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Evaluation of Layer-by-layer Thin Film of PDADMAC: Alcian Blue and PSS Using Surface Plasmon Resonance and Optical Waveguide Spectroscopies

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1. Introduction

Optical waveguide (OWG) spectroscopy [1,2] is known as a powerful technique to observe optical absorption properties of thin films, and the method should be useful for thin film evaluation and sensors. The OWG spectroscopy is quite sensitive since the evanescent field of the guided light is absorbed repeatedly by a thin film on the core. However, it is difficult to estimate the film thickness by the OWG spectroscopy only. Previously [3], we proposed an OWG sensor with surface plasmon resonance (SPR) technique [4,5]. The sensor allows us to obtain the optical absorption and thickness of a thin film simultaneously. In this study, in-situ observation of layer-by-layer (LbL) thin film deposition of water-soluble dye and transparent polymer mixture was performed using the sensor. The amount of dye and polymer in the film were evaluated.

2. Experimental details

The prepared sensor in this study is shown in Fig. 1. A BK-7 slide glass with 45-nm-thick Ag, 5-nm-thick Au and 50-nm-thick poly(methyl methacrylate-co-methacrylic acid) (PMMA-co-PMAA) films was used as a waveguide sensor. PMMA-co-PMAA is hardly soluble in water but contains carboxyl groups, so an LbL deposition by electrostatic interaction can be carried out on the surface. Additionally, PMMA-co-PMAA is transparent and its refractive index is similar to BK-7 substrate. The optical property of dye can be observed at the sensor surface without metal films by the OWG spectroscopy. Furthermore, the SPR condition at Au surface can be controlled by the thickness of the PMMA-co-PMAA film. In this study, the PMMA-co-PMAA film thickness was adjusted to induce SPR at longer wavelength compared to dye absorption. The light absorption due to dye and SPR can be observed at separate wavelength region, so the optical property and thickness can be investigated by OWG and SPR spectroscopies, respectively. SPR phenomena can be observed for p-polarized light component. The s-polarized component of the output light (I_S) was observed before film deposition and the p-polarized component was also observed (I_P) before and after film deposition. The output light spectrum (light absorption) due to dye and SPR is shown using $\log_{10}(I_S/I_P)$.

Cationic phthalocyanine derivative, alcian blue (AB), cationic poly(diallyldimethylammonium chloride) (PDADMAC) and anionic poly(styrenesulfonate) (PSS) were used for LbL film deposition. PDADMAC and PSS are transparent in visible region. At first, aqueous solutions of PDADMAC and PSS (5.0 mg/ml) were prepared and PDADMAC/PSS LbL film with two-bilayers was deposited on PMMA-co-PMAA layer. Then, mixed aqueous solution of PDADMAC (5.0 mg/ml) and AB (1.0 mg/ml) was prepared and LbL film with mixed layer of PDADMAC and AB (shown as PDADMAC:AB hereinafter) and PSS layer was deposited. The depositions were conducted by injecting aqueous solution alternately in the cell and the sensor surface was rinsed twice using pure water before solution exchange.

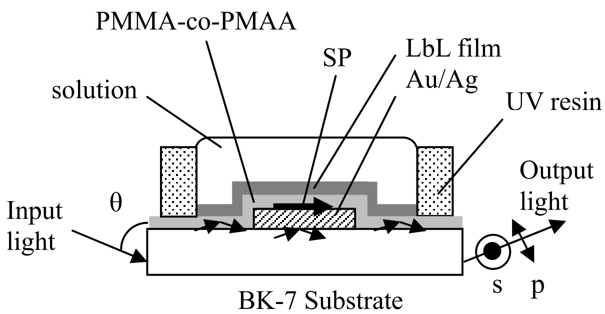

Fig. 1. The measuring setup used in this study.

