

Surface Plasmon Resonance Spectroscopic Comparison of Spiroxazine Monolayer and Polymeric Thin Film

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ABSTRACT: Photochromic dye has recently attracted much interest in optical applications because of its reversible photoswitching properties by light irradiation. To apply those aspects of photochromism to actual photonic devices, the form of the thin film must be favorable to the photochromic molecular system. In this study, a polymeric thin film and self-assembled monolayer were constructed with a photochromic spiroxazine derivative that is well known for its good fatigue properties. Their photoisomerization properties were characterized through surface plasmon resonance (SPR). As a result of ultraviolet irradiation to these thin

films, the SPR angle shift clearly appeared as the optical thickness (Refractive index \times Geometrical thickness) change in both of the films. The Fresnel calculation based on measurement results showed that the angle shift of the polymeric thin film mainly corresponded to the change of the refractive index. For the spiroxazine monolayer, the geometrical thickness change caused the resonance angle to shift dominantly. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3459–3465, 2003

Key words: photochemistry; monolayer; thin films

INTRODUCTION

Photochromic dye has remarkable photofunctional properties in that the absorption spectra can be changed reversibly by light irradiation. This photoisomerization also results in various physical and chemical property changes, such as changes in the refractive index, dielectric constant, and the molecular geometric and electronic structure.¹ These photoswitching properties can be applied to various optical applications such as all-optical switches and optical memory.²

On the basis of these outstanding properties of photoisomerization, to apply the photochromic molecular system to actual photonic devices, the system must cooperate with another rigid system such as a polymer matrix, organic–inorganic hybrid glass, or substrate with a linker.^{3–5} This cooperative system has been mainly shaped into the form of a thin film that may be easily manipulated and may fabricate photonic applications. Among various photochromic thin-film formation techniques, the

Langmuir–Blodgett method and self-assembled monolayer (SAM) method have drawn focus recently because they are known as the most appropriate techniques for functional monomolecular layer fabrication.⁶ Particularly, much attention has been paid to the photochromic ultrathin film and its application to optical storage devices because photochromic Langmuir–Blodgett films and SAMs can offer the opportunity for the photocontrol of polymer chain organization and orientation.^{7,8}

Traditionally, the characterization of photochromic ultrathin films has been achieved by means of diverse tools such as electrochemical analysis, X-ray analysis, atomic force microscopy (AFM), and optical analysis [ellipsometry, ultraviolet–visible (UV–vis) spectrometry, surface plasmon resonance (SPR)].^{9,10} Among these tools, because it is recognized as a highly sensitive technique that offers precise characterization results for ultrathin films, SPR has been widely used to determine optical constants and for the real-time monitoring of molecular binding events.¹¹ Thus, the physical properties of photochromic thin films can be successfully characterized with respect to the change in the optical constant with the SPR method.⁹

The object of this study was to investigate the photochromic changes in the spiroxazine SAM with the SPR method and to analyze the experimental results in terms of the SPR angle shift with Fresnel

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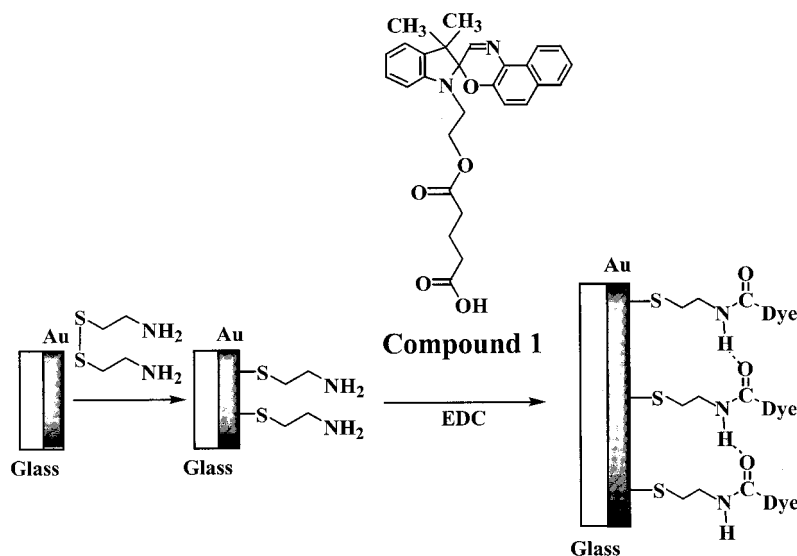


Figure 1 Schematic representation of the build-up of the spiroxazine SAM on Au.

equations.¹² To clarify the meaning of photochromic change more clearly, the results of the SAM were compared with those of a spiroxazine dispersed polymeric thin film.

