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Attenuated total reflection and emission due to surface plasmon excitation of layer-by-layer ultrathin films containing azo-dye

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Abstract

The properties of attenuated total reflection (ATR) and emission due to surface plasmon (SP) excitation were investigated for the alternate layer-by-layer ultrathin films self-assembled on Ag thin films using polycation (poly(diallyldimethylammonium chloride), PDADMAC) and azo-dye (Direct Red 80, DR80). The emission light had peaks at the same angles as the resonant angles of the ATR curves and the shapes of the emission spectra also corresponded to those of the ATR curves, and the emission was considered to be mainly due to the SP excitation mediated by the surface roughness of Ag thin films. The structure of the PDADMAC/DR80 layer-by-layer films was found to change due to the photoisomerization of DR80 molecules by the irradiation of polarized visible light, and the surface roughness of the layer-by-layer films was also found to increase by the irradiation and hardly to change after 5-min irradiation.

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1. Introduction

Many studies on electronic and optical devices of organic ultrathin films have been carried out. For the development of organic ultrathin film devices with high quality and efficiency, it is quite important particularly to evaluate the structure of organic ultrathin films and to investigate the properties and functions. The attenuated total reflection (ATR) method utilizing surface plasmon (SP) excitation at the interface between metal thin films and dielectric ultrathin films is one of the very useful measurement techniques to evaluate dielectric properties of ultrathin films [1]. Many works using ATR measurements have been reported on the evaluation of structure and optical properties of organic ultrathin films on metal thin films [2-5] and on the estimation of the orientations of liquid crystal (LC) molecules in LC cells [6-8]. The ATR method has also been investigated for device applications such as photoelectric cells [9-11] and gas sensors [12-14] because of strong electric fields at the interface between metal thin films

and organic ultrathin films due to SP excitations. 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 [15– 17]. 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 [16-20]. 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 [16-20]. The emission observed by the reverse irradiation will be used as a new sensing technique and is very useful for application to new organic nano-devices.

Organic ultrathin films containing photoisomerizable molecules, e.g. azo-dyes are excellent and attractive for application to optical devices such as optical storage media, optical switching and so on. The *trans-cis* photoisomerization of azobenzene groups of azo-dyes

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DR80

Fig. 1. Chemical structures of the molecules of polycation (PDAD-MAC) and azo-dye (DR80) used for the deposition of layer-by-layer films in this work.

introduces alignment of the molecular long axis in a direction perpendicular to the direction of polarized irradiation light [21–23]. Using these phenomena, the controlled alignment of LC molecules in an LC cell display configuration that has been demonstrated [21–23]. In the previous article, 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 [24]. The alternate self-assembly deposition technique is useful for controlling film thickness and is applicable to preparing multilayer films containing many other photo-functional molecules [25,26].

In this article, ATR and emission properties due to SP excitation were investigated for self-assembled layerby-layer ultrathin films containing low molecular weight azobenzene dye (Direct Red 80, DR80). The structural change of the layer-by-layer films due to photoisomerization has been also investigated. The measurement of scattered light due to SP excitation [27–30] was also carried out in order to obtain the information about the surface roughness of the layer-by-layer films.

2. Experimental details

2.1. Preparation of layer-by-layer ultrathin films

Chemical structures of the polycation and the dye used in this experiment are shown in Fig. 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 four azobenzene groups per molecule exhibiting photoisomerization. PDAD-MAC was used to prepare self-assembled alternate laverby-layer films with 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 approximately 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 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. A complete description has been reported elsewhere [25,26]. For the deposition of the layer-by-layer films, the substrates were immersed in the solutions for 15 min at 22.0 °C. The alternate films were prepared with 3, 5 and 7 bilayers of PDADMAC/DR80.

2.2. Experimental method

Fig. 2 shows the Kretschmann configuration [1] for the measurements utilizing SP excitation. The configuration for the ATR and scattered light [29,30] measurements is shown in Fig. 2a and the configuration for the emission measurement [16–20] is shown in Fig. 2b. A half-cylindrical prism (BK-7) was used and the samples



Fig. 2. Kretschmann configurations for the measurements utilizing SP excitation. (a) and (b) show the methods of the ATR and scattered light measurements and the emission measurement, respectively.



