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Optical properties and molecular orientation of self-assembled monolayer using surface plasmon resonance spectroscopy

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Abstract

We report evidence of photoisomerization-induced changes in thin films of spiroxazine-alkanethiol self-assembled monolayers (SAM) by surface plasmon resonance (SPR). Geometry optimization by MO calculations reveals that the tilt angle of spiroxazine moiety is around 30°. © 2001 Published by Elsevier Science Ltd.

Keywords Self-assembled monolayer (SAM), Spiroxazine dye, Photochromism; Surface plasmon resonance (SPR), Tilt angle; Molecular orientation

1. Introduction

A photochromic compound is characterized by its ability to undergo a reversible colour change. Interest in the photochromism of organic materials began to increase substantially around 1940. The principal studies of photochromic compounds involved acquiring an insight into mechanisms of the photoprocesses, determining the structures of the uncoloured form and the coloured form, and developing synthetic methods. The development of time-resolved or flash spectroscopy and, more recently, the use of laser photophysical means opened new approaches to study of the excited states and transient species involved in the photoreactivity of photochromic molecules.

Recently, photochromic materials have gained much attention, and they now constitute an active research area because of their tremendous importance in biological phenomena and in their potential applications in the areas of linear and nonlinear optics [1].

Although the photochromism of spiropyran has been extensively studied [2,3], little work has been carried out on spironaphthoxazine dyes. These two classes of compounds are similar in many respects. However, the replacement of the benzopyran ring by a naphthoxazine ring result in spironaphthoxazine having the advantage of greatly improved resistance to prolonged UV irradiation,

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which confers a much more commercial importance on them [4].

Ultrathin organic films are of considerable interest because of their potential technological applications in the fields of surface coatings, sensors and optoelectronics [5]. These films are commonly formed using Langmuir–Blodgette (LB) deposition or self-assembly techniques (SAMs) based on chemisorption. The monolayers prepared from sulfur containing species, such as thiols and disulfides, at gold surfaces have been especially well studied because of their tendency toward forming quasi-crystalline monolayers with well-defined structures [6]. Although most of the studies have been accomplished for SAMs without functional groups, such as alkanethiolate SAMs, increasing interest has been directed toward SAMs containing chromophores for optical applications [7]. We have previously reported the synthesis and self-assembly of the photochromic spiroxazine dye-containing alkanethiol with an amide group incorporated into the backbone [8] (Fig. 1).

Surface plasmon resonance (SPR) has been recently demonstrated as an effective optical technique for chemical sensing. A number of SPR configuration systems have been reported such as immunoassay [9], liquid [10], gas [11], and thin film [12]. SPR is an optical process in which light satisfying a resonance condition excites a charge-density wave that is propagating along the interface between a metal and a dielectric material. Surface plasmon can be excited by the attenuated-total-reflectance (ATR) method, as proposed by Kretschmann [13]. Also reported is the photoinduced refractive index change of a self-assembled, spiroxazine monolayer based on SPR [14]. In this paper, we report the optical properties and molecular orientation, of a SAM of UV-sensitive spiroxazine deposited gold, using SPR spectroscopy.

2. Experimental

The measurements were performed with a home made Kretschmann configuration apparatus (Fig. 2). Details on the preparation of the spiroxazine-containing alkanethiol self-assembled monolayer on gold for SPR measurements can be found elsewhere [8,14].

The glass slide with a spirooxazine-containing SAM formed on Au surface and prism ($n = 1.515$, Sigma, BK 7) were loaded on a computer-controlled rotating stage. Optical contact between the prism and slide glass in achieved by a refractive index matching fluid ($n_D = 1.515-1.517$, Merck). The p-polarized He–Ne laser at 633 nm was used as a probe beam. Reflected intensity via prism was measured with the photodiode detector (Ando Electric Co. Ltd., AQ-1976) and optical multimeter (Ando Electric Co. Ltd., AQ-1135E). The angle was regulated by the automatic-motorized rotary stage controller with a resolution of 0.004°. A high-pressure mercury lamp (Ushio, SP3-250D) was used as the UV radiation source and was calibrated with a monochromator at 366 nm. In order to investigate the photochromic properties of SAMs, the UV light source is switched with shutter and radiated on the SAMs layer.

