Nonlinear Optical Susceptibility of Tetra-tert-butyl-Vanadyl-phthalocyanine Films Laminated by Langmuir-Blodgett Method

Saburo Uchida, Vijay T. Chitnis, Hideo Furuhashi,
Akinori Maeda, Goro Sawa, Kenzo Kojima, Asao Ohashi,
Shizuyasu Ochiai, Yoshiyuki Uchida and Teruyoshi Mizutani*
Aichi Institute of Technology, Yachigusa, Yakusa-cho, Toyota 470-0392, Japan
Fax: +81-565-48-8121, e-mail: uchiday@aitech.ac.jp
*Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan

Organic nonlinear optical tetra-tert-butyl-Vanadyl-phthalocyanine ((t-Bu)$_4$VOPc) films were laminated by the Langmuir-Blodgett (LB) method and their nonlinear optical susceptibility was measured by the Maker-fringe method. The solvent used to desolve (t-Bu)$_4$VOPc was 1, 2-dichloroethane. The monolayer on the surface of water was transferred to a glass substrate by the vertical dipping method. The surface pressure was kept constant at 18 mN/m selected from the surface pressure area isotherm of the monolayer. In this way, 30 monolayers of VOPc films were laminated. The UV/Vis spectra for each film were similar in the Q band region. Therefore, the structure of each monolayer of the multilayer stack was similar. The molecular size of the VOPc is 2.2x2.2x0.2 nm^3. The molecular films were aligned almost perpendicular to the substrate, as estimated from the limiting molecular area of 0.44 nm^2/molecule. The third harmonics of the VOPc film were measured by the Maker-fringe method. The nonlinear optical susceptibility from the peak of the third harmonic intensity was estimated at about 10^{-10} esu.
Keywords: Langmuir-Blodgett film, Vanadyl-phthalocyanine film, nonlinear optical susceptibility, Maker-fringe method

1. INTRODUCTION

The information-based society of the 21st century is hungry for a lot of information at high speed. Multi-directional high-speed information processing can be realized using optical techniques involving nano-technology. Because of molecular level device technology, much information can be packed into a small region. Our research aimed at determining the suitability of tetra-tert-butyl-Vanadyl-phthalocyanine ((t-Bu)$_4$VOPc) film for the development of devices such as optical A/D converters, logic gates, optical memory, etc. Therefore, it was necessary to study the physical properties of this material.

We fabricated VOPc films using the Langmuir-Blodgett (LB) technique [1] and characterized them by the Maker-fringe method [2]. In the Maker-fringe method, a thin film sample is exposed to a high power laser and the nonlinear optical susceptibility is measured. This is estimated by comparison with the measurement performed for the quartz crystal glass as standard. Fang et al. [3] developed a suitable equation for the estimation of susceptibility of VOPc as a single crystal, using the data obtained by

Maker-fringe method. We modified [4] that equation and developed a new equation for conditions, in which the measurements could be made at high, as well as at low optical energy density of the laser beam. This equation was used to calculate the susceptibility of large number of VOPc films prepared by the Molecular Beam Epitaxy method [5].

In this paper, we present the fabrication of VOPc films using the LB technique and measurement of their nonlinear optical susceptibility.

2. EXPERIMENTAL SETUP FOR THE LB TECHNIQUE

The LB technique is widely used for the fabrication of monolayers, which can be used to form multiplayer stacks. This is achieved by spreading the material under consideration onto the water surface to form a molecular monolayer and gradually transferring it to the glass substrate, by lowering or raising the substrate through the monolayer interface. This is done by the appropriate choice of material with hydrophobic and hydrophilic head groups of the molecule.

We used a moving barrier type system for

fabrication of LB films. The sample liquid was spread over the surface of water in the tray of the system, and the surface pressure was monitored by compressing the liquid surface using a computer-controlled compressor. The substrate was gradually pulled out of the liquid to carry the monolayer film of the sample liquid to the substrate.

