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Chemical Resistivity and Micro-fabrication of Organic Monolayer Directly Attached to Silicon

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1. Introduction

Organic Self-assembled monolayer (SAM) formed through the chemical reaction between 1-alkene and hydrogen-terminated silicon in an attractive material for molecular electronics devices, since the monolayer is directly attached to silicon through Si-C bonds without inserting a silicon oxide layer¹. Many researchers have reported on structural configurations and chemical bonding states of such SAMs². In addition, the SAMs covalently attached to Si substrates with Si-C bonds are expected to have better chemical resistivities particularly to hydrofluoric acid (HF) than alkylsilane SAMs which are fixed on oxide-covered silicon substrates through Si-O-Si bonds^{2(e)}. 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 (NH₄F) solutions.

2. Results and Discussion

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 80°, which agrees with that of hydrogen-terminated silicon³. The root mean square roughness of the etched silicon substrate was ca. 0.25 nm. Figure 1 shows Si_{2p} spectra before and after the HF etching measured by x-

ray photoelectron spectroscopy. Two peaks corresponding to bulk Si (ca. 100 eV) and SiO₂ (ca. 104 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 alkylated as follows. The hydrogen-terminated silicon substrate and 1-hexadecene was sealed into an autoclave of which volume was 100 cm³. 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, which was modified for the use under reduced pressures, had been evacuated down to a pressure of 50 Pa, it was heated to be hexadecene molecules react with Si-H groups on the substrate, resulting in the alkyl monolayer formation ($\text{SiH} + \text{CH}_2 = \text{CHC}_{14}\text{H}_{29} \rightarrow \text{SiC}_{16}\text{H}_{33}$). After the alkylation, the silicon substrates were ultrasonically cleaned in toluene, methanol and deionized water in order to remove physical-adsorbents. 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 molecular chains in the SAM are probably more highly oriented perpendicular to the substrate and/or more densely packed than in similar

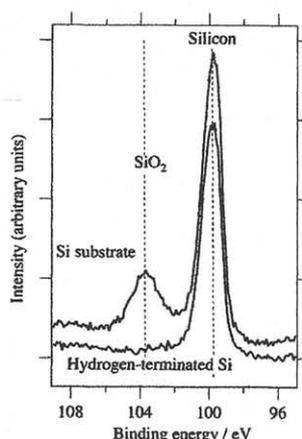


Fig.1 Spectra of Si_{2p} measured by x-ray photoelectron spectroscopy.

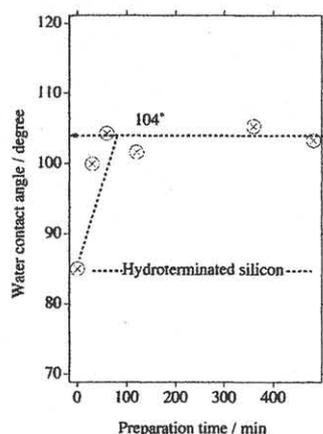


Fig.2 Relationship between water contact angle and CVD time.

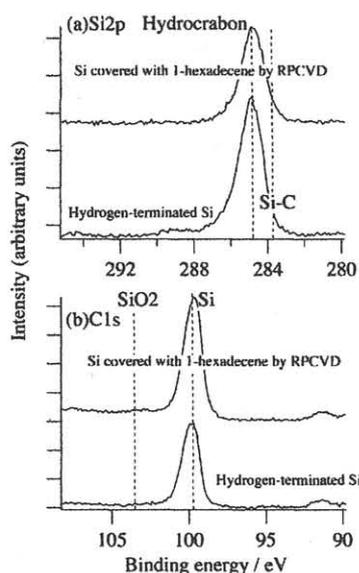


Fig.3 Spectra of Si_{2p} and C_{1s} by measured by x-ray photoelectron spectroscopy.

SAMs reported previously, because the water contact angle of 104° is closer to the ideal value of the CH₃-terminated surface⁴. Figure 3 shows Si_{2p} and C_{1s} xps spectra before and after the alkylation. The spectra of Si_{2p} before and after the alkylation were not changed at all, indicating that we succeeded in preventing the hydrogen-terminated silicon substrate from being oxidized. Locations of the C_{1s} peaks before and after the alkylation are identical, while the intensity increases after the alkylation. These results 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 NH₄F aqueous solutions were examined. The concentrations of HF and NH₄F were 5 and 45 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 NH₄F 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 decreases down to ca. 85°. The ODS-SAM is concluded to be completely removed from the substrate due to the HF etching for only 2min. On the other hand, the water contact angle of HD-SAM is hardly changed. The water contact angle remains 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 NH₄F solution drastically becomes lower and then reached ca. 80° after 2 min as similarly to the results in the HF solution. However the water contact angle of HD-SAM decreases slower than ODS-SAM. The water contact angle is still around 95° even after 10 min. These

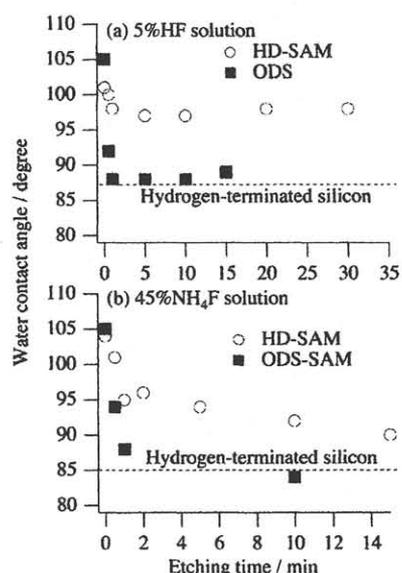


Fig.4 Relationship between water contact angle and etching time.

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 NH₄F 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 resists film in acid and base solutions.

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References

- [1] D.D.M. Wayner and R.A. Wolkow, *J. Chem. Soc., Perkin Trans. 2*, 2002, 1, 23.
- [2] (a) M.R. Linford and C.E.D. Chidsey, *J. Am. Chem. Soc.*, 1993, **115**, 12631. (b) M.R. Linford, P. Fenter, P.M. Eisenberger and C.E.D. Chidsey, *J. Am. Chem. Soc.*, 1995, **117**, 3145. (c) J. Terry, M.R. Linford, C. Wigren, R.Y. Cao, P. Pianetta and C.E.D. Chidsey, *Appl. Phys. Lett.*, 1997, **71**, 1056. (d) J. Terry, M.R. Linford, C. Wigren, R.Y. Cao, P. Pianetta, C.E.D. Chidsey, *J. Appl. Phys.*, 1999, **85**, 213. (e) A.B. Sieval, R. Linke, G. Heji, G. Meijer, H. Zuilhof and E.J.R. Sudholter, *Langmuir*, 2001, **17**, 7554. (f) R.L. Cicero, C.E.D. Chidsey, G.P. Lopinski, D.D.M. Wayner and R.A. Wolkow, *Langmuir*, 2002, **18**, 305. (g) E.E. Quayum, T. kondo, S. Nihonyanagi, D. Miyamoto and K. Uosaki, *Chem. Lett.*, 2002, **2**, 208.
- [3] E. Kondoh, M.R. Baklanov, F. Jonckx and K. Maex, *Mat. Sci. Semicon. Proc.* **1**, 1998, 107.
- [4] A.B. Sieval, V.V.H. Zuihof and E.J.R. Sudholter, *Langmuir*, 1999, **15**, 828.