

Depth Profiling of Ultra Thin Film Using Laser Induced Fluorescence Spectroscopy under Normal Incidence Conditions Based on the Reciprocal Principle

Xing-Zheng WU, Takehiko KITAMORI, Norio TERAMAE,[†] and Tsuguo SAWADA*

Department of Industrial Chemistry, Faculty of Engineering,
The University of Tokyo, 7-3-1 Hongo, Bunkyo, Tokyo 113

[†] Department of Applied Chemistry, Faculty of Engineering,
Nagoya University, Gokisocho 1, Chigusa-ku, Nagoya 464

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Depth profiling for thin film sample using laser induced fluorescence spectroscopy under normal incidence conditions, based on the principle of reciprocity, was studied. A laminated Langmuir–Blodgett model film sample (187 nm in thickness) with a concentration depth profile which varies as a stair-like function with 20.8 nm steps was prepared. Using this model film sample, observation angle dependence of fluorescence intensity was compared with theoretical results based on the principle of reciprocity, and it was shown that the principle held for the thin film sample having a continuous concentration depth profile. Secondly, these data were used to reconstruct the concentration depth profile by the least square method. The quantitative concentration depth profiling results obtained for the model film sample were satisfactory. This method can be used for film samples thinner than the wavelength of the excitation light and its spatial resolution in the depth direction is estimated to be in the order of a nanometer.

The importance of measurements of local concentration depth profiles and three-dimensional profiles with resolution in submicrometer or nanometer regions has been emphasized in many technological fields such as electronic devices,¹⁾ solid surface physics,²⁾ and cell biology.³⁾ Optical spectroscopical concentration depth profiling methods should be non-destructive, non-contact methods without using a high vacuum system. Attenuated total reflection infrared (ATR IR) adsorption spectroscopy⁴⁾ and total internal reflection fluorescence spectroscopy⁵⁾ are well known non-destructive depth profiling methods. Although it is estimated theoretically that the ATR IR method has a depth resolution about one-tenth that of the wavelength,⁵⁾ practical analysis for thin film samples thinner than the wavelength used is difficult. Total internal reflection fluorescence spectroscopy has been used to determine concentration depth profiling of proteins adsorbed at a solid/liquid interface,⁶⁾ depth distribution of fluorescent species in silk fabrics,⁷⁾ and the concentration ratio of a fluorophore between a two layer film sample.⁸⁾ However, until now only qualitative results or results for a simple concentration depth profile model, such as a uniform concentration distribution, have been reported.

Recently, Suci and Reichert⁹⁾ have studied the reciprocity in an angular pattern of fluorescence, and they have investigated the possibility of depth profiling, using Langmuir–Blodgett (LB) films, for the sample having a uniform concentration depth profile.¹⁰⁾ For such film samples in which fluorophores were uniformly distributed over a range of 52.8 nm, i.e., a rectangular profile, the central position of the rectangular profile could be accurately determined, which demonstrated the possibility of determining the width of the rectangular distribution profile. This

depth profiling method using variable angle fluorescence data is attractive, since it can be used for the concentration depth profile of a film sample thinner than the wavelength of the excitation light, with highest sensitivity applying laser as the beam source. However, as actual samples usually have a complicated concentration distribution, it is important to study the validity of this method for the thin film sample which has a concentration depth profile varying continuously with distance from the surface.

In the present study, a 187 nm thick LB film sample, having a concentration depth profile which varies as a stair-like function with 20.8 nm steps, was prepared as the model sample. By using variable observation angle fluorescence data obtained under normal incidence conditions, it is shown that the reciprocal principle holds for the sample having a nonuniform concentration depth profile. Then the profile is determined by applying this method.

Method Outline

According to the reciprocal principle for fluorometry proposed by Suci and Reichert,⁹⁾ as shown in Fig. 1, fluorescence intensity $F(\theta)$ measured at the observation angle θ under normal incidence conditions is expressed as,

$$F(\theta) = k \int_0^t C(z) T(\theta, z) dz, \quad (1)$$

where $C(z)$ is the concentration distribution in the depth direction z , t is the thickness of the sample, and k is a constant related to spectroscopical parameters such as absorption coefficient and fluorescence quantum yield. The function $T(\theta, z)$ is defined as a transmission function, and its functional form has been given by a

