

# Alkyl Self-assembled Monolayer Prepared on Hydrogen-terminated Si(111) through Reduced Pressure Chemical Vapor Deposition : Chemical Resistivities in HF and NH<sub>4</sub>F Solutions

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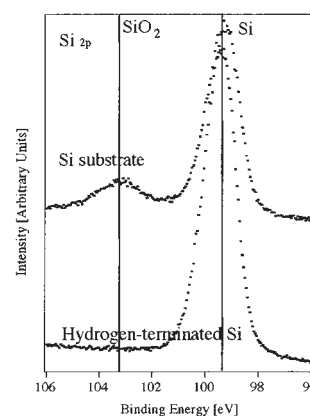
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Hexadecyl self-assembled monolayers have been prepared on hydrogen-terminated Si(111) substrates through reduced pressure chemical vapor deposition. Chemical resistivities to HF and NH<sub>4</sub>F of SAMs were studied.

Organic self-assembled monolayer (SAM) formed through the chemical reaction between 1-alkene and hydrogen-terminated silicon is an attractive material for molecular electronic devices, since the monolayer is directly attached to silicon through Si–C bonds without inserting a silicon oxide layer.<sup>1</sup> Many researchers have reported on structural configurations and chemical bonding states of such SAMs.<sup>2</sup> Hydrofluoric acid (HF) and ammonium fluoride (NH<sub>4</sub>F) solutions are frequently used as etching reagents when various shapes are fabricated on silicon wafers for electronic devices. The high chemical resistivities of SAMs as a resist film to the etching solutions allow us to fabricate the complex and super-fine shapes on silicon wafers. In the case of alkylsilane SAMs fixed on oxide-covered silicon substrates through Si–O–Si bonds, these solutions rapidly destroy the bonds. The SAMs covalently attached to Si substrates with Si–C bonds are expected to have better chemical resistivities to the solutions than alkylsilane SAMs due to absence of Si–O–Si bonds.<sup>2e)</sup> However, chemical resistivities of the 1-alkene SAMs have not been studied in detail. We have prepared 1-alkene SAM on hydrogen-terminated Si(111) substrates through reduced pressure chemical vapor deposition (RPCVD), and have elucidated the resistivities in HF and ammonium fluoride (NH<sub>4</sub>F) solutions in order to show potential for a resist film.

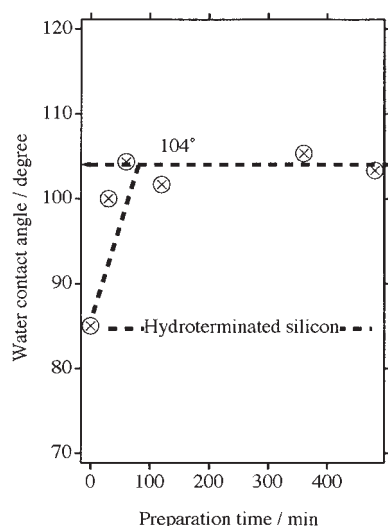
Silicon (111) substrates (p-type) were cleaned ultrasonically in acetone, methanol and deionized water in that order. The substrates were further etched in aqueous HF solution (5 vol%) at 70 °C. The water contact angle of the substrate etched for 3 min was about 85°, which agrees with that of hydrogen-terminated silicon.<sup>3</sup> The root mean square roughness (RMS) of the etched silicon substrate was obtained by atomic force microscopy (Seiko Instruments Inc., SPA-300HV+SPI-3800N). The RMS was ca. 0.25 nm. Figure 1 shows Si<sub>2p</sub> spectra before and after the HF etching measured by X-ray photoelectron spectroscopy (XPS; Shimadzu ESCA-3300). The take-off angle of photoelectron was 90° in this study. Two peaks corresponding to bulk Si (ca. 99.3 eV) and SiO<sub>2</sub> (ca. 103.3 eV) were confirmed in the spectrum before the HF etching. On the other hand, only a peak of bulk Si was confirmed in the spectrum after the HF etching. These results show that the native oxide was completely removed from the silicon substrate, and the substrate was terminated with hydrogen.

1-Hexadecene (Tokyo Kasei Co. Ltd.) was used as a precursor. The hydrogen-terminated Si(111) substrates were

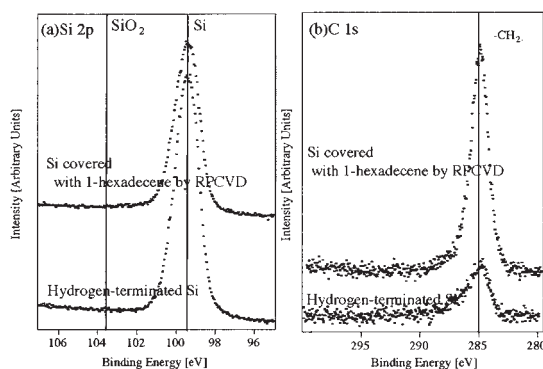


**Figure 1.** Si<sub>2p</sub> spectra of silicon substrate and hydrogen-terminated silicon measured by X-ray photoelectron spectroscopy.