EXPERIMENTAL

Materials preparation

Spiroxazine containing a long alkyl chain (compound **1**) was designed and synthesized according to a previously reported method, and its monolayer was prepared with the following procedure (Fig. 1).^{13,14}

For substrate preparation, after the glass slide (18 × 18 mm) was immersed in a cleaning detergent for 10 h, it was cleaned with deionized water in an ultrasonic cleaner for 10 min and dried for 30 min at 80°C. Au was then coated by electron-beam evaporation with a thickness of 50 nm after 3 nm nickel–chromium deposition on the glass slide. The Au coated glass was then immersed in a 1.0×10^{-2} M cystamine hydrochloride aqueous solution for 2 h and rinsed with deionized water. In addition, the cystamine adsorbed glass was treated with a 1.0×10^{-2} M methanolic solution of 1-ethyl-3-[3-(dimethylamino) propyl] carbodiimide (EDC) and 5.0×10^{-4} M spiroxazine dye for 12 h. The resulting monolayer was rinsed with deionized water and dried out in N₂ gas.

A polymeric thin film composed of poly(methyl methacrylate) (PMMA; molecular weight = 120,000; Aldrich) and **1** was dissolved in toluene (Aldrich, Milwaukee, WI). Its casting solution was spin-coated (5000 rpm) on the Au-deposited glass slide as a substrate described previously and baked at 110°C for 1 h. The weight ratio of PMMA to dye was 9:1.

Thin-film characterization

To confirm the monolayer formation, Fourier transform infrared reflection absorption spectroscopy (FTIR RAS), AFM, UV–vis spectroscopy and the contact angle measurement were used as described next.

FTIR RAS measurements were carried out with a Nicolet Magma-IRTM 500 spectrometer (Nicolet, Madison, WI). A narrow-band HgCdTe detector, cooled with liquid nitrogen, was used to detect the reflected light. A Graseby Space grazing angle reflectance accessory (Orlando, FL) equipped with a polarizer was used at 80°. All of the spectra were collected with 2 cm⁻¹ resolutions.

The topographic images of the monolayer surfaces were collected in the contact mode with a scanning probe microscopy (SPM-LS) manufactured by Park Scientific Instruments (Sunnyvale, CA). The silicon nitride cantilevers had a nominal spring constant of about 0.05 N/m, and the scanning parameters were adjusted to obtain clear images revealing the effects of the monolayer on the Au surface.

A multichannel photodiode detector (Otsuka Electronics, MCPD 1000, Osaka, Japan) with an ultraviolet (UV) irradiation apparatus (high-pressure mercury lamp, Ushio, SP3-250D, Tokyo, Japan) was used to acquire the visible absorption spectrum of the monolayer under UV irradiation. Because of the very slow photoswitching speed of the spiroxazine monolayer in air, only the visible spectra before and after UV irradiation (1 h) were compared. The photochromic spectrum of the polymeric thin film also was characterized with the same method. Its absorbance change was recorded by scanning spectra at various time intervals (1–5 s) until the spectra were saturated.

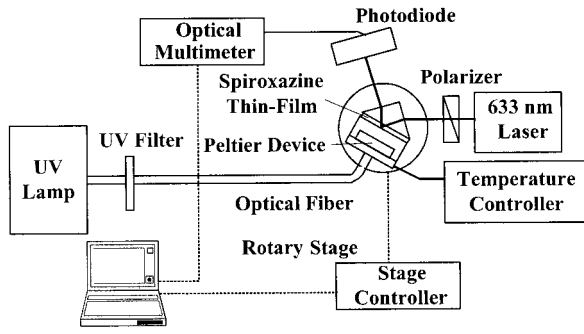


Figure 2 Experimental setup diagram of the SPR measurement.