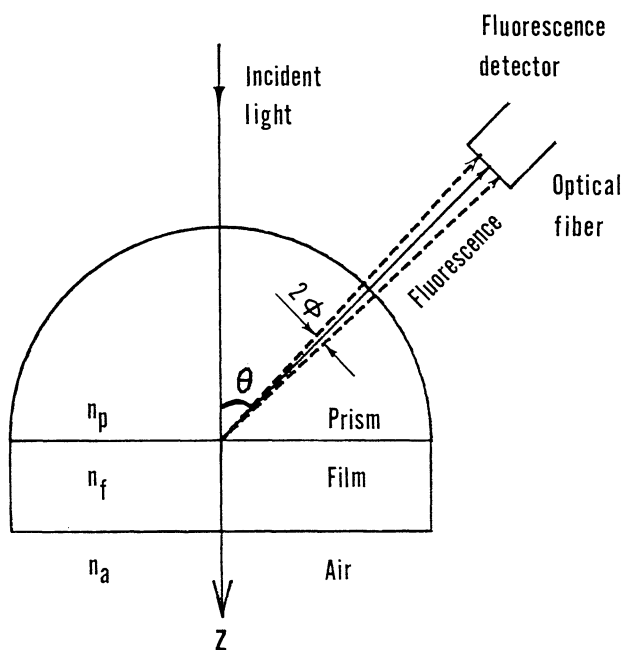


Fig. 1. Schematic of laser induced fluorescence spectroscopy under normal incidence conditions based on the reciprocal principle.

theoretical analysis of the multiple reflection of the electromagnetic waves between the prism/film and film/air interfaces.⁹⁾

Suci and Reichert verified the propriety of the reciprocity described by Eq. 1 using the sample in which a fluorophore is localized at a certain distance z_0 from the surface. As the fluorophore localizes at z_0 , the concentration distribution $C(z)$ becomes $C_0\delta(z-z_0)$, and Eq. 1 becomes

$$F(\theta, z_0) = kC_0T(\theta, z_0). \quad (2)$$

They measured the observation angle dependence of the fluorescence intensity $F(\theta, z_0)$ and compared it with the calculated value of $T(\theta, z_0)$ to show the propriety of the transmission function $T(\theta, z)$. In addition, they applied it to a uniform concentration distribution with which $F(\theta)$ is the integrated form of $T(\theta, z)$.¹⁰⁾

In the present study, we tried to obtain the concentration distribution $C(z)$ from the measured data $F(\theta)$ and the relationships described in Eq. 1. The function $C(z)$ can be obtained by solving the inverse integral of Eq. 1, because $T(\theta, z)$ is known theoretically and $F(\theta)$ is given experimentally. However, the inverse problem of the convolutions, as it well known, does not always have an analytical solution, and the numerical method is frequently confronted with the problem of divergence and precision. Then, a numerical fitting method was applied to obtain $C(z)$. If the physical and chemical processes leading to the concentration distribution can be guessed, a general functional form of $C(z)$ is roughly estimated. For example, $C(z)$ is an

error function type for a diffusion limiting process, and an exponential one for a chemical kinetics system. Hence, an exact function $C(z)$ is obtained by the following numerical fitting, which utilizes the least square method. The functions $F_{\text{cal}}(\theta)$ and $F_{\text{mea}}(\theta)$ are defined as the calculated function $F(\theta)$ for a guessed or trial function $C(z)$ and an experimentally obtained one, respectively. The exact form of $C(z)$ is determined by minimizing the following value of s ,

$$s = \sum_i [F_{\text{mea}}(\theta_i) - F_{\text{cal}}(\theta_i)]^2 / g_{\theta_i}, \quad (3)$$

where i means the i -th measurement data, and g_{θ_i} is a weight factor. In the present report, this fitting method was used to obtain $C(z)$.

Experimental

A block diagram of the experimental set up is shown in Fig. 2-A. An argon-ion laser provided the excitation light ($\lambda_i=488$ nm). The laser output power was adjusted to about 10 mW. A quarter-wave plate and a polarizer were used to adjust the polarization of incident light. The laser beam was modulated with a chopper. The chopped beam was focused on the focal plane of hemicylindrical prism ($n_p=1.88$ at 587.6 nm). The prism was 1 cm in diameter and 2 cm in length. The hemicylindrical prism was mounted on the rotating stages as shown in Fig. 2-B. Both the rotating stages and hemicylindrical prism were coaxially adjusted. An optical lightguide (50 cm length; 0.11 cm bundle diameter; step index type glass fiber; 0.57 numerical aperture) was used to collect the fluorescence transmitted through the prism. One end of the optical lightguide was fixed at the focal plane of the prism and the other end was coupled with a monochromator. A film polarizer was placed in front of the optical lightguide. The film polarizer restricted the collected fluorescence to the perpendicularly polarized component. A photomultiplier (Hamamatsu R928) was used as a detector. The signal from the photomultiplier was fed into and amplified with a lock-in amplifier.