In the present experiment, we used VOPc as the sample, as performed by Komatsu et al. [6, 7], to prepare the LB films. This molecule has a phthalocyanine link with the butyl group at the four corners, as shown in Fig. 1. The molecular weight of this organic molecule [V(C$_{48}$H$_{48}$N$_8$)O] is 804. The structure of the molecule is similar to that of a shuttlecock. The size of the phthalocyanine link is 1.4 nm and the height with V=O is 0.2 nm. The length of the group at the corner of the phthalocyanine link is 0.38 nm. Thus, the total length of the (t-Bu)$_4$VOPc molecule is 2.2 nm [8]. This molecule with attached C-H groups was specially selected to obtain the hydrophilic and hydrophobic parts for the formation of LB films.
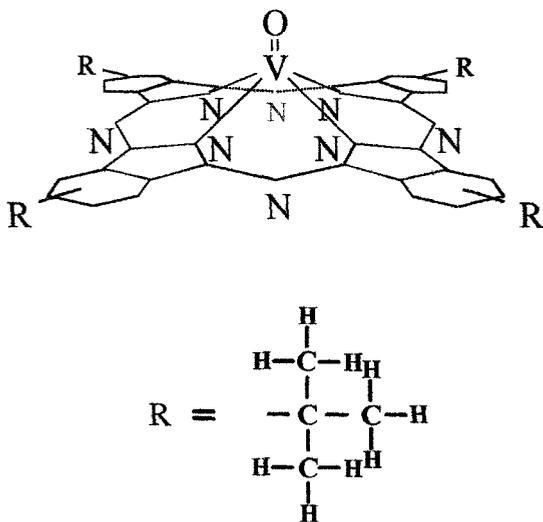
Fig. 1 Molecular structure of the tetra-tert-butyl-Vanadyl-phthalocyanine ((t-Bu)$_4$VOPc).

The VOPc was dissolved in 1, 2-dichloroethane. The substrate was made of 50 mm x 50 mm glass. The tray of the LB film system was cleaned with acetone and ultrapure water. After that, ultrapure water was poured into it. The experiment was conducted in an air-conditioned room. The temperature was maintained at 22-24 °C . The sample was added to the solvent and an 80 mg/liter solution was prepared. This was slowly poured onto the surface of the water in the tray of the LB system. The liquid was compressed at the rate of 8 mm/min and the substrate was pulled up

at the rate of 6 mm/min. The length of the coated film was 20 mm. The surface pressure (π) and the surface area (A) were measured and the curves were plotted using a computer. An example of the π-A curve is shown in Fig. 2. The surface pressure was maintained at 18 mN/m. The multiplayer stacks of 30 monolayers were fabricated by pulling the substrate perpendicular to the surface of the water with a Z-type layered structure. The hydrophilic molecular group stuck to the glass.
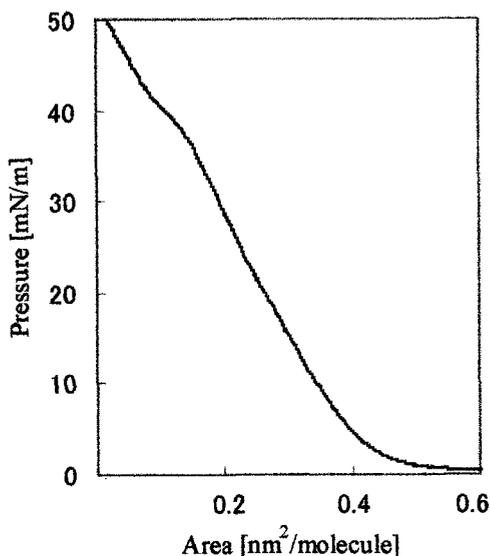
Fig. 2 Surface pressure-area (π-A) isotherm of the sample under consideration.

The molecular area was estimated by extrapolating the linear portion of the curve up to the x-axis and was 0.44 nm^2/molecule.

The sample film with an area 50 mm x 20 mm was set aside for about two hours to dry. The process was repeated to form several stacks of LB films.

3. MAKER-FRINGE METHOD

A polarized beam from a high power laser was incident on the VOPc thin film deposited on a glass substrate. The interaction of the high power polarized light with the film material causes a change in the frequency of the laser beam. The light source of the Maker-fringe system was a Nd:YAG laser with a wavelength of 1064 nm, a pulse width of 5 ns and an optical power output of 455 mJ. The pulse rate was maintained at 10 Hz. The laser beam was polarized in the perpendicular plane. The third harmonic component was detected using an interference filter and a photomultiplier. The incident angle of the laser beam was changed using a computer-controlled stage, within a range of –50 to +50 degree with 0.1 or 1 degree resolution. A neutral density filter was used to reduce the

power of the laser. The pulse rate of the laser was monitored by an oscilloscope and the data was fed into the computer to estimate the average intensity over ten pulses. The laser beam was focused using a lens with a focal length of 150 mm. The length of the beam waist at the focal point was 3.4 mm.

4. CHARACTERISTICS OF THE THIRD HARMONIC INTENSITY FOR DIFFERENT INCIDENT ANGLES

Figure 3 shows the intensity of the third harmonic component of the light passed through the LB film with 30 monolayers for different incident angles of the laser beam.

