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ATTENUATED TOTAL REFLECTION AND EMISSION PROPERTIES OF SELF-ASSEMBLED LAYER-BY-LAYER FILMS CONTAINING AZOBENZENE DYE

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Self-assembled layer-by-layer films were fabricated on Ag-evaporated glass substrates using Direct Red 80 (DR80) azobenzene dye and poly (diallyldimethylammonium chloride) (PDADMAC). The properties of attenuated total reflection (ATR) and emission due to surface plasmon excitation were investigated. The ATR was measured for the Kretschmann configuration of a prism/Ag/layer-by-layer film structure and the emission through the prism was measured when the sample was excited by reverse irradiation in the Kretschmann configuration. The peak angles of the emission spectra almost agreed with the resonant angles of the ATR curves. The shapes of the emission spectra also corresponded to the ATR curves. The structural change of the self-assembled films due to photoisomerization of DR80 molecules was also investigated. From the ATR measurements, the structure of the self-assembled films was found to change due to the photoisomerization by the irradiation of polarized visible light. The surface roughness of the self-assembled films due to the photoisomerization was examined from the scattered light measurements.

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Keywords: attenuated total reflection; azobenzene dye; emission; poly(diallyldimethylammonium chloride); self-assembled layer-by-layer film; surface plasmon excitation

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INTRODUCTION

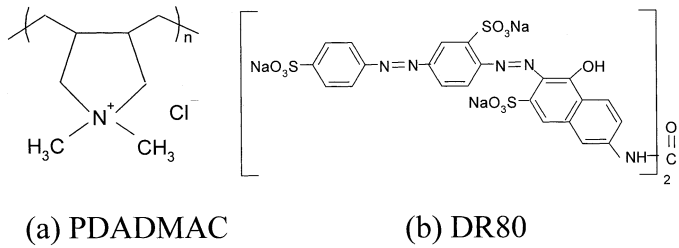
Azobenzene dyes which are photoisomerizable molecules are excellent materials for application to optical devises such as optical storage media, optical switching and so on. The trans-cis photoisomerization of azobenzene groups introduces alignment of the molecular long axis in a direction perpendicular to the direction of polarized irradiation light [1–3]. Using these phenomena, the controlled alignment of Liquid Crystal (LC) molecules in an LC cell display configuration has been demonstrated [1–3]. In the previous paper, photo-induced surface gratings of alternate self-assembled layer-by-layer ultrathin films containing azobenzene dyes were fabricated and the alignment properties of LC molecules on these films were investigated [4]. The alternate self-assembly deposition technique is a versatile method and is applicable to many other photo-functional molecules [5,6].

The investigation of properties of organic ultrathin films is very important and many studies on electrical and optical devices of organic ultrathin films have been carried out. For the development of organic ultrathin film devices with high efficiency, it is quite important particularly to evaluate the structure and optical functions of the ultrathin films. The Attenuated total reflection (ATR) measurement utilizing Surface plasmon (SP) excitation at the interface between metal thin films and dielectric ultrathin films is one of very useful methods to evaluate dielectric properties of ultrathin films of several or several tens nanometer thick [7]. There are many reports using ATR measurements that evaluate structure and optical properties of organic ultrathin films on metal thin films, and estimate orientations of liquid crystal molecules [8–11]. The ATR methods have been also investigated for device applications of organic ultrathin films because of strong optical absorption and strong electric fields due to SP excitations [12–16]. Recently, emission light at a resonant angle region of SP excitations was observed through the prism in the ATR Kretschmann configuration, when metal ultrathin films on the prism or organic ultrathin films on metal films were directly irradiated from air by a laser beam [17–20]. The emission light for organic dye films was not only monochromatic, but also the spectra changed with emission angles where the emission light was measured through the prism [19–23]. 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 [19–23].

In this paper, ATR and emission properties due to surface plasmon excitation were investigated for self-assembled layer-by-layer films containing low molecular weight azobenzene dye. The structural change of the self-assembled films due to photoisomerization has been also investigated. The measurement of scattered light due to surface plasmon excitation [24–26] was also carried out in order to obtain the information about the surface roughness of the self-assembled films.