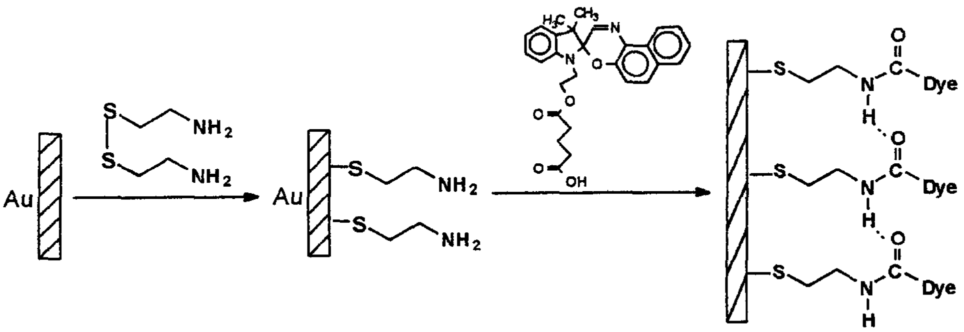

Fig. 1. Stepwise organization of a spiroxazine dye monolayer on Au layer.

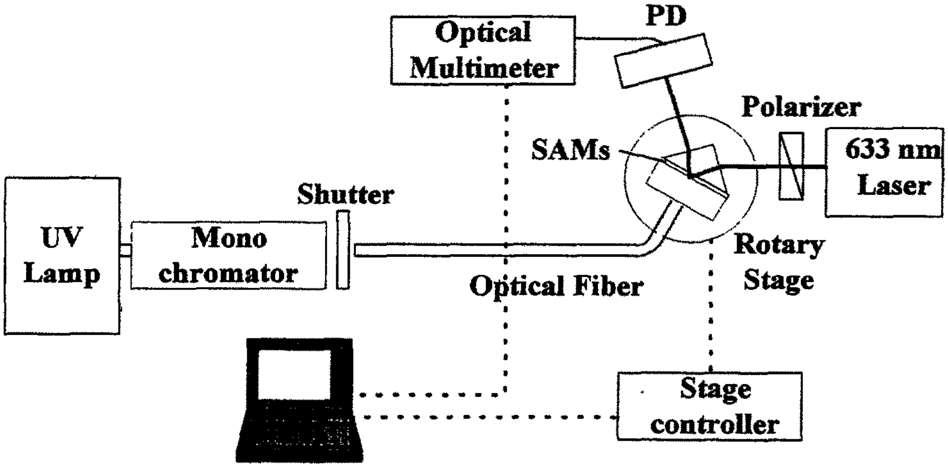

Fig. 2. Experimental setup for the SPR measurements of spiroxazine SAMs.

3. Theory

The four-layer system, composed of prism, metal film (gold), dielectric monolayer, and external dielectric environment, is shown in Fig. 3. This diagram has been used to model the typical Kretschmann configuration for exciting the SPR. Especially, in order to estimate the thickness of spiroxazine monolayer formed on the gold surface and to confirm the changes of the thickness and/or refractive index, the four-layer model and following equations are used to fit into the experimental results, before and after UV photo switching.

Usually, a system such that depicted in Fig. 3 can be described with a characteristic matrix, as shown below [15].

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

where

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

Here, E_0^+ and E_0^- represent the positive incident wave and the negative reflected wave in 0th medium, respectively. Also, E_3^+ indicates the positive transmitted wave in 3rd medium. Since there is no negative wave in the 3rd medium, we put $E_3^- = 0$. For calculating Eq. (1), the phase term δ_m and Fresnel coefficient r_m, t_m can be considered as the complex quantity, described below as Eqs. (3)–(5), under the condition of an arbitrary incidence angle, absorbing media, and p-polarization.