The incident angle and the observation angle can be varied by adjusting the relative position of the two rotating stages. In the experiment, the incident angle was kept at 0° , while the observation angle θ was changed from 15° to 80° with 1° steps. The absolute value of the observation angle was determined as follows; rotating the upper stage from the location at which the laser beam is in normal incidence condition to that at which the reflected beam irradiated on the center of the fiber. The value of the observation angle is double the upper rotating stage angle. As shown in Fig. 1, the uncertainty ϕ at the observation angle θ is determined by the fiber bundle size and the distance between the fiber and the irradiation point. For this system, ϕ is estimated to be $\pm 0.7^\circ$.

Sample. The method of Langmuir-Blodgett deposition used was the same as described elsewhere.¹¹⁾ The two species used to fabricate the model film sample were icosanoic acid (eicosanoic acid) (analytical grade, Kanto Kagaku) and N,N' -dioctadecylrhodamine B (DORB) (Nippon Kankoh-Shikiso Kenkyusho).¹²⁾ Aqueous cadmium sulfate solutions (5×10^{-5} mol dm⁻³) was used as a subphase. A benzene solution of

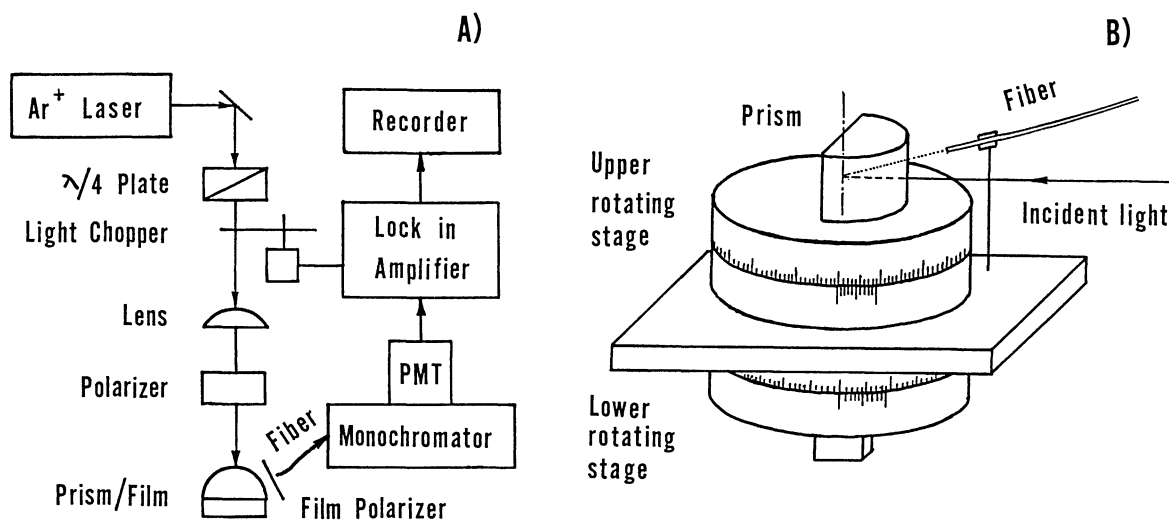


Fig. 2. Schematic diagram of the experimental setup including a detailed optical arrangement of the detection unit.



Fig. 3. Concentration depth profile of the model LB film sample.

icosanoic acid and mixtures of icosanoic acid and DORB with a certain molar ratio were spread on the subphase in a Langmuir trough (Kyouwakagaku). The LB layers were deposited onto the prism at a film pressure of $25\text{--}30 \times 10^{-3} \text{ N m}^{-1}$. The prism surface was first precoated with seven layers of cadmium icosanoate to ensure the surface was uniform and hydrophobic. Secondly, eight layers of 7% DORB (the unit of DORB concentration is the molar percent) and cadmium icosanoate mixture were deposited. Then another eight layers of 6% DORB and cadmium icosanoate mixture were deposited. This procedure was repeated eight times to laminate layers of DORB in which the concentration was being changed from 7% to 0% as shown in Fig. 3. The total number of monolayers was 71.

