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Surface Oxide Protection of Si(111) in Solution by the Surfactant Molecules

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Abstract

It has been attempted to immobilize organic mono layer on semiconductor surface as functional materials. Silicon surface was especially noticed to develop highly efficient and functional devices, and the silicon devices were expected for the immobilized surface with organic layer. Then we have attempted the immobilization by the mono layer on the hydrogen terminated silicon surface with the alkyl base indicated hydrophobic by using a surfactant. We have observed interactions of immobilized molecules and organic molecules adsorbed on hydrogen terminated Si(111), which is aerosol OT as known surfactant and 4-cyanophenol as shown amphipathic molecule. The aerosol OT inhibited oxidation of Si(111) surface by adsorption to the hydrogen terminated surface to indicate hydrophobic. The 4-cyanophenol made the surface oxide by adsorption, and was desorbed by forming hydrophilic Si surface. In the case of the mixed solution by the aerosol OT and 4-cyanophenol, the aerosol OT controlled the surface oxidation on the hydrogen terminated Si against the 4-cyanophenol.

Keywords

Adsorption, Silicon, Hydrogen Termination, Amphipathic, *In-Situ* ATR-FTIR

1. Introduction

It has been attempted to immobilize organic mono layer on metal or semiconductor surface etc. as functional materials [1] [2] [3] [4] [5]. Si surface was especially noticed to develop highly efficient and functional devices, and the Si devices were expected for the immobilized surface with organic layer. The typically functional organic layer was known as a biological membrane, which is an amphipathic material in consisting of hydrophobic and hydrophilic bases [6] [7]. The structure has double layer, which the two phosphatides face mutually on the hydrophobic bases in consisting of two alkyl chains [8] [9]. It would show an ideal model to analyze the function of the biological membrane by replacing the unilateral phosphatide with a hydrogen terminated Si (H-Si) surface. The H-Si surface is obtained by etching Si wafer with HF and NH_4F solution to peel oxide layer on the surface [10] [11] [12]. Then we have attempted the immobilization by the mono layer on the H-Si surface with the alkyl base indicated hydrophobic by using a surfactant.

On the other hand, behaviors have been investigated about co-adsorption between alkyl thiol and aromatic thiol on Au substrate by some groups. The adsorbed form was known as $\sqrt{3}\times\sqrt{3}$ structure in the alkyl thiol by itself, and was reported about domain structure in the co-adsorption with the alkyl thiol and aromatic thiol, which have tried to produce an electrode with the controlled domain structure, however the adsorption mechanism is not clearly [13] [14] [15]. We have attempted the analysis of the co-adsorption mechanism for an aerosol OT as an amphipathic organic molecule known to surfactant and 4-cyanophenol as aromatic molecule on the Si(111) surface by *in-situ* ATR-FTIR.

2. Experimental

The Si substrate has used a single crystal semiconductor as n-Si(111), and been cut at 50 × 17 nm with mirror polishing at 45˚ for the either side as ATR prism in **Figure 1**. The substrate was treated RCA washing with conc. H_2SO_4 + 30% H_2O_2 mixed solution, and immersed in 5% HF solution for 5 min and 25% NH_4OH + 30% H_2O_2 mixed solution at 80˚C for 10 min. The sample was applied as ATR prism simultaneously, and measured by 45˚ as an angle of IR incidence in flowing H_2O. Next, the sample was treated with hydrogen termination by flowing 5% HF solution for 10 min, and smoothed atomically on the surface by flowing 40% NH_4OH solution for 7 min as measuring in-situ ATR-FTIR. Furthermore, the sample was measured by flowing 4-cyanophenol as the adsorbed aromatic molecule, or flowing 4-bis(2-ethylhexyl)sodium sulfosuccinate solution (aerosol OT) as the immobilized organic molecule with two alkyl chains known as a surfactant. We performed experimental patterns of (1) flowing only 4-cyanophenol solution, (2) flowing mixed 4-cyanophenol and aerosol OT solution, and (3) flowing 4-cyanophenol solution after adsorb aerosol OT by flowing it.

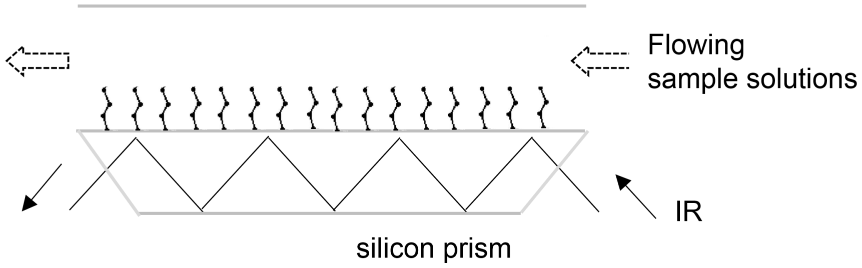

Figure 1. A cell of *in-situ* ATR-FTIR by a cross section.

