *in situ* in aqueous solution.

Spectra of Si-CH_x on the Si surface was obtained at the aerosol OT concentration of 1×10^{-4} M, 1×10^{-3} M, 1×10^{-2} M *in situ* in **Figure 4**. The spectra showed CH_x 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 CH₃ relatively compared with the CH₂ peaks, nevertheless, the methyl base is less than the methylene base. **Figure 5** showed peak area of CH_x *in situ* in the flowing aerosol OT, which saturation time of

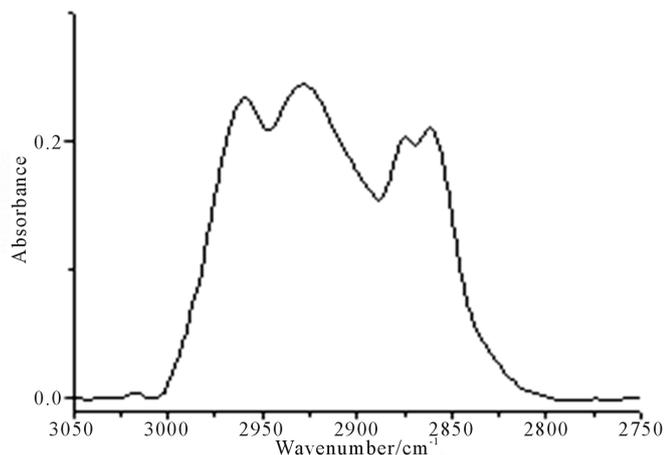


Figure 3. Absorption spectra of the aerosol OT about CH_x peaks.

