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Surface plasmon resonance spectroscopy as a probe of photo-induced switching in self-assembled spiroxazine monolayer

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Abstract

Evidence is presented of photo-induced reversible changes in the a spiroxazine dye in the surface plasmon resonance angle of a self-assembled monolayer (SAM) on gold. The resonance angle shift of the SAM of spiroxazine dye increased with increasing refractive index of the solvent. Also reported is evidence of photoisomerization-induced structural change in cast films of spiroxazine dye. © 2001 Published by Elsevier Science Ltd.

Keywords: Self-assembled monolayer; Spiroxazine; Surface plasmon resonance; Cast film; Refractive index

1. Introduction

Surface plasmon resonance (SPR) is well known as a powerful and inexpensive optical method for the study of interfacial phenomena [1]. 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, such as silver or gold, and a dielectric material. When the light is polarized with its electric field in the plane of incidence, the field causes collective oscillations of the electrons in the metal layer and results in bunching of these electrons. At the surface plasmon resonance angle, the energy of the metal surface coincides with the incident photon and the charge density wave. The photon energy is then transferred to the surface plasmon waves, which result in energy loss from reflected intensity. This phenomenon can be observed as a sharp dip in the reflected light intensity. Outside the metal, an evanescent electric field exists. This evanescent wave is part of the internally reflected light beam and partially penetrates into the lower refractive index medium. The evanescent wave can interact optically with compounds that are close to the surface or at the surface. Changes in the optical properties of this region will influence the SPR angle, this accounts for the usefulness of SPR for optical switching.

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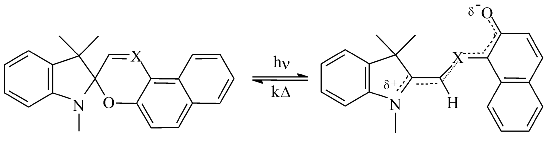
$$A \underset{h\nu',\ \Delta}{\overset{h\nu}{\rightleftharpoons}} B$$

The light-induced reversible isomerization between two forms having different absorption spectra are referred to as photochromism and compounds capable of these reactions are called photochromic molecules [2].

Recently, photochromic materials have gained appreciable attention and they now constitute an active research area because of their tremendous importance in biological phenomenon and their potential applications in the area of linear and nonlinear optics.

The two isomers differ from not only in the adsorption spectra but also in refractive indices, dielectric constants, oxidation/reduction potentials, and geometric structures. The instant property changes imparted by photoirradiation without processing lead to their use in various optoelectronic devices [3,4], such as optical memory, photo-optical switching, and display. Although much effort has been extended thus far, photochromic molecules still await practical applications. One of the major reasons for this lack of industrial applications of photochromic materials, particularly organic photochromic compounds, is their poor durability.

Although the photochromism of the spiropyran system has been extensively studied [5,6], only little work has been carried out on spiroxazine dyes. While these two classes of compound are similar in many respects, the replacement of the benzopyran ring by a naphthoxazine ring results in a spironaphthoxazine having the advantage of greatly improved resistance to prolonged UV irradiation. This confers a great importance to the spironaphthoxazine compounds [7].



colorless form colored photomerocyanine

X = CH ; spiropyran
X = N ; spiroxazine

Self-assembled monolayer (SAMs) on metal surfaces have received much attention because of the importance of establishing how the surface properties can be altered by light and how the behavior of a SAM is affected by its structural rigidity [8,9].

We have previously reported the synthesis and self-assembly of the photochromic spiroxazine dye-containing alkanethiol substituent with an amide group incorporated in the backbone [10]. Also reported has been the photoinduced thickness change of a self-assembled spiroxazine monolayer based on SPR [11]. This paper concerns the photoinduced switching of a SAM of photochromic spiroxazine deposited gold using different hydrocarbon solvent such as pentane, hexane, heptane and octane, using SPR spectroscopy. We also report the photochromism exhibited by the dye in cast film.

