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Excitations of Multiple Surface Plasmons and Emission Light in Nanostructured LB Films

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Surface plasmon (SP) excitations have been investigated in the attenuated total reflection (ATR) Kretschmann configuration of prism/metal /organic dye LB ultrathin films. Emission light through the prism was 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 and metal ultrathin films in the Kretschmann configuration. The emission properties coincided with resonant conditions of SP excitations in the ATR Kretschmann configuration. It was thought that multiple SPs were excited at the interface of metal and LB films and some of multiple SPs were transferred to emission light corresponding to the resonant conditions of SPs in the ATR method. It is thought that the phenomenon due to multiple SP excitations is very useful for application to new devices.

Key words: surface plasmon excitation, attenuated total reflection, Kretschmann configuration, Emission light, LB film.

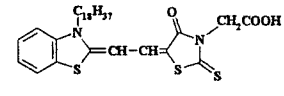
1. INTRODUCTION

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 [1-4] and as one of sensing methods [2, 5]. The ATR methods have been also investigated for device applications, because of strong optical absorption and strong electric fields due to SP excitations [6, 7]. 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 [8, 9]. The emission light depended upon resonant conditions of SPs in the Kretschmann configuration of prism Ag film/ Rhodamine-B (RB) Langmuir-Blodgett (LB) film, and it was thought that multiple SPs were excited by means of the direct excitation of RB film by a laser beam, that is, reverse irradiation [10, 11].

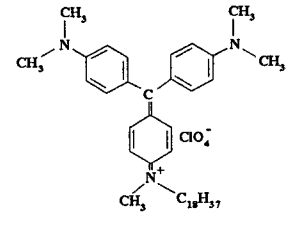
In this paper, surface plasmon (SP) excitations have been investigated in the attenuated total reflection (ATR) Kretschmann configuration of prism/metal /organic dye LB ultrathin films. Emission properties due to SP excitations were reported in the reverse irradiation of the Kretschmann configuration with nanostructured LB ultrathin films.

2. EXPERIMENTAL

MC and CV were used as organic dye molecules in this study. The molecular structures are shown in Fig.1. The MC is one of cyanine dyes having photoconductive effect. MCs have been studied for photoelectric cells [7]. The CV is one of triphenylmethyl groups. Langmuir-Blodgett (LB) films of the MC and the CV were prepared by LB dipping method. These molecules were mixed with arachidic acid (C20) for excellent LB depositions and the molar ratio in these LB monolayers was [MC or CV]: [C20] =1:2.



(a)



(b)

Fig.1 Chemical structures of the dye molecules; (a) merocyne (MC) and (b) crystal violet (CV).

The both LB thin films were deposited on C20 LB films with 2 monolayers on cover glasses coated with vacuum-evaporated Ag thin film. Ag thin film was used as SP active layer and the thickness was about 50nm. The C20 LB films were used for the following better depositions, and the thickness of the C20 monolayer was 2.76 nm [3].

Figures 2 (a) and (b) show the ATR Kretschmann configuration and the reverse irradiation. A half-cylindrical prism (BK-7 n=1.522 at 488 nm) was used in this study, and samples of the Ag/organic 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 controlled by a computer. 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.

Emission light through the prism was also observed using a sharp cut filter below about 520 nm when the sample was excited by the reverse irradiation in the Kretschmann configuration, as shown in Fig.2 (b). The sample was irradiated at the vertical incident angle by a p-polarized Ar^+ laser beam at 488nm [10, 11]. The spectra of the emission light were measured at various emission angles where the light was observed.

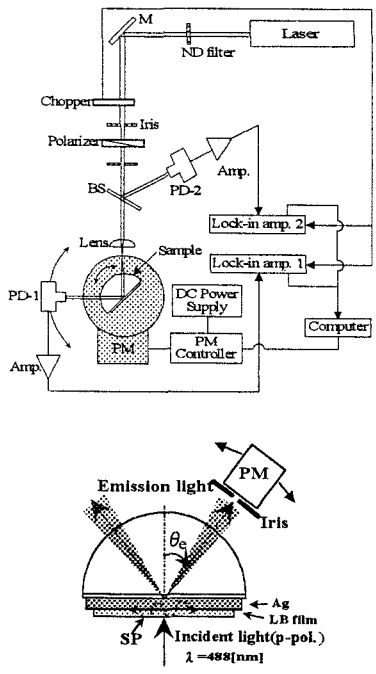


Fig.2 A measuring system for the ATR Kretschmann configuration (a) and the reverse irradiation (b).

3. RESULTS AND DISCUSSION

3.1 ATR and emission properties

Figure 3 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}) shifted toward higher angle as the laser wavelengths for the measurements became shorter. The relation between the θ_{SP} and the wavelengths was caused by a dispersion property of SP in the Kretschmann configuration.

