

Study of the fluorinated self-assembled monolayer by photoemission and NEXAFS spectroscopies

The study of surface modification using the fluorinated self-assembled monolayer (F-SAM) has attracted significant interest for a wide range of applications because its surface covered by F-SAM has good properties of anti-adherence, lubrication, and water resistance [1]. In the field of nanoimprint lithography, which is a promising method of fabricating various nanostructures at low cost and with a high throughput by pressing a mold, F-SAM has been used as an antisticking layer of nanoimprint molds to avoid resist adhesion [2]. Since the antisticking layer of a nanoimprint mold repeatedly comes into direct contact with the resist in the process of nanoimprint lithography, it is critical to obtain information on the surface of the F-SAMs, the interface between the F-SAMs and the Si substrate, and the molecular orientation in F-SAMs. Therefore, we have measured the photoemission spectra to clarify the electronic structures, such as the chemical compositions and components, on the surface of F-SAMs. In addition, the near-edge X-ray absorption fine structure (NEXAFS) spectra of F-SAMs with different thicknesses were measured to investigate the molecular orientation.

Four kinds of F-SAMs denoted as FAS-3, FAS-9, FAS-13, and FAS-17 were prepared from the fluorinated silane coupling agent $\text{CF}_3(\text{CF}_2)_n(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$ with $n=0, 3, 5,$ and $7,$ respectively [3]. The number after FAS means the number of F atoms. With increasing number of F atoms, the length of the C-C chain arising from the $(\text{CF}_2)_n$ part increases. The schematic diagrams of the four kinds of F-SAMs with different chain lengths are shown in Fig. 1. All photoemission and NEXAFS spectra were measured at BL07B end station of the NewSUBARU synchrotron radiation facility, University of Hyogo.

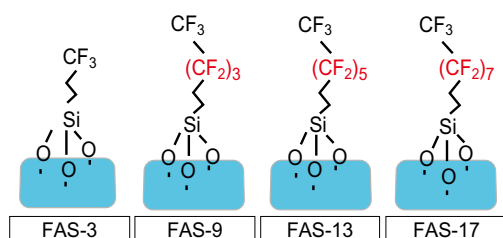


Fig. 1. Four kinds of F-SAMs with different chain lengths.

In Fig. 2, the photoemission spectra (dots) of the C 1s core-level region in four kinds of F-SAMs with different chain lengths are plotted. In the photoemission spectra of the C 1s core level, three peaks at 292, 286, and 284.5 eV were observed in FAS-3 although four peaks at 293, 291, 286, and 284.5 eV were observed in FAS-9, FAS-13, and FAS-17. With increasing chain length, the intensity of the peak at 291 eV increased while the intensities of the peaks at 293 and 286 eV did not change. On the basis of the chemical compositions of the four kinds of F-SAMs with different chain lengths, the four peaks at 293, 291, 286, and 284.5 eV in FAS-9, FAS-13, and FAS-17 were assigned to the CF_3 , CF_2 , CH_2 , and C-C components, respectively. In FAS-3, the peak at 292 eV was assigned to the CF_3 component, since there is no C-C chain arising from the $(\text{CF}_2)_n$ part, as shown in Fig. 1. To clarify further details of the chemical environments, the curve fitting analysis for the photoemission spectra of the C 1s core level was performed by a least-square method. The best-fit curves (lines) of the four kinds of F-SAMs with

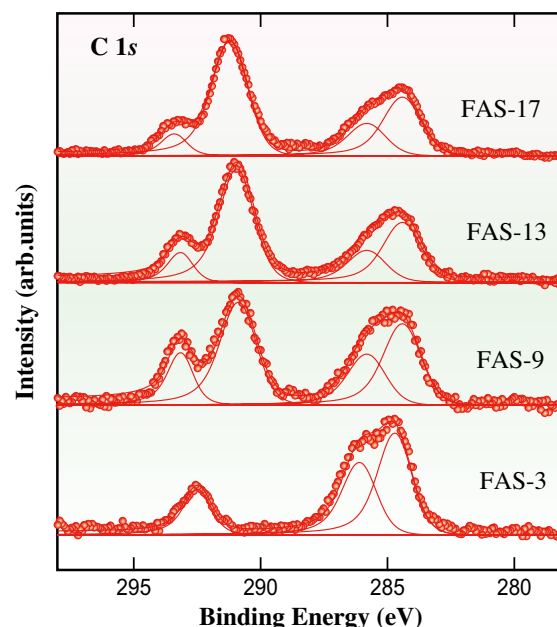


Fig. 2. Photoemission spectra (dots) of the C 1s core-level region in four kinds of F-SAMs with different chain lengths. The fitted results (lines) are also plotted for each photoemission spectrum.

