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$_2$O 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 NH$_4$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.

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. H₂SO₄ and 30% H₂O₂ mixed solution immersing at 10 min, and 5% HF, NH₄OH and H₂O₂ mixed 80°C solution at 10 min, and washed pure water. Finally, the substrate was immersed in boiling up with solution of conc. H₂SO₄ and 30% H₂O₂ solution at 10 min to form SiO₂ 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% NH₄F 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 H₂O adsorption on the Si surface in flowing pure water [10]-[12]. Di-2-ethylhexyl sulfosuccinate sodium salt (aerosol OT) as surfactant is C₈H₁₇COOCH₂CH₂(COOC₈H₁₇)SO₃Na, which the spectrum is assigned to 3467 cm⁻¹ (O-H stretching vibration), 2957 cm⁻¹ (CH₃ asymmetry), 2926 cm⁻¹ (CH₂ asymmetry), 2858 cm⁻¹ (CH₂ symmetry), 1735 cm⁻¹ (C=O stretching vibration), 1459 cm⁻¹ (CH₂ 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.](image)

![Figure 2. ATR-FTIR spectra of hydrogen-terminated Si(111) surface of (a) ex situ; (b) in situ in aqueous solution.](image)
Spectra of Si-CH\textsubscript{x} on the Si surface was obtained at the aerosol OT concentration of \(1 \times 10^{-4} \text{ M}, 1 \times 10^{-3} \text{ M}, 1 \times 10^{-2} \text{ M}\) \textit{in situ} in Figure 4. The spectra showed CH\textsubscript{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 CH\textsubscript{3} relatively compared with the CH\textsubscript{2} peaks, nevertheless, the methyl base is less than the methylene base. Figure 5 showed peak area of CH\textsubscript{x} \textit{in situ} in the flowing aerosol OT, which saturation time of
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 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 H$_2$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 H$_2$O molecules by adsorption to the Si surface, and AFM images will support them.

References


