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Humidity Sensing Using Surface Plasmon Excitation in Fluorescent Microsphere Films

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In this study, thin films of 100-nm polystyrene (PS) microspheres mixed with polyvinyl alcohol (PVA) were prepared, and changes in the attenuated total reflection (ATR) using surface plasmon (SP) excitation due to humidity adsorption were investigated. The PS microspheres contained luminescent dyes, and SP emission light due to these dyes was also observed. The sample configuration was prism /Ag film (50 nm) / sphere film structure. The ATR dip and SP emission peak angles shifted in line with the adsorption and desorption of humidity. Furthermore, the intensity of the SP emission light changed, and this was considered to be a result of the PVA swelling due to humidity adsorption. The humidity response of the ATR and SP emission light was repeatedly observed. The adsorbed mass was also monitored using a quartz crystal microbalance.

Key words: attenuated total reflection, surface plasmon, emission light, microsphere, sensing

1. INTRODUCTION

Surface plasmons (SPs) are coupling mode of free electrons and light [1]. The attenuated total reflection (ATR) method utilizing the resonance excitation of SPs can be used for sensing and evaluating ultrathin films [2-4]. In the measurement of ATR, the Kretschmann configuration (prism / metal film / dielectric film structure) is generally used. When the metal film is irradiated through the prism by p-polarized light at an angle that satisfies the conditions of SP resonance excitation, reflected light is attenuated. The reflection curve as a function of the incident angle (i.e. the ATR property) strongly depends on the metal film and the media adjacent to the metal film [1-4].

Furthermore, some of the energy of SP excitation is emitted as far-field light to the SP resonant angle through a prism in the ATR configuration [5-8]. In particular, SP emission light due to fluorescent molecules adjacent to the metal film has been reported [7, 8]. In such cases, the near-field light of the excited fluorescent dye [9] induces SPs, and the SP emission light has the wavelength components of the dye's photoluminescence. SP emission light can be applied to various optical devices, sensors and the like.

In this study, a polystyrene (PS) microsphere film with polyvinyl alcohol (PVA) was prepared, and changes in the ATR and SP emission light properties due to humidity adsorption were investigated for sensing application. The microspheres contained fluorescent dyes, and SP emission light was observed due to these dyes. The adsorbed mass was also monitored using a quartz crystal microbalance (QCM).

2. EXPERIMENTAL DETAILS

2.1. Sample preparation

100-nm PS spheres containing fluorescent dyes were purchased from Moritex Co. Japan and were used for film preparation. A thin film of Ag with a thickness of about 50 nm was deposited on microscopic cover glass (BK-7) using the vacuum evaporation method. A thin film of PS spheres with PVA (sphere:PVA film) was deposited onto the Ag film using the spin-coating method with H_2O containing 0.04 mg/ml of PVA and 0.2 mg/ml of PS spheres. Near-field light from the excited luminescent dye in the spheres can induce SPs at the metal surface [9]. The PVA is also considered to adsorb humidity and improve sensitivity.

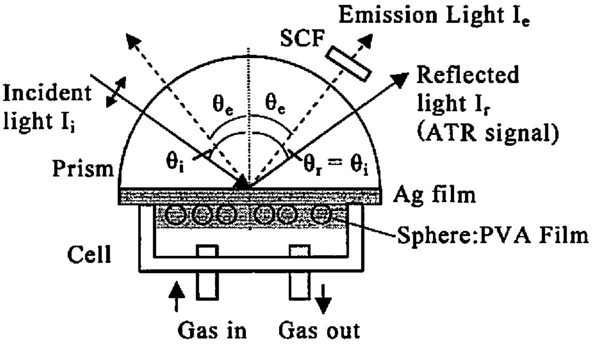


Fig. 1. Sample configuration for the measurement of ATR and SP emission light properties.

2.2. Methods of measurement

2.2.1. ATR curves

Figure 1 shows the ATR configuration in this study. The glass substrate with the sphere:PVA film was attached to the bottom of a half cylindrical prism (BK-7, n = 1.522 at 488.0 nm) using index matching oil (the glass substrate is not shown in Fig. 1). Ar^+ (λ = 488.0 nm) and He-Ne (λ = 632.8 nm) laser beams were used as incident light. The intensities of incident light I_i and reflection light I_r were automatically measured while changing incidence angle θ_i, and ATR curves were obtained.

The film thickness and dielectric constant of the sphere:PVA film can be changed through the adsorption of various gases. In this study, changes in the properties of the ATR due to humidity adsorption were investigated. The sample surface was covered with a plastic case as shown in Fig. 1, and nitrogen gas at different humidities (described as dry N_2 and wet N_2) was fed in. The humidity values for the dry and wet N_2 were about 15% and 75% respectively.