2. Experimental

Measurements were performed with a home-made Kretschmann configuration apparatus (Fig. 1). Details of the preparation of the spiroxazine-containing alkanethiol self-assembled monolayer on gold for SPR measurements can be found elsewhere [10,11].

A slide glass with a spiroxazine-containing SAM formed on a gold 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 was achieved by a refractive index matching fluid ($n_D = 1.515$–1.517, Merck). The *p*-polarized He–Ne laser at 670 nm was used as 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 the SAMs, the UV light source was switched and radiated the SAMs layer. All solvents were pumped into the sample cell.

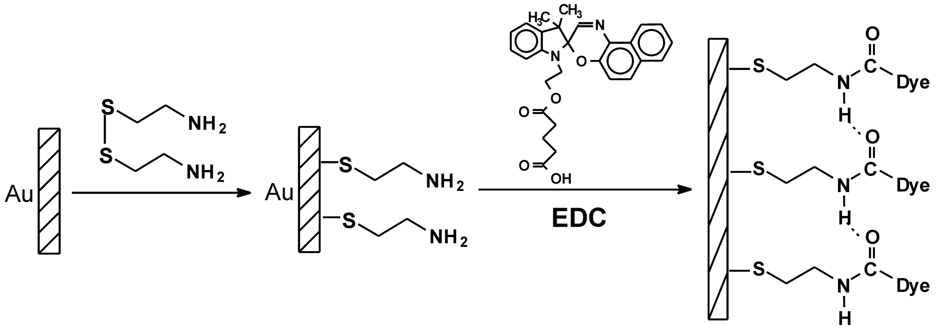


Fig. 1. Stepwise organization of a spiroxazine dye monolayer on Au layer. EDC, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride.

3. Results and discussion

3.1. Photoinduced switching in self-assembled spiroxazine monolayer

In surface plasmon resonance, the resonance angle in very sensitive to variation in the medium outside the metal film. We have previously reported the preparation and surface properties of a photochromic spiroxazine dye monolayer on gold [10,11].

The spiroxazine-alkanethiol used in this study to form SAMs is shown schematically in Fig. 2. The 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 and the spiroxazine dye was then coupled to the base monolayer, as described [10,11].

According to Fourier transform infra-red reflection absorption spectroscopy (FTIRAS) [11], the hydrocarbon chains are inclined normally from the surface. We have previously reported that the change in thickness of a monolayer was the dominant factor which can give rise to change in the resonance angle [11]. The spectra obtained were fitted to Fresnel theory by assuming the "idealized layer model" according to which, the layers are considered to be isotropic and the substrate is envisaged as being perfectly flat. The calculated thickness for the SAM before and after UV irradiation were 16–12 Å, respectively (i.e. the thickness change of SAM was 4 Å after UV irradiation). However, the resonance angle shift

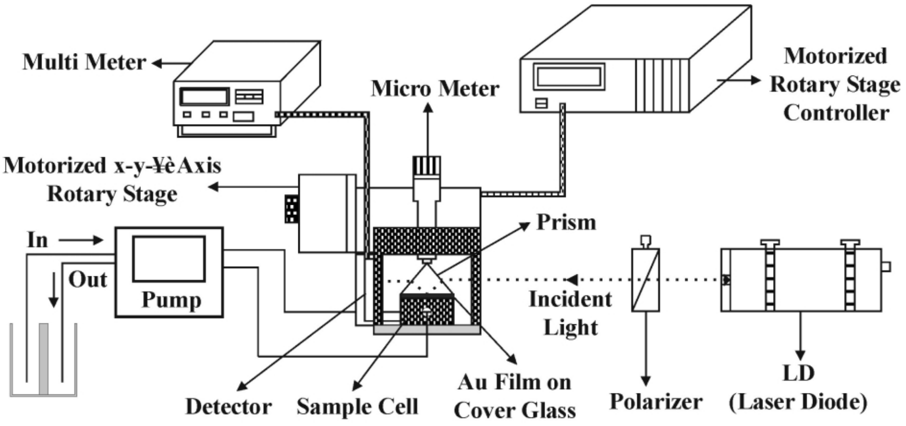


Fig. 2. Experimental setup for measuring SPR angle shift of SAMs.

highly depended on the change of refractive index of the polymeric film containing the spiroxazine dye [12]. The resonance angle of the situation before irradiation and the situation after irradiation were 42.66 and 42.62° (0.04° shift) under air.