EXPERIMENTAL DETAILS

Chemical structures of the polycation and the dye used in this experiment are shown in Figure 1. The poly(diallyldimethylammonium chloride) (PDADMAC) polycation and the Direct Red 80 (DR80) azobenzene dye were obtained commercially from Aldrich Chemical Company, Inc. DR80 contains azo groups exhibiting photoisomerization. PDADMAC was used to prepare self-assembled films of well-defined thickness and order. Both molecules were thoroughly soluble in aqueous solution and a concentration of 0.01 M was used for the self-assembly depositions. Ag thin films with the thickness of around 50 nm were deposited on cover glass substrates by a vacuum evaporation method. The surfaces of the Ag-evaporated glass substrates were then functionalized with 3-aminopropyltriethoxysilane (Aldrich Chemical Company, Inc.) prior to the alternate deposition of PDADMAC/DR80. The layer-by-layer adsorption of the PDADMAC/DR80 self-assembled films was carried out. The procedure was as follows: the molecular layers of the PDADMAC and the DR80 were alternately deposited from these solutions with 0.01 M on the substrates. A complete description has been reported elsewhere [5,6]. For the deposition of the self-assembled layer-by-layer films, the substrates were immersed in the solutions for 15 minutes at 22.0°C. The alternate films with 3, 5 and 7 bilayers of PDADMAC/DR80 were prepared.



(a) PDADMAC (b) DR80

FIGURE 1 Chemical structures of molecules used for self-assembled layer-by-layer films.

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Figure 2 shows the Kretschmann configuration [7] for the measurements utilizing SP excitation. The configuration for the ATR and scattered light measurements [24–26] is shown in Figure 2 (a) and the configuration for the emission measurement [17–23] is shown in Figure 2(b). A half-cylindrical prism (BK-7) was used and the samples of PDADMAC/DR80 self-assembled films on Ag-evaporated glass substrates were attached to the bottom of the prism using a matching oil. The prism with the sample was mounted on a computer-controlled goniostage and the incident angles θ_i was changed by rotating the goniostage 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 as a function of the incident angle θ_i 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, the intensity of the scattered light was observed as a function of the scattering angle θ_s when the incident angle θ_i of the laser beam was set as the resonant angles of the ATR curve. Emission due to SP excitation 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 θ_e. In the measurements, p-polarized laser beams from He-Ne and Ar^+ lasers with the wavelengths of 632.8 and 488.0 nm, respectively, were used.

The high dichroism of the PDADMAC/DR80 self-assembled films is due to the photoisomerization of DR80 by irradiation of polarized light [4,27,28]. The structural change due to photoisomerization of DR80 molecules has been investigated in-situ during irradiation of polarized light of the halogen lamp at 300 W.

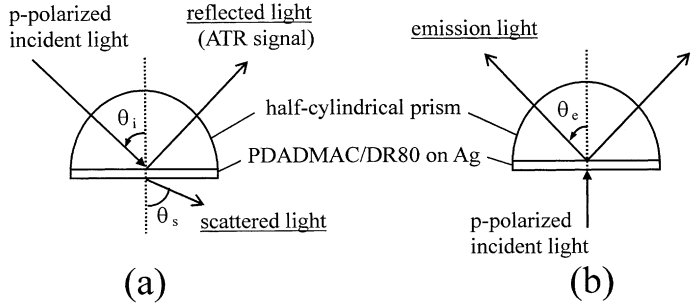

FIGURE 2 Kretschmann configurations for the measurements utilizing surface plasmon excitation. (a) shows the method of the ATR and scattered light measurements and (b) shows the method of the emission measurement.

