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Multiple Surface Plasmon Excitations and Emission Light due to Reverse Irradiation in Kretschmann Configuration with Nanostructured Dye LB Films

Susumu Toyoshima[a], Futao Kaneko[b,c*], Toshiharu Sato [a], Kazunari Shinbo [b,c], Keizo Kato[b,c], Yasuo Ohdaira[b,c] and Takashi Wakamatsu[d]

[a] Graduate School of Science and Technology, Niigata University, Niigata 950-2181 Japan
[b] Dept. of Electrical and Electronic Eng., Niigata University, Niigata 950-2181 Japan
[c] Center for Transdisciplinary Research, Niigata University, Niigata 950-2181 Japan
Fax: 81-25-262-6741, e-mail: fkaneko@eng.niigata-u.ac.jp
[d] Dept. of Electrical Eng., Ibaraki National College of Technology, Hitachinaka 312-8508 Japan
Fax: 81-29-271-2918, e-mail: wakamatu@ee.ibaraki-ct.ac.jp

Surface plasmon (SP) excitations and emission light due to reverse irradiation have been investigated in Kretschmann configuration of prism/metal/organic dye LB films. Nanostructures and optical properties of dye LB films have been evaluated using the attenuated total reflection (ATR) measurement. Emission light through the prism was also observed using direct irradiation of a laser beam from air to the LB films, that is, reverse irradiation. Intensities and spectra of the emission light through the prism strongly depended upon emission angles and nanostructures of dye LB films. The dispersion property of the SPs was calculated using the anomalous dispersion property due to the strong absorption peak of the merocyanine LB film. The emission properties coincided with the resonant conditions of SP excitations in the configuration below the angular frequency corresponding to the wavelength of the strong absorption peak. It was thought that multiple SPs were excited at the interface of the metal and the LB films and some of multiple SPs were transferred to emission light corresponding to the resonant conditions of SPs in the ATR method. The emission light from rod-like dye molecules was also observed by means of reverse irradiation of p- and s-polarized laser beams. It is thought that the phenomenon due to multiple SP excitations is very useful for application to new optical nano-devices.

Key words: surface plasmon resonance, Kretschmann configuration, merocyanine LB film, emission light, surface plasmon excitation.

1. INTRODUCTION

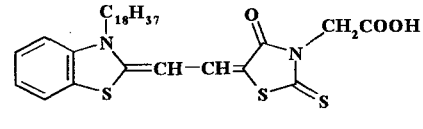
The surface plasmon resonance (SPR) method, that is, the attenuated total reflection (ATR) method has attracted much attention for measurements and sensing, since surface plasmons (SPs) resonantly excited at ultrathin metal surfaces are strongly influenced by conditions of the surfaces [1,2]. The ATR measurements utilizing SP excitations have been used to evaluate structure and optical properties of organic ultrathin films on metal ultrathin films, to estimate orientations of liquid crystal molecules, and as one of sensing methods [1, 2]. The ATR methods have been also investigated for device applications, because of strong optical absorption and strong electric fields due to SP excitations [3].

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 ultrathin films were directly irradiated from air by a laser beam, that is, reverse irradiation [4-6]. The emission light depended upon resonant conditions of SPs in the Kretschmann configuration of prism/ metal film/ dye molecular film and dye molecules [7,8].

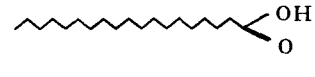
In this paper, emission light has been investigated for merocyanine (MC) Langmuir Blodgett (LB) film in the reverse irradiation at two polarized laser beams of 488.0 nm. The emission light was reported depending upon the polarized planes of the laser used in the reverse irradiation.

2. EXPERIMENTAL DETAILS

Merocyanine (MC) was used as an organic dye, showing photoluminescence (PL). MC LB films were prepared by LB dipping method. Figures 1 (a) and (b) show the chemical structure of MC dye and arachidic acid (C20). MC LB films were deposited on C20 LB films with two monolayers on cover glasses covered with evaporated Ag film of thickness about 50 nm. MC dyes were mixed with C20, MC:C20 =1:2, for the excellence MC LB deposition. The C20 LB films with two layers on the Ag films were used for the following better depositions of the MC LB films. The thickness of the C20 monolayer was 2.76 nm [6]. The Ag thin film was used as SP active layer.



(a)



(b)

Fig.1 Chemical structures of the dye molecules; (a) merocyanine (MC) and (b)arachidic acid (C20).

