24BG010 BL-13

Determination of organic molecular film thickness on gold substrates using soft X-ray photoelectron spectroscopy

Shogo Tendo[a], Kakuto Yoshioka, Akinobu Niozu, Shohei Asakura, Yuri Ohura, and Shin-ichi Wada

[a]*Graduate School of Advanced Science and Engineering, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*

[b]*Graduate School of Humanities and Social Sciences, Hiroshima University, Higashi-Hiroshima 739-8524, Japan*

[c]*Research Institute for Synchrotron Radiation Science, Hiroshima University, Higashi-Hiroshima 739-0046, Japan*

Keywords: Self-assembled monolayer (SAM), X-ray photoelectron spectroscopy (XPS), Thickogram analysis.

Self-assembled monolayers (SAMs) enable nanoscale surface functionalization by taking advantage of molecular design flexibility, and are expected to have a wide range of applications including electronic devices, catalysts, biosensors, and solar cells [1]. The electronic conductivity, surface energy, and reactivity of SAMs vary significantly depending on molecular film thickness and orientation. Therefore, precisely determining these structural properties is essential for the design and application of SAMs. In this study, we determined the molecular film thickness using X-ray photoelectron spectroscopy (XPS) and evaluated its validity based on molecular orientation angles determined by near-edge X-ray absorption fine structure (NEXAFS) spectroscopy and structural optimization through density functional theory (DFT) calculations.

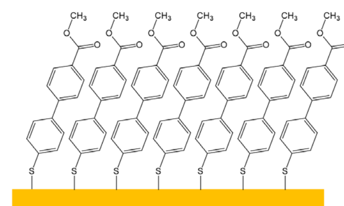

FIGURE 1. Graphical image of MBP SAM.

The experiments were conducted at HiSOR BL-13, a bending magnet beamline suitable for analyzing surfaces composed of light elements. The target samples were SAMs formed by chemisorption via thiol groups onto gold substrates, consisting of six different molecules with varying aromatic backbone structures, each terminating in a methyl ester group. In this study, the methodology for determining film thickness is presented using biphenyl (MBP) SAMs as an example, as shown in FIGURE 1. A wide-scan XPS spectrum of MBP SAMs, acquired with a hemispherical electron energy analyzer at a photon energy of 396 eV, is shown in FIGURE 2.

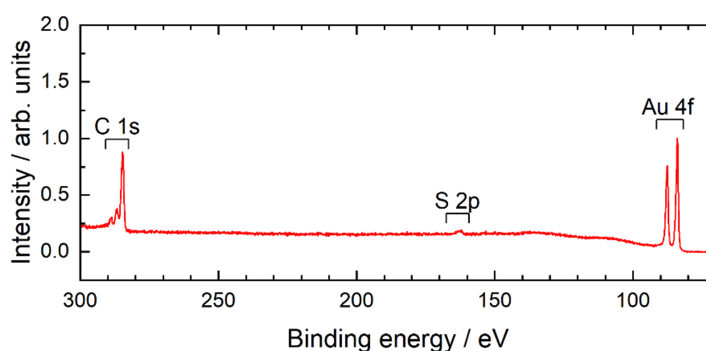

FIGURE 2. Wide-scan XPS spectrum of MBP SAM. The spectrum was acquired at a photon energy of 396 eV, with the intensity normalized to the Au $4f_{7/2}$ peak.

Since photoelectrons undergo inelastic scattering within the molecular film, the intensity of the Au 4f photoelectron peak, I_{Au}, is expressed by equation

$$I_{\mathrm{Au}} = s_{\mathrm{Au}}\exp(-t/\lambda_{\mathrm{Au}}\cos\theta), \tag{1}$$

where t represents the molecular film thickness and θ is the emission angle (0° in this study). The intensity of the C 1s photoelectron peak, I_{C}, is given by equation

$$I_{\mathrm{C}} = s_{\mathrm{C}}\exp(-t/\lambda_{\mathrm{C}}\cos\theta). \tag{2}$$