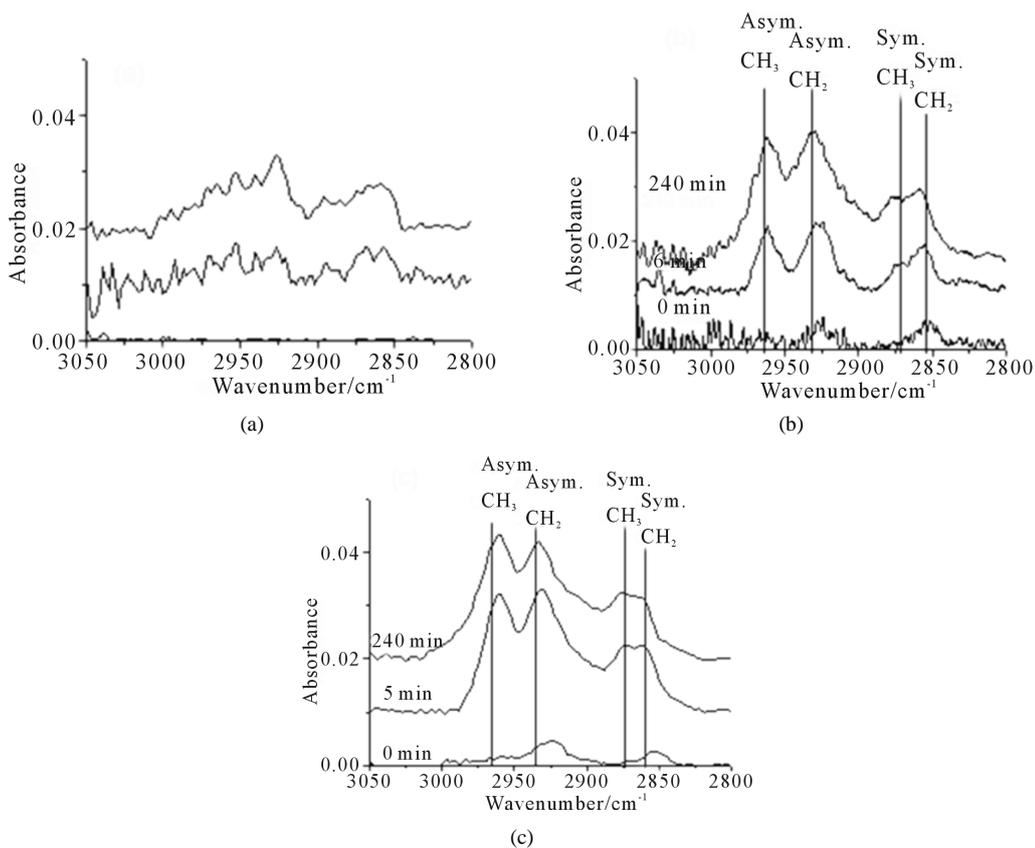


Figure 4. *In situ* ATR-FTIR spectra of the Si surface under the flowing aerosol OT at the concentration of (a) 1×10^{-4} M; (b) 1×10^{-3} M and (c) 1×10^{-2} M.

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 H₂O molecules.

Figure 7 shows AFM images on the Si(111) surface after measuring *in situ* ATR-AFM with flowing (a): 1×10^{-4} M and (b): 1×10^{-2} M aerosol OT for 90 min. The surface was rough in the concentration of 1×10^{-4} M, and was smooth in that of 1×10^{-2} M. These results will indicate difference of amounts of adsorption, and will adsorb densely and orientationally in the case of flowing the 1×10^{-2} M aerosol OT. Hence, the hydrogen-terminated Si(111) surface would prevented the oxidation from attacking the H₂O molecules by adsorption the aerosol OT, which will be efficient with the higher concentration to larger coverage as shown in **Figure 8**.

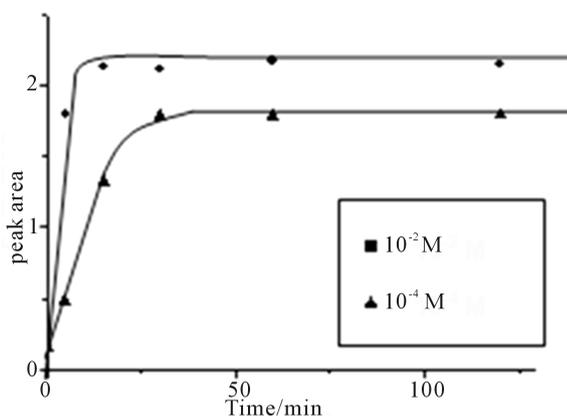


Figure 5. Time course of the CH_x peaks area in **Figure 4**.