Fig. 3 shows the SPR curves for the SAM with the photochromic spiroxazine dye before and after exposure to UV (366 nm) radiation under different solvents. When the medium outside the gold layer is pentane, hexane, heptane and octane, the resonance

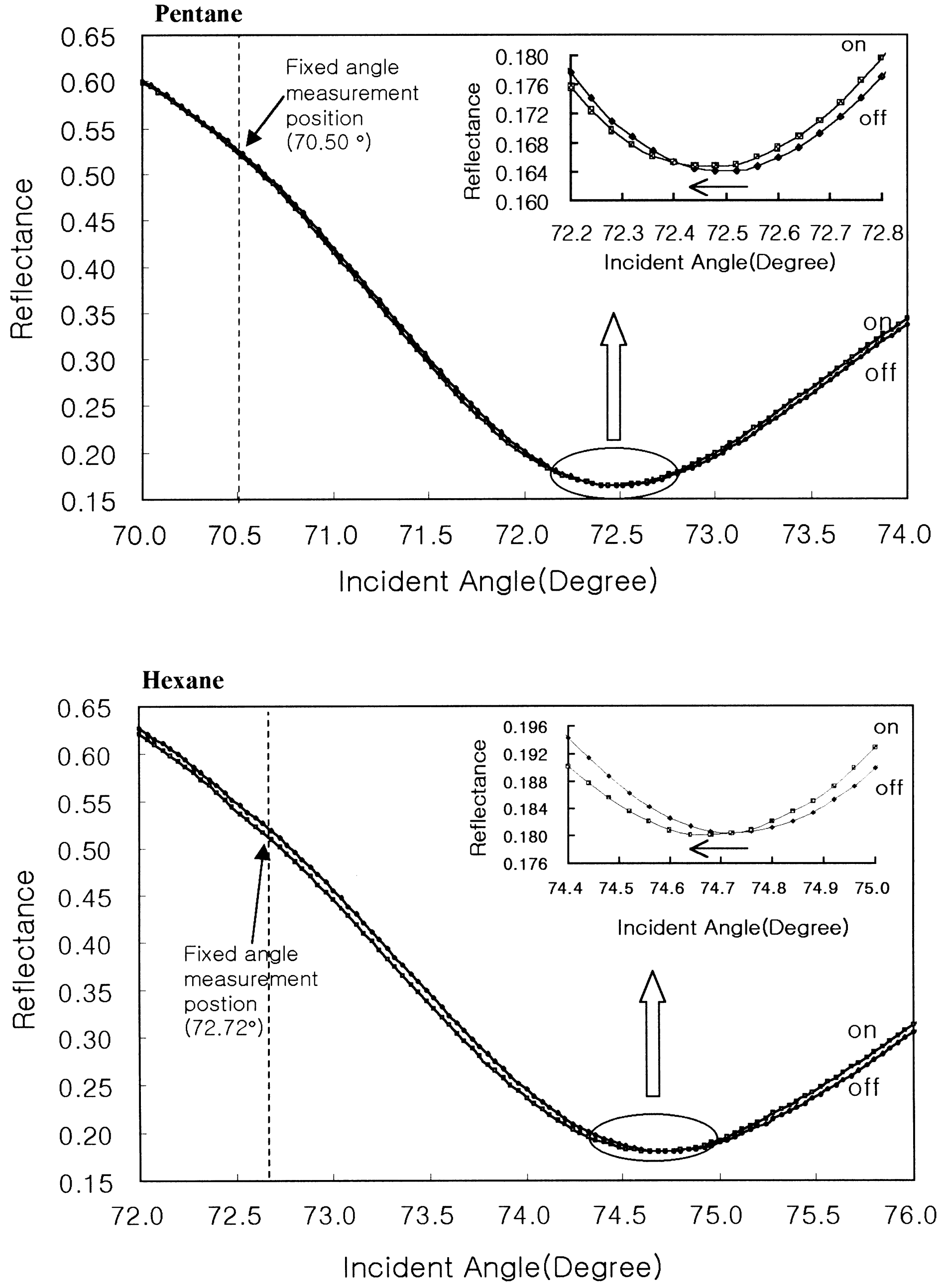
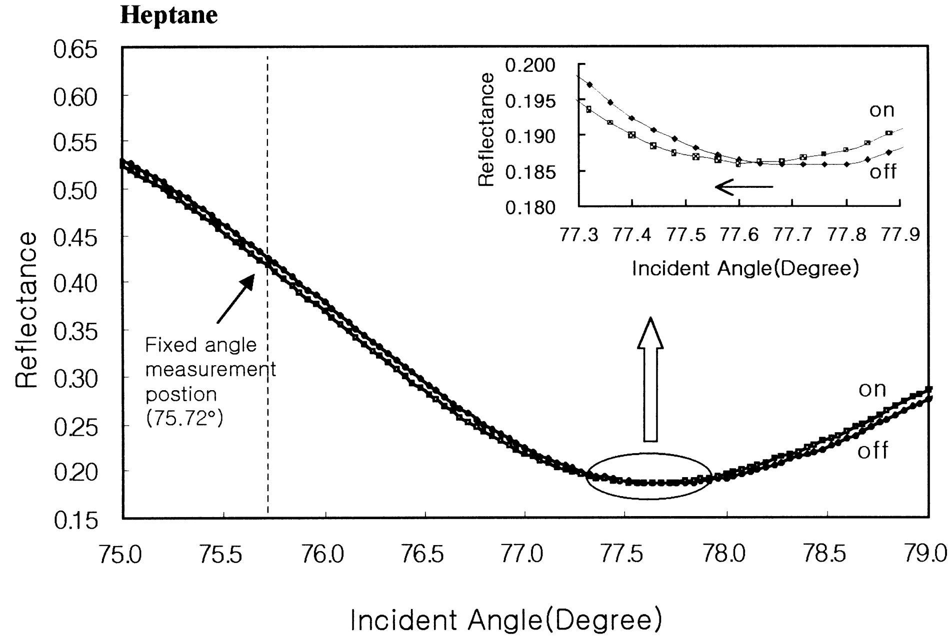