For the measurements of surface wettability and surface functionality, the water contact angles of the bare gold, cystamine–gold, and spiroxazine–cystamine gold were measured at room temperature with a contact angle goniometer (Erma, Inc., model G-I type, Tokyo, Japan).

Instrumentation for SPR characterization

The SPR measurement setup is shown in Figure 2. Both a dye-doped polymer and a monolayer on the Au surface were index-matched with a BK7 prism (refractive index, $n = 1.515$ at 633 nm). The p -polarized He–Ne laser at 633 nm was used as a probe beam. The reflected intensity via the prism was measured with a photodiode detector (ANDO Electric Co., Ltd., AQ-1976, Kanagawa, Japan) 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, Shizuoka, Japan, 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). During the SPR measurements, the temperature was kept at $25 \pm 0.1^\circ\text{C}$ by a temperature controlling system with a Peltier module.

Calculation model with fresnel equations¹²

Figure 3 describes the four-layer system composed of a prism, metal film (gold), dielectric film (spiroxazine polymeric film or monolayer), and external dielectric environment (air). This diagram has been used for the model of a typical Kretschmann configuration for SPR excitation.¹⁵ In particular, to investigate the photochromic change in the spiroxazine thin film, we applied the four-layer model and the following equations to our study.

Usually, the system displayed in Figure 3 can be represented with the following characteristic matrix:

$$\begin{pmatrix} E_0^+ \\ E_0^- \end{pmatrix} = \prod_{m=1}^3 \frac{C_m}{t_m} \begin{pmatrix} E_3^+ \\ E_3^- \end{pmatrix} \quad (1)$$

where

$$C_m = \begin{pmatrix} e^{i\delta_{m-1}} & r_m e^{i\delta_{m-1}} \\ r_m e^{-i\delta_{m-1}} & e^{-i\delta_{m-1}} \end{pmatrix} \quad (2)$$

where E_0^+ and E_0^- represent the positive-going incident wave and negative-going reflected wave in the 0th medium, respectively. Also, E_3^+ indicates the positive-going transmitted wave in the 3rd medium. Because there was no negative going wave in the 3rd medium (E_3^-), we set E_3^- at 0. To calculate eq. (1), the phase term (δ_m) and Fresnel coefficient (r_m), t_m was considered the complex value described in eqs. (3)–(5) under the conditions of arbitrary incidence angle, absorbing media, and p polarization, respectively:

$$\delta_{m-1} = \frac{2\pi}{\lambda} (n_{m-1} - jk_{m-1}) d_{m-1} \cos \theta_{m-1} \quad (3)$$

$$r_m = g_m + jh_m$$

$$\equiv \frac{n_{m-1} \cos \theta_m - n_m \cos \theta_{m-1}}{n_{m-1} \cos \theta_m + n_m \cos \theta_{m-1}} (n_m = n_m - jk_m) \quad (4)$$

$$t_m = 1 + g_m + jh_m \quad (5)$$

where j is an imaginary number, g_m and h_m are real and imaginary parts of Fresnel coefficients, λ is the wavelength of the incident wave, d_m is the thickness of the layer, n_m is the complex refractive index, n_m is the real part of the refractive index, k_m is the imaginary part of the refractive index (extinction coefficient), and θ_m is the incident angle at the m th medium, respectively. Furthermore, the incident angles in each interface determined by Snell's law are also complex if an angle is over the critical value.¹⁶ As a result, the manipulation of complex angles must be included in the evaluation of eq. (1).

$$\text{Writing the matrix product } \prod_{m=1}^3 C_m = \begin{pmatrix} a & b \\ c & d \end{pmatrix}$$

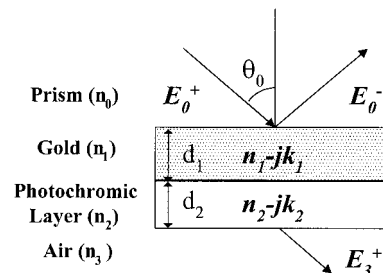


Figure 3 Kretschmann configuration for SPR excitation.

