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Evaluation of Structure and Emission Property of Alternate Self-Assembled Ultrathin Films Containing Azo-Dye by Surface Plasmon Excitation Method

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Alternate self-assembled ultrathin films were fabricated on Ag-evaporated glass substrates using azobenzene dye (Direct Red 80, DR80) and poly(diallyldimethylammonium chloride) (PDADMAC). The attenuated total reflection (ATR) and emission due to surface plasmon excitation were investigated. The ATR properties were measured for the Kretschmann configuration of a prism/Ag/self-assembled film structure and the emission through the prism was measured when the sample was excited by reverse irradiation. From the ATR properties, the structure of the PDADMAC/DR80 self-assembled films was evaluated. From the emission spectra, it was found that the shapes and the peak angles almost corresponded to the shapes and the resonant angles of the ATR curves. The structural change of the self-assembled films due to photoisomerization was also investigated using scattered light measurement.
Key words: alternate self-assembled film, azo-dye, attenuated total reflection, emission, scattered light

1. INTRODUCTION

For the development of organic molecular devices with high efficiency, it is quite important particularly to evaluate the structure of organic ultrathin films and to investigate the properties and functions. The surface plasmon (SP) excitation method at the interface between metal thin films and dielectric ultrathin films is quite useful for the evaluation of dielectric properties and structure of ultrathin films [1]. Many works using attenuated total reflection (ATR) measurements have been reported on the structure and optical properties of organic ultrathin films on metal thin films [2-4]. The ATR method has been also investigated for device applications such as photoelectric cells and gas sensors because of strong electric fields at the interface between metal thin films and organic ultrathin films due to SP excitations [5-7]. Recently, emission light at a resonant angle region of SP excitations was observed through the prism in the ATR Kretschmann configuration, when metal thin films on the prism or organic ultrathin films on metal thin films were directly irradiated from air by a laser beam [8-10]. The emission light depended upon resonant conditions of SPs in the Kretschmann configuration, and it is considered that multiple SPs were excited for organic dye films by means of the direct excitation of organic dye films by a laser beam, that is, reverse irradiation [8-10].

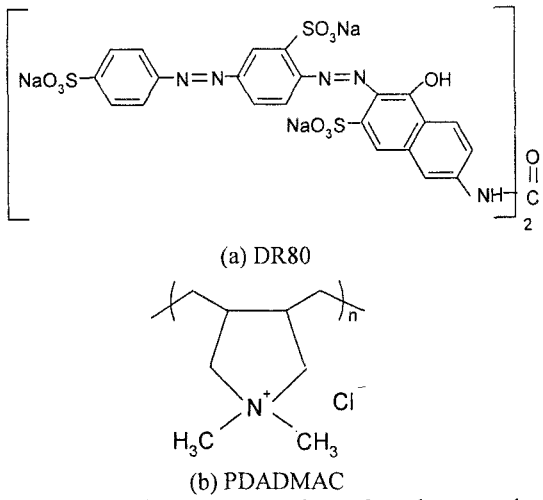
Photoisomerizable molecules e.g. azo-dyes are excellent and attractive materials for application to optical devices. The photoisomerization of azo-dyes introduces alignment of the molecular long axis in a direction perpendicular to the direction of polarized irradiation light. In the previous paper, photo-induced surface gratings of alternate self-assembled ultrathin films containing azo-dyes were fabricated and the alignment properties of liquid crystal molecules on these films were investigated [11].

In this paper, ATR and emission properties due to surface plasmon excitation were investigated for alternate self-assembled ultrathin films containing azobenzene dye (Direct Red 80, DR80). The structural change of the films due to photoisomerization has been also investigated. The measurement of scattered light due to surface plasmon excitation [12] was also carried out in order to obtain the information about the surface roughness of the self-assembled films.

2. EXPERIMENTAL

2.1 Preparation of alternate self-assembled ultrathin films

Chemical structures of the polycation and the azo-dye used in this work are shown in Fig. 1.



(a) DR80

(b) PDADMAC

Fig. 1. Molecular structures of DR80 azobenzene dye and PDADMAC polycation used in this work.