When the molar ratio of dye to icosanoic acid is less than 10%, the mixed monolayers and multilayers have a similar

structure to cadmium icosanoate LB films.^{11,13} The reported thickness of a monolayer of cadmium icosanoate and the refractive index of the multilayers are 2.64 nm and 1.53, respectively.¹¹ Thus the total film thickness can be estimated from the number of monolayers, and it was calculated to be 187 nm. The multilayers deposited onto the curved part of the prism were removed with an acetone-soaked wadding¹⁴ to prevent interference with the fluorescence measurement.

The fluorescence peak of the model sample appeared at 580 nm, and this peak was used in the following experiments.

Results and Discussion

To verify the propriety of the reciprocity for a nonuniform $C(z)$, fluorescence dependence on the observation angle was measured for the model sample under normal incident conditions, and the results were compared with the theoretical values calculated using Eq. 1. The experimental results are plotted in Fig. 4. As the concentration distribution $C(z)$ for the model sample shown in Fig. 3 is written as follows,

$$C(z) = \begin{cases} 0\% & 0 \leq z \leq 7d \\ (8-j) & 8jd \leq z \leq 8(j+1)d, j = 1, 2, 3, \dots, 8 \end{cases} \quad (4)$$

where d is the thickness of the monolayer, 2.64 nm, then the theoretical value $F_{\text{cal}}(\theta)$ can be calculated by substituting Eq. 4 into Eq. 1 (the values of the parameters and material constants are described in the experimental section). The calculated results are shown by a solid line in Fig. 4. The theoretical values agree well with the experimental results, where the most appropriate value of k in Eq. 1 is $2.3 \times 10^{-3} (\%^{-1} \text{ nm}^{-1})$. Therefore, the propriety of the reciprocity is confirmed for the nonuniform concentration distribu-

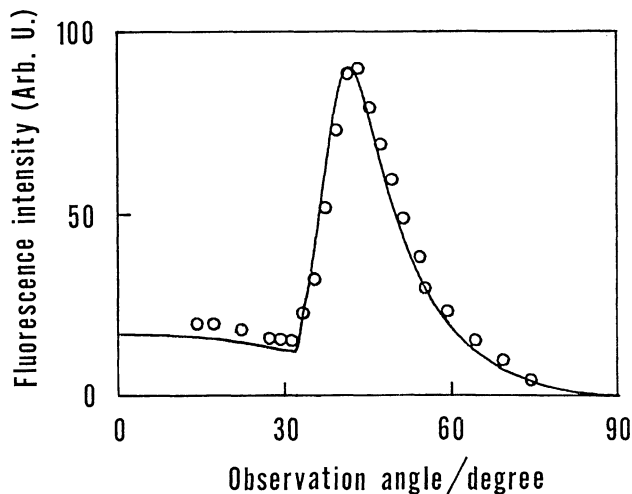


Fig. 4. Theoretical and experimental results of the angular dependency of the fluorescence intensity measured for the model sample. The theoretical values are described by the solid line, and the experimental results are plotted as circles.

tion, and it is proved that the reciprocity described in Eq. 1, which has been partially verified for localized and uniform concentration distribution, is applicable to a general functional form of $C(z)$. These results suggest that the arbitrary concentration depth profile $C(z)$ can be obtained from Eq. 1.

Next, concentration depth profiling which was proposed in the method outline section, based on the reciprocal theory, was examined. As mentioned in the method outline section, $C(z)$ can be obtained from the least square method of Eq. 3, when the functional form of $C(z)$ is roughly estimated. In the present case, the linear function,

$$C(z) = Az + B, \quad (5)$$

is assumed to be a trial function, and the constants A (% nm⁻¹) and B (%) which give the nearest form to the actual distribution shown in Fig. 3 are tentatively obtained from Eq. 3. Using the data presented in Fig. 4 and the most appropriate value of k obtained above, the constants A and B are obtained as -0.04% nm⁻¹ and 8.0%, respectively, and the reconstructed line is shown in Fig. 5 with the actual distribution indicated by a dashed line. The obtained result $C(z)$ reconstructs well the absolute value of the concentration, and shows the decreasing profile. Hence the calculated concentration depth profile of DORB in the model sample is considered to be reasonable, and the propriety of the present depth profiling method is verified.