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

$$r_m = g_m + jh_m \equiv \frac{\mathbf{n}_{m-1}\cos\ \theta_m - \mathbf{n}_m\cos\ \theta_{m-1}}{\mathbf{n}_{m-1}\cos\ \theta_m - \mathbf{n}_m\cos\ \theta_{m-1}}, \tag{4}$$

$$(\mathbf{n}_m = n_m - jk_m)$$

$$t_m = 1 + g_m + jh_m \tag{5}$$

Here, λ, d_m, $\mathbf{n}_m$, n_m, k_m, θ_m are the wavelength of incident wave, the thickness of layer, the complex refractive index, the real part of refractive index,

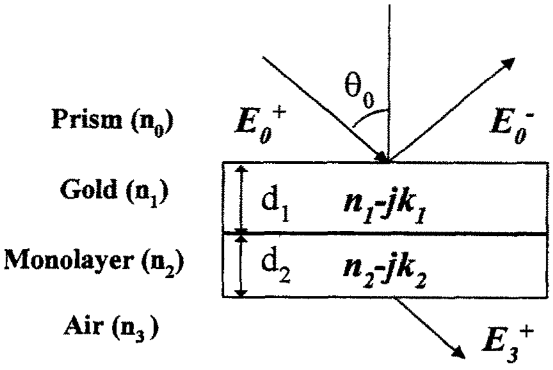

Fig. 3 A diagram of a four-layer system for exciting surface plasmon.

the imaginary part of refractive index, and the incident angle at mth medium, respectively. Furthermore, the incident angles in each interface determined by the Snell's law are also complex if an angle is over critical value. So, the manipulation to complex angles must be included for the evaluation of Eq. (1) as $\sin\,\theta_m = a_m + jb_m$.

Writing the matrix product $\prod_{m=1}^{3} C_m = \begin{pmatrix} a & b \\ c & d \end{pmatrix}$ in Eq. (1), we finally obtain the reflectance that is given by

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

Using the reflectance formulae (6) depending on the incident angles, the real and imaginary parts of the refractive index and the thickness of the gold layer can be determined by fitting the previous equations to the experimental results for the clean gold surfaces. The best-fitted values can be used to estimate the thickness of the monolayer and to investigate the resonance angle changes according to the UV irradiation.

4. Results and discussion

The spiroxazine–alkanethiol used in this study to form SAMs is shown schematically in Fig. 1. Stepwise chemical assembly of a spiroxazine monolayer on gold was performed by covalent linkage to a cystamine-monolayer-modified gold surface. A cystamine monolayer was first assembled onto a gold surface. The spiroxazine dye was coupled to the base monolayer, as recently described [16].

Infra-red spectroscopy is an ideal probe of structure and orientation in the deposited films because of its sensitivity to chemical properties and to physical properties.

Fourier transform instrumentation and the pioneering works of Francis and Ellison [17], and Greener [18], on the analysis of adsorbates on metal surface, reflection-absorption spectroscopy (RAIRS, also known as IRRAS) began to develop towards its current status as a routine laboratory technique.

The p-polarized light used in the FTIRRAS experiments, only interacts with vibrational modes perpendicular to the surface (a tilt angle of 0°), the C–H bonds would be nearly parallel to the surface and not absorb much p-polarized light. On the other hand, a tilt angle greater than zero would orient the C–H bonds more perpendicular to the surface and thereby increase the absorbance (peak area). Band assignments for FT-IR spectra in KBr and the SAM of the spiroxazine dye before irradiation has been studied by Kim et al. [8]. The intense band at 2923 and 2852 cm^{-1} are assigned to $-\mathrm{CH}_2-$ asymmetric and symmetric stretching mode of the hydrocarbon chains and the 2960 cm^{-1} band is of $-\mathrm{CH}_3$ asymmetric stretching mode in KBr. These frequencies are in agreement with those reported by other workers [19,20].