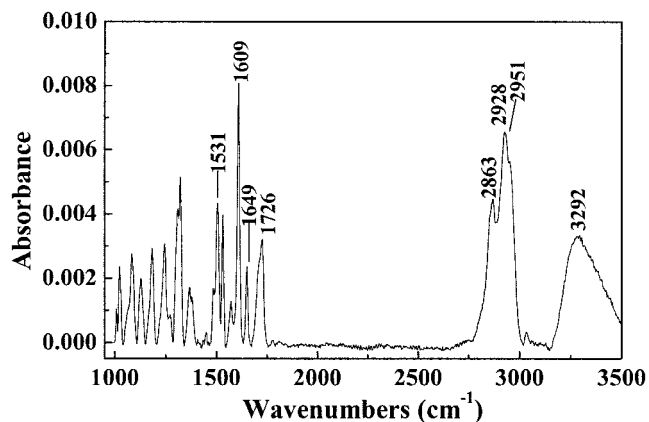


Figure 4 FTIR RAS spectra of the spiroxazine monolayer.

in eq. (1), we obtain the reflectance, which is given by

$$R = \frac{(E_0^-)(E_0^-)^*}{(E_0^+)(E_0^+)^*} = \frac{cc^*}{aa^*} \quad (6)$$

The Fresnel mismatch with the experimental results can be resolved by consideration of the transmittance at each prism face.

To estimate the optical constants of each layer, first the previous equations should be applied to fit the reflectance curve of bare gold. Then, the best-fit values can be used to estimate the thickness and the refractive index of the photochromic thin films. However, if one of these parameters cannot be determined before, an ambiguity exists in their separate determination. Because the optical thickness ($n_m \times d_m$) in δ_m has many pairs of values (n_m, d_m) to the given reflectance curve,

one of them must be fixed before the Fresnel calculation to remove any uncertainty.

On the basis of the previous procedures, the photochromic change in the spiroxazine SAM was investigated in terms of the resonance angle shift ($\Delta\theta$) with the SPR method. With the experimental results and calculations with the Fresnel equations, we analyzed the physical meaning of the photochromic change in terms of optical parameters such as the refractive index and thickness.

RESULTS AND DISCUSSION

Spiroxazine monolayer and polymeric thin-film formation

As shown in Figure 4, the FTIR RAS result showed strong N—H stretching (amide A) at 3293 cm^{-1} , C=O stretching (amide I) at 1649 cm^{-1} , and N—H in-plane bending (amide II) at 1531 cm^{-1} . The bands of 2928 and 2863 cm^{-1} were assigned as the asymmetric C—H stretching mode of a methylene group and the symmetric C—H stretching mode of a methylene group, respectively. A C—H asymmetric stretching band of the CH_3 group was observed at 2951 cm^{-1} . The peak positions of methylene stretching bands are usually affected by molecular conformation so that the peaks of the monolayer appear at higher frequencies than that of the solid. The C=O stretching (amide I) at 1649 cm^{-1} and band broadening of N—H stretching at $3300\text{--}3500 \text{ cm}^{-1}$ may have been due to hydrogen bonding. These results supported the formation of hydrogen bonding between spiroxazine derivatives.

Furthermore, the peak intensity of the bands indicated that the hydrocarbon chains were largely in-

