A Slab-Optical-Waveguide Absorption Spectroscopy of Langmuir-Blodgett Films with a White Light Excitation Source

Kenji Kato,* Akiko Takatsu, Naoki Matsuda, Reiko Azumi, and Mutsuyoshi Matsumoto
National Institute of Materials and Chemical Research, 1-1, Higashi, Tsukuba, Ibaraki 305

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A novel slab optical waveguide (SOWG) technique with a white light excitation source was applied to the spectroscopy of LB monolayer samples. Absorption spectra of a Cu-porphyrin complex in LB films at concentrations of 0.1-0.5 monolayers were observed in the wavelength range of 380 to 650 nm. Polarized spectra giving information on the molecular orientation in the ordered thin films were also measured.

In recent years, slab optical waveguide (SOWG) techniques have been applied to optical sensing of surface chemical species and chemical reactions.[1-3] Bohn[4] and Itoh[5] recently reviewed the analytical spectroscopic application of SOWG. The SOWG act as an internal reflection element (IRE) used in the attenuated total reflection (ATR) spectroscopy. The SOWG has a very thin core layer and realizes a much larger number of total reflection in the core and higher sensitivity than conventional ATR spectroscopy. But most research has addressed the fabrication of chemical sensors where the measurements are generally carried out at a fixed wavelength. Swalen et al. reported point by point measurements at several fixed wavelengths using multiline lasers to obtain the absorption spectra of the LB films.[6] In this communication, we will demonstrate that a usual white light source can be used for the measurements of the absorption spectra of LB films on SOWG. The SOWG also allows one to control the polarization of the incident beam and perform linear dichroism experiments.

A SOWG was fabricated by an ion-exchange process from slide glass (S-1214, Matsunami, 24 mm×76 mm×1 mm) in molten potassium nitrate at 420° C for 30 min.[7] Prisms (Kogaku Giken, LaSF-08, n=1.8785 at 633 nm, 5 mm (width)×4 mm (height)×15 mm (length), base angle=53.7°) were used to couple the light beam into the SOWG and di-iode methane (n_{D20}=1.74) was used as coupling liquid. In the measurements of polarized spectra, non-fluorescent slide glass (S-3314, Matsunami) was used to fabricate a SOWG.

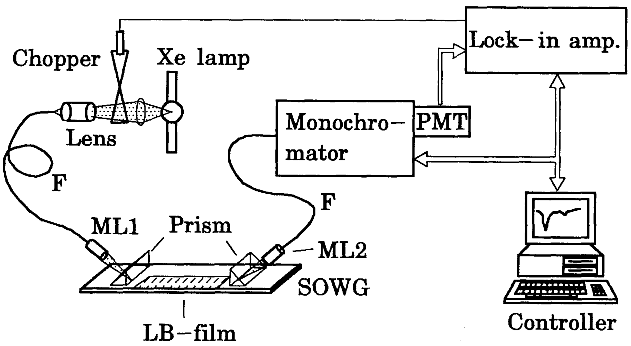

Figure 1. Schematic diagram of the slab optical waveguide spectrometer. The SOWG was placed horizontally on a gonio stage. Micro−lenses (ML1,2) attached at the ends of optical fibers (F) were mounted on mechanical XYθ − stages.

The experimental setup is schematically shown in Figure 1. The excitation source was a 500 watts xenon lamp. Its beam was modulated by a mechanical chopper and was introduced into a multi-mode optical fiber (core diameter =100 μm) through a microscope objective lens. A micro-lens (ML1, Selfoc micro-lens, Nippon Seat Glass) was attached at the other end of the optical fiber and the exit beam from ML1 was focused at the 90° corner of the incoupling prism. Outcoupled beam was collected by the second micro-lens attached at the other optical fiber and was led to a monochromator (CT-50, Nihon Bunko) equipped with a photomultiplier (R2949, Hamamatsu Photonics). Polarization of the transmitted light was set to transverse magnetic mode (TM) or transverse electric mode (TE) using a polarizer placed after the outcoupling prism. Signal from the photomultiplier was preamplified and analyzed with a lock-in amplifier.