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RESULTS AND DISCUSSION

Figures 3(a) and (b) show the ATR properties measured at 632.8 and 488.0 nm, respectively, for the PDADMAC/DR80 self-assembled films with different number of bilayers. 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 is considered to be due to the increase of both thickness and real part of complex dielectric constant of the self-assembled films with the number of bilayers. The dips of the ATR curves become shallower with the increase of the number of bilayers. This is considered to be due to the increase of imaginary part of complex 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 self-assembled films is found to be larger than that for 3- and 5-bilayer self-assembled films. This is thought to indicate that the adsorption of molecules becomes more stable in the self-assembly deposition with the number of bilayers. 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 emission lights observed as a function of the emission angle through the prism from the PDADMAC/DR80 self-assembled films with different number of bilayers are shown in Figure 4(a) and (b) indicate the results measured at 632.8 and 488.0 nm, respectively. Since the

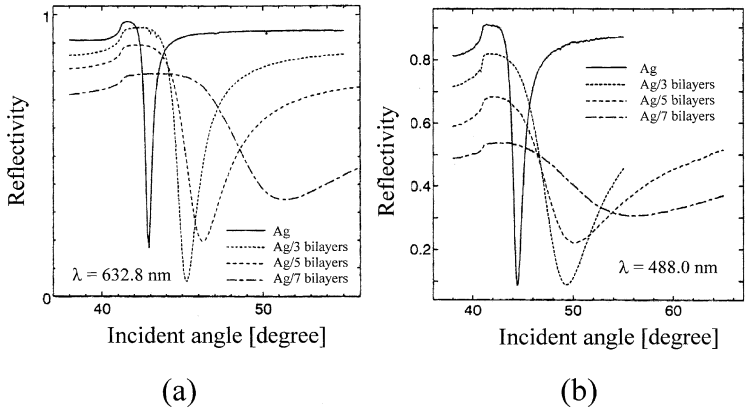

FIGURE 3 ATR properties of the PDADMAC/DR80 self-assembled films with different number of bilayers. (a) and (b) show the results measured at 632.8 and 488.0 nm, respectively.

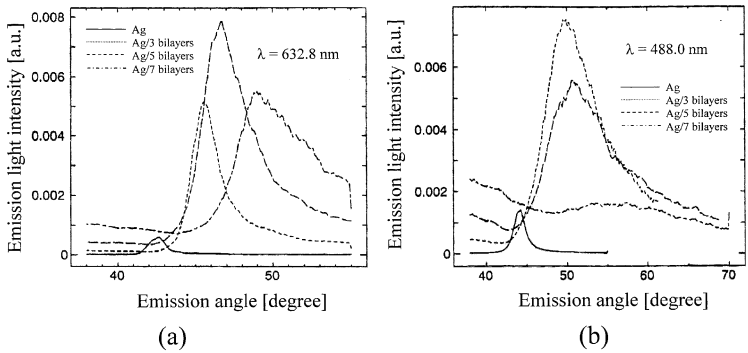

FIGURE 4 Emission lights through the prism from the PDADMAC/DR80 self-assembled films with different number of bilayers as a function of the emission angle. (a) and (b) show the results measured at 632.8 and 488.0 nm, respectively.

photoluminescence could not be observed for the self-assembled films, the emission light is thought to originate mainly in the incident laser light. The peak angles of the emission in Figures 4(a) and (b) agree well with the resonant angles of the ATR curves shown in Figures 3(a) and (b). The shapes of the emission spectra also correspond to the ATR curves. These results indicate that the decoupled light comes from SP modes excited at the interface between Ag thin films and the self-assembled films and that the emission is mainly due to the SP excitation mediated by the surface roughness of Ag thin films [18,21].

The dependences of ATR properties of 7-bilayer PDADMAC/DR80 self-assembled film on irradiation time of polarized visible light were measured. Figure 5(a) and (b) show the results measured at 632.8 and 488.0 nm, respectively. From the ATR curves measured at 632.8 nm, it is found that the resonant angles hardly change with the irradiation time but the depths of the dips change, and that the depth of the ATR curve for 5-min irradiation is the shallowest. From the ATR curves measured at 488.0 nm, it is found that the resonant angles gradually increase with the irradiation time and the depths of the dips also become larger with the irradiation time. It is considered that these are related to the changes of surface roughness and imaginary part of dielectric constant of the self-assembled films caused by the photoisomerization of DR80 molecules. The difference in the ATR properties of (Figs. 5) (a) and (b) due to the wavelengths of incident light is considered to be mainly concerned with the optical absorbance of the self-assembled films.