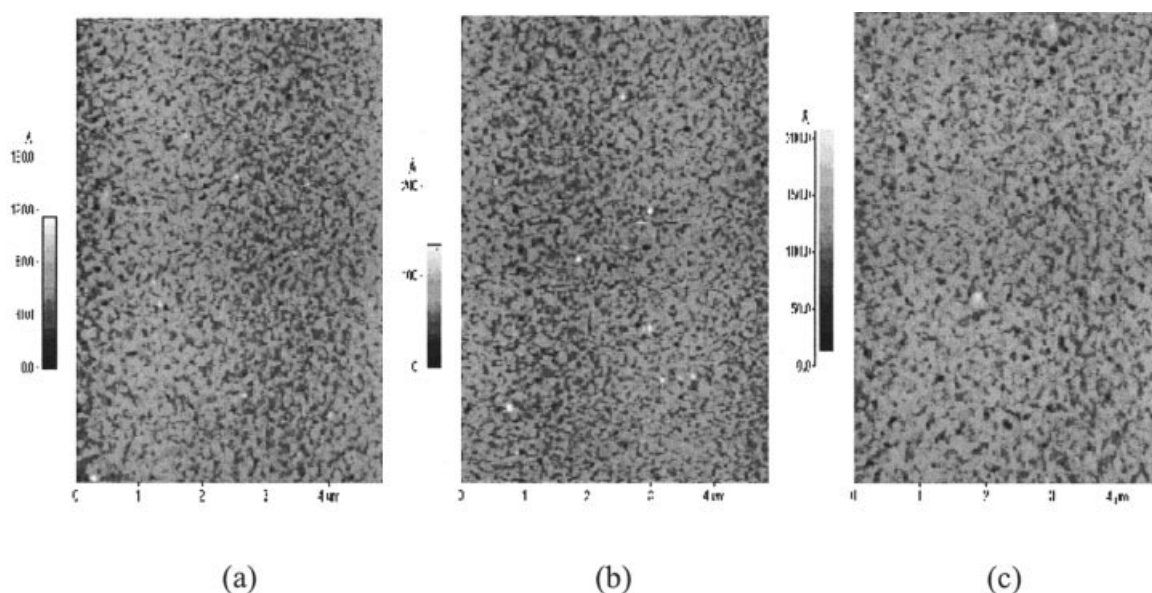
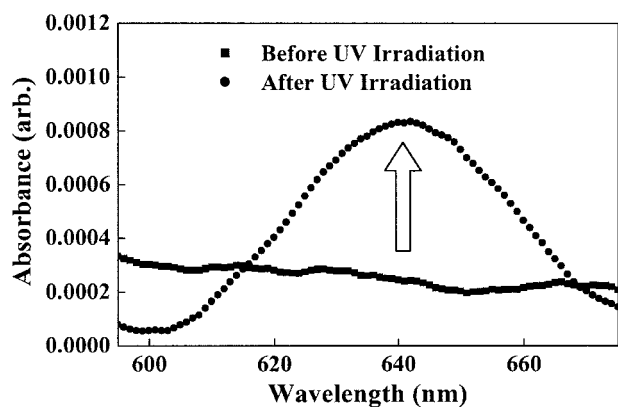
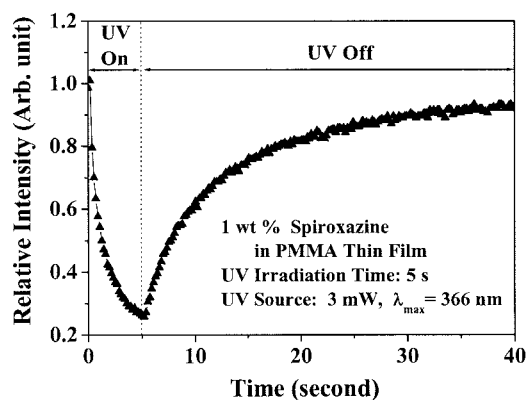


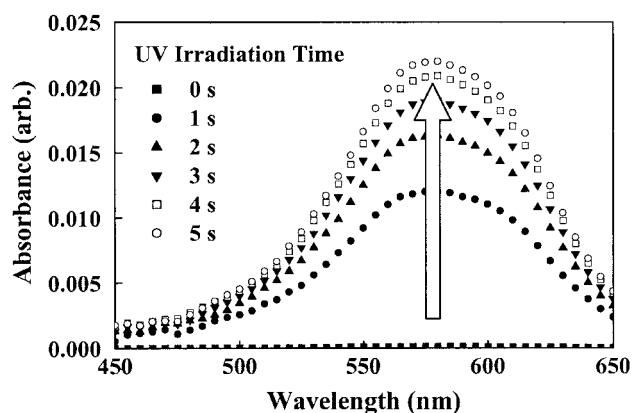
Figure 5 AFM images of bare (a) Au, (b) cystamine SAMs on a Au chip, and (c) spiroxazine-cystamine SAMs on a Au chip.