The optical energy density of the laser beam is very high at the focal point, which reduces at positions away from it. The glass substrate would be damaged due to high energy density, if it is kept at the focal point. Therefore, the glass substrate was kept away from the focal point with the film side away from the incident laser beam. The third harmonic component due to the glass substrate is shown in Fig. 4.
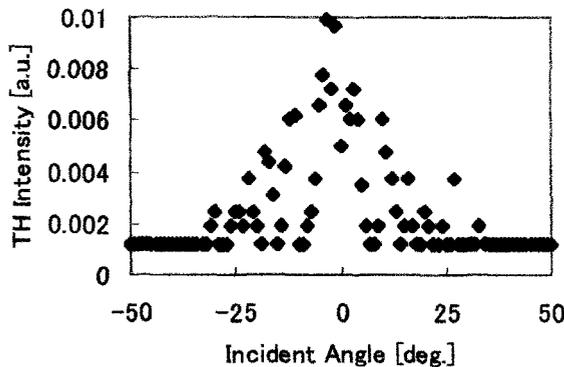
Fig. 3 Third harmonic characteristic of the LB film with 30 monolayers.

5. CALUCLATION OF THE THIRD HARMONIC NONLINEAR OPTICAL SUSCEPTIBILITY

Fang et al. [3] calculated the nonlinear susceptibility for the VOPc single crystal. We modified their equation for different optical energy densities, corresponding to the positioning of the substrate with respect to the focal point.

$$|\chi^{(3)}|=12A_2/A_1 l_c(3\omega)/\lambda_\omega|\chi_r^{(3)}|$$

$$(I_m(3\omega)/I_r(3\omega))^{1/2}AB \qquad (1)$$

$$A=|n\tilde{}_{3\omega}+1/n_{3\omega}{}^r+1|(n_\omega+1)^3/(n_\omega{}^r+1)^3$$

$$B=((n_\omega-n_{3\omega})^2+(k_{3\omega})^2/$$

$$(1-\exp(-\alpha d/2))^2+(\Delta\Psi)^2\exp(-\alpha d/2))^{1/2}$$

$$n\tilde{}_{3\omega}=n_{3\omega}+j k_{3\omega}$$

$$\Delta\Psi=6\pi(n_\omega-n\tilde{}_{3\omega})d/\lambda_\omega$$

Where, $\chi_r^{(3)}$ is the third harmonic susceptibility of the quartz crystal glass, $I_m(3\omega)$ and $I_r(3\omega)$ are third harmonic intensities of sample and standard quartz crystal glass, A_1 and A_2 are cross sectional areas of the laser beam at standard and sample positions, respectively, $l_c(3\omega)$ is the coherent length of the standard, λ_ω is the wavelength of the laser, α is the absorption coefficient of the sample at the wavelength corresponding to the third harmonic. n_ω and $n\tilde{}_{3\omega}$ are refractive indices of the sample at laser frequency and at its third harmonic. $n_\omega{}^r$ and $n_{3\omega}{}^r$ are refractive indices of the standard at laser frequency and at its third harmonic. $n_{3\omega}$ and $k_{3\omega}$ are real and imaginary parts of the refractive index $n\tilde{}_{3\omega}$, $\Delta\Psi$ is proportional to the difference between the refractive indices corresponding to laser frequency and its third harmonic, and d is the thickness of the sample.

6. DISCUSSION
6.1 Structure of VOPc film

The shuttlecock structure of VOPc film is shown in Fig. 1. The VOPc film has absorption in

Fig. 4 Third harmonic characteristic of the glass substrate.
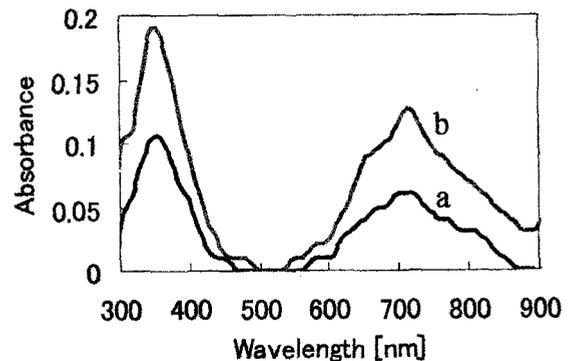
Fig. 5 UV/Vis absorption spectra of the LB films (a: 20 monolayers, b: 30 monolayers).

the Q band within a range of 500 – 800 nm, corresponding to its structure. Griffiths et al. [9] proposed that the structural arrangement and orientation of the VOPc film be classified as three phase formations. Jin et al. [10] also conclude by some estimated results that absorption peaks of 680 nm and 740 nm correspond to phase I and that of 830 nm corresponds to phase II. It was also confirmed that the absorption peak of 810 nm is obtained by epitaxy film and that of 780 nm is obtained by pseudoepitaxy films fabricated by the Molecular Beam Epitaxy method.