A single or double layer assembly of a mixture of Cd-icosanoate $(CH_3(CH_2)_{18}COO)_2Cd$ and Cu-porphyrin complex (*meso*-tetrakis(3,5-di-*t*-butylphenyl)porphinatocopper(II)) was transferred onto the SOWG by the Langmuir-Blodgett technique. Detailed description about the LB films was given in the previous report.[8] For the mixture of Cu-porphyrin and Cd-icosanoate with molar rations of 1.5:10 and 1.5:100, the coverage of Cu-porphyrin molecule in the monolayer was calculated to be 0.46 and 0.1 monolayer, respectively, from the surface pressure-area isotherm.

The LB film was deposited onto a half area of SOWG as depicted in Figure 1, sample size on the SOWG was 40 mm (length) and 12 mm (width). Coupling prisms were located across the two regions on the SOWG, with and without the LB film. By translating the SOWG, the transmission spectra of the two regions were measured separately. Absorption spectra of the LB films were obtained from the ratio between these transmission spectra.

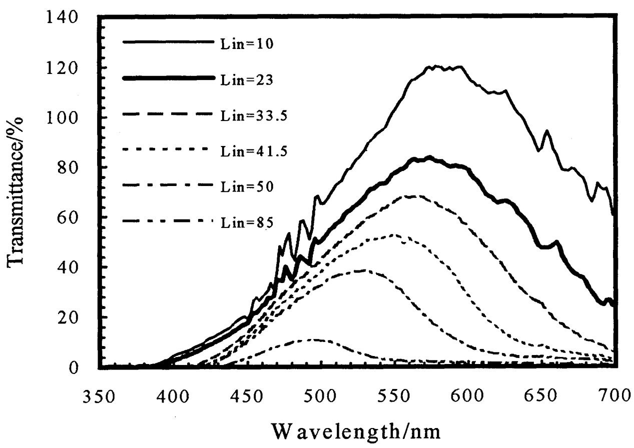

Figure 2. Transmission spectra of SOWG with no sample layers for various distances between the micro-lens (ML1) and the incoupling prism (L_{in}/mm).

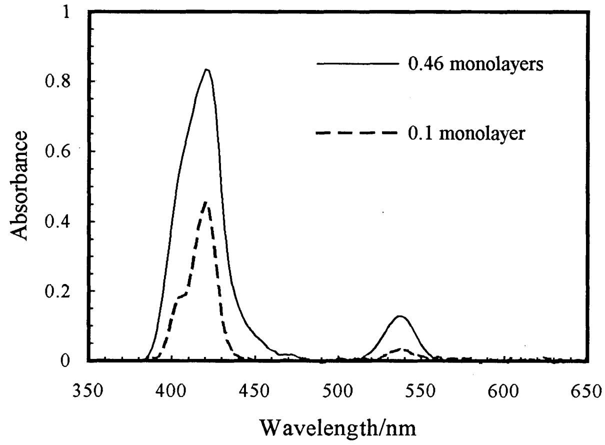

Figure 3. Absorption spectra of Cu-porphyrin in the LB films. The solid line and the dotted one correspond to a concentration of 0.46 and 0.1 monolayer, respectively.