The main experimental error factor of this system is the uncertainty of the observation angle. As stated in the experimental section, the uncertainty ϕ at observation angle was estimated to be $\pm 0.7^\circ$. The recon-

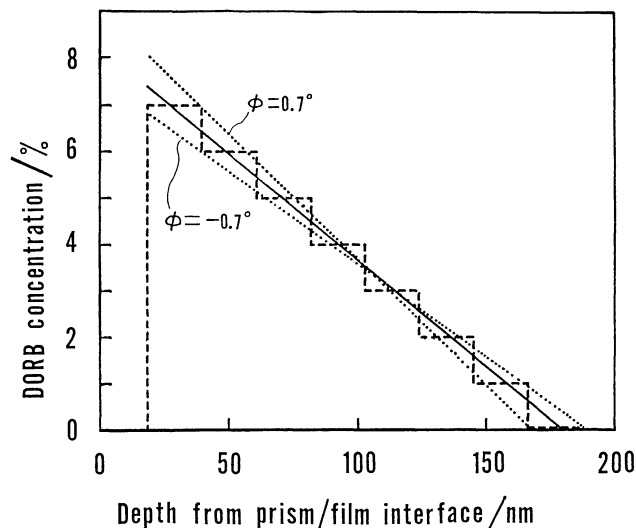


Fig. 5. Reconstructed concentration depth profile for the model film sample. The solid and dashed lines represent reconstructed and actual $C(z)$ values, respectively. The dotted lines represent the error region of the reconstructed results given by the experimental uncertainty of the observation angles.

structed results in which uncertainty was taken into consideration are shown in Fig. 5 with dotted lines. These reconstructed results become better when a fiber with smaller bundle size is used to reduce the uncertainty of the observation angle. In this experiment, the concentration changes of 20 nm steps in a 187 nm thick sample shown in Fig. 3 can be recognized. Considering the experiment errors in Fig. 5, although the exact value of the spatial resolution in the depth direction is not given, a resolution of less than 20 nm can be expected for the present method. It is no exaggeration to say that the present experiment is the first which obtains a quantitative depth profile for a thin film thinner than the excitation wavelength using a nondestructive spectroscopic technique. For thin film samples with thickness on the order of a wavelength or thinner, this method is particularly meaningful, since other optical depth profiling methods such as photoacoustic spectroscopy¹⁵⁾ cannot easily yield information on depth profiling for such thin film samples.

As stated above, the reconstructed concentration depth profiling results would become better when a fiber with a smaller bundle size is used. A smaller bundle size also leads to a decreased signal to noise ratio. A detailed discussion on the application limits of the present method, which are considered to be restricted by the experimental conditions such as the uncertainty and accuracy of the observation angle and signal to noise ratio, will be reported elsewhere.

Although the absolute value of A (% nm⁻¹) and B (%) were obtained for the present model film sample, it is generally difficult to know k for the actual samples.

Hence only a relative concentration depth profile can be obtained using the least square method.

The present method is similar to the conventional ATR method, where variable incident angle data are used to reconstruct $C(z)$.^{4,5,7)} For a bulk sample, the ATR method has been proved to be effective. However, in the conventional ATR method, only total internal reflection occurring at the prism/film interface shown in Fig. 1 is considered, thus only the data obtained beyond the critical angle can be used to reconstruct $C(z)$. For the film sample with a thickness on the order of the incident light wavelength or the thinner, such as our model film sample, the conventional ATR method in which only consider evanescent wave decays from prism/film interface exponentially cannot be applied. It is also necessary to consider the reflection effect which occurs at the film/air interface for the evanescent wave. On the other hand, in the present method, $T(\theta, z)$ is derived by considering multiple reflection occurring at the interfaces of the prism/film and film/air shown in Fig. 1,¹⁰⁾ so data at any observation angle can be applied to samples which are thinner than the excitation wavelength or the evanescent wave.

In summary, concentration depth profiling using fluorescence spectroscopy under normal incidence conditions based on the reciprocal principle was demonstrated for a 187 nm thick film sample. The present depth profiling method had a high spatial resolution and could be used for ultra thin film samples. Using normal incidence conditions, it was possible to obtain a local three-dimensional profile by scanning the excitation beam. In addition, dynamics and kinetics of the fluorophore can be measured if array detectors are applied to obtain various angular data simultaneously. Therefore, this method is expected to be a useful one for analytical and

spectroscopical studies of thin films and surfaces.

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