(a)



(a)

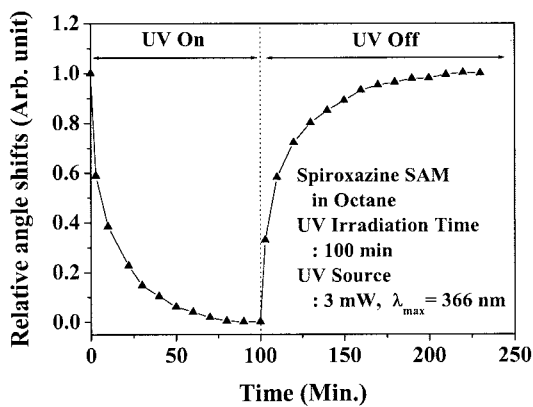


(b)

Figure 6 UV-vis spectra of the (a) spiroxazine monolayer and (b) polymeric thin film in air before and after UV irradiation.

clined from the gold surface. In addition, the AFM measurement results guaranteed that the cystamine and spiroxazine layer were successfully deposited on the gold surface. The root mean square roughness was 10.4 Å (gold), 12.5 Å (cystamine-gold), and 15.9 Å (spiroxazine-cystamine-gold; Fig. 5).

The UV-vis spectra of the monolayer and polymeric thin film containing spiroxazine are shown in Figure 6. As expected, the closed spiroxazine form was reversibly changed into an open merocyanine form in both cases because of photoswitching. The maximum absorption wavelengths appeared under UV irradiation around 640 nm [monolayer; Fig. 6(a)] and 580 nm [polymeric thin film; Fig. 6(b)]. These results could be due to the absorption wavelength of spiroxazine being affected by polarity of its circumstance. A different neighbor environment can alter a species' ability to absorb a given wavelength of radiation.¹⁷



(b)

Figure 7 Time-course curve of spiroxazine in the (a) polymeric film and (b) SAM.

As shown in Figure 7, the photoisomerization speed of spiroxazine in the SAM was slower than that of spiroxazine in the polymeric film. In case of the polymeric film, the polymer matrices offered free volume for the photoisomerization of spiroxazine. In contrast, the spiroxazine SAM, which had a densely packed structure, could

TABLE I
Water Contact Angle of Surface-Modified Au Measured by the Contact Angle Goniometer

Substrate	Contact angle (°)
Gold surface	83 ± 2
Cystamine-gold (monolayer I)	78 ± 3
Spiroxazine (closed)-cystamine-gold (monolayer II)	62 ± 2
Spiroxazine (open)-cystamine-gold (monolayer III)	55 ± 2

TABLE II
Theoretical Comparison of the Resonance Angle Shift
Corresponding to the Change of the Refractive
Index and Geometrical Thickness

	Fixed parameter	Changing parameter	$\Delta\theta$ (°)
Polymeric film	$n_p = 1.491$	$\Delta d_p = 1$ nm	0.066
	$d_p = 466$ nm	$\Delta n_p = 0.01$	0.753
SAM	$n_s = 1.500$	$\Delta d_s = 1$ nm	0.131
	$d_s = 1.5$ nm	$\Delta n_s = 0.01$	0.0027

n_p = refractive index of the polymeric film; d_p = geometrical thickness of the polymeric film; n_s = refractive index of the SAM; d_s = geometrical thickness of the SAM.

not offer a sufficient free volume. Therefore, the photoisomerization speed of the spiroxazine SAM was slower than that of spiroxazine in the polymeric film.¹

The contact angle measurement results are shown in Table I. Each surface-modified monolayer (I, II, and III) was more hydrophilic than that of the gold surface. The cystamine-gold surface had a contact angle of 78°, indicating that the amino-group-terminated system was more polar than the gold surface. The smaller contact angle of 62° observed in the spiroxazine-cystamine-gold may have been due to the structure of the spiroxazine monolayer. The amide group was itself very polar, and the presence of the high densities of the amide groups could have made the surface of the monolayer hydrophilic. Under UV irradiation, the contact angle of monolayer III was smaller than that of monolayer II. This was because the surface of monolayer III was more hydrophilic than monolayer II.

