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Yoshiki Hirata [a] , Takahito Inoue [b] , Hiroshi Yokoyama [b] & Fumio Mizutani [a]

[a] National Institute of Bioscience and Human-Technology (NIBH), 1-1 Higashi, Tsukuba, Ibaraki, 305-8566, Japan

[b] Electro Technical Laboratory (ETL), 1-1 Umezono, Tsukuba, Ibaraki, 305, Japan

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YOSHIKI HIRATA[a], TAKAHITO INOUE[b], HIROSHI YOKOYAMA[b] and FUMIO MIZUTANI[a]

[a]*National Institute of Bioscience and Human-Technology (NIBH), 1–1 Higashi, Tsukuba, Ibaraki 305–8566, Japan; and* [b]*Electro Technical Laboratory (ETL), 1–1 Umezono, Tsukuba, Ibaraki 305, Japan*

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Scanning Maxwell stress Microscopy (SMM) which is a type of scanning probe microscopy designed to image microscopic electrical properties. have been applied to study the local surface potential distribution in photochromic spiropy ran dye Langmuir-Blodgett (LB) films. Using linear dependence between effective dipole moment and surface potential, structural change has been studied during photoisomerization.

Keywords: Scanning Maxwell-stress Microscopy: Surface Potential; Spiropyran; Photochromism

INTRODUCTION

Recently, organic materials with photochromic responses have attracted considerable attention ascribed to their potentials as high density memory devices and molecular switches. It is known that spiropyran (SP) dyes in Langmuir-Blodgett films change to the photomerocyanine (PMC) form as a result of UV irradiation, and visible light irradiation causes the reverse change to spiropyran form[1]. These optical and electrical properties in LB films strongly depended on their film structure and environments. Recently several scanning probe microscope investigations have been focused such fields. The

Scanning Maxwell stress Microscopy (SMM) is a dynamic electric force microscopy, operated at the off-resonant frequency of the cantilever, and has been demonstrated to have a capability to image local surface charge and potential at a resolution of sub-micron[2-4]. In this work, we presents visualization of local surface potential distribution in LB films and surface potential change during photo isomerization.

EXPERIMENTS

1',3'-Dihydro-3',3'- dimethyl- 6-nitro- 1'-octadecyl- 8-docosanoyl oxymethylspyro [2H-1-benzopyran-2,2'-[2H]indol] was used for amphiphilic spiropyrane dye. The sample films were prepared by the LB method from spreading of mixed chloroform solution of dye and arachidic acid with molar ratio of 1 : 2. For topographic and surface potential measurements, the monolayer was deposited onto a silicon (111) at surface pressure of 35 mNm^{-1}. For the light source, a filtered Xe lamp and black light were used. The SMM consists of a commercial AFM (NanoscopeIIIa, Digital Instruments), two lock-in amplifiers and a function generator. Cantilevers with Pt sputtered Silicon tips were used for SMM measurements. The principles of SMM are described elsewhere[2-3]. Molecular modeling and calculations were performed on Macspartan plus (Wavefunction Inc.,) software.

RESULTS AND DISCUSSION

Figure 1 (a) and (b) present the images of the topography and local surface potential distribution on a mixed LB film of spiropyran and arachidic acid. One can see two different height islands declared A and B in topographic image. Previous experiments, pure arachidic acid LB film deposited at 35 mNm^{-1} gives same domain height, shape and surface potential with domain A. Therefore, these two components of monolayer may aggregate separately. The absolute values of surface potential compared with the bare silicon substrate are about -438 mV for arachidic acid (domain A) and +475 mV for spiropyran (domain A).

