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Photoelectron Mean Free Path in Langmuir-Blodgett Film Estimated from Angular Dependence of X-Ray Photoelectron Spectra

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The Langmuir-Blodgett (built-up) film of barium stearate was prepared and its angular dependence of X-ray photoelectron spectra was obtained. A simple layer model was proposed to evaluate angular dependence of X-ray photoelectron spectra. The electron mean free path of C_{1s} photoelectron (kinetic energy of ca.965 eV) was determined from comparison between experimental and calculated take-off angle dependences of intensity of C_{1s} spectra.

Structure and properties of Langmuir-Blodgett (built-up) films have been paid great attention in these days. This is due to the fact that the control of molecular assembly can be easily achieved by the preparation technique developed by Langmuir[1] and Blodgett.[2] Though applications for electronconductor, semiconductor and so on have been tried by several authors,[3,4] little investigations have been done on the structural characterization of those built-up films.

The X-ray photoelectron spectroscopy (XPS) is a useful technique to characterize the surface structure of solids. The evaluation of photoelectron mean free path in the built-up film is important since photoelectron mean free path determines the analytical depth of XPS. Also, the channeling phenomenon of emitted photoelectron through the intermolecular channel of oriented molecule in built-up film has been observed.[5] This phenomenon should be verified through the measurement of X-ray photoelectron spectra of well-characterized built-up films. In this study, the Langmuir-Blodgett (built-up) film of fatty-acid with a long alkyl chain was prepared and the angular dependent X-ray photoelectron spectra was measured in order to estimate photoelectron mean free path in the LB film.

Long-chain fatty-acid used was stearic acid (Fluka Co, Ltd.). A benzene solution of stearic acid was spread on the surface of aqueous solution of 3×10^{-5} M $BaCl_2$ and 4×10^{-4} M $KHCO_3$ with a pH of 7.0-7.2 at 290 K. The monolayer of barium stearate on the aqueous solution of $BaCl_2$ and $KHCO_3$ was kept at the constant pressure of 3.0×10^{-2} N m^{-1} at which the monolayer was in a condensed solid phase. The multilayers of barium stearate were built-up on the polystyrene film according to the Langmuir-Blodgett method. The built-up film with 40 monolayers was obtained as Y-membrane. Orientation of long-chain fatty-

acid molecules in the built-up film was confirmed by wide-angle X-ray diffraction. The Bragg spacing of the each reflection agreed well with the reported value.[6, 7] This indicates that the molecular assembly of the built-up film prepared is appropriate for the model material of XPS measurements. The X-ray photoelectron spectra of the built-up films were obtained with Shimadzu ESCA750. X-Ray source was MgK_{α} which was operated at 8 kV and 30 mA. The samples were attached on the probe which were cooled to 243 K to avoid chemical degradation and evaporation of fatty acid molecules during XPS measurements. Also, the introduction of barium ions in hydrophilic group improves the stability of built-up film. Spectra were obtained in a digital form. Curve fitting of the spectra was accomplished using a non-linear least square method.[8] A Gaussian-Lorentzian function was assumed for this curve fitting process.

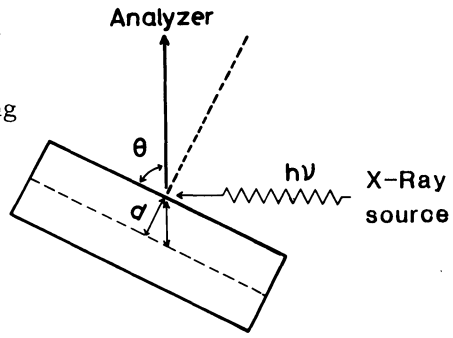

Fig. 1. Relationship between the incident X-ray beam and the emitted photoelectron.

Figure 1 shows the relationships between the incident X-ray beam and the emitted photoelectron, where θ, λ, and d are the take-off angle of the emitted photoelectron, the photoelectron mean free path, and the sampling depth, respectively. The sampling depth, d, is proportional to the photoelectron mean free path and $\sin\theta$, as described by the equation of $3\lambda\sin\theta$. Therefore, an information on the elemental depth profile from the outermost surface becomes more precise with a decrease in the take-off angle. Figure 2 is the C_{1s} spectra of the built-up film of barium stearate, measured with the take-off angles of 15, 30, and 90 degrees. The C_{1s} peak observed at 285.0 eV is attributed to neutral carbon of a long alkyl chain. The small C_{1s} shoulder observed at around 288.3 eV is assigned to carbonyl carbon in a hydrophilic group. The relative intensity of carbonyl carbon in the total C_{1s} intensity decreased with an decrease in the take-off angle. This indicates that a hydrophilic carbonyl group does not exist in the air-facing ultrathin layer of the built-up film.

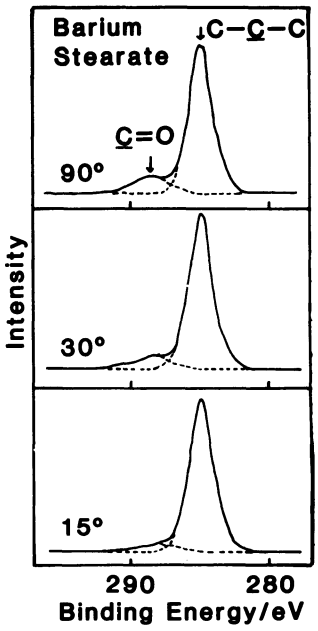

Fig. 2. The angular dependent C_{1s} spectra for the Langmuir-Blodgett(built-up) film of barium stearate at 243 K.