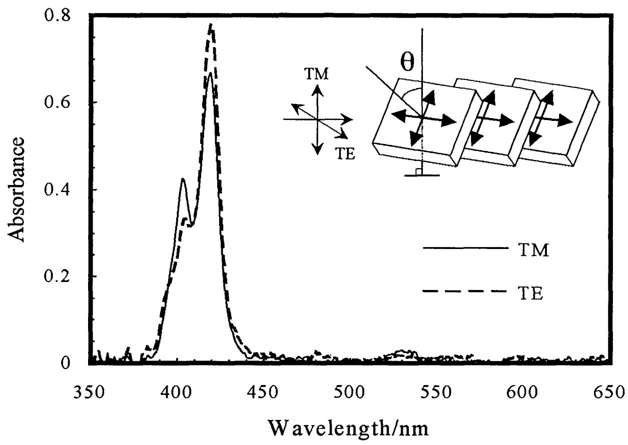

Figure 4. Polarized absorption spectra of a double layer LB film with a molar ratio of 1.5:100. Solid and dotted lines show the results obtained by TM and TE polarized arrangements, respectively. The insert shows a schematic view of porphyrin aggregates in the LB film. The average tilt angle(θ) of the porphyrin plane with respect to the surface normal is about 60°.[8]

The SOWG used in this study had a single mode at 633 nm. The effective thickness was estimated to be about 3 μm.[7] Coupling angle of incident light beam with SOWG changes with the light wavelength due to the change in the propagation angle in the core and also to the change in refractive indices. It suggests that we can couple a white light beam over a wide spectral range by applying the light beam with various incident angle simultaneously. Transmission spectra of SOWG at various incident angles were measured at fixed distances between the micro-lens (ML1) and the incoupling prism (L_{in}=23 mm) and between the second micro-lens (ML2) and the outcoupling prism (L_{out}=10 mm). Peak position of the transmission spectrum was shifted from 420 to 690 nm by changing the incident angle from 37.8° to 35.6° away from the plane of the SOWG. Figure 2 shows transmission spectra with various L_{in} at a fixed incident angle (36.8°). As the L_{in}-value decreased, the bandwidth of the transmission spectra became wider, because the variation of incident angle increased with decreasing L_{in}. Assuming that the effective diameter of the micro-lens is 1 mm and that L_{in} is 23 mm, the variation of incident angle was calculated to be about 2.5° which is wide enough to transmit a white light beam over the visible light region.

Absorption spectra of Cu-porphyrin in the LB films at concentrations of sub-monolayer levels were shown in Figure 3. Soret band of Cu-porphyrin located at 415 nm in *n*-hexane splits into two peaks in the LB film[8] due to aggregate formation. In Figure 3, a peak and a shoulder were observed at 420 nm and at 404 nm, respectively. Absorbance at 420 nm for the 1.5:100 mixed monolayer sample was 0.45. That is about 138 times larger than that obtained from the conventional high sensitive spectrophotometer (HSSP-1, Nihon Bunko). Absorbance at 540 nm for the 1.5:100 and 1.5:10 mixed monolayer samples were 0.030 and 0.128, respectively, so that the absorbance ratio (0.128/0.030=4.3) agrees well with that (4.6) of the coverage of the Cu-porphyrin molecule in these monolayer samples. The peak at 420 nm for the 1.5:10 mixed monolayer sample seems to be saturated.

Information on the molecular orientation can be obtained by using polarization arrangements. Figure 4 shows the polarized absorption spectra of a double monolayers LB film on the SOWG. Polarized spectra obtained in TE and TM mode correspond to conventional s- and p-polarized spectra, respectively. In this measurement, shoulders at 404 nm were clearly resolved, because non-fluorescent slide glass was used as substrate of SOWG and the transmittance in the violet region (380 to 420 nm) was improved. It was obvious that the peak at 420 nm is stronger in TE mode and the shoulder at 404 nm becomes more distinguished in TM mode. This anisotropy of the absorption bands can be well explained by the aggregation model of the porphyrin molecules in the LB films which considers two transition dipole moments: the one at ca. 420 nm is almost parallel to the surface, and the other at ca. 404 nm is tilted with respect to the surface normal (insert of Figure 4).

A new slab optical waveguide (SOWG) technique with a white light excitation source was demonstrated. This method enable us to measure the absorption spectra of thin films at low concentration of absorbing molecules, and also useful to obtain the information on the molecular orientation in the samples. Further studies are now in the progress.

References and Notes

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