3. Results and Discussion

3.1. Flowing to Only 4-Cyanophenol

Figure 2 shows *in-situ* ATR-FTIR spectra on the hydrogen terminated Si surface under flowing to 1 × 10^{-3} M 4-cyanophenol solution. A peak was observed at 2234 cm^{-1} based on cyano group, and would be weak by desorption with time passes. Si-H peak intensity also decreased with desorption of the cyano group, which would indicate oxidation of the Si surface gradually with 4-cyanophenol desorption. The aromatic group of 4-cyanophenol will be adsorbed on the Si-H surface to indicate hydrophobic. Then, the Si surface may be oxidated by adsorption with H_2O molecule simultaneously to inhibit strong polarity based on cyano and hydroxyl group.

Similarly, Figure 3 shows the spectrum on SiO_2 substrate indicating hydrophilic under flowing 5 × 10^{-3} M 4-cyanophenol solution. The larger peak of cyano group based on 4-cyanophenol on the hydrogen terminated Si was obtain than that of SiO_2, which would have the advantage of hydrophobic surface.

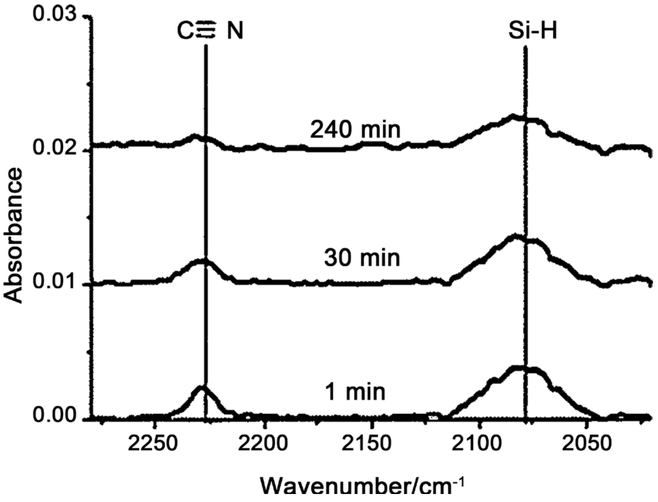

Figure 2. Spectra under flowing to 1 × 10^{-3} M the 4-cyanophenol solution on the hydrogen terminated Si(111) surface.

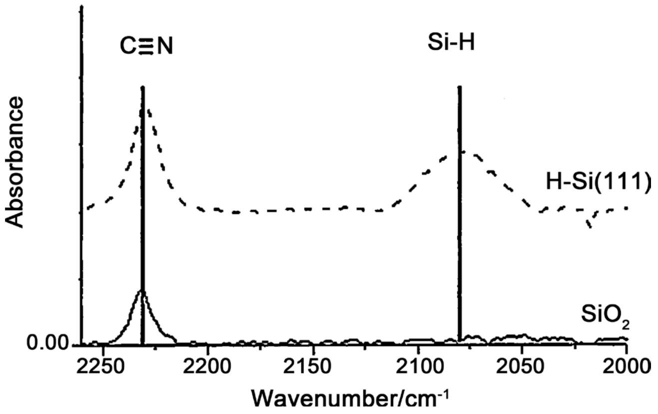

Figure 3. Spectra under flowing to 5 × 10^{-3} M the 4-cyanophenol solution on the SiO_2 surface and hydrogen terminated Si(111) surface as broken line.

3.2. Flowing to 4-Cyanophenol and Aerosol OT

At first, spectra was reported by flowing 1 × 10^{-2} M aerosol OT on the H-Si(111), which observed spectra on assigned to CH_x stretching vibration based on the aerosol OT, and the peak intensity increased with time passes [16]. This result would show adsorption of the aerosol OT onto the hydrogen terminated Si surface over time. In this study, the spectra were measured under the flow of the 4-cyanophenol and aerosol OT mixed solution at variation with time as shown in **Figure 4**. The concentration of the 4-cyanophenol solution is 1 × 10^{-3} M, 3 ×