The dependence of scattered lights on the irradiation time of polarized visible light was also measured in order to examine the surface roughness of the PDADMAC/DR80 self-assembled films. The result for the 7-bilayer

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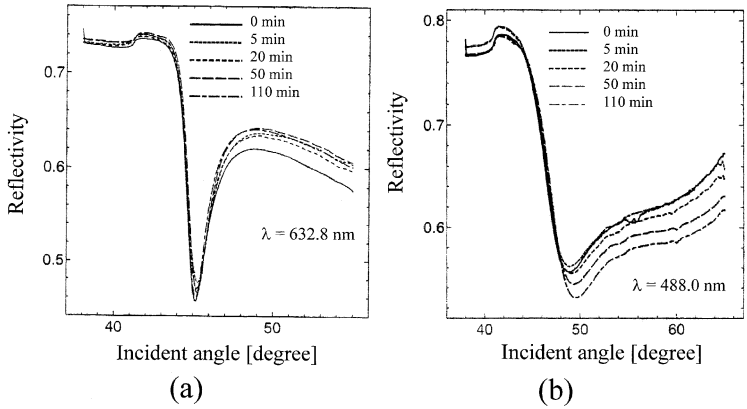

FIGURE 5 Dependence of ATR properties of 7-bilayer PDADMAC/DR80 self-assembled film on irradiation time of polarized visible light. (a) and (b) show the results measured at 632.8 and 488.0 nm, respectively.

self-assembled film measured at 632.8 nm is shown in Figure 6. It is found that the scattered light intensities increase after irradiation and hardly change after 5-min irradiation. This means that the surface roughness of the self-assembled film increased by the irradiation of polarized visible light and hardly changed after 5-min irradiation. The change of the ATR curves after 5-min irradiation shown in Figures 5(a) and (b) is thought to be due to the change of the dielectric constant of the self-assembled film.

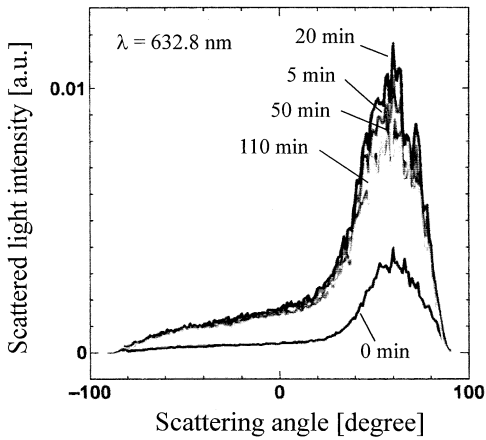

FIGURE 6 Dependence of scattered lights from 7-bilayer PDADMAC/DR80 self-assembled film measured at 632.8 nm on irradiation time of polarized visible light.

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CONCLUSION

The ATR and emission properties due to SP excitation were investigated for the PDADMAC/DR80 self-assembled layer-by-layer films. The structural change of the self-assembled films due to photoisomerization was also investigated. The peak angles of the emission lights agreed well with the resonant angles of the ATR curves. The shapes of the emission spectra due to SP excitation from the PDADMAC/DR80 self-assembled films also corresponded to the ATR curves. From the ATR measurements, the structure of PDADMAC/DR80 self-assembled films was found to change due to the photoisomerization by the irradiation of polarized visible light. From the scattered light measurements, it was also found that the surface roughness of PDADMAC/DR80 self-assembled films increased by the irradiation of polarized visible light and hardly changed after 5-min irradiation. More detail study on the structure of the self-assembled films utilizing SP excitation is now under way.

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