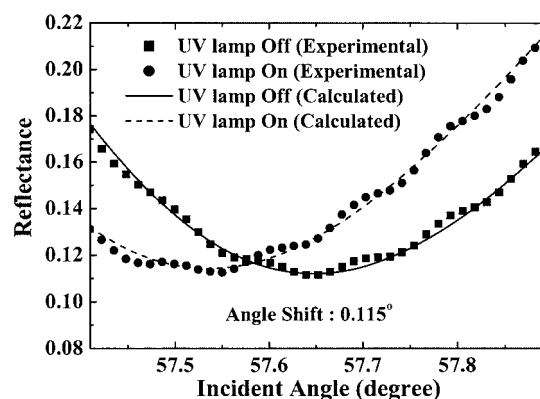
SPR angle shifts of the spiroxazine monolayer and polymeric thin film

As expected, the results of the UV-vis spectrum and contact angle measurements indicated that the significant $\Delta\theta$'s were also observed on UV irradiation, although the switching time of the monolayer was longer than that of the polymeric film in air (Fig. 8). The solid and dashed lines in the figure indicate the results fit with the Fresnel equations. Through these calculated SPR curves, we examined the $\Delta\theta$'s with respect to the change in the refractive index and the thickness of the thin layers. As described earlier, the absolute refractive index and the thickness of the samples could not be determined simultaneously. However, the change in the refractive index and the thickness corresponding to the photochromic change of the samples could be expressed well enough with the $\Delta\theta$'s. Thus, the physical meaning of the photochromic change could be understood by means of the $\Delta\theta$'s.

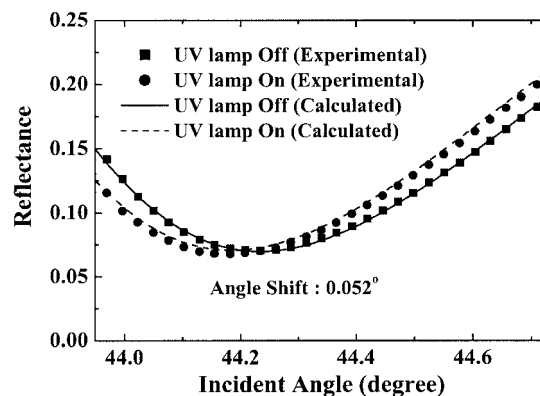
It is well known that the $\Delta\theta$'s of a polymeric film containing photochromic dye are affected by changes in the refractive index, especially from n_m .² Subsequently,

the photochromic change in the spiroxazine polymeric thin film can be described as the refractive index change. Theoretical comparison of the $\Delta\theta$ corresponding to the change in the refractive index with the fixed geometrical thickness and to the change in geometrical thickness with a fixed refractive index supported this fact. As shown in Table II, the change in the refractive index was more effective in causing $\Delta\theta$'s than that of a geometrical thickness change in the polymeric film. From the results of previous Fresnel calculations with eqs. (1)–(6), Figure 8(a) shows that a refractive index change of 0.00148 corresponded to a $\Delta\theta$ of 0.115°.

In contrast to the polymeric thin film, the angle shift of a monolayer containing a spiroxazine dye could not be expressed by a refractive index change only. As shown in Figure 8(b), the photochromic change in the monolayer could be described by an optical thickness change. When the refractive index of the spiroxazine monolayer was assumed to be 1.5,



(a)



(b)

Figure 8 SPR angle shifts of the (a) spiroxazine polymeric thin film and (b) monolayer in air before and after UV irradiation.