Fig. 3. Resonance angle shift of SAMs upon UV irradiation.


Heptane

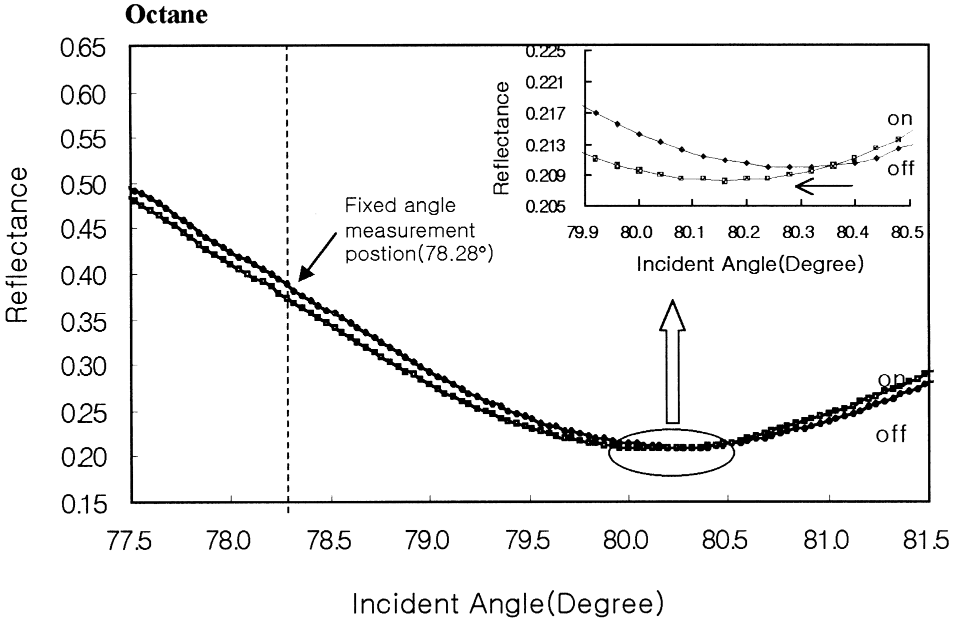

Octane

Fig. 3. (*continued*)

angles, before and after UV irradiation, were 72.50–72.46° (0.04° shift), 74.72–74.67° (0.05° shift), 77.76–77.66° (0.10° shift) and 80.28°–80.16° (0.12° shift), respectively.

The observed resonance angle shift induced by UV irradiation can be rationalized by the formation of the photoinduced ring opened merocyanine form. The shift in incident angle increased with the number of carbons in the hydrocarbon backbone of the solvent used (Fig. 4).

It is well known that resonance angle shift is affected by a change of refractive index [13]. The refractive index (η) of solvents used in this study were 1.358 (pentane), 1.375 (hexane), 1.386 (heptane) and 1.398 (octane). As shown in Fig. 5, the resonance angle shift of the monolayer increases markedly upon increasing refractive index of the solvents (Fig. 5)

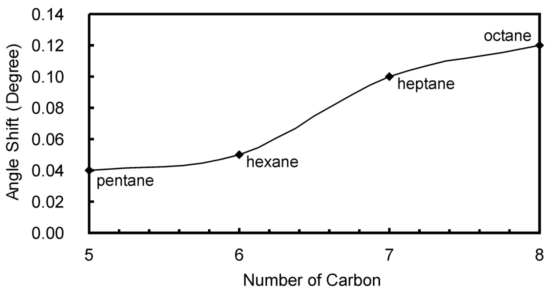


Fig. 4. Effect of number of carbon of solvent on resonance angle shift.

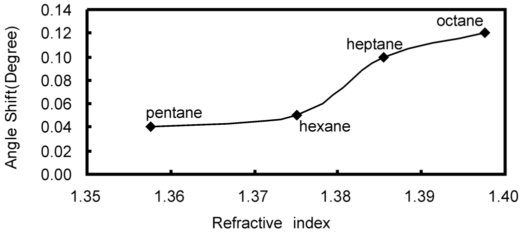


Fig. 5. Effect of refractive index of solvent on resonance angle shift.

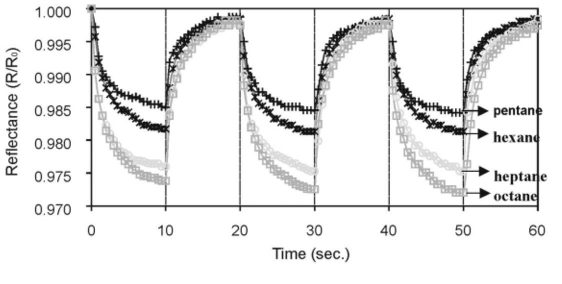


Fig. 6. Effect of successive exposure and reversal cycles for a SAM using hydrocarbon solvents.

