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Evaluation of Structure and Gas Response in Porphyrin Langmuir-Blodgett Films by Attenuated Total Reflection Measurements

Keizo Kato, Hitoshi Araki, Kazunari Shinbo [1], Futao Kaneko [1],
Colin M. Dooling [2] and Tim H. Richardson [2]

Graduate School of Science and Technology, Niigata University
Ikarashi 2-8050, Niigata 950-2181, Japan
Phone: +81-25-262-6724 Fax: +81-25-262-6741 E-mail: keikato@eng.niigata-u.ac.jp
[1] Department of Electrical and Electronic Engineering, Niigata University
Ikarashi 2-8050, Niigata 950-2181, Japan
[2] Applied Molecular Engineering Group, Department of Physics & Astronomy, University of Sheffield
Hounsfield Road, Sheffield S3 7RH, UK

1. Introduction

The investigation of properties in organic thin films is very important and many studies on electrical and optical devices of organic thin films have been reported [1]. Some attention has been guided towards organic thin films as candidates for gas sensors. The ability of monitoring toxic gases in a wide range of environments has become very important. However, the majority of such organic sensors have exhibited relatively slow gas response time and incomplete recovery after gas exposure. Porphyrins and their derivatives [2] have been investigated by many researchers. Recently, a class of tetraphenyl porphyrins has shown promise as useful sensing materials [3].

The attenuated total reflection (ATR) measurement utilizing surface plasmon excitation at the interface between metal thin films and dielectric ultrathin films is one of very useful methods to evaluate the dielectric properties of ultrathin films [4,5]. Some efforts have been made to detect toxic gases using ATR method [6]. It is very important to investigate response to toxic gases of organic thin films and its mechanism. In this study, the porphyrin Langmuir-Blodgett (LB) films were prepared at a very fast deposition rate and the ATR properties were measured in order to evaluate the film structure and the NO_2 gas response.

2. Experimental

The porphyrin molecule used in this work is 5,10,15,20-tetrakis(3,4-bis[2-ethylhexyloxyphenyl])-21H,23H-porphine (EHO) [7] and is shown in Fig.1. The EHO molecules were spread from a chloroform solution of concentration 0.129 mg/ml onto a water subphase. The pH and the temperature of the subphase were 6.2 and 296 K, respectively. The EHO LB films were deposited on Ag evaporated glass substrates by vertical dipping method with a very fast deposition rate of 1000 mm/min. The surface pressure was 15 mN/m.

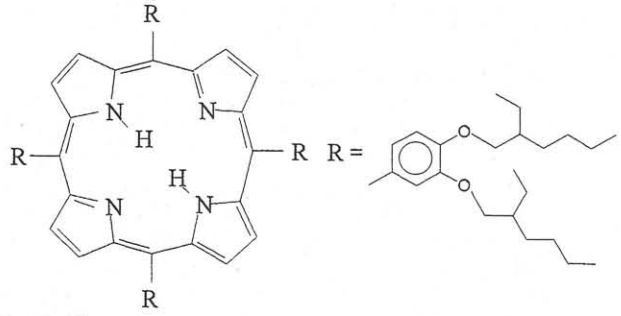

Fig. 1. Chemical structure of porphyrin (EHO) molecule used in this work.

The EHO LB films were brought into optical contact with a half-cylindrical glass prism. The ATR sample has the Kretschmann configuration and the measurements were carried out at room temperature in N_2 and NO_2 gases. He-Ne and Ar^+ laser with wavelengths of 632.8 nm and 488 nm, respectively, were used as the incident radiation. The p-polarized laser beam was directed onto the back surface of the Ag thin film through the prism. The reflectivities were obtained as a function of the incident angle from the ratio of the intensity of the reflected beam to that of the incident beam.

3. Results and Discussions

Fig. 2 shows the temporal evolution of the absorption spectrum of an EHO LB film during exposure to 4.4 ppm NO_2 gas. The EHO LB film was prepared on a glass substrate at 3 excursions in the deposition process and contains 6 monolayers nominally. One excursion represents one downstroke through the air-water interface followed by one upstroke. The absorption spectrum contains a sharp

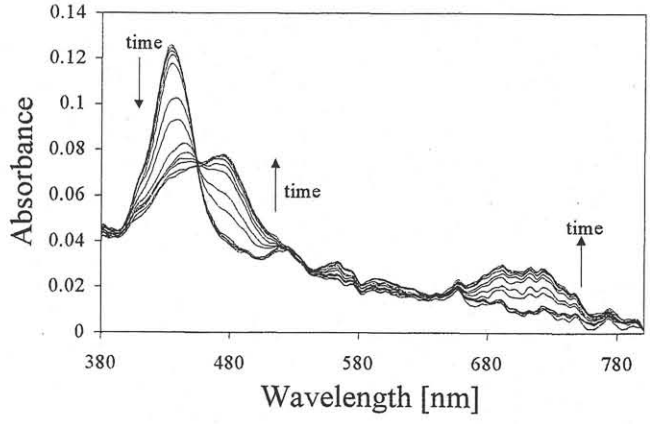

Fig. 2. Temporal evolution of the absorption spectrum of the 3 excursion EHO LB film during exposure to 4.4 ppm NO_2 gas. These data were collected every 4 s during the exposure.