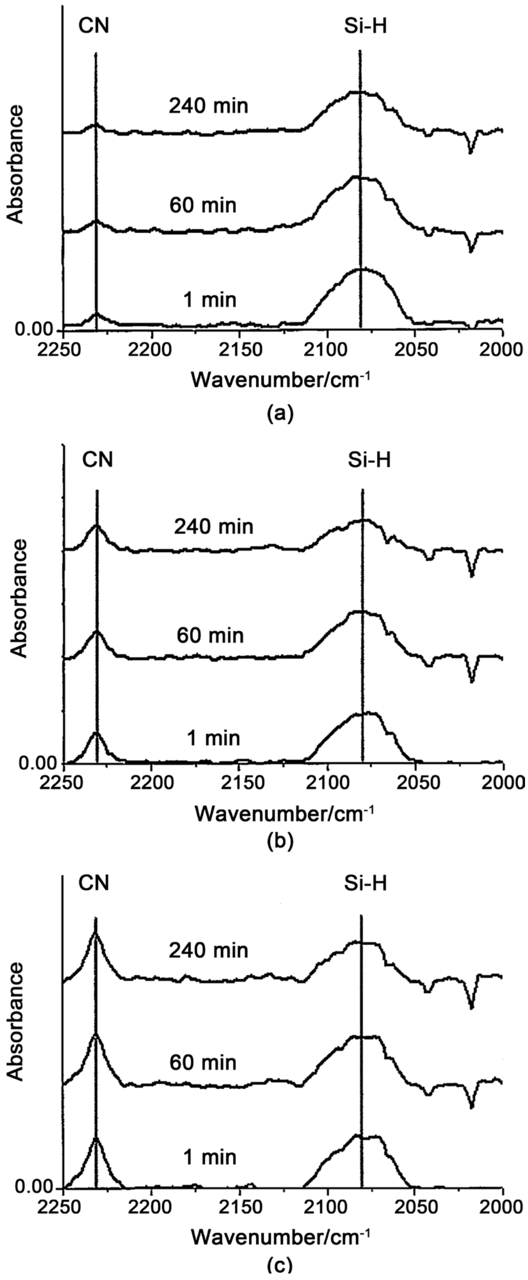

Figure 4. Spectra under flowing to the 4-cyanophenol solution at the concentration of (a) 1 × 10^{-3} M; (b) 3 × 10^{-3} M and (c) 5 × 10^{-3} M with including the 1 × 10^{-2} M aerosol OT solution.

10^{-3} M and 5×10^{-3} M, and that of the aerosol OT solution is 1×10^{-2} M. The peak intensity of cyano group based on 4-cyanophenowas increased with more thickness in the solution, which would show much adsorption of the 4-cyanophenol onto the hydrogen terminated Si surface. On the other hand, the peak intensity of the cyano group hardly changed at the time passes in comparing with Figure 2. This result will indicate that the 4-cyanophenol is keeping adsorption on the Si surface because the aerosol OT layer makes the adsorbed 4-cyanophenol protect by taking in the layer like a biological membrane. By contact, the peak intensity of Si-H decreased slowly, and plotted the decrease rate as referencing the peak area at 1 min as shown in Figure 5. The higher concentration of 4-cyanophenol solution made the Si-H peak intensity decrease. These results show proceeding to the oxidation of the Si surface, and may indicate an influence of H_2O adsorption by the 4-cyanophenol like the mechanism in Figure 2.

Spectra on assigned to CH_x stretching vibration based on the aerosol OT is showed in Figure 6. The peak intensity did not increase with time passes in spite

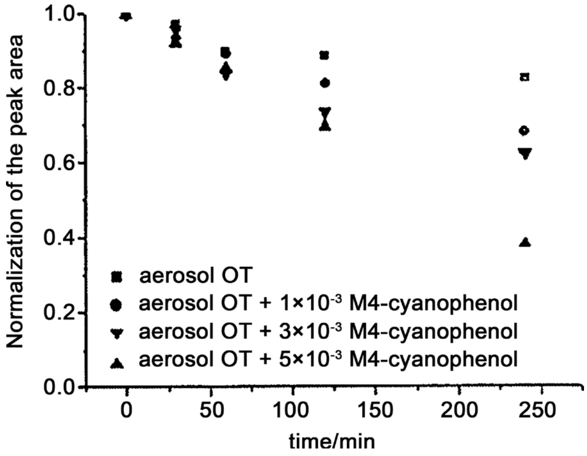

Figure 5. Normalization plots of the decreasing peak area with time course.

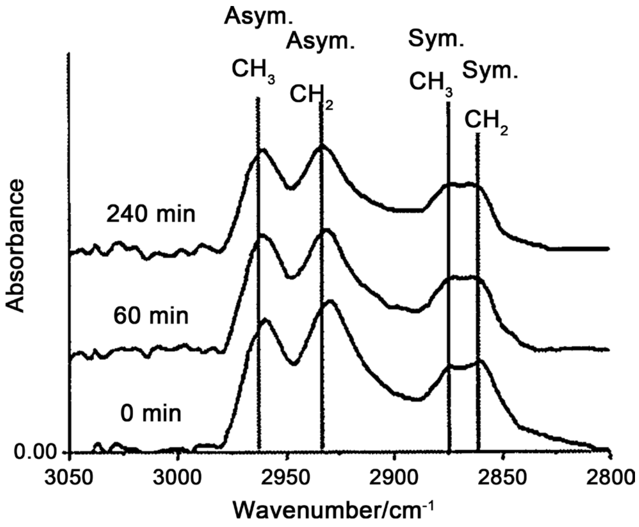

Figure 6. CH_x spectra based on the aerosol OT under flowing the 3×10^{-3} M 4-cyanophenol and 1×10^{-2} M aerosol OT mixed solution.