Fig. 3. Experimental system of the ATR, scattered light and emission measurements.

of PDADMAC/DR80 films on Ag-evaporated glass substrates were attached to the bottom of the prism using a matching oil. The experimental system for the ATR, scattered light and emission light measurements is shown in Fig. 3. The prism with the sample of PDADMAC/DR80 films was mounted on a computercontrolled goniostage and the incident angles θ_i was changed by rotating the goniostage using a pulse motor for the ATR and scattered light measurements, the ppolarized 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 (PD1) as a function of the incident angle θ_i of the laser beam. The intensity of the incident light was also monitored using another photodiode (PD2). 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 by a photomultiplier (PM) 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 layer-by-layer film. The intensity of the emission light was observed through the prism as a function of the emission angle θ_{e} . In this work, 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 films is due to the photoisomerization of DR80 molecules by irradiation of linearly polarized visible light [24,31,32]. 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.

3. Results and discussion

3.1. UV-vis spectroscopy of PDADMAC/DR80 films

UV-vis absorption spectra measured for the PDAD-MAC/DR80 layer-by-layer ultrathin films are shown in Fig. 4. The peak approximately 550 nm is attributed to the $\pi-\pi^*$ transition for a *trans* configuration of DR80 molecules [26]. Since the aqueous solution of DR80 shows absorption peak at 528 nm [26], the aggregation of dye molecules are considered to occur and the red-shift behavior suggests the formation of J-aggregates of DR80 molecules. Absorption spectra after 30-min irra-



Fig. 4. UV–vis absorption spectra of the PDADMAC/DR80 ultrathin film. Solid and dashed lines represent the absorption parallel and perpendicular to the polarization direction of the irradiated light, respectively. Absorption spectra after 30-min irradiation of linearly polarized visible light are also shown.

diation of linearly polarized visible light are also shown in Fig. 4. The absorbance parallel to the polarization direction of the irradiated light decreases larger than the perpendicular. This indicates that the *trans-cis* photoisomerization is induced mainly parallel to the polarization direction of irradiated light and *trans*-forms remain perpendicular with respect to the polarization of irradiated light, so that the long axis of the dye oriented predominantly perpendicular with respect to the polarization. By the irradiation of the layer-by-layer films with linearly polarized visible light, therefore, it is considered that an in-plane reorientation of DR80 molecules occurs and the anisotropic alignments are produced.

3.2. ATR properties of PDADMAC/DR80 films

The ATR properties measured at 632.8 and 488.0 nm for the PDADMAC/DR80 films with different number of bilayers are shown in Fig. 5a and b, respectively. The



Fig. 5. ATR properties of the PDADMAC/DR80 films with different number of bilayers. (a) and (b) show the results measured at 632.8 and 488.0 nm, respectively.



Fig. 6. Emission light intensities through the prism from the PDAD-MAC/DR80 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.

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 layer-by-layer films. This result indicates that both thickness and real part of complex dielectric constant of the layer-by-layer 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 complex dielectric constant of the layer-by-layer 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 [33]. 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 layer-by-layer films with the increase of the number of bilayers. The difference between the wavelengths of incident light in the ATR properties of Fig. 5a and b is considered to be mainly concerned with the optical absorbance of the films shown in Fig. 4.



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

3.3. Emission light from PDADMAC/DR80 films

Fig. 6a and b show the emission light observed as a function of the emission angle through the prism from the PDADMAC/DR80 layer-by-layer films with different number of bilayers using the incident laser light of 632.8 and 488.0 nm, respectively. Since the photoluminescence could not be observed for the layer-by-layer films, the emission light is thought to originate mainly in the incident laser light. The peak angles of the emission spectra in Fig. 6a and b agree well with the resonant angles of the ATR curves shown in Fig. 5a and b, respectively. The shapes of the emission spectra also correspond to the ATR curves. The coincidence between the peak angles in the emission spectra and the resonant angles in the ATR curves confirms that the decoupled light comes from SP modes excited at the interface between Ag thin films and the layer-by-layer films. Therefore, the emission is considered to be mainly

due to the SP excitation mediated by the surface roughness of Ag thin films [17,34]. The difference between the wavelengths of incident light in the emission properties of Fig. 6a and b is also considered to be mainly concerned with the optical absorbance of the films in Fig. 4 as well as the result of ATR measurements in Fig. 5a and b. But the exact mechanism to explain the emission spectra has not been clarified yet and will be investigated in near future.