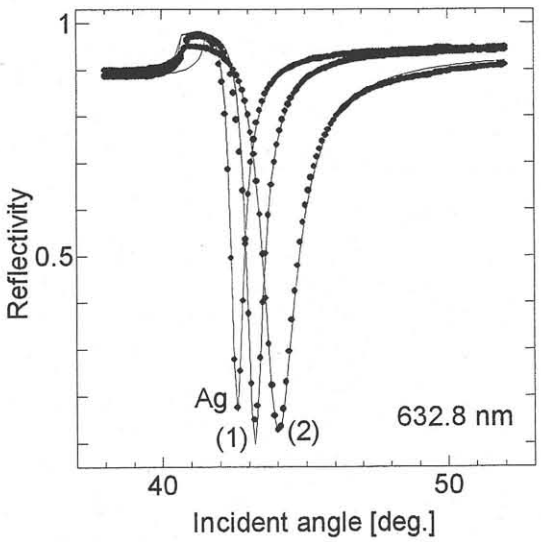

Fig. 3. ATR properties of the EHO LB films on Ag measured at 632.8 nm in N_2 gas. (1) and (2) indicate the results for the 1 and 2 excursion LB films, respectively. The dots and curves represent the experimental and theoretical results, respectively.

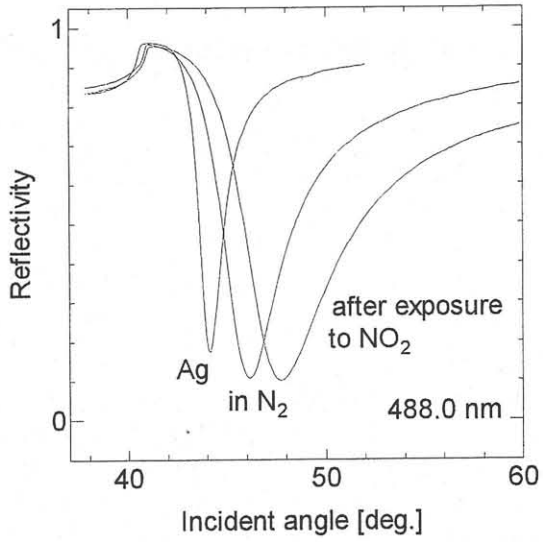

Fig. 4. ATR curves of the 1 excursion EHO LB film measured at 488.0 nm in N_2 and after 60 min exposure to 100 ppm NO_2 gas.

Soret band at 434 nm with satellite Q-bands at the wavelengths in the range of 500 - 650 nm. After exposure to NO_2 gas, the intensity at around 430 nm became weaker. On the contrary, the intensities at around 475 nm and 700 nm grew after exposure to NO_2 gas. The absorption spectrum reversed several hours after switching off the NO_2 gas stream at room temperature, but this recovery process could be accelerated with moderate heating. The optical absorption spectra of the EHO LB films have been found to be highly sensitive to NO_2 gas [7].

Fig. 3 shows the ATR properties of the Ag thin film and the EHO LB films on the Ag thin films. The thickness and the complex dielectric constants of the EHO LB films were evaluated from the ATR properties at 632.8 nm. The thicknesses of 1 and 2 excursion EHO LB films were significant larger than that expected ones based on a monolayer thickness of around 1.3 nm. The evaluated thicknesses were thought to be concerned with the island structure [8] of the EHO LB films. The large difference in the evaluated complex dielectric constants was found to exist between the 1 and 2 excursion EHO LB films. This difference was also considered to be caused by the structure and to be related to the growth mechanism of the EHO molecules. The ATR properties measured at 488.0 nm were different from those at 632.8 nm and they were considered to be related to the dispersion properties [9] due to the optical absorption band of the EHO LB films.

Fig. 4 shows the ATR curves for the 1 excursion EHO LB film measured at 488.0 nm in N_2 and after 60 min exposure to 100 ppm NO_2 gas. After the exposure to NO_2 gas, the resonant angle increased and the half width of the resonance became larger. The change after the exposure to NO_2 gas in the ATR curves measured at 488 nm was larger than that at 632.8 nm. This result means that the response for the ATR properties measured at 488.0 nm is more sensitive to NO_2 gas than those measured at 632.8 nm.

4. Conclusions

ATR properties were measured for EHO LB films deposited at a very fast deposition rate of 1000 mm/min, and the structure and response to NO_2 gas was investigated. The thickness and the complex dielectric constants of the EHO LB films evaluated from the ATR properties measured at 632.8 nm were thought to be concerned with the island structure of the EHO LB films. The ATR properties at 488.0 nm were considered to be related to the dispersion properties due to the optical absorption band of the EHO LB films. From the NO_2 gas response measurements, the ATR properties at 488.0 nm were found to be more sensitive to NO_2 gas than those at 632.8 nm.

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