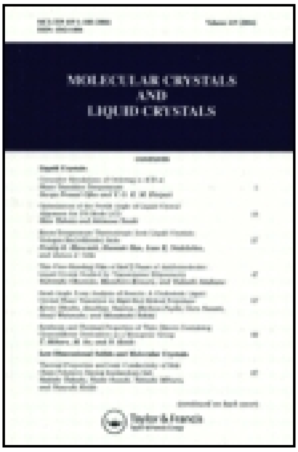

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Multiple Surface Plasmon Excitations in Molecular Thin Films on Silver Films in the Kretschmann ATR Configuration

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Multiple Surface Plasmon Excitations in Molecular Thin Films on Silver Films in the Kretschmann ATR Configuration

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Emission light through the prism has been investigated from the Kretschmann configuration of the prism/ Ag thin film/ rhodamine-B (RB) LB film in the resonant excitation of the attenuated total reflection (ATR) measurement. The emission light and the spectra strongly depended upon the emission angles where the light was observed. The emission properties corresponded to the dispersion property of the resonant excitations of surface plasmons (SPs) in the ATR configuration. It was concluded that the emission light was caused by multiple excitations of SPs in the ATR configuration. It is thought that the phenomenon will be used as a new sensing device.

Keywords Surface plasmon excitation; Attenuated total reflection; Surface plasmon resonance; Kretschmann configuration; Rhodamine-B LB film; Emission light

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 exciting at ultrathin metal surfaces are strongly influenced by conditions of the surfaces [1]. The ATR measurements utilizing the 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 a sensing method [1-4]. The ATR method has been also investigated for device applications, because of strong optical absorption and strong electric fields, that is, evanescent fields when SPs are resonantly excited [5].

Recently, emission light at a resonant angle region of SP excitations was observed through the prism in the Kretschmann configuration of the ATR measurements, 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, by means of the reverse irradiation [6,7]. In this paper, emission light properties from the prism have been investigated for the ATR Kretschmann configuration of prism/ Ag thin film/ rhodamine-B (RB) Langmuir-Blodgett (LB) film in the conventional ATR method.

EXPERIMENTAL DETAILS

A well-known laser dye, that is, RB was used as an organic dye molecule for the LB dipping method. RB molecules, purchased from NIPPON KANKOH-SHIKISO KENKYUSHO CO. LTD., were mixed with arachidic acid (C20) to obtain better LB structure. The molar ratio of the mixture was [RB]: [C20] =1:5. The RB LB films with ten monolayers were deposited on cover glasses with evaporated Ag films of about 50 nm thick. The procedure of the LB deposition has been reported [6, 7].

Figure 1 shows the Kretschmann configuration of the ATR measurements and a measuring system [1]. A half-cylindrical prism (BK-7 n=1.522 at 488 nm) was used and the sample of the Ag/RB LB film on a cover glass was attached to the bottom of the prism using a matching oil. The prism was located on a rotating stage and the incident angles of laser beams were automatically controlled by a computer. The ATR properties, that is, reflectivities were detected using a photodiode as a function of the incident angle of the laser beams. In this research, emission light through the prism was also investigated for the Kretschmann ATR configuration. The emission spectra between 530 and 670 nm using a spectrometer with an optical fiber were measured as a function of the emission angle in the resonant SP excitation of an Ar^+ laser at 488.0 nm.

RESULTS AND DISCUSSIONS

ATR Properties at Various Wavelengths

Figure 2 shows the ATR properties for the Kretschmann configuration of the prism/ Ag film/ RB LB film at various wavelengths using Ar^+ lasers at 488.0 nm and 514.5 nm and He-Ne lasers at 594.1, 612.0 and 632.8 nm. The incident angles at the minimum reflectance that were the resonant ones of the SPs were 54.6, 51.7, 48.2, 47.0 and 46.9 degrees at 488.0, 514.5, 594.1, 612.0 and 632.8 nm, respectively. The resonant angles shifted toward higher angles as the laser wavelengths became shorter. The relation between the resonant angles and the wavelengths shows the dispersion property of the SPs in the Kretschmann configuration. The dispersion property between the wavenumbers, k_x , of the SPs in the propagating direction of the film surface and the angular frequencies ω of the laser wavelengths can be calculated from the equations:

$$k_x = n_P\, k \sin\theta sp \quad \text{and} \quad \omega = k\, c,$$

where n_P is the refractive index of the prism, $k(=2\pi/\lambda)$ the wavenumbers of the laser

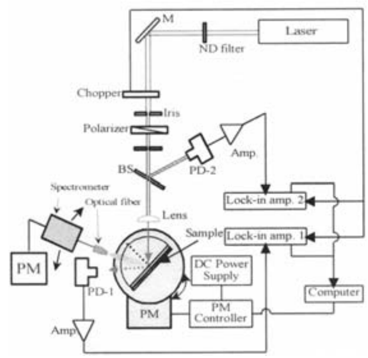

FIGURE 1 Kretschmann ATR configuration and a measuring system.

