

We have developed derivatization X-ray Photoelectron Spectroscopy (XPS) as a means of analyzing the silanol group, which is capable of improving the friction properties of silicon containing diamond-like carbon (DLC-Si).¹⁾

A derivatization reagent must have both a large number of fluorine atoms and only one reacting point, so that it can be reliably detected by XPS and self-polymerization can be avoided. Therefore, we selected tridecafluoro-1,1,2,2-tetrahydrooctyl dimethylchlorosilane (FOCS) as the derivatization reagent for the silanol group. The model samples used for this study were H-, OH- and H/OH- (mixture of H and OH) terminated silicon wafers. The H-terminated silicon wafers were prepared by dipping silicon (100) wafers into a 0.5-vol% aqueous solution of hydrofluoric acid to remove the naturally occurring layers of oxide and to hydrogenate their surfaces. The H/OH-terminated silicon wafers were prepared by dipping H-terminated silicon wafers into ion-exchanged water, and the OH-terminated silicon wafers were prepared by dipping silicon (100) wafers into a solution of $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$ (1:4). The water contact angles for these wafers were determined to be 76° (H-terminated), 34° (H/OH-terminated) and 18° (OH-terminated), respectively.

Derivatization reactions were performed by dipping the model samples into a 1-vol% FOCS solution in chloroform for 1 hour at room temperature. Subsequently, the model samples were

washed with chloroform to remove any unreacted FOCS. These samples were then dried in the XPS preparation chamber. The fluorine content was determined by XPS (PHI-5500MC) with monochromated Al $K\alpha$ X-rays at 150 W. The diameter of the irradiating X-ray was $400\ \mu\text{m}$, the take-off angle was 70° , and the base pressure was below 3×10^{-7} Pa.

The fluorine concentrations on the surfaces of the derivatized model samples are shown in **Fig. 1**. The order of the detected fluorine concentration is clearly related to the amount of the surface silanol groups (Si-OH), while the reproducibility is good. This result indicates that the amount of the silanol groups can be evaluated using this FOCS derivatization technique.

We tried to apply this technique to the analysis of the mechanism of low-friction DLC-Si. The relationship between the fluorine concentration and the friction coefficient of DLC-Si is shown in **Fig. 2**. This result indicates that the silanol group acted so as to reduce the friction coefficient of DLC-Si.

In conclusion, we have developed derivatization XPS using FOCS that enables us to evaluate silanol groups on the surfaces of materials. By applying this technique, we were able to obtain important information about the low-friction mechanism of DLC-Si.

References

- 1) Takahashi, N., et al. : J. Surf. Sci. Soc. Jpn., **26-8**(2005), 492

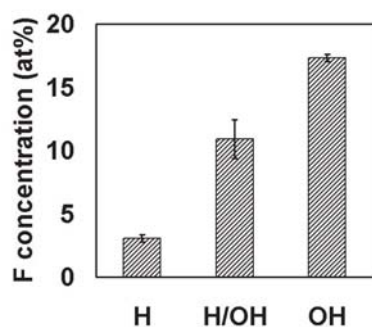


Fig. 1 Fluorine concentration of derivatized surface of silicon wafers.

H : terminated by H
H/OH : terminated by mixture of H and OH
OH : terminated by OH

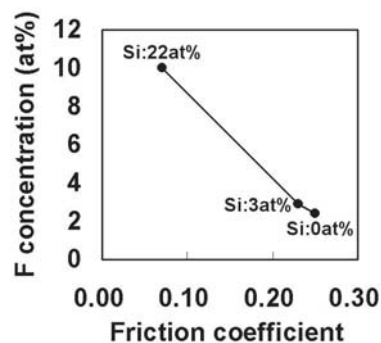


Fig. 2 Relationship between fluorine concentration and friction coefficient on surface of DLC-Si coatings (0-, 3- and 22-atomic% Si concentration).