3.4. ATR properties of PDADMAC/DR80 films by photoisomerization

Fig. 7a and b shows the dependences of ATR properties measured at 632.8 and 488.0 nm for 7-bilayer PDADMAC/DR80 film on irradiation time of linearly polarized visible light, respectively. From the ATR curves measured at 632.8 nm, it is found that the resonant angles hardly change with the irradiation time



Fig. 8. Dependence of angular spectra of scattered light intensities from 7-bilayer PDADMAC/DR80 film measured at 632.8 nm on irradiation time of linearly polarized visible light.

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 is found that the resonant angles gradually increase with the irradiation time and the depth of the dips also become larger with the irradiation time. 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 expected by the optical absorbance by the irradiation of linearly polarized visible light shown in Fig. 4.

3.5. Scattered light from PDADMAC/DR80 films

Scattered light due to SP excitation [27–30] was also measured in order to examine the surface roughness of the PDADMAC/DR80 layer-by-layer films. The dependence of angular spectra of the scattered light intensities for the 7-bilayer film measured at 632.8 nm on irradiation time of linearly polarized visible light is shown in Fig. 8. The scattered light intensities are found to increase after irradiation and hardly change after 5min 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 angular spectrum of the scattered light intensities in the range of $-90^{\circ} < \theta_{s} < 0^{\circ}$ is thought to be mainly caused by the surface roughness of Ag films [28-30], the increase of the scattered light intensities in the range of $-90^{\circ} < \theta_s < 0^{\circ}$ seems to indicate the increase of the surface roughness and structural change of the Ag films by the irradiation of linearly polarized visible light. But the change of the scattered light intensities in the range of $-90^{\circ} < \theta_{s} < 0^{\circ}$ is much smaller than that in the range of $0^{\circ} < \theta_{s} < 90^{\circ}$ 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 as shown in Fig. 7a and b is thought to be mainly due to the change of the dielectric constant of the layer-by-layer film by the photoisomerization of DR80 molecules.

4. Conclusion

The ATR and emission properties due to SP excitation were investigated for the PDADMAC/DR80 layer-bylayer ultrathin films. The structural change of the layerby-layer films due to photoisomerization was also investigated. The peak angles of the emission lights agreed well with the resonant angles of the ATR curves, and the emission was considered to be mainly due to the SP excitation mediated by the surface roughness of Ag thin films. The shapes of the emission spectra due to SP excitation from the PDADMAC/DR80 films also corresponded to 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 measurements, 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. The study on more detail structure and emission properties due to SP excitation of the layer-by-layer films after photoisomerization is now under way.

References

- [1] V.M. Agranovich, D.L. Mills (Eds.), Surface Polaritons, North-Holland, Amsterdam, 1982.
- [2] F. Kaneko, S. Honda, T. Fukami, K. Kato, T. Wakamatsu, K. Shinbo, S. Kobayashi, Thin Solid Films 284–285 (1996) 417.
- [3] K. Kato, H. Saiki, H. Okuchi, F. Kaneko, T. Wakamatsu, K. Shinbo, S. Kobayashi, Thin Solid Films 284–285 (1996) 420.
- [4] K. Kato, Y. Aoki, K. Ohashi, K. Shinbo, F. Kaneko, Jpn. J. Appl. Phys. 35 (1996) 5466.
- [5] T. Fukami, F. Kaneko, K. Shinbo, T. Wakamatsu, K. Kato, S. Kobayashi, Mol. Cryst. Liq. Cryst. 327 (1999) 103.
- [6] G.J. Sprokel, R. Santo, J.D. Swalen, Mol. Cryst. Liq. Cryst. 68 (1985) 29.
- [7] A. Baba, F. Kaneko, K. Shinbo, K. Kato, S. Kobayashi, T. Wakamatsu, Jpn. J. Appl. Phys. 37 (1998) 2581.
- [8] A. Baba, F. Kaneko, K. Shinbo, T. Wakamatsu, K. Kato, S. Kobayashi, Mater. Sci. Eng. C 8–9 (1999) 145.
- [9] T. Wakamatsu, K. Saito, Y. Sakakibara, H. Yokoyama, Jpn. J. Appl. Phys. 36 (1997) 155.
- [10] K. Shinbo, T. Ebe, F. Kaneko, K. Kato, T. Wakamatsu, IEICE Trans. Electron. E83-C (1999) 1081.