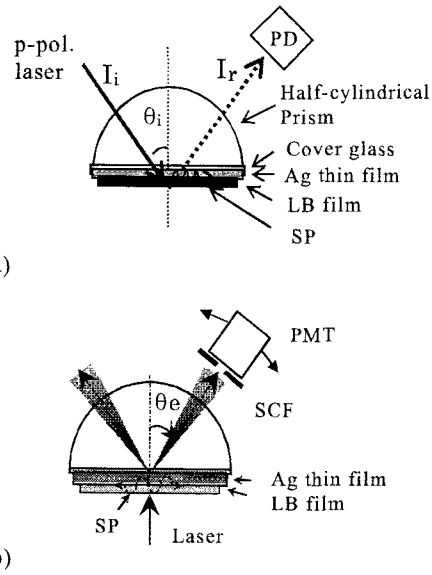


Fig.2 A measuring system for the ATR (a) and the emission light due to the reverse irradiation method in the Kretschmann configuration (b).

Figures 2 (a) and (b) show the measuring system for the ATR and emission light due to the reverse irradiation method in the Kretschmann configuration, respectively. A half-cylindrical prism (BK-7 n=1.522 at 488 nm) was used in this study, and the samples of the Ag/LB film on cover glasses were attached to the bottom of the half-cylindrical prism using a matching-oil. The prism was located on a rotating stage and the incident angle of a laser beam was automatically changed by a computer control system. Reflectance intensity to incident one Ir/Ii, that is, the ATR signal was measured as a function of the incident angle, θ_i, of the laser beam. Ar^+ lasers (λ=488.0 nm and 514.5 nm) and He-Ne lasers (λ=594.1 nm and 632.8 nm) were used.

In the reverse irradiation method, the samples were irradiated at the vertical incident angle by p- and s- polarized Ar^+ laser beams at 488.0 nm as shown in Fig.2 (b). Emission light through the prism was observed with and without a sharp cut filter below about 520 nm as a function of emission angle, θe, where the light was observed [6-11]. Spectra of the emission light were measured at various emission angles. Emission light through the prism was also observed at resonant SP excitations in the conventional ATR method as shown in Fig.2 (a) [7, 8].

3. RESULTS AND DISCUSSION

3.1 Absorption and ATR properties

Figure 3 shows the absorbance and the PL of MC LB film on a slide glass covered with C20 monolayer and the absorbance of solution of MC. The MC LB film shows an absorbance peak due to J-aggregation at about 600 nm, which is the higher wavelength than that of the solution, and it has a strong PL peak at around 630 nm, excited by an Ar^+ laser at 488 nm.

Dispersion properties of complex dielectric constants for the MC LB film were calculated from the absorption spectrum of the MC LB film in Fig.3 using Kramers-Kronig relationship [9]. Figure 4 shows the dispersion properties of the dielectric constants and the anomalous dispersion of the real part was observed due to the strong absorption peak at about 600 nm [9]. Since there were a dip in the short wavelength region and a peak in the long one around the absorption peak in the real part, it is thought that the anomalous dispersion affects ATR properties and SP excitations for organic dye films with a strong and sharp absorption peak.

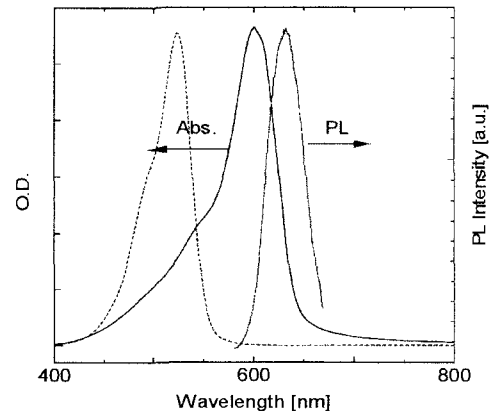


Fig.3 Absorption and PL spectra of MC LB film deposited on slide glass and absorption of chloroform solution of MC dyes.

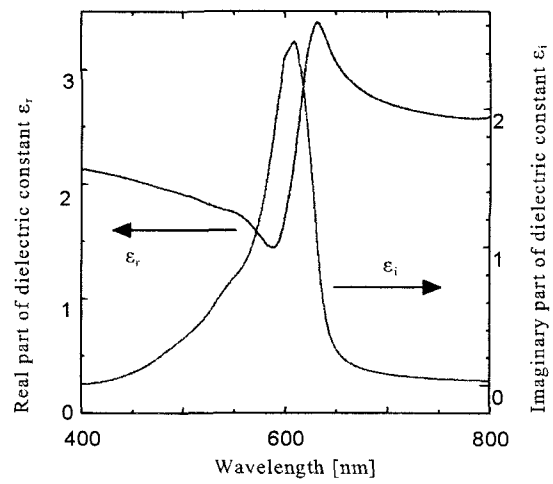


Fig.4 Anomalous dispersion properties of complex dielectric constants calculated from the absorption using Kramers-Kronig relationship.

