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Evaluation of Phthalocyanine Layer-by-layer Film Deposition Using Surface Plasmon Resonance and Optical Waveguide Spectroscopies

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1. Introduction

The surface plasmon resonance (SPR) spectroscopy [1,2] is known as a useful technique for evaluation of dielectric constants and/or thickness of thin films. The surface plasmon (SP) is a coupled mode of a light and a collective oscillation of free electrons on a metal surface. The SP excitation can be induced by an evanescent field of a totally reflected light, and a prism coupler is commonly used. However, the prism prevents a miniaturization of a sensor, and it is not desirable for practical use. In contrast, the SP excitation can be also induced on an optical fiber or optical waveguide. Studies of SPR fiber and waveguide sensors have been reported [3], and simple and compact sensors can be developed. The property of the sample film can be sensitively evaluated under SPR condition, but an absorption spectrum cannot be easily investigated.

The optical waveguide (OWG) spectroscopy [4-6] is a powerful method to observe optical absorption properties of thin films and is quite sensitive because the evanescent field of a guided light is absorbed repeatedly by a thin film on the core. Furthermore, the optical absorption occurs in the penetration depth of the evanescent field from the core (typically several hundreds nanometers). The optical absorption spectrum can be obtained even in a colored solution by using the OWG method, and the method should be useful for thin film evaluation and sensors. However, it is difficult to estimate the film thickness on the waveguide core by the OWG spectroscopy only, especially for dyes forming various aggregates. The thickness should be obtained from other measurement.

Recently, we proposed a hybrid sensor of SPR and optical waveguide (OWG) spectroscopies [7]. By measuring the output light from the single waveguide, the film thickness and the optical absorption spectrum were obtained simultaneously. In previous work, a dye film deposition by spray method was observed in air. The sensor should be also used in a liquid or in a vacuum. In this study, electrostatic layer-by-layer (LbL) film deposition of water-soluble copper phthalocyanine (CuPc) was investigated to demonstrate the effectiveness of the sensor in aqueous solution. By using the sensor, film deposition process in the solution can be observed in detail.

2. Experimental details

Figure 1 shows the structure of the sensor in this study. The sensor consists of a BK-7 slide glass as the substrate, an vacuum evaporated gold film with 50-nm-thick and a spin-coated poly(methyl methacrylate-co-methacrylic acid) (PMMA-co-PMAA, Aldrich) film with 41-nm-thick on the substrate. Then, a solution cell for LbL film deposition was set on the sensor (not shown in the figure). A LbL film deposition was carried out using cationic Alcian Blue, pyridine variant (CuPc, Aldrich) and anionic poly(sodium 4-styrenesulfonate) (PSS, Aldrich). Alcian Blue is a derivative of copper phthalocyanine and is used because it is transparent at 750 nm and longer wavelength region, which is used for SPR observation. PMMA-co-PMAA is almost transparent in the measurement region (550-1000 nm) and has anionic carboxyl groups. Moreover, PMMA-co-PMAA hardly solve in water, which is used for the fabrication of the LbL films. The LbL film was deposited by electrostatic interaction between the substrate surface and molecules in the aqueous solutions (1mg/ml).

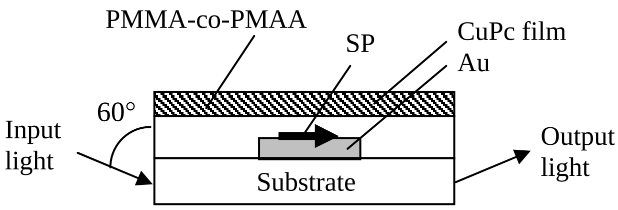

Fig. 1. The sample structure prepared in this study.

Transverse electric (TE) and transverse magnetic (TM) polarized white lights were used for the measurements. A TE polarized light was entered to the substrate from the edge before the deposition of the LbL film, and the output light was used as the reference. Then, the attenuation of output light due to dye absorption and SPR was observed, using the evanescent wave of the TM polarized light. The SPR wavelength depends on the incident angle, thicknesses and dielectric constants of the gold and the PMMA-co-PMAA films. By controlling the thickness of the PMMA-co-PMAA film to excite SPs at longer wavelength than the dye absorption band, the optical absorption of the LbL film and the SP excitation can be separately observed.