The magnitude of electron mean free path in the built-up film was estimated from the variation of the intensity ratio of the carbonyl carbon to the total carbon atoms in C_{1s} with the take-off angle. This was done by comparing the measured intensity ratio with the calculated one. It is possible from the result mentioned above to obtain

the experimental intensity ratio of oxygen to carbon atoms. Since the magnitude of photoelectron mean free path depends on the kinetic energy value of photoelectron, it is difficult to evaluate the theoretical intensity ratio of oxygen to carbon. With respect to the evaluation of the theoretical intensity ratio of the carbonyl carbon to the total carbon atoms in C_{1s}, an instrument throughput function and photoelectric cross-section corrections were not necessary to be considered. Thus, the relative intensity ratio of carbonyl carbon to the total carbon atoms was evaluated from a simple layer model. The magnitude of photoelectron mean free path estimated in this study is limited to the case of C_{1s} photoelectron with the kinetic energy value of ca. 965 eV. A simple layer model was proposed in order to calculate the angular dependence of C_{1s} spectra. Figure 3 shows the layer model for the built-up film of long-chain fatty-acid. The location of each carbon atom along the chain axis in the built-up film is evaluated from the result of the wide angle X-ray diffraction. Since the atomic concentration distribution can be defined from this layer model, the variation of the XPS intensity with the take-off angle can be calculated from the following equations.

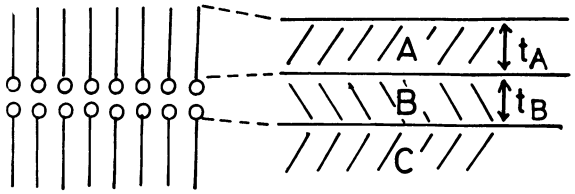

Fig. 3. The layer model for the built-up film of barium stearate.

$$I_A \propto N_A\lambda(1-\exp(-t_A/\lambda\sin\theta)) \quad (1)$$

$$I_B \propto N_B\lambda(1-\exp(-t_B/\lambda\sin\theta))\exp(-t_A/\lambda\sin\theta) \quad (2)$$

$$I_C \propto N_C\lambda\exp(-t_B/\lambda\sin\theta)\exp(-t_A/\lambda\sin\theta) \quad (3)$$

where A , B, and C represent the alkyl carbon in the outermost layer, the carbonyl carbon in hydrophilic group, and the alkyl carbon in the second layer, respectively, as shown in Fig. 3. N_A, N_B, and N_C are the concentrations of each carbon in each phase, which are assumed to be constant. t_A and t_B are the thickness of each layer obtained from the wide-angle X-ray diffraction and the literature data.[6, 7] The relative intensity from carbonyl carbon can be calculated from the following equation.

$$X=I_B/I_{total} \quad (4)$$

where I_{total} is the total intensity of C_{1s}. These calculations were carried out by applying these equations up to the seventh layer. It is verified that the contribution to the spectra from the inner-layer is negligible in this case. Figure 4 shows the angular dependences of the experimental intensity ratio of carbonyl carbon to the total C_{1s} for built-up film of barium stearate and the calculated one(solid line) based on the layer model represented in Fig. 3. The relative intensity at each angle

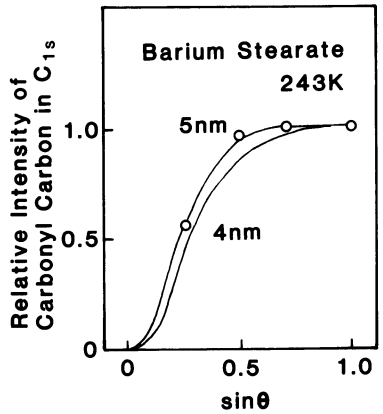

Fig. 4. The variation of the relative fraction of carbonyl carbon in the total C_{1s} for the built-up film of barium stearate with the take-off angle of photoelectron. (o: observed, solid line: calculated)

was normalized by the relative intensity at the take-off angle of 90 degree. The experimental data agreed considerably well with the calculated curve in the case that the magnitude of photoelectron mean free path for C_{1s} (kinetic energy of ca. 965 eV) was assumed to be 4.9 nm. Similar magnitudes of electron mean free path in built-up films are obtained for other built-up films which have various chemical structures.[9] Brundle et al. reported the mean free path of 3.6 nm in cadmium arachidate for the photoelectron with kinetic energy value of ca. 1120 eV.[10] The built-up film employed by Brundle et al. was prepared on the metal substrate which emits photoelectron with a certain kinetic energy. Thus, if one would like to get the magnitude of electron mean free path for C_{1s} photoelectron, one should use the clean carbon substrate which is difficult to prepare. However, the analytical procedure employed for this study has the advantage that the sample preparation is very simple and also the patching effect due to the evaporation of molecules can be negligible. The magnitude of electron mean free path is quite similar to that estimated from the Ashley parameter[11, 12] which is based on the bulk property of the solids. In the case that the photoelectron generated in inner layers of built-up film emitted through the intermolecular channel of built-up films, the angular dependence of C_{1s} spectra would be very small. Therefore, it may be reasonable to conclude that channeling phenomenon of photoelectron is not prominent in the built-up film of fatty acid with a long alkyl chain.

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