Figure 5 shows the ATR properties at various laser wavelengths for the Ag/C20 (2 layers)/MC (16 layers) LB thin film. Minima due to resonant excitations of SP were observed in the ATR properties. The resonant angles of the SP (θ_{SP})

were about 61°, 58°, 59° and 55° for the wavelengths of 488.0 nm, 514.5 nm, 594.1 nm and 632.8 nm, respectively. The dip at the resonant angle for 594.1 nm was shallow and observed at a higher incident angle than that for 514.5 nm. It was thought that the property was caused by the anomalous dispersion in the dielectric constants due to the strong and sharp absorption of the MC LB film at about 600 nm.

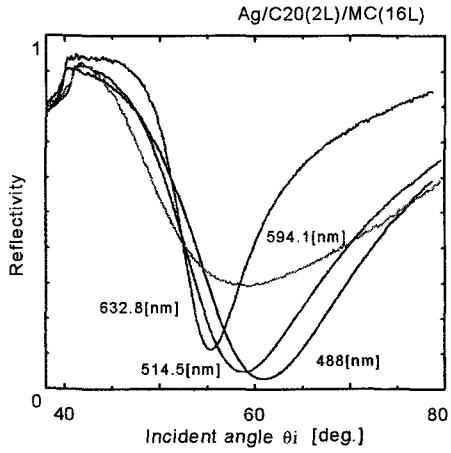


Fig.5 ATR properties for Ag/C20 (2 layers)/MC (16 layers) at various wavelengths.

3.2 Surface plasmon emission light

Figure 6 shows emission light as a function of the emission angle, θe, for the prism/Ag/C20 (2layers)/MC (16layers) LB film in the reverse irradiation of s- and p-polarized laser beams at 488.0 nm. A sharp cut filter below 520 nm was used in the measurement because the emission light without the filter mainly contained the laser wavelength at 488.0 nm [8]. The emission light

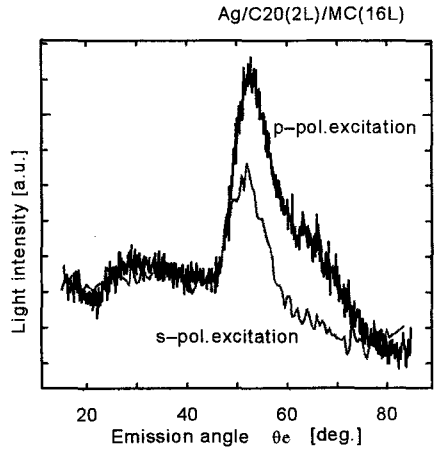


Fig.6 Emission light with a sharp cut filter as a function of the emission angle, θe, for the prism/Ag/C20 (2layers)/MC (16layers) LB film by the reverse irradiation of s- and p-polarized laser beams at 488.0 nm.

using the filter was observed between 45° and 60° in the emission angle and the peaks were about 52° due to the irradiation of the s- and p-polarized laser beams. The emission peak by the p-polarized laser beam was larger than that by the s-polarized one.

Figures 7 (a) and (b) show the spectra of the emission light by the reverse irradiation of p- and s-polarized laser beams at 488.0 nm, respectively. The emission light strongly depended on the emission angles, θe. The intensities of the emission light were weak and the spectra were not clear, but the spectra were similar and each spectrum in Figs.7 almost corresponded to a part of the PL spectrum of the MC LB film between 600 nm and 700 nm. The intensities of the emission light by the p-polarized laser beam were larger than those by the s-polarized one.

The emission peaks by the p-polarized laser with the electric fields parallel to the observation plane were larger than those by the s-polarized one with the field perpendicular to the plane. Since orientations of the MC dyes were thought to be almost uniform in the LB film plane, it is tentatively estimated that some MC dyes having the long axis parallel to the polarized plane of the laser were mainly excited by the reverse irradiation and the excited dyes induce anisotropic SPs propagating along the Ag surface, which can be observed mainly in the observation plane of the half-cylindrical prism.