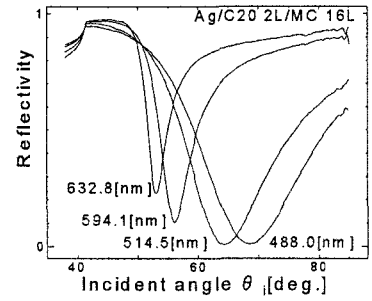


Fig.3 ATR properties at various laser wavelengths for the Ag/C20(2L)/MC(16L).

Figures 4 (a) and (b) show emission light through the prism as a function of the emission angle and the emission spectra at various emission angles in the reverse irradiation of a laser beam at 488 nm for the Ag/C20(2 layers)/MC (16 layers) LB thin film. A peak in the emission light in Fig.4 (a) was observed at about 50° and the spectra were measured at round 50°. The spectra strongly depended on the emission angles and were related to the photoluminescence (PL) property of the MC LB films[12]. Each spectrum almost corresponded to a part of the PL spectrum of the MC LB films showing a peak at about 600nm [12].

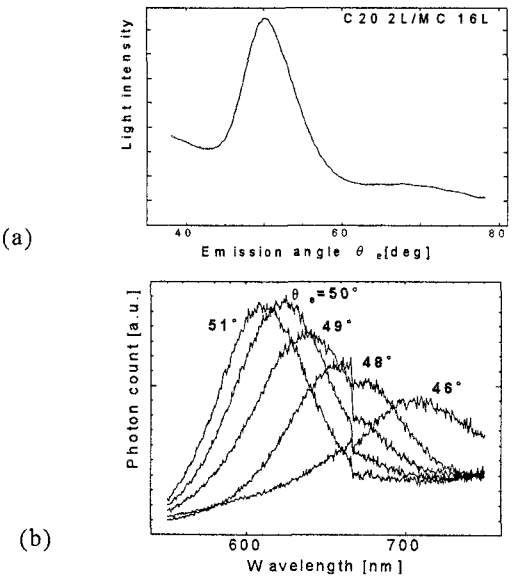


Fig.4 Emission light as a function of the emission angle (a) and the spectra at various emission angles (b) in the reverse irradiation.

The dispersion property of SP calculated from the emission peaks in Fig.4 (b) was compared with the calculated one from the ATR properties in Fig.3. Figure 5 shows the dispersion properties for the ATR curves and the emission spectra[10-12]. Open circles and black dots indicate the properties for the ATR measurements and the emission spectra, respectively. The dispersion property of the emission light agreed well to one of the ATR measurements.

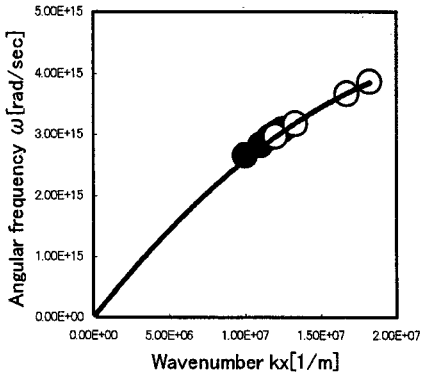


Fig.5 Dispersion properties calculated from the ATR curves (O) and the emission spectra (●).

It was thought that multiple SPs were simultaneously excited by the reverse irradiation and the emission light was generated due to the dispersion property of SP in the Kretschmann ATR configuration of the prism/Ag/C20/MC LB film. Similar emission light through the prism has been reported for the Ag/Rhodamine-B LB film by the resonant excitations of SPs in the conventional ATR method and the calculated dispersion properties also coincided with one of the ATR measurements[10-12].

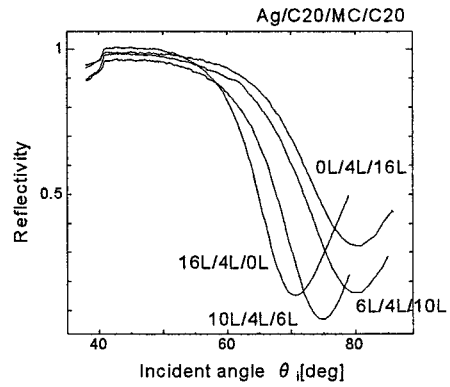
These emission spectra also depended upon organic dye molecules and the structures in the configuration[10-12]. Inoue et al. have reported an analytic treatment of light emission properties of electric and magnetic multipoles near dielectric surfaces and evaluated basic optical near-field problems such as electric dipole radiation[13]. Their analysis indicates that surface electromagnetic modes with evanescent fields localized at the surface are induced when separation between dipoles and the surface is smaller than the wavelength of light [13]. 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 multiple SPs, and the multiple SPs are converted to emission light at the resonant SP conditions in the Kretschmann configuration.