of flowing into the 4-cyanophenol solution. The reason would be suitable for the aerosol layer adsorbed on the hydrogen terminated Si surface, because a behavior of the aerosol layer is reported in the presence of organic thiol molecule on the Au substrate, and the results will be similar to ours [14].

3.3. Flowing to 4-Cyanophenol after Immobilizing Aerosol OT

Spectra were indicated under flowing to the 3 × 10^{-3} M 4-cyanophenol solution after the 1 × 10^{-2} aerosol OT solution as shown in Figure 7. The peak intensity of cyano group based on 4-cyanophenol hardly changed at time passes, which would protect the adsorption of the 4-cyanophenol onto the Si surface by the aerosol OT layer. Thus, the 4-cyanophenol will not slip into the aerosol OT layer at time passes by the immobilization on the Si surface. Furthermore, the Si surface will not be oxidation not to decrease in the peak intensity of the Si-H at time passes.

Spectra on assigned to CH_x stretching vibration based on the aerosol OT is showed after adding the 4-cyanophenol solution in Figure 8. The peak intensity

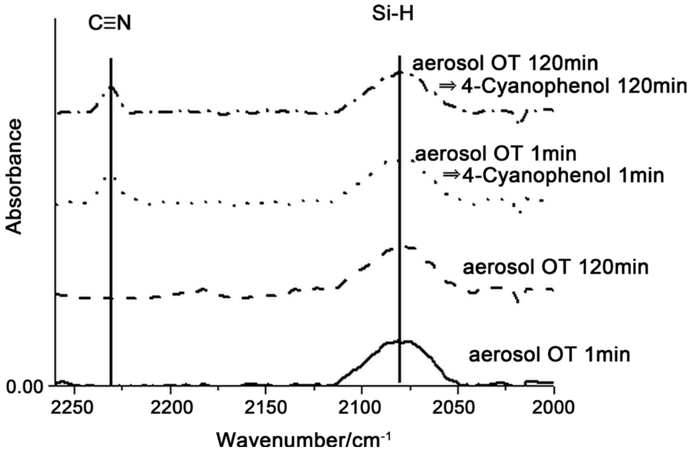

Figure 7. Spectra under flowing to the 1 × 10^{-2} M aerosol OT solution, and the 3 × 10^{-3} M 4-cyanophenol solution after to the 1 × 10^{-2} M aerosol OT solution.

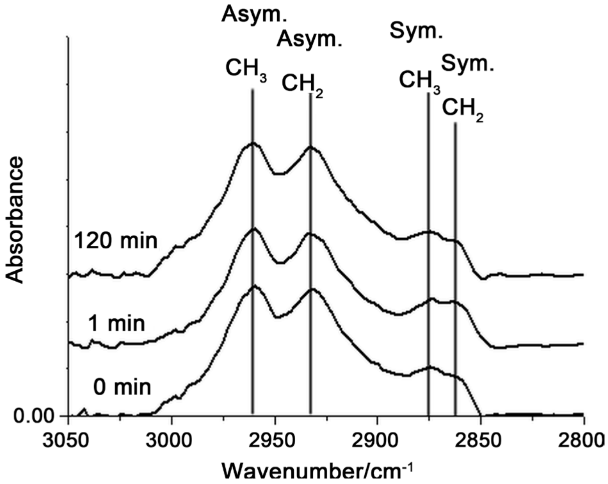

Figure 8. CH_x spectra based on the aerosol OT under flowing the 3 × 10^{-3} M 4-cyanophenol and 1 × 10^{-2} M aerosol OT mixed solution.

also did not change for the flow of the 4-cyanophenol solution. This result would show that the aerosol OT layer on the Si surface was not be influenced by the 4-cyanophenol.

4. Conclusion

The 4-cyanophenol was adsorbed onto the hydrophobic surface by the hydrogen terminated Si, and was desorbed by the hydrophilic surface to oxide on the surface. These results might show that the 4-cyanophenol brought H_2O molecule by the cyano and hydroxyl group onto the Si surface, and the H_2O molecule made the surface oxide. The aerosol OT will adsorb by the alkyl chain shown as the hydrophobic onto the surface, furthermore the layer will protect oxidation of the Si surface and will prevent the layer slipping in the presence of the 4-cyanophenol.

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