2.3.2. SP emission light

In the ATR Kretschmann configuration, part of the SP energy can be converted to far-field light (SP emission light) [5-8]. In this study, SP emission light was also observed as shown in Fig. 1. The incident light excites the fluorescent dyes in the PS spheres, and the near-field light of the excited dye induces SPs and SP emission light. Emission light was observed as a function of emission angle θ_e, and should be strongly observed around the SP resonant angle [5-8]. The SP emission light has the wavelength components of the dye's photoluminescence. In measurement, emission light is also observed due to SPs being excited by incident laser beams because of surface roughness, even without the contribution of the dye [5]. Such SP emission light has the same wavelength as the incident light. A sharp-cut filter (SCF) eliminating excitation light wavelength was therefore set in front of the detector to observe the SP emission light due to dyes, as shown in Fig. 1.

The PVA film of the fabricated sample adsorbs various gases, and the SP excitation of the dye molecules can be changed. In this study, changes in the properties of SP emission light due to humidity adsorption were investigated.

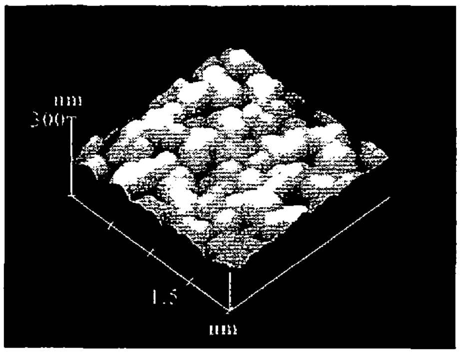


Fig. 2. AFM image of the Sphere:PVA film.

2.3.3 Quartz crystal microbalance (QCM) method

The resonance frequency of a quartz crystal oscillator is changed for the adsorption of the materials. The QCM method can detect relatively small changes in the mass of adsorption materials [10, 11]. In this study, sphere:PVA films were deposited onto a crystal oscillator (oscillation frequency: 5 MHz) in the same way as for measurement of the ATR and SP emission light properties. Changes in the oscillation frequency as a result of humidity adsorption were observed.

3. RESULTS AND DISCUSSION

3.1 AFM image, optical absorption and photoluminescence spectra

Figure 2 shows an AFM image of the sphere:PVA film. PS spheres can be observed in the film. The diameter of the observed spheres (200 nm) was larger than the original value of 100 nm. This was considered to be a result of the PVA coating.

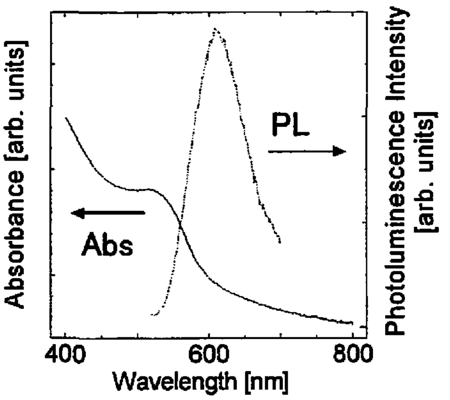
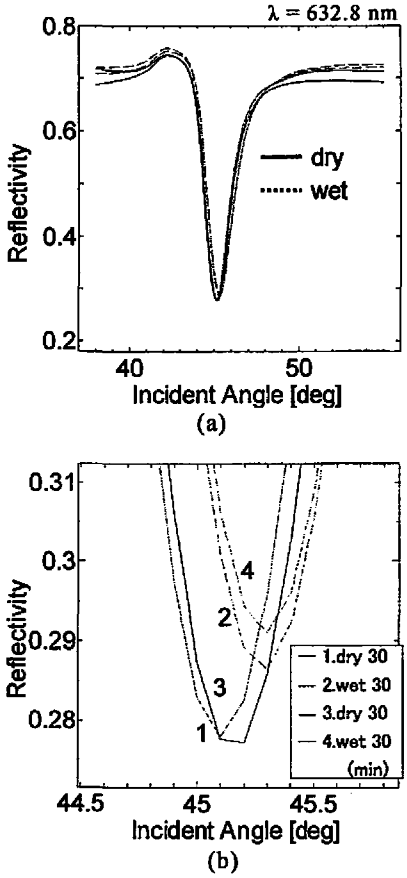


Fig. 3. Optical absorption and PL spectra of the Sphere:PVA film.



(a)

(b)

Fig. 4. The ATR properties of the sphere:PVA film observed after exposure to dry and wet N_2 for 30 minutes in turn (a), and the properties around the dip angle (b).