The dispersion property, that is, a relationship between wavenumber of SP and angular

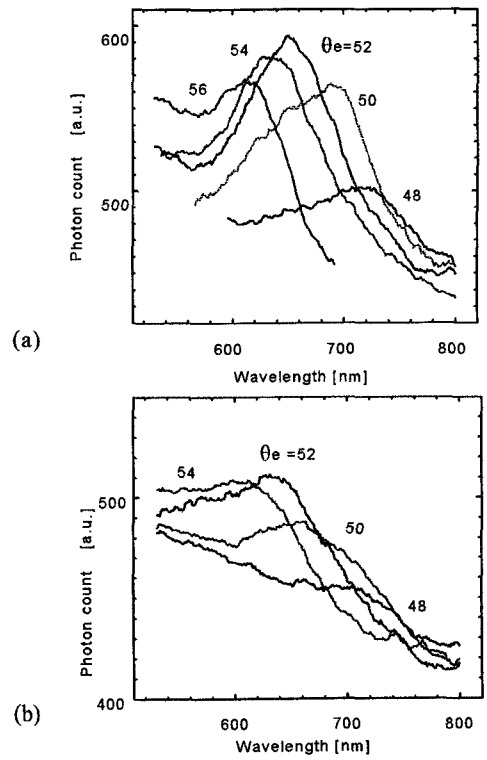


Fig.7 Emission spectra at various emission angles for the prism/Ag/C20 (2layers)/MC (16layers) LB film by the reverse irradiation of p- (a) and s-polarized (b) laser beams at 488.0 nm.

frequency was calculated from the emission angles, θe, and the peak wavelengths in the emission spectra, assuming that θe is θsp [7, 8]. The dispersion property was also calculated from the ATR properties in Fig.5 using the laser wavelengths and θsp. We also calculated a dispersion curve of the SPs using the anomalous dispersion property of the dielectric constants for the MC LB film as shown in Fig.4 [1, 2].

Figure 8 shows these dispersion properties of the SPs. There were some perturbations due to the anomalous dispersion in the dielectric constants at the angular frequency corresponding to the wavelength of about 600 nm where MC LB film showed the strong absorption. The dispersion properties of the emission light agreed well with one of the ATR measurements below the angular frequency of about 600 nm. It was thought that SPs were excited in the reverse irradiation and the emission light was generated due to the dispersion property of SP in the ATR Kretschmann configuration. Similar emission light properties have been reported for Ag/ rhodamine B LB films in the Kretschmann configuration [7]. These emission spectra also depended upon organic dye molecules and LB structures in the configuration [7, 8]. There was some difference between the calculated curve and that from the ATR measurement above the angular frequency of about 600 nm in Fig.8. It is not clear, but we think that it is caused by some difference between the optical absorption due to in-plane dyes in the MC LB film and the SP excitations due to evanescent waves in the configuration and/or orientations of MC dyes in the direction of the thickness of the LB film. The detail analysis is now under way.

Inoue and Hori have reported an analytic treatment of the light emission properties of electric and magnetic multipoles near dielectric surfaces and evaluated the basic optical near-field problems such as electric dipole radiation [10]. Their analysis indicates that surface electromagnetic modes with evanescent fields localized at the surface are induced when the

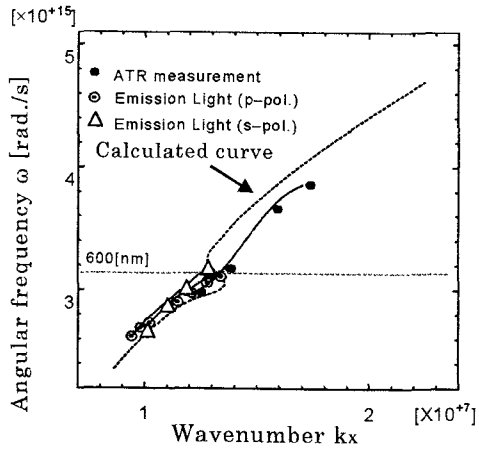


Fig.8 Dispersion properties between wavenumber of SPs and angular frequency calculated from ATR and the emission spectra for the prism/Ag/C20 (2layers)/MC (16layers) LB film.

separation between dipoles and the surface is smaller than the wavelength of light. Therefore, it is estimated that polarizations of organic dye molecules excited by the laser irradiation induce vibrations of free electrons at the metal surface producing SPs, and the SPs are converted to emission light at the resonant SP conditions in the Kretschmann configuration [7, 8].

Since SP emission light due to dye molecules is related to energy transfer in nano-distance from molecules and metal surface and conversion from SPs in near field optics into far field optics [11], it is thought that the phenomenon due to multiple SP excitations is very useful for applications to new optical nano-devices.

4. CONCLUSION

Emission light properties were investigated for the prism/Ag/C20/MC LB thin films in the reverse irradiation at two polarized laser beams of 488.0 nm. The emission peaks by the p-polarized laser were larger than those by the s-polarized one. It is thought that anisotropic surface plasmons are induced from rod-like MC molecules excited by polarized laser beams. The dispersion property of the SPs was calculated using the anomalous dispersion property due to the strong absorption peak. The phenomenon due to SP excitations is thought to be very useful for application utilizing SPs.

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