3.2 ATR and emission properties for nanostructured LB films

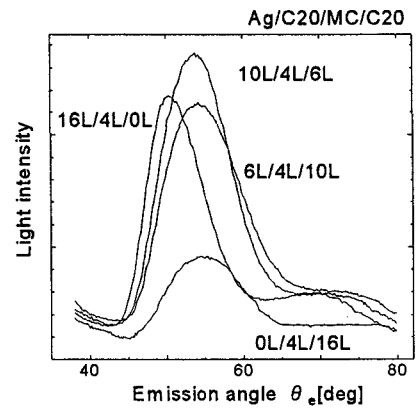
Figures 6 (a) and (b) show ATR and emission properties due to position of MC LB film with 4 layers in hetero LB films of C20/MC/C20, of which numbers of the total layers were 20 on Ag thin films. For example, Arabic numerals of 10L/4L/6L in Figs.6 represent numbers of layers for the C20 on Ag film, MC and C20 LB films, respectively. The properties strongly depended upon the position of the MC LB film.

The resonant angles, θ_{SP}, shifted toward higher angles as the position of the MC layers became closer to the Ag surface as shown in Fig.6 (a). The results show that the ATR method is very sensitive to position of dye molecules and the MC LB films in strong evanescent fields near the metal surface cause the large shifts in the ATR properties.

Figure 6 (b) shows emission light from prism/Ag/C20/MC/C20 samples. The emission properties also depended upon the position of the MC LB films, and the intensities increased with the separation between the MC and Ag films and showed a maximum at the separation of C20 with 10 monolayers, that is, about 28 nm. Pockrand et al.[8] reported a similar separation dependence using irradiation of an s-polarized laser beam, but in our results any emission was not observed for incident laser s-polarized perpendicular to the observation plane. It is thought that the property may be caused by anisotropy of excited MC molecules and/or the aggregations.



(a)



(b)

Fig.6 ATR (a) and emission (b) properties from prism/Ag/C20/MC/C20 with various separations between Ag and MC films.

It is tentatively estimated that small emissions are due to non-radiative energy transfer or charge transfer [14] from the excited MC to the metal film in the small separations and due to smaller induced charges on the metal film in the large separations. Inoue et al. have reported that surface electromagnetic modes localized at the surface are induced by dipoles with electromagnetic waves[13] and have suggested that the dipole-surface interaction will be very important for device applications utilizing near field optics in future [15]. It is thought that the phenomenon is very useful for nanostructured device applications.

3.3 Emission light property from Ag/hetero LB film of MC/CV

Figure 7 shows spectra of emission light from the prism/Ag/hetero LB film of MC/CV at various emission angles in the reverse irradiation. The MC and CV monolayers in the hetero LB film with 16 monolayers were deposited alternately on C20 with 2 monolayers. The emission spectra also depended on the emission angles. There was no emission light below about 600 nm and the spectra were distributed around 700 nm. Since the spectra in Fig.7 were different from ones in Fig.4 (b), the spectra were not due to MC molecules, but due to CV molecules. Any emission light from prism/Ag/ CV LB film without MC molecules was not observed in the reverse irradiation. Therefore, it was thought that this phenomenon was caused by some energy transfer from MC to CV such a dipole-dipole interaction [14, 16]. As the spectra are very sensitive to surface conditions such as kinds of molecules, molecule-molecule interaction, layer structures and/or thickness[10-12], it is thought that this phenomenon is useful for application to a new sensing device.

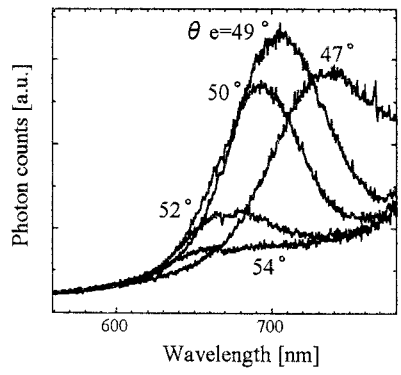


Fig.7 Spectra of emission light from the prism/Ag/hetero LB film of MC/CV at various emission angles in the reverse irradiation.

4. CONCLUSION

Emission light was observed for the MC film and the hetero LB film of MC and CV on Ag films using the reverse irradiation in the Kretschmann configuration. It was estimated that the emission light was caused by multiple excitations of SPs. Excitations of the SPs strongly depended upon the separation between the MC LB films and the Ag film. It was thought that the emission light from the hetero film of MC and CV was due to energy transfer from MC to CV molecules. It is thought that the phenomenon is useful for application to a new luminescent device and sensors.

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