The Direct Red 80 (DR80) azo-dye contains four azobenzene groups per molecule exhibiting photoisomerization. The poly(diallyldimethyl-ammonium chloride) (PDADMAC) polycation was used to prepare alternate self-assembled films with well-defined thickness and order. Ag thin films with the thickness of about 50 nm were deposited on cover glasses by a vacuum evaporation method. The surfaces of the Ag-evaporated glass substrates were then functionalized with 3-aminopropyltriethoxysilane prior to the alternate deposition. The layer-by-layer adsorption of PDADMAC/DR80 films was carried out as follows: the molecular layers of the PDADMAC and the DR80 were alternately deposited from these solutions with 0.01 M on the substrates. For the self-assembly deposition, the substrates were immersed in the solutions for 15 minutes at 22.0°C.

2.2 Experimental method of ATR, scattered light and emission measurements

The Kretschmann configuration [1] was used for the ATR, scattered light and emission measurements. A half-cylindrical prism (BK-7) was used and the samples of PDADMAC/DR80 films on Ag-evaporated glass substrates were attached to the bottom of the prism using a matching oil. The prism with the sample of PDADMAC/DR80 films was mounted on a computer-controlled goniostage and the incident angles was changed by rotating the goniostage using a pulse motor for the ATR and scattered light measurements, the p-polarized laser beams are directed on to the back surface of the Ag thin film through the prism. The intensity of the reflected light of the incident laser beam was detected by a photodiode as a function of the incident angle of the laser beam. The reflectivity, that is, the ATR value was obtained from the ratio of intensities of incident and reflection lights. For the scattered light measurement [12], the intensity of the scattered light was observed by another photodiode as a function of the scattering angle when the incident angle of the laser beam was set as the resonant angles of the ATR curve. Emission due to SP excitation [8-10] was also measured when a p-polarized laser beam was perpendicularly irradiated from the air to the front surface of the self-assembled film. The intensity of the emission light was observed through the prism as a function of the emission angle. In this work, p-polarized laser beams from He-Ne (wavelength λ = 632.8 nm) and Ar^+ (λ = 488.0 nm) lasers were used.

3. RESULTS AND DISCUSSION

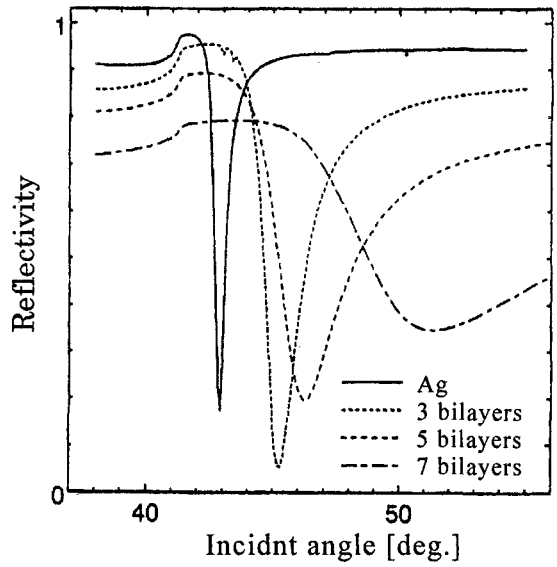
3.1 ATR properties of PDADMAC/DR80 films

The ATR properties measured at 632.8 nm and 488.0 nm for the PDADMAC/DR80 films with different number of bilayers are shown in Figs. 2 (a) and (b), respectively. The ATR curves of Ag thin films are also shown in the figures. The resonant angles of the ATR curves increase with the number of bilayers of the self-assembled films. This result indicates that both thickness and real part of dielectric constant of the self-assembled films increase with the number of bilayers. The resonance of the ATR curves becomes shallower with the increase of the number of bilayers. This is considered to be due to the increase of imaginary part of dielectric constant of the self-assembled films with the number of bilayers. The shift of the resonant angles between the ATR curves for 5- and 7-bilayer films is found to be larger than that for 3- and 5-bilayer films. This is thought to indicate that the adsorption of molecules becomes more stable in the self-assembly deposition with the number of bilayers [13]. The reflectivities in the initial region lower than the resonant angles of ATR curves decrease with the number of bilayers. This seems to be caused by the increase of light scattering in the self-assembled films with the increase of the number of bilayers. The difference between the wavelengths of incident light in the ATR properties is considered to be mainly concerned with the optical absorbance of the self-assembled films [14].