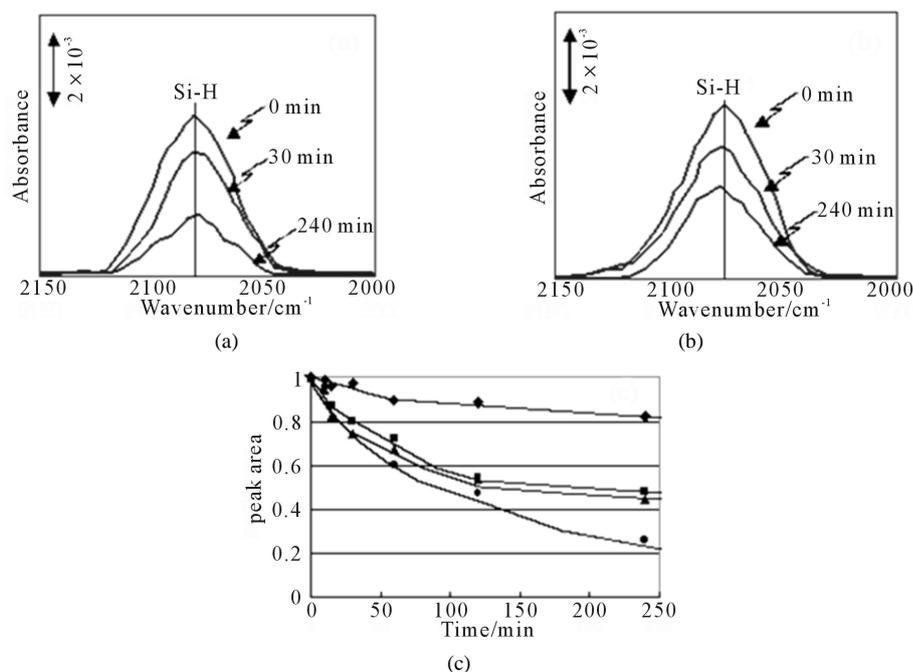


Figure 6. *In situ* ATR-FTIR spectra of the Si-H peaks on the hydrogen-terminated Si(111) under the flowing (a) aqueous solution and (b) aerosol OT. Time course of normalized peak area is in (c) at the concentration of \blacklozenge ; 1×10^{-2} M, \blacksquare ; 1×10^{-3} M, \blacktriangle ; 1×10^{-4}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

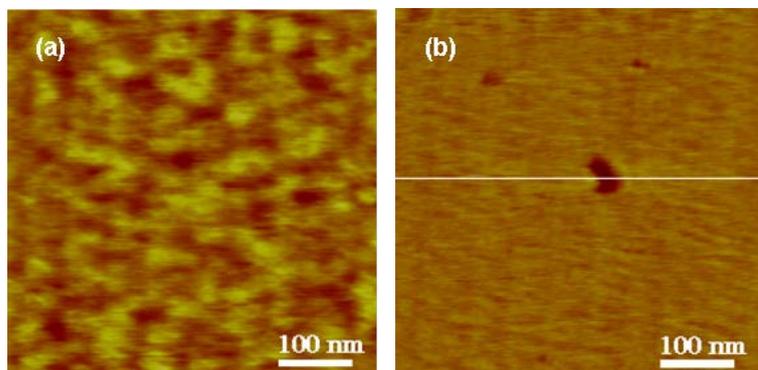


Figure 7. AFM images after the measuring samples in the aerosol OT at the concentration of (a) 1×10^{-4} M and (b) 1×10^{-2} M.

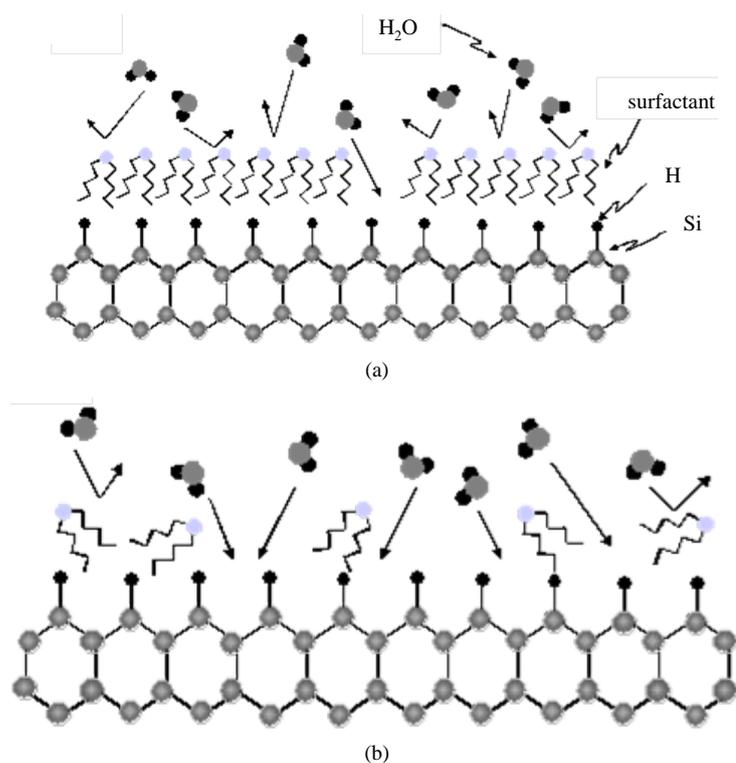


Figure 8. Mechanism of preventing the oxidation by interaction between surfactant and H_2O molecules on the hydrogen-terminated Si(111) surface at (a) 1×10^{-2} M and (b) 1×10^{-4} M.

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 H_2O molecules by adsorption to the Si surface, and AFM images will support them.

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