λ_{Au} and λ_{C} denote the inelastic mean free paths (IMFPs) of Au 4f and C 1s photoelectrons, respectively, while s_{Au} and s_{C} represents their corresponding detection sensitivities. The sensitivity ratio of s_{Au} / s_{C} was determined using hexadecanethiol SAMs of known molecular film thickness (17.3 Å) [2]. Based on these equations (1) and (2), Cumpson derived the Thickogram equation

$$\ln\left(\frac{I_{\mathrm{C}}\, s_{\mathrm{Au}}}{I_{\mathrm{Au}}\, s_{\mathrm{C}}}\right) = \ln\sinh\left(\frac{1}{2\lambda_{\mathrm{C}}\cos\theta}\right) + \left[\left(\frac{E_{\mathrm{C}}}{E_{\mathrm{Au}}}\right)^{0.75} - \frac{1}{2}\right]\frac{t}{\lambda_{\mathrm{C}}\cos\theta} + \ln 2 \tag{3}$$

for film thickness determination using XPS [3].The IMFP ratio was estimated using an empirical formula based on the ratio of kinetic energies: $\lambda_{\mathrm{C}}/\lambda_{\mathrm{Au}} = (E_{\mathrm{C}}/E_{\mathrm{Au}})^{0.75}$. Further data analysis was performed using the electron spectroscopy analysis software COMPRO12, developed by Yoshihara. [4], leading to the determination of an MBP SAM thickness of 14 Å. The film thickness was estimated based on the determination of the molecular orientation angle using NEXAFS spectra and the calculation of molecular length via DFT. Figure 3 shows the polarization-dependent NEXAFS spectra at the carbon K-edge. The absorption intensity of the π* peak increased and that of the σ* peak decreased when the angle of incidence of soft X-rays was varied from 20° to 90°. This dependence indicates that the molecules are oriented upright on the substrate. From the fitting analysis of the first peak with an excitation energy of about 285 eV to the π* orbital of the phenyl ring, the molecular orientation angle was determined to be 19°. The film thickness predicted from this orientation angle, the molecular length (12 Å) calculated using DFT (B3LYP/6-31G**), and the S–Au bond length (2.3 Å [5]) was 14 Å, which agreed with the result of Thickogram analysis. This agreement validates the method for determining the thickness of organic molecular films using XPS.

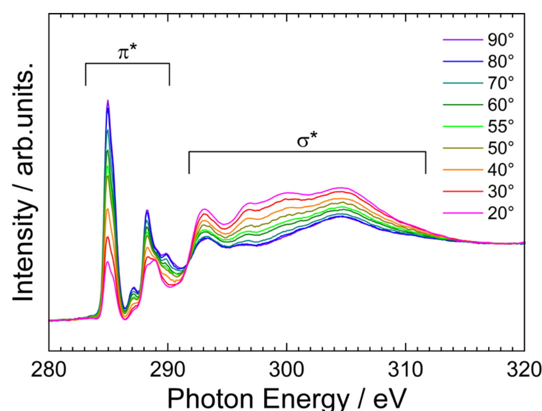

FIGURE 3. NEXAFS spectra of MBP SAM at the carbon K-edge. The polarization dependence was measured by varying the incident angle of soft X-rays from 20° (grazing incidence) to 90° (normal incidence) relative to the substrate.

Thickogram analysis was found to be applicable not only to SAMs on gold substrates but also to SAMs on nanoparticle surfaces [6]. This suggests that the method is a valuable tool for evaluating the thickness of organic thin films in fields requiring nanoscale molecular film control, such as electronic devices, catalysts, and biosensors.

REFERENCES

[1] J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, and G. M. Whitesides, Chem. Rev. **105**, 1103 (2005).
[2] H. A. Biebuyck, C. D. Bain, and G. M. Whitesides, Langmuir **10**, 1825 (1994).
[3] P. J. Cumpson, Surf. Interface Anal. **29**, 403 (2000).
[4] K. Yoshihara, JSA **23**, 138 (2017).
[5] C. Battocchio, F. Porcaro, S. Mukherjee, E. Magnano, S. Nappini, I. Fratoddi, M. Quintiliani, M. V. Russo, and G. Polzonetti, J. Phys. Chem. C **118**, 8159 (2014).
[6] S. Tendo, A. Niozu, K. Yoshioka, M. Tabuse, J. Adachi, H. Tanaka, and S. Wada, Phys. Chem. Chem. Phys. **27**, 388 (2025).