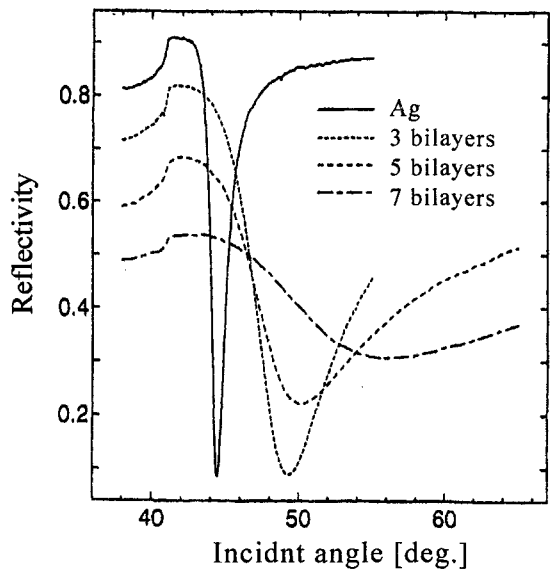
3.2 Emission light properties of PDADMAC/DR80 films

Figure 3 shows the emission light measured at 632.8 nm as a function of the emission angle through the prism from the PDADMAC/DR80 films with different number of bilayers. The peak angles of the emission spectra agree well with the resonant angles of the ATR curves shown in Fig. 2 (a). The shapes of the emission spectra also correspond to the ATR curves. This result indicates that the emission light is due to the SP excitation [8-10].

The difference between the wavelengths of incident light in the emission properties was also observed and was considered to be mainly concerned with the optical absorbance of the films as well as the ATR properties in Fig. 2.



(a) λ = 632.8 nm



(b) λ = 488.0 nm

Fig. 2. ATR properties of the PDADMAC/DR80 films with different number of bilayers.

3.3 ATR and scattered light properties of the PDADMAC/DR80 films by photoisomerization.

The high dichroism of the PDADMAC/DR80 films is due to the photoisomerization of DR80 molecules by irradiation of linearly polarized visible light [11, 15]. The structural change due to photoisomerization of DR80 molecules has been investigated in-situ during irradiation of linearly polarized visible light of the halogen lamp at 300 W. Figure 4 shows the dependence of ATR properties on irradiation time of linearly polarized visible light measured at 632.8 nm for 7-bilayer PDADMAC/DR80 film. It is found that the resonant angles hardly change with the irradiation time but the depths of the dips change, and the depth of the ATR curve for 5-min irradiation is the shallowest. From the ATR curves measured at 488.0 nm, it was found that

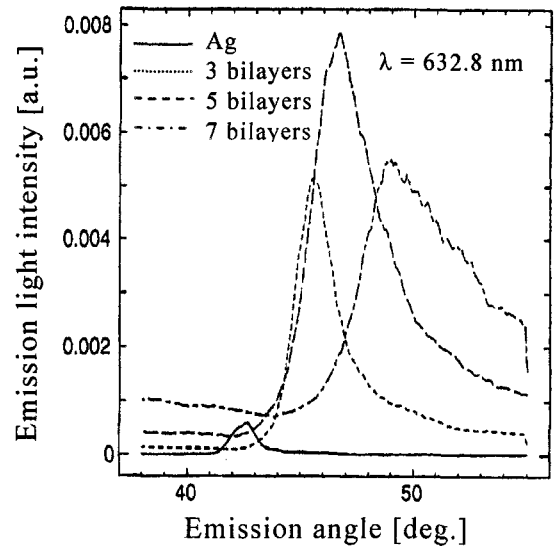


Fig. 3. Emission light measured at 632.8 nm as a function of the emission angle for the PDADMAC/DR80 films with different number of bilayers.