Figure 3 shows the optical absorption and photoluminescence (PL) spectra of the sphere:PVA film. In optical absorption spectra, a broad peak due to dye was observed at about 530 nm. For the PL measurement, Ar^+ laser beam (λ = 488.0 nm) was used for the excitation. Red luminescence with a peak at about 610 nm was observed.

3.2 ATR properties

Figure 4(a) shows the ATR properties of sphere:PVA film after the exposure to dry and wet N_2 for 30 minutes in turn. Figure 4(b) shows that around the ATR dip angle. The dip angle in dry N_2 was located approximately 45°. The dip shifted to high angle side and the depth became shallow after exposure to wet N_2. The dip almost recovered to original state after exposure to dry N_2. Changes of the ATR curve were repeatedly observed. Film thickness and dielectric constants of Ag and sphere:PVA films were obtained from fitting with theoretical curves [12] to experimental ones and were shown in Table I. The Film thickness slightly increased with humidity adsorption, and it was considered to be due to swelling of PVA.

Table I. Thickness and dielectric constants of Ag and Sphere:PVA films obtained from curve-fitting.

	Thickness (nm)	Dielectric constant
Ag	47.3	-17.0+i0.58
Sphere:PVA (1.Dry)	31.3	1.55+i0.09
Sphere:PVA (2.Wet)	34.9	1.52+i0.08
Sphere:PVA (3.Dry)	31.5	1.56+i0.11
Sphere:PVA (4.Wet)	34.2	1.54+i0.08

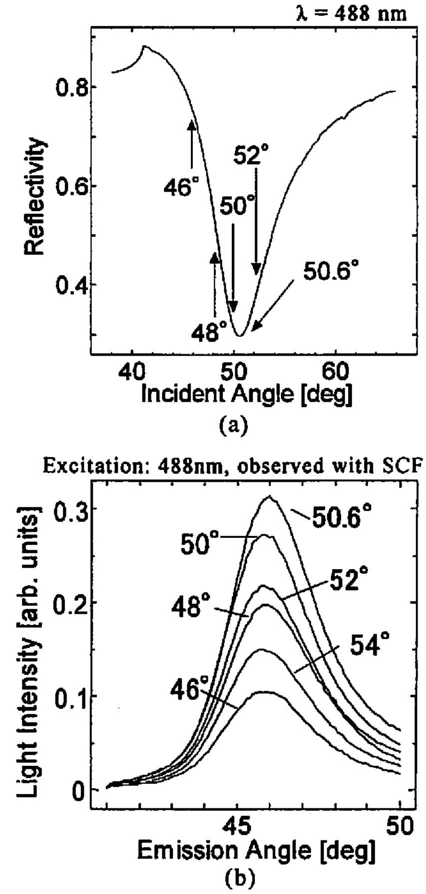
3.3. SP emission light properties

3.3.1. Incident angle dependence

Emission light due to dye luminescence was observed as shown in Fig. 1. An Ar^+ laser beam (λ = 488.0 nm) was used for excitation, and was irradiated at various incident angles. A sharp-cut filter (SCF) that eliminates excitation light wavelengths was used for measurement, enabling observation of only the SP emission light due to the excited fluorescent dye molecules.

Figure 5 (a) shows the ATR curve of the sphere:PVA film for the Ar^+ laser beam (λ = 488.0 nm). The ATR curve has a reflectivity dip at around 50° due to SP excitation by the laser beam. When SPs are excited, a strong electric field is induced adjacent to the metal, and dyes in the spheres on the metal can also be strongly excited. The excited dyes induce SPs and emission light. Figure 5 (b) shows the emission light curves for the Ar^+ laser beam incidence at various angles. Strong emission light was observed when the laser beam was irradiated at around the ATR dip angle.

The ATR dip angle (i.e. the SP resonant angle) in Fig. 5 (a) is different from that in Fig. 4 because it depends on the wavelength of the incident light [7, 8]. The SP emission light in Fig. 5 (b) is induced by dye luminescence with a peak at around 610 nm as shown in Fig. 3. As the SP emission light curve peaks at the SP resonant angle, the peak angle of the emission light in Fig. 5 (b) is close to the ATR dip angle of Fig. 4 (632.8 nm) rather than that of Fig. 5 (a) (488.0 nm).



(a)

(b)

Fig. 5. The ATR properties (a), and SP emission light properties at various incident angles in the neighborhood of the ATR dip (b).

3.3.2. Humidity adsorption

The properties of SP emission light after exposure to dry and wet N_2 for 30 minutes in turn are shown in Fig. 6 (a). Fig. 6 (b) shows the emission light around the peak angle. The incident angle of the excitation laser beam was set at 50.6° to obtain strong emission light.