Figure 5 shows the UV/Vis spectra of the VOPc films for different thickness. The spectral response shows two peaks at 350 nm and 710 nm. Film thickness is calculated by the absorbance of 350 nm and is proportional to the number of monolayers [8]. The absorption at 710 nm is attributable to the structural arrangement and orientation of the LB film.

6.2 Molecular stack of monolayers

The π-A characteristic shown in Fig. 2 indicates monolayer formation on water surface. If this monolayer formation is inadequate, multiplayer stacks cannot be formed. The limiting molecular area estimated from the π-A curve of Fig. 2 is 0.44 nm²/molecule. The cross section of the molecule is 2.2 x 0.2 nm², which indicates that the molecules are standing vertical to the water surface. The side view of the molecular organization of the monolayer on the substrate is schematically shown in Fig. 6.
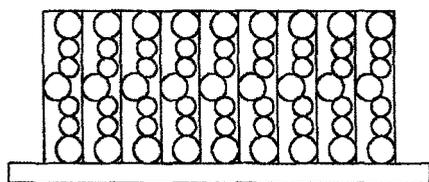
Fig. 6 A model of molecular organization of the monolayer on the substrate.

6.3 Nonlinear Optical Susceptibility

The third harmonic characteristics of the sample are resultant of the characteristics of the LB film and the substrate. Since the third harmonic content due to glass is very small, the resultant third harmonic susceptibility was due to the LB film. The characteristic was symmetrical with peak at 0 degree. The third harmonic component is directly proportional to the square of the thickness of the LB film.

The third harmonic susceptibility of the LB film was calculated using Equation 1. The beam

cross-sectional area at the LB film position was $A_2=1.5 \times 10^5$ µm² and at the position of standard was $A_1=52$ µm². The optical susceptibility was estimated as 1×10^{-10} esu. The susceptibility of VOPc film laminated by LB method was of the same order as that of the VOPc single crystal prepared by Fang et al. using Molecular Beam Epitaxy method [3]. This indicates that our multilayer formation was almost like a crystal.

7. CONCLUSION

We discussed here the fabrication of multiplayer stacks of 30 monolayer $(t-Bu)_4VOPc$ films obtained by the LB method. The third harmonic optical susceptibility of the sample was 1×10^{-10} esu, as estimated by the Maker-fringe method. Since this was of the order of single crystal VOPc, we conclude that the monolayers are aligned to form the multilayer stack.

REFERENCES

[1] G. Roberts, "Langmuir-Blodgett Films", Plenum Press, New York (1990).
[2] J. Jerphagnom and S. K. Kurtz, *J. Appl. Phys.*, **41**, 1667-1681 (1970).
[3] S Fang, H. Tada and S. Mashoko, *Appl. Phys. Lett.*, **69**, 767-769 (1996).
[4] A. Maeda, N. Okumura, H. Furuhashi, T. Yoshikawa, Y. Uchida, K. Kojima, A. Ohashi, S. Ochiai, M. Ieda and T. Mizutani, *Trans. IEICE.*, **J82-C-1**, 195-204 (1999) in Japanese.
[5] Y. L. Jin, Q. Jiang, G. Sawa, Y. Uchida, K. Kojima, A. Ohashi, S. Ochiai and T. Mizutani, *Proc. SPIE*, **4905**, 423-431 (2002).
[6] T. Komatsu, T. Kuriyama, T. Takamura and Y. Shimoyama, *J. Surface Science*, **19**, 284-287 (1998) in Japanese.
[7] T. Matsuura, T. Komatsu, E. Hatta and Y. Shimoyama, *Jpn. J. Appl. Phys.*, **39**, 1821-1825 (2000).
[8] A. Fukui, H. Furuhashi, T. Yoshikawa, A. Maeda, S. Ochiai, Y. Uchida, K. Kojima, A. Ohashi and M. Ieda, *Bull. Aichi Institute of Technology*, **33B**, 9-15 (1998) in Japanese.
[9] C. H. Griffiths, M. S. Walker and P. Goldstein, *Mol. Cryst. & Liq. Cryst.* **33**, 149-170 (1976).
[10] Y. L. Jin, H. Furuhashi, H. Nakano, Y. Uchida, K. Kojika, A. Ohashi, S. Ochiai and T. Mizutani, *Proc. SPIE*, **5277**, (2003) in press.