alkylated as follows. The hydrogen-terminated silicon substrate and 1-hexadecene was sealed into an autoclave of which volume was 100 cm<sup>3</sup>. The volume of 1-hexadecene put into the autoclave was determined to be 4 μL in order to avoid being condensed in the autoclave. After the autoclave process, which was modified for the use under reduced pressures, had been evacuated down to a pressure of 10 Pa, it was heated to be hexadecene molecules react with Si–H groups on the substrate, resulting in the alkyl monolayer formation ( $\text{SiH} + \text{CH}_2 = \text{CHC}_{14} \rightarrow \text{SiC}_{16}\text{H}_{33}$ ). After the alkylation, the silicon substrates were ultrasonically cleaned in toluene, methanol and deionized water in order to remove physical-adsorbates. Figure 2 shows the relationship between water contact angle and CVD time. The water contact angle reached a saturated one (= 104°) after the alkylation for 60 min. The surfaces completely covered with CH<sub>3</sub> and CH<sub>2</sub> groups have ideal water contact angles of 110° and 104°, respectively. The CH<sub>3</sub>-terminated SAM has the water contact angle below 110° since the molecular chains of SAM actually have a certain tilt angle. The water contact angle of 104° is slightly small compared with the value of alkylsilane SAM (= 108°). However, this water contact angle is bigger than those of alkene SAM reported previously.<sup>4</sup> In the case of SAMs onto hydrogen-terminated silicon, the water contact angle would depend on the face of silicon substrate, the number of H–Si bonds and so on. Figure 3 shows Si<sub>2p</sub> and C<sub>1s</sub> XPS spectra before and after the alkylation. The spectra of Si<sub>2p</sub> before and after the alkylation were not changed at all except for the intensities, indicating that we succeeded in preventing the hydrogen-terminated silicon substrate from being oxidized. Locations of the C<sub>1s</sub> peaks before and after



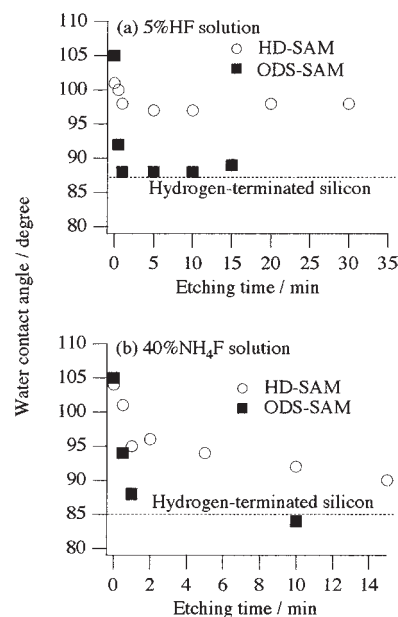
**Figure 2.** Relationship between water contact angle and CVD time.



**Figure 3.**  $\text{Si}_{2p}$  and  $\text{C}_{1s}$  spectra of 1-hexadecene SAM measured by X-ray photoelectron spectroscopy.

the alkylation are identical, while the intensity increases after the alkylation. These results indicate that the alkylation of the hydrogen-terminated silicon substrate is accomplished without forming the oxide.

Resistivities of the 1-hexadecene SAM (HD-SAM) to HF and  $\text{NH}_4\text{F}$  aqueous solutions were examined. The concentrations of HF and  $\text{NH}_4\text{F}$  were 5 and 40 vol%, respectively. Figures 4(a) and (b) show the changes in water contact angles when the HD-SAM samples were immersed in the HF and  $\text{NH}_4\text{F}$  solutions at 25 °C, respectively. For control experiments, an organosilane SAM prepared from octadecyltrimethoxysiloxane (ODS-SAM) on oxide-covered silicon substrates was also examined in the same solutions. As shown in Figure 4(a), the water contact angle of ODS-SAM drastically decreased down to ca. 85°, which is the water contact angle of hydrogen-terminated silicon. This indicates that the organic layer and silicon oxides layer would be removed from silicon substrate. On the other hand, the water contact angle of HD-SAM was hardly changed. The water contact angle remained at around 98° even after immersing for 30 min in the HF solution. As shown in Figure 4(b), the water contact angle of ODS-SAM in the  $\text{NH}_4\text{F}$  solution drastically became lower and



**Figure 4.** Relationship between water contact angle and etching time.

then reached ca. 80° after 2 min as similarly to the results in the HF solution. However, the water contact angle of HD-SAM decreased lower than ODS-SAM. The water contact angle was still around 95° even after 10 min. These chemical resistivities of HD-SAM originate in the covalent Si–C bond.

In conclusion, we have successfully prepared HD-SAM through RPCVD and evaluated its chemical resistivities in the HF and  $\text{NH}_4\text{F}$  solutions. The water contact angle of HD-SAM immersed in these solutions remained for a longer time than ODS-SAM. HD-SAM is expected to work as a high performance monolayer resist film in acid and base solutions.

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