different chain lengths are also shown. Figure 3 shows the NEXAFS spectra of the four kinds of F-SAMs with different chain lengths. Several peaks were observed at the photon energies of 285, 289, 290, 292, 295, and 299 eV. With increasing chain length, the intensities of the peaks at 292 and 299 eV increased while that of the peak at 289 eV decreased. On the other hand, the intensities of the peaks at 285, 290, and 295 eV were almost unchanged with increasing chain length. This indicates that the peaks at 292 and 299 eV are derived from the $(CF_2)_n$ part of F-SAMs. In addition, the peaks at 292, 295, and 299 eV in this study were assigned to the $\sigma^*(C-F)$, $\sigma^*(C-C)$, and $\sigma^*(C-F)$ transitions from the C 1s core level, respectively [4]. The peak at 289 eV was also assigned to the $\sigma^*(C-H)$ transition arising from the $(CH_2)_2$ part of the F-SAMs. When the incidence angle θ increased from 0 to 75°, the intensities of the peaks at 292 and 299

eV assigned to the $\sigma^*(C-F)$ transitions decreased while that of the peak at 295 eV assigned to the $\sigma^*(C-C)$ transition increased. Since the direction of the electric field in synchrotron radiation is parallel to the surface in the case of $\theta = 0^\circ$, the incidence angle dependence indicates that the $\sigma^*(C-F)$ and $\sigma^*(C-C)$ orbitals in F-SAMs are parallel and perpendicular to the surface, respectively. Therefore, it is considered that the C-C chain in the $(CF_2)_n$ part of F-SAMs is perpendicular to the surface.

In summary, the electronic structures of four kinds of F-SAMs with different chain lengths were investigated by photoemission and NEXAFS spectroscopies. Not only the chemical compositions and components but also the molecular orientation in the F-SAMs were clarified in this study. These results would be useful in the fields of application, such as nanoimprint lithography.

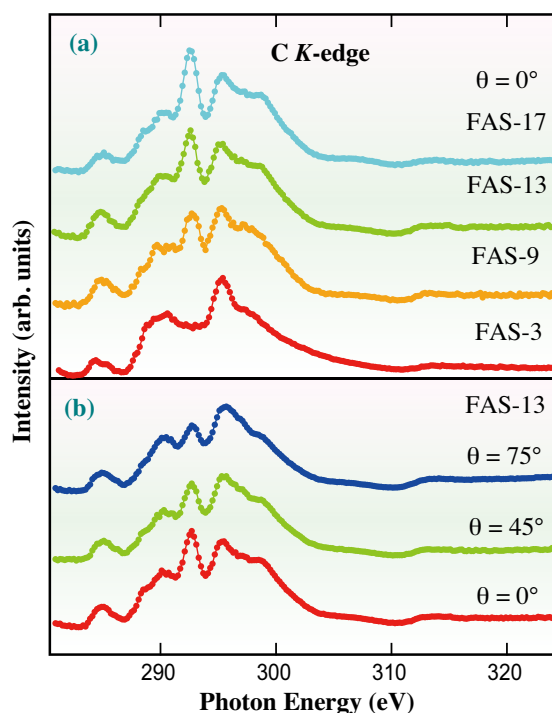


Fig. 3. (a) C K-edge NEXAFS spectra of four kinds of F-SAMs with different chain lengths. (b) C K-edge NEXAFS spectra in FAS-13 as a function of the incidence angle of the synchrotron radiation to the surface normal.

Yuichi Haruyama

Laboratory of Advanced Science and Technology
 for Industry, University of Hyogo

Email: haruyama@lasti.u-hyogo.ac.jp

References

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