On changing from dry to wet N_2, the peak shifted to the high angle side and the intensity decreased. The emission light curve then almost returned to the original state after exposure to dry N_2. Changes in the properties due to humidity adsorption were repeatedly observed. In the properties of the SP emission light, large peak intensity changes, as well as changes in the SP resonance angle can be observed. Emission light is considered to be very useful for sensing.

The reason for the light intensity change in Fig. 6 has not yet been clarified. However, it is considered to be a result of the swelling of the PVA. We have reported that SP excitation due to fluorescent dye molecules strongly depends on the distance between the metal surface and the dyes [7]. Since the near-field light from the excited dyes strongly decays with distance, the SP induced by near-field light weakens when the dyes are far from the metal surface. When the PVA that coats the spheres adsorbs humidity, the PVA swells and the distance between the metal and the spheres increases. This increase in distance should result in low SP emission light.

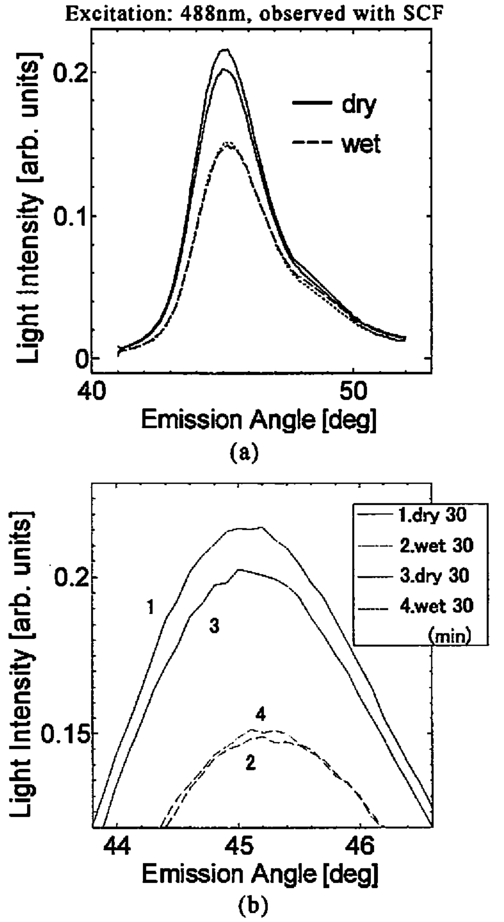


Fig. 6. The properties of SP emission light after exposure to dry and wet N_2 for 30 minutes in turn (a) and the properties around the peak angle (b).

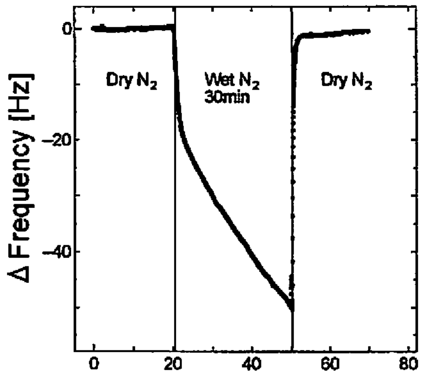


Fig. 7. Changes in the QCM frequency before and after exposure to wet N_2.

3.4 QCM properties

For evaluation of the adsorbed quantity, a PS:PVA film was prepared on a QCM, and changes in the oscillation frequency resulting from exposure to dry and wet N_2 were observed. The oscillation frequency decreased over time with the inflow of wet N_2, and a shift of -50 Hz was observed after 30 minutes as shown in Fig. 7. The adsorbed mass on the QCM surface was calculated as approximately 0.9 μg/cm^2. The oscillation frequency returned quickly after exposure to dry N_2.

SP excitation enables the detection of various gases such as alcohols, as well as humidity. Additionally, combining SP excitation and QCM methods allows detailed evaluation of adsorption.

4. CONCLUSION

The ATR and SP emission properties were investigated, and were found to change according to the adsorption and desorption of humidity. The dip angle in the ATR properties shifted to the higher angle side with the inflow of wet N_2 gas, which suggested an increase in the film thickness. This was considered to be a result of the PVA swelling due to humidity adsorption. The peak angle of SP emission light also shifted to the high angle side, and the peak intensity decreased. It was estimated that the distance between the metal and the dye increased as a result of humidity adsorption, and the light intensity in turn decreased. The change in the peak intensity was large, and should be useful in sensing. Furthermore, the quantity of water adsorbed by the inflow of wet N_2 was calculated as about 0.9 μg/cm^2 from the change in the QCM oscillation frequency.

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