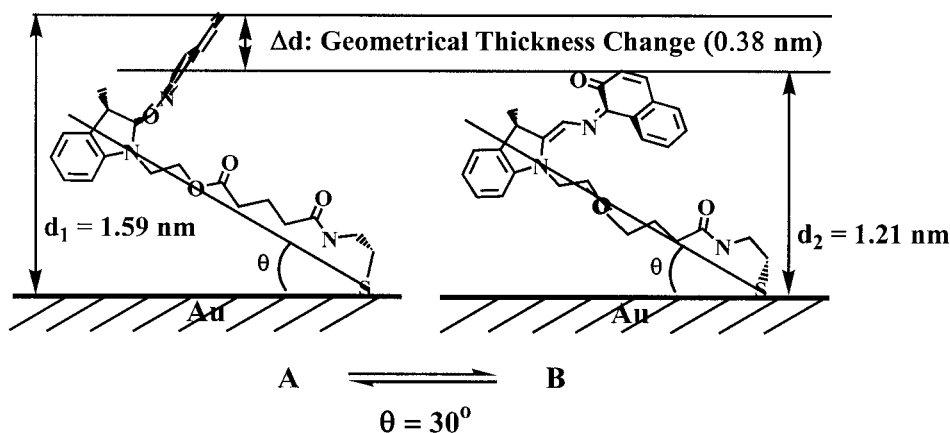


Figure 9 Schematic representation of a spiroxazine monolayer before and after UV irradiation through MOPAC AM1 optimization.

the $\Delta\theta$ of the spiroxazine monolayer after UV irradiation could be described by a geometrical thickness change of 0.4 nm (1.6 \rightarrow 1.2 nm) so that the optical thickness change was 0.6 nm [Refractive index (1.5) \times Geometrical thickness (0.4 nm)]. However, although the ambiguity of the analysis to the angle shift of the monolayer still existed, we could be easily evaluated through comparing the degrees of change in both the refractive index and geometrical thickness by following the results of the calculation to the spiroxazine monolayer with eqs. (1)–(6). As shown in Table II, the change in geometrical thickness was more effective in causing $\Delta\theta$'s than that of the refractive index in the SAM. This indicates that the dominant contribution to the $\Delta\theta$ of spiroxazine SAM was not the refractive index change but the geometrical thickness of the monolayer.

These results were in agreement with the contact angle measurement results. UV radiation can convert a spiroxazine form to a photomerocyanine form. The oxazine ring opening causes a geometrical thickness change in the monolayer and creates a more hydrophilic surface than that of the closed form. The result of the geometric optimization with molecular mechanics (MM2) followed by an Austin Model 1 (AM1) level approximation on Molecular Orbital Package (MOPAC) also confirmed this photoswitching behavior (Fig. 9). The interatomic distances by the AM1 method for tilt angle (θ) are shown in Figure 9, where d_1 and d_2 correspond to the interatomic distance before and after irradiation, and Δd is the difference between d_1 and d_2 . The thicknesses of the SAM calculated by SPR ($d_1 = 1.60 \text{ nm}$, $d_2 = 1.20 \text{ nm}$, and $\Delta d = 0.4 \text{ nm}$) were well reproduced by the AM1 method at $\theta = 30^\circ$. At $\theta = 30^\circ$, $d_1 = 1.59 \text{ nm}$, $d_2 = 1.21 \text{ nm}$, and $\Delta d = 0.38 \text{ nm}$, as calculated by the AM1 method. However, no significant change in Δd was observed between 0 and 90° , where the carbonyl group of an opened spiroxazine moiety was directed to the surface of gold. Figure 9 depicts the geometrical thickness change caused by UV irradiation: 0.38 nm (1.59 \rightarrow 1.21

nm) at a tilted angle of 30° . Thus, the results of SPR measurement and calculation agreed well with the geometry and structure of the spiroxazine–alkanethiol–gold monolayer optimized by the AM1 method.

CONCLUSIONS

The results indicate that the monolayer and the polymeric film containing spiroxazine had significant photoswitching properties caused by UV irradiation. In the case of the spiroxazine-doped polymeric film, the refractive index change was a major physical parameter in photoswitching. However, in the spiroxazine monolayer, the geometrical thickness change caused by photoisomerization was the dominant factor.

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