The FTIRRAS showed that the bands of 2928 and 2863 cm^{-1} are assigned as an asymmetric –C–H stretching mode of a methylene group and the symmetric –C–H stretching mode of a methylene group, respectively. Also, the –C–H asymmetric stretching band of the $-\mathrm{CH}_3$ group is observed at 2951 cm^{-1}. It is particularly notable that the intensities of the bands due to the $-\mathrm{CH}_2-$ asymmetric and symmetric stretching modes become much stronger in FTIRRAS than in the transmission spectra. From these results it may concluded that the molecular axis are tilted considerably from the surface normal in the SAM. The technique of SPR is based on the optical changes that occur at interfaces between a thin metal film and a dielectric medium just outside the metal film due to, for example, adsorption. SPR has been widely used to determine the thickness of adsorbed layers on metal surfaces [21].

Fig. 4 shows the SPR curves for SAM with photochromic spiroxazine dye both before and after irradiation of UV light (366 nm). The resonance angles of the situation before irradiation and the situation after irradiation were 44.234 and 44.182°, respectively. The resonance angle shift induced by UV irradiation can be rationalized by the formation of the photoinduced opened-spiroxazine form. The spectra obtained were fitted to Fresnel theory by assuming the "idealized layer model". In this model, the layers are considered to be isotropic and the substrate is envisaged as being perfectly flat. The solid and dotted line indicates the results fitted with the Fresnel equations to the

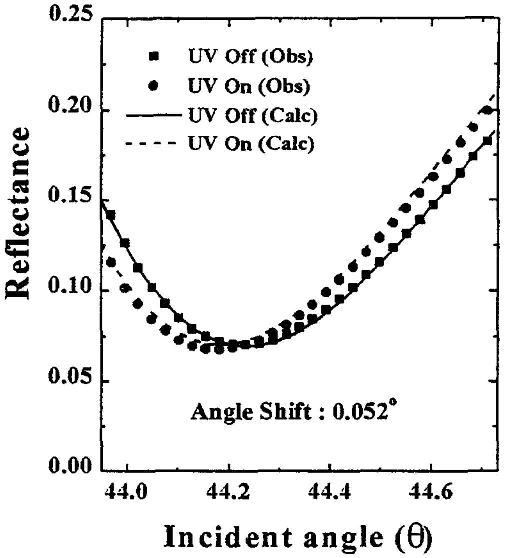

Fig 4 Resonance angle shifts of monolayer containing spiroxazine before and after UV irradiation

experimental results in consideration of the complex refractive index of samples. In a polymeric thick film, with an approximate thickness of several hundred nanometers, it is well known that resonance angle shifts of thick film are affected by the refractive index change [22]. In contrast with these facts, the SAM had the small change of resonance angle shifts, 0.00028° to the refractive index changes of 0.001 as a result of the previous calculation. It is considered that the explicit factor for the resonance angle shifts of monolayer is not the refractive index changes but the thickness changes. A refractive index of 1.5 for the films was assumed for use in the thickness calculation. In the fitting procedure, the real and imaginary components of the relative permittivity of the layer are kept fixed and the thickness (d) is calculated. The calculated thickness for the SAM before and after irradiation were 1.6 nm and 0.4 nm, respectively, i.e. the thickness change of SAM was 1.2 nm after UV irradiation. A qualitative interpretation of solvent shift is possible by considering the difference in dipole moment between the ground and excited state of the organic molecule. As the solvent polarity increased, a bathochromic shift was observed (i.e. positive solvatochromism).

The positive solvatochromism indicates that the structure of the open chain form which absorbs near 600 nm is keto type structure. Fig. 5 shows that the optimized geometry before and after irradiation of spiroxazine-containing alkanethiol, where the structure of opened spiroxazine takes the keto type structure based on positive solvatochromism. Geometry optimizations was carried out using MM2 (molecular mechanics) followed by an AM1 level approximation on MOPAC. If the spiroxazine-containing alkanethiol oriented perpendicularly to the surface on gold, the axial interatomic distances before and after irradiation were 1.97 and 1.95 Å, respectively. The interatomic distances by the AM1 method for tilt angle θ are shown in Figs. 5 and 6, where d_1 and d_2 correspond to the interatomic distance of before and after irradiation, and Δd is the difference between d_1 and d_2.