3. Results and discussion

Figure 2 shows experimental output light spectra for the LbL thin films of CuPc and PSS on the sensor. The y-axis value was obtained from the following equation in the similar manner with the calculation of the conventional absorption,

$$Abs = -\log_{10}(I_{TM}/I_{TE}) \qquad (1)$$

where I_{TM} is the intensity of the TM polarized output light, and I_{TE} is the reference light intensity of the TE polarized output light before the LbL film deposition. Curves 1-6 show the spectra for the LBL film of 1-6 bilayers, respectively. Clear peaks are observed at 600 and 830 nm, which are due to dye absorption (Q band of CuPc) and SP excitation, respectively. The optical absorptions of CuPc and SP excitation can be separately observed by controlling PMMA-co-PMAA film thickness, as shown here. With the LbL film deposition, the peak at 600 nm increased almost linearly. At the same time, the SPR wavelength shifted to the longer wavelength side. Qualitatively, SPR peak exhibits a blue-shift with increase of thickness or dielectric constant (real part) of the deposited film. The thickness of the LbL film was calculated to be 2.6 nm. For the calculation, the dielectric constants of Ag film for various wavelengths were obtained from a literature [8]. The absorption at blue to green light region (400-550 nm) is not shown in the figure, since the absorption of gold film is remarkable and the signal to noise ratio was poor. However, by using silver film for SP excitation, absorption at this wavelength region should be observed. The in-situ observation of film deposition and evaluation of other dye film deposition are also carried out.

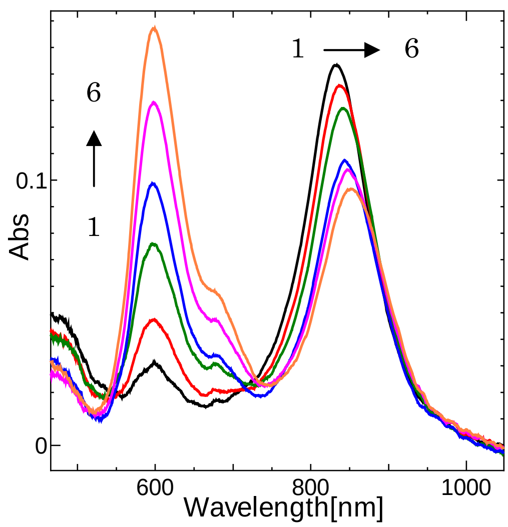

Fig. 2. Experimental output light spectra for the deposited LbL films on the sensor.

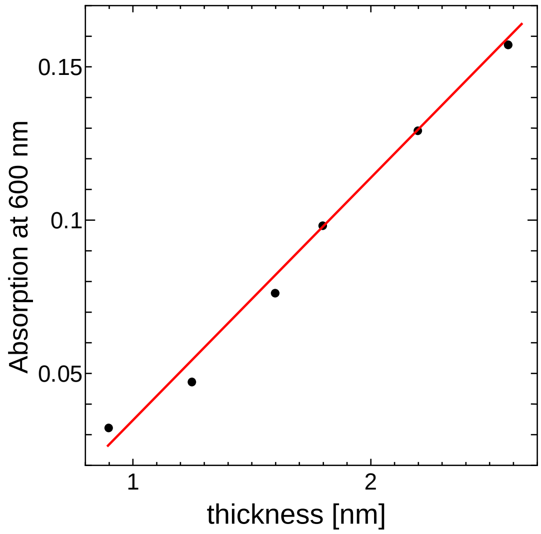

Fig. 3. Relationship between the peak intensity and the estimated thickness of LbL film.

3. Conclusions

In this study, measurements of optical property and thickness for CuPc LBL film were carried out by surface plasmon resonance and optical waveguide spectroscopies. It was confirmed that simultaneous measurement can be carried out in aqueous solution using this method. The sensor is simple and easy to prepare, and should be useful for investigation of film deposition process.

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