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UV-Sensing Characteristics of Monolayer and Polymeric Thin-Film Containing a Spiroxazine

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Abstract
We constructed a polymeric thin-film and a self-assembled monolayer containing a photochromic spiroxazine derivative. Their photoisomerization properties by UV irradiation are characterized by surface plasmon resonance (SPR) and Fresnel calculation.

Keywords photochromism; spiroxazine; surface plasmon resonance; optical thickness

INTRODUCTION

Spiroxazine dye has remarkable photochromism in that absorption spectra can be changed reversibly by light irradiation.[1] In order to apply this photo-functional molecular system to actual photonic devices, it has cooperated with a planar rigid system like Self-Assembled Monolayer (SAM) and a polymeric membrane.[2] Many characterization tools have been used for confirming their film formation and their photo-function. Among various characterization

tools of photochromic thin-film, SPR has been recently recognized as a highly sensitive technique that can precisely investigate optical properties of organic thin-films.[3]

The object of our investigation was to examine the photochromic change of spiroxazine SAM and a polymeric membrane using the SPR method and Fresnel equations in terms of SPR angle shift.

EXPERIMENTAL

Spiroxazine containing a long alkyl chain (**1**) and its monolayer on Au surface were prepared according to a previously reported method (Figure 1(a)).[4] Polymeric thin-film composed of poly(methyl methacrylate) (PMMA, M.W. = 120,000, Aldrich) and spiroxazine with a long alkyl chain (**1**) was dissolved in toluene (Aldrich). Its casting solution was spin-coated (5000 rpm) on an Au-deposited glass slide as a substrate described above and baked at 110° C for one hour. The weight ratio of PMMA and dye was 9:1.

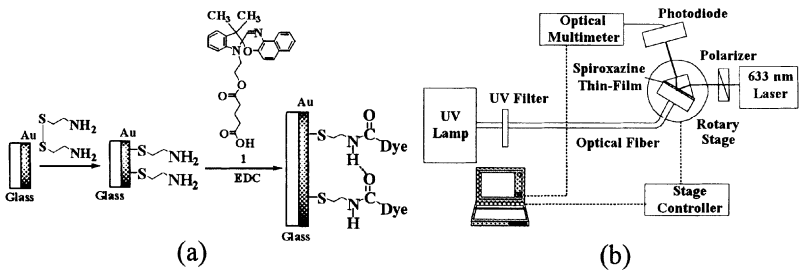

FIGURE 1 (a) Spiroxazine Monolayer build-up on Au surface. (b) Experimental setup diagram of SPR.

To confirm the monolayer formation, Fourier transform infrared reflection absorption spectroscopy (FTIR RAS), contact angle measurement, UV-Visible spectroscopy and Atomic Force Microscopy (AFM) were used according to a previously reported method.[4-5]

The SPR measurement setup is shown in Figure 1(b). Both a dye-doped polymer and a monolayer on the Au surface were index-matched with a BK7 prism (n = 1.515 at 633 nm). A p-polarized He-Ne laser at 633 nm was used as a probe beam. Reflected intensity via the prism was measured with a photodiode detector (ANDO Electric Co. Ltd., AQ-1976) and an optical multimeter (ANDO Electric Co. Ltd., AQ-1135E).

The incident angle into the prism varied with the motorized rotary stage and its controller (Suruga Seiki, D80, minimum resolution: 0.004). A high-pressure mercury lamp (Ushio, SP3-250D) was used as the UV radiation source and was calibrated with a UV pass filter (center wavelength, 360 nm).

RESULTS AND DISCUSSION

We recently reported the results of the above characterization such as spiroxazine SAM formation on Au surface (FT IR-RAS) and its reversible photochromic change under UV irradiation (contact angle measurement, UV-Visible spectroscopy and AFM). [4-5] As mentioned in those reports, UV irradiation clearly induces the spiro linkage opening in the spiroxazine monolayer.

Through the SPR curves fitted with experimental results, we can examine resonance angle shifts with respect to the change of the refractive index (RI) and thickness of thin layers (Figure 2).

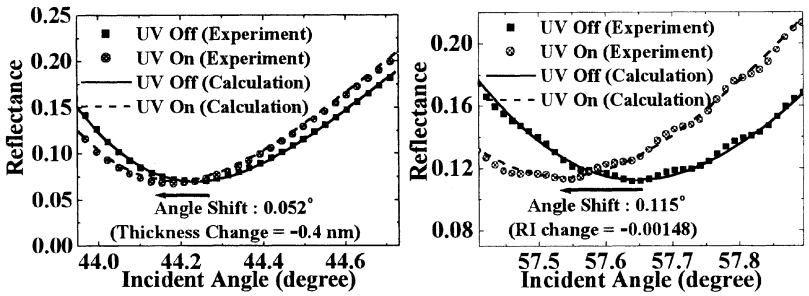

FIGURE 2 SPR angle shifts of (a) spiroxazine SAM and (b) polymeric film under UV irradiation.

According the previous study, it is known that the SPR angle shift for photoisomerization of a photochromic molecule is related to the optical thickness (RI × geometrical thickness) change.[3] The ambiguity of each parameter can be resolved by introducing a different dielectric environment method and a multi-wavelength method.[6] In this study, we evaluated the optical thickness change using only the Fresnel calculation.

As a result of Fresnel calculation to the angle shift presented in

Figure 2, an optical thickness change by photoisomerization can be evaluated as follows. Assuming the refractive index of a spiroxazine monolayer to be 1.5, the resonant angle shift of the spiroxazine monolayer can be caused by a geometrical thickness change of 0.4 nm (the optical thickness change = 0.6 nm), because a refractive index change of 0.001° corresponds to an SPR angle shift of 0.00028°, while a geometrical thickness change of 0.1 nm corresponds to SPR angle shift of 0.013° according to the calculation (Figure 2 (a)).

However the photochromic change in the spiroxazine polymeric thin-film is well known to be the refractive index change considering the random orientation of the PMMA matrix (Figure 2 (b)).[7]

In conclusion, the monolayer and polymeric film containing spiroxazine has significant photoswitching properties by UV irradiation. In the case of the spiroxazine-doped polymeric film, the refractive index change can be a major physical parameter of photoswitching. However, in the spiroxazine monolayer, the geometrical thickness change caused by photo-isomerization is the dominant factor.

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