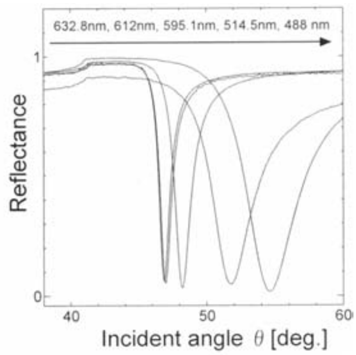

FIGURE2 ATR properties at various wavelengths; 488.0, 514.5, 594.1, 612.0 and 632.8 nm..

wavelengths λ in the air, c the light velocity in the air, and θsp the resonant angles of the SP excitations[1]. Open circles in Fig.3 show the dispersion property of the SPs calculated using the equations from the ATR properties at various wavelengths in Fig.2.

Emission Light through the Prism due to Multiple Surface Plasmon Excitations

Emission light through the prism was observed below the reflection angle in the conventional ATR measurement using the Ar^+ laser at 488 nm when the SP was resonantly excited at resonant angle of 54.6 degree in the Kretschmann ATR configuration as shown in Fig.1. The emission spectra are shown in Fig.4 and strongly depended on the emission angles where the emission light was observed from the prism. The dispersion property of the emission light was also calculated assuming that the emission angles are the resonant angles and the peak wavelengths are the wavelengths in the equations, and is shown as triangles in Fig.4. This calculated property agreed well to one of the ATR measurements.

Symmetrical emission light through the prism was observed for the same sample in the reverse irradiation, that is, when the RB LB film on the metal film was directly irradiated from air by a laser beam [6,7]. The spectra at various emission angles in the reverse irradiation were very similar to ones in Fig.4 [6,7]. The dispersion property of the emission light in the reverse irradiation was also calculated and the property was in agreement with the other ones [7].

These properties indicated that the emission light through the prism in the resonant excitation of the ATR measurement was caused by SP excitations in the Kretschmann ATR configuration. Therefore, it was concluded that multiple SPs were simultaneously excited and the emission light was generated due to the dispersion property of SPs in the Kretschmann ATR configuration. It has not been clarified yet, but emission spectra also depended upon organic dye molecules and the structures on the metal thin film in the configuration [7] and it is tentatively estimated that polarizations of organic dye molecules on the metal thin film excited by the evanescent fields or the direct irradiation of the laser beam induce vibrations of free electrons at the metal surface producing multiple SPs.

It is thought that the phenomenon may be used as a new sensing device as the spectra due to multiple SP excitations are very sensitive to surface characteristics on metal films in the Kretschmann ATR configuration.

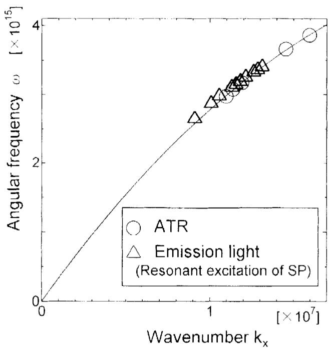

FIGURE 3 Dispersion properties of the SPs calculated from the ATR properties and the emission property.

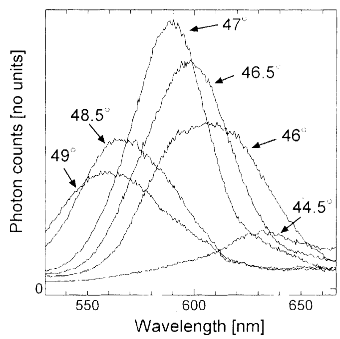

FIGURE 4 Spectra of the emission light at various emission angles due to the resonant excitation.

CONCLUSION

Emission light through the prism was observed from the Kretschmann configuration of the prism/ Ag thin film/ rhodamine-B (RB) LB film in the resonant excitation of the ATR measurement. The emission properties corresponded to the dispersion property of the resonant excitations of SPs in the ATR configuration. The emission light was caused by multiple excitations of the SPs. It is thought that the phenomenon will be used as a new sensing device.

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