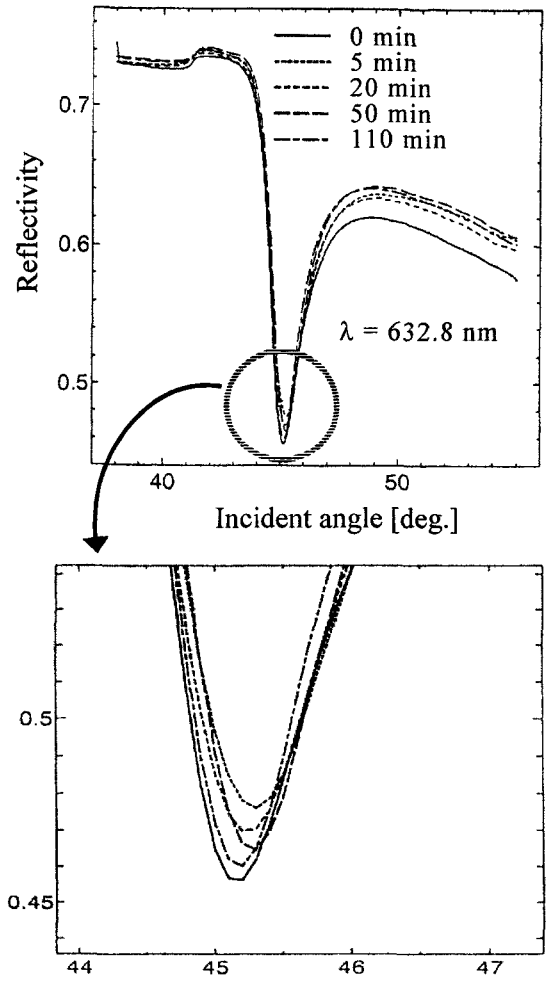


Fig. 4. Dependence of ATR properties on irradiation time of linearly polarized visible light measured at 632.8 nm for 7-bilayer PDADMAC/DR80 film.

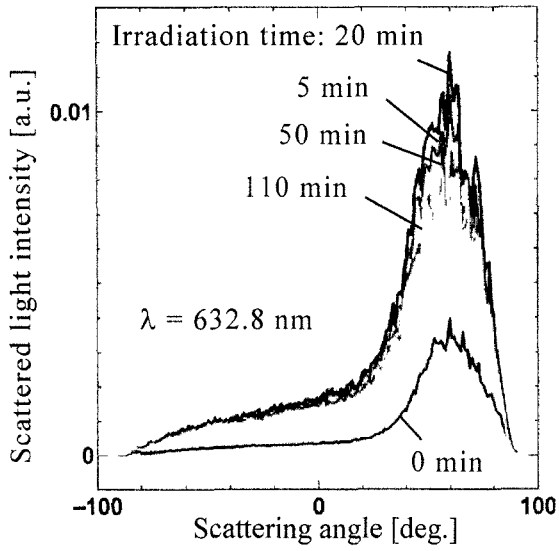


Fig. 5. Dependence of angular spectra of scattered light intensities on irradiation time of linearly polarized visible light measured at 632.8 nm for 7-bilayer PDADMAC/DR80 film.

the resonant angles gradually increased with the irradiation time and the depths of the dips also became larger. These are considered to be related to the changes of surface roughness and imaginary part of dielectric constant of the films caused by the photoisomerization of DR80 molecules. It is also thought to be concerned with the anisotropic alignments of DR80 molecules expected by the optical absorbance by the irradiation of linearly polarized visible light [13].

Scattered light due to SP excitation [12] was also measured in order to examine the surface roughness of the PDADMAC/DR80 films. The dependence of angular spectra of the scattered light intensities on irradiation time of linearly polarized visible light measured at 632.8 nm for the 7-bilayer film is shown in Fig. 5. The scattered light intensities are found to increase after irradiation and hardly change after 5-min irradiation. This means that the surface roughness of the film increased by the irradiation of linearly polarized visible light and hardly changed after 5-min irradiation. Since the scattered light intensities in the negative range of scattering angle are thought to be mainly caused by the surface roughness of Ag films [12], the increase of the scattered light intensities in the negative range seems to indicate the increase of the surface roughness and structural change of the Ag films. But the change of the scattered light intensities in the negative range is much smaller than that in the positive range and the increase of the scattered light intensities is thought to be mainly caused by the change of the PDADMAC/DR80 films due to the photoisomerization of DR80 molecules. From this result, the changes of the ATR curves after 5-min irradiation shown in Fig. 4 is thought to be mainly due to the change of the dielectric constant of the PDADMAC/DR80 film by the photoisomerization of DR80 molecules.

4. CONCLUSION

The ATR and emission properties due to SP excitation were investigated for the PDADMAC/DR80 self-assembled films. The change of the structure due to photoisomerization was also investigated. It was found that the shapes and the peak angles of the emission spectra due to SP excitation almost corresponded to the shapes and the resonant angles of the ATR curves. From the ATR measurements, the structure of PDADMAC/DR80 films was found to change due to the photoisomerization by the irradiation of polarized visible light. From the scattered light measurement, it was also found that the surface roughness of PDADMAC/DR80 films increased by the irradiation of polarized visible light and hardly changed after 5-min irradiation.

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