3. Results and discussion

Figure 2 shows output light spectra of the LbL film of PDADMAC/PSS (2-bilayers) and successive PDADMAC:AB/PSS. The peak at 600 nm is due to AB absorption and the intensity increased with PDADMAC:AB/PSS film deposition. The peak at 680 nm is due to SPR, and it also exhibited red-shifts with deposition. The peaks of dye and SPR are relatively close in this figure; however, they can be more separated by using thicker PMMA-co-PMAA layer.

Kinetic responses of light absorption at 600 nm and SPR wavelength are shown in Fig. 3. The light absorption at 600 nm mainly increased by PDADMAC:AB layer deposition, while the absorption intensity did not increase with transparent PSS deposition. In contrast, the kinetic curve of SPR wavelength responded to every film deposition. The combination of SPR method to OWG sensor enables to detect transparent molecule adsorption.

Figure 4 shows relationship between thickness and number of bilayers. The thickness of the film was evaluated from the SPR wavelength. The thickness of PDADMAC/PSS film (2-bilayers) was small, however, those of PDADMAC:AB/PSS layers were remarkably large. That is, although the concentration of PDADMAC for cationic electrolyte solution was constant (5.0 mg/ml), addition of AB (1.0 mg/ml) induced significant change. The reason has not been clarified yet, but it is considered that some cohesion would occur among molecules in mixed solution and enhance molecular adsorption.

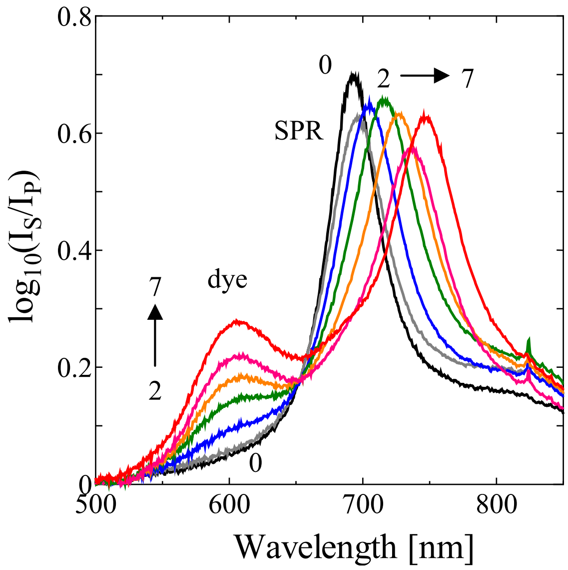

Fig. 2. Output light spectra before and after the LbL film deposition.

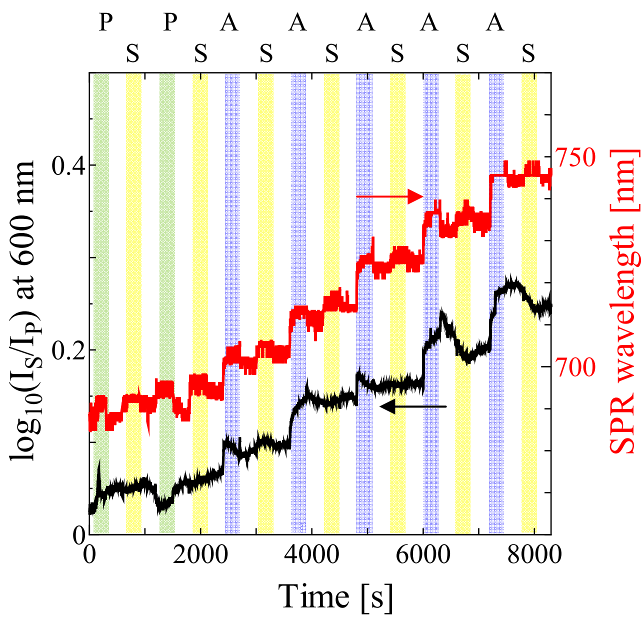

Fig. 3. Kinetic response of light absorption at 600 nm and SPR wavelength (p; PDADMAC, A; PDADMAC:AB, S;PSS, rinses with pure water were carried out in-between).