After 30 min UV irradiation, surface potential difference between domain C and D became less contrast as shown in Fig 2 (b), whereas corresponding

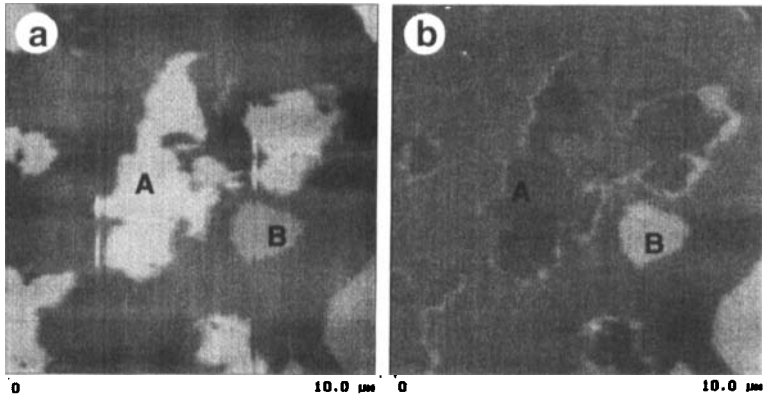

FIGURE 1 The topographic (a) and surface potential (b) images (10 x 10 μm^2 scan size) of spiropyran and arachidic acid mixed monolayer acquired with an as-deposited. The glayscale ranges are 20 nm (a) and 1500 mV. (See Color Plate IV at the back of this issue)

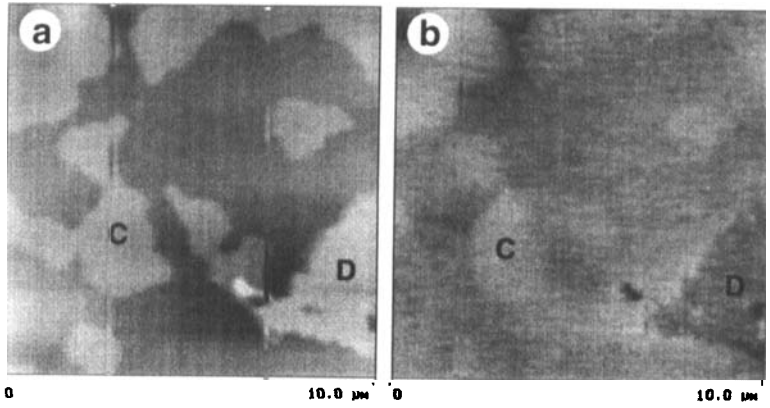

FIGURE 2 The topographic (a) and surface potential (b) images (10 x 10 μm^2 scan size) of spiropyran and arachidic acid mixed monolayer acquired after UV irradiation. The glayscale ranges are 20 nm (a) and 1500 mV. (See Color Plate V at the back of this issue)

domain heights were unchanged before UV irradiation. Since spiropyran changes to the amphotericly charged photomerocyanine form as a result of UV irradiation, this difference seems to be due to changing in the molecular orientation and electrical structure. To estimate these structural and electrical change, we try to interpret apparent surface potential by semi quantitative analysis.

The surface potential ΔV relative to the bare silicon surface can be correlated with the molecular area A and the effective perpendicular component of the dipole moment per molecule $\mu_\perp$ by equation : $\Delta V = \mu_\perp / A\varepsilon_0$ [5-6]. Using thisrelationship, measured surface potentials obtained from SMM are converted to molecular orientation information with the surface normal component of molecular dipole moment. For calculation easy, we assume that molecules were rigid and they have total dipole moment along the long axis of molecule. Tilted angles are obtained from comparing between obtained dipole moment and calculated one.

Table 1 shows surface potential and the calculated tilt angle along the molecular long axis. This result indicates that molecular tilt angle is changed about 17 ° during photoisomerization. This difference corresponds to over 20 % height change of domains. On the other hand, measured SMM topographic data indicates that height change at most 5 ~ 6 %. For precious estimation of orientational information, real molecular area and relative permitivity are needed.

TABLE I Measured surface potential data for amphiphilic compounds

Compound	Surface potential	Molecular area	Tilt angle
arachidic Acid	- 438 mV	55 Å^2	64 °
spiropyran	+ 475 mV	138 Å^2	65 °
photomerocyanine	+ 210 mV	162 Å^2	48 °

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