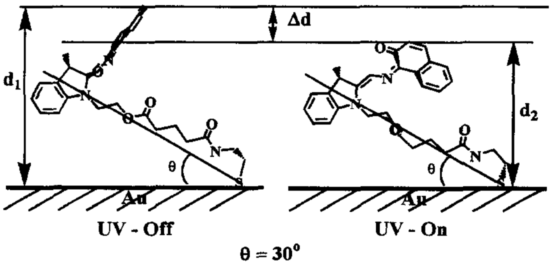

Fig. 5 Optimized geometry and schematic representation of SAMs before and after UV irradiation

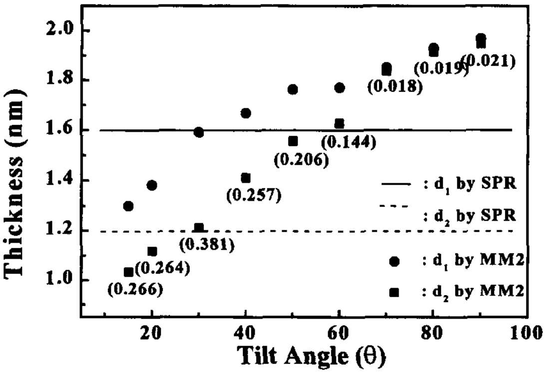

Fig. 6. Relationship between the tilt angle and SAM film thickness Thickness change shown in parentheses

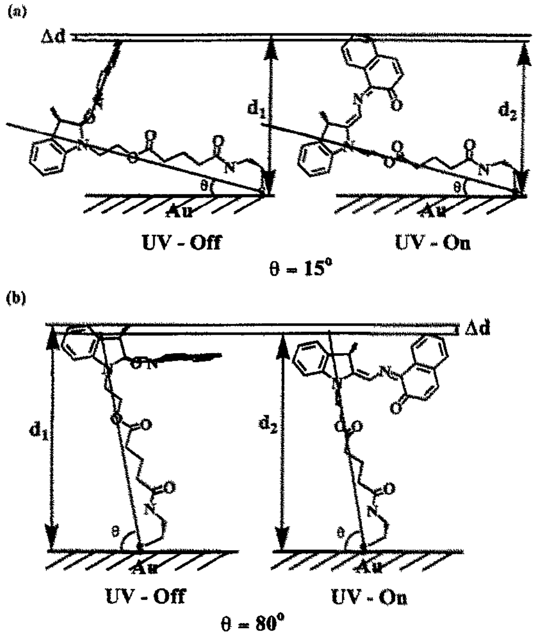

Fig. 7. Optimized geometry and the structure of a spiroxazine–alkanethiol–gold monolayer: (a) $\theta = 15°$; (b) $\theta = 80°$.

As seen from Fig. 6, increase in tilt angle causes an increase in d_1 and d_2. The fact that the calculated thickness of SAM by SPR, $d_1 = 1.6$ nm, $d_2 = 1.2$ nm and $\Delta d = 0.4$ nm is well reproduced by AM1 method at $\theta = 30°$. At $\theta = 30°$, $d_1 = 1.592$ nm, $d_2 = 1.211$ nm and $\Delta d = 3.81$ nm by AM1 method. However, no significant change in Δd is observed between 0 and 90°, where the carbonyl group of opened spiroxazine moiety directed to the surface of gold (Fig. 7).

It is not always easy to delineate an exact picture of the molecular orientation of organic dye in the SAM film, but it may possible to suggest the molecular orientation of spiroxazine alkanethiol as shown in Fig. 5 from the present results.

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