- [11] K. Kato, H. Tsuruta, T. Ebe, K. Shinbo, F. Kaneko, T. Wakamatsu, Mater. Sci. Eng. C 22 (2002) 251.
- [12] R. Casalini, J.N. Wilde, J. Nagel, U. Oertel, M.C. Petty, Sensors Actuators B 57 (1999) 28.
- [13] K. Kato, C.M. Dooling, K. Shinbo, T.H. Richardson, F. Kaneko, R. Tregonning, M.O. Vysotsky, C.A. Hunter, Colloids Surf. A 198–200 (2002) 811.
- [14] K. Kato, H. Araki, K. Shinbo, F. Kaneko, C.M. Dooling, T.H. Richardson, Jpn. J. Appl. Phys. 41 (2002) 2779.
- [15] T. Kume, S. Hayashi, K. Yamamoto, Mater. Sci. Eng. A 217– 218 (1996) 171.
- [16] T. Nakano, T. Wakamatsu, H. Kobayashi, F. Kaneko, K. Shinbo, K. Kato, T. Kawakami, Mol. Cryst. Liq. Cryst. 349 (2000) 235.
- [17] K. Kato, M. Terakado, K. Shinbo, F. Kaneko, T. Wakamatsu, Thin Solid Films 393 (2001) 97.
- [18] F. Kaneko, T. Nakano, M. Terakado, K. Shinbo, K. Kato, T. Wakamatsu, Mol. Cryst. Liq. Cryst. 377 (2002) 53.
- [19] T. Nakano, M. Terakado, K. Shinbo, K. Kato, F. Kaneko, T. Kawakami, T. Wakamatsu, Jpn. J. Appl. Phys. 41 (2002) 2774.
- [20] F. Kaneko, T. Nakano, M. Terakado, K. Shinbo, K. Kato, T. Kawakami, T. Wakamatsu, Mater. Sci. Eng. C 22 (2003) 409.
- [21] K. Ichimura, Y. Suzuki, T. Seki, A. Hosoki, K. Aoki, Langmuir 4 (1988) 1214.

- [22] W. Gibbons, P. Shannon, S. Sun, B. Sweltin, Nature 351 (1991) 49.
- [23] M. Schadt, K. Schmit, V. Hozinkov, V. Chifrinnov, Jpn. J. Appl. Phys. 31 (1992) 2155.
- [24] F. Kaneko, T. Kato, A. Baba, K. Shinbo, K. Kato, R.C. Advincula, Colloids Surf. A 198–200 (2002) 805.
- [25] R.C. Advincula, A. Baba, F. Kaneko, Polym. Mater.: Sci. Eng. Prepr. 81 (1999) 95.
- [26] R.C. Advincula, E. Fells, M.K. Park, Chem. Mater. 13 (2001) 2870.
- [27] E. Fontana, R.H. Pantel, Phys. Rev. B 37 (1988) 3164.
- [28] Y. Naoi, M. Fukui, J. Phys. Soc. Jpn. 58 (1989) 4511.
- [29] Y. Aoki, K. Kato, K. Shinbo, F. Kaneko, T. Wakamatsu, IEICE Trans. Electron. E81-C (1998) 1098.
- [30] Y. Aoki, K. Kato, K. Shinbo, F. Kaneko, T. Wakamatsu, Thin Solid Films 327–329 (1998) 360.
- [31] R.C. Advincula, D. Roitman, C. Frank, W. Knoll, A. Baba, F. Kanako, Polym. Prepr. 40 (1999) 467.
- [32] J. Ishikawa, A. Baba, F. Kaneko, K. Shinbo, K. Kato, R.C. Advincula, Colloids Surf. A 198–200 (2002) 917.
- [33] K. Shinbo, J. Ishikawa, A. Baba, F. Kaneko, K. Kato, R.C. Advincula, Jpn. J. Appl. Phys. 41 (2002) 2753.
- [34] S. Hayashi, T. Kume, T. Amano, K. Yamamoto, Jpn. J. Appl. Phys. 35 (1996) L331.