Fig. 6 shows the changes in reflectivity (R/R_0) in response to UV-on and UV-off states. Rapid online monitoring of these changes is possible if one records the reflected intensity as a function of time at a fixed angular position; 70.50° in pentane, 72.72° in hexane, 75.72° in heptane and 78.28° in octane, as marked by the arrow in Fig. 3.

A large number of spiroxazine dyes have been found to be photochromic in solution. As the spiroxazine dye in a SAM is similar to a quasi-crystaline state, hence, thermal reversion in air is sometimes incomplete and can take many hours. In hydrocarbon solvent, the spiro form returns to the merocyanine form upon removal of the light source. The reason why the rise time is longer than the fall time is explained that quantum efficiency of the reversal process is lower than that of forward case like a previously reported study [14]. Thermal relaxation always regenerated the original state, thus indicating the full reversibility of the photoisomerization-induced optical and structural changes in self-assembled monolayer of spiroxazine dye system. The change in the reflectivity (R/R_0) in going from the merocyanine to the spiro forms diminishes with decreasing number of carbons of the solvent used; the order of R/R_0 after UV irradiation as follows: octane < heptane < hexane <pentane. These illumination cycles can be repeated many times. The technique is sensitive enough to monitor the repeated switching induced in a monolayer.

3.2. Solid state photochromism

Photochromic organic crystals are interesting not only for the design of new materials for optical data processing and storage [15], but also because the photoinduced molecular transformations might be used to gain control over other physical properties in the solid state. Spectra in Fig. 7 show the IR transmission spectra of spiroxazine dye for SAM in the cast film before and after UV irradiation.

A cast film of spiroxazine dye was prepared from chloroform solution on a CaF_2 plate. Upon irradiation with UV light (366 nm) for 5 min, new bands at 1188 cm^{-1} appeared. A band at 1188 cm^{-1} may arise from conjugated C–O stretching in the naphthalene ring. After the removal of the UV irradiation the peak disappeared with 5 min.

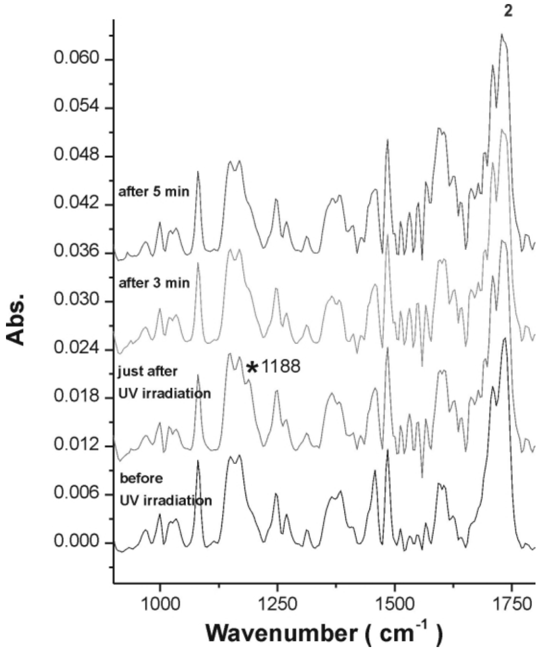
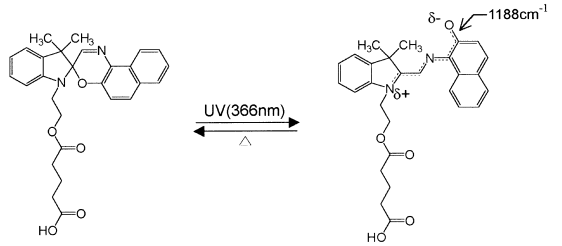


Fig. 7. Infra-red trasmission spectra of spiroxazine for SAM in CaF_2 before and after UV irradiation.



The photochemical reversibility of this system has been examined by the irradiation with 366 nm light for the photoisomerization and in dark. It is apparent that the photochromic system of the spiroxazine dye for SAM is phtochemically reversible at least up to 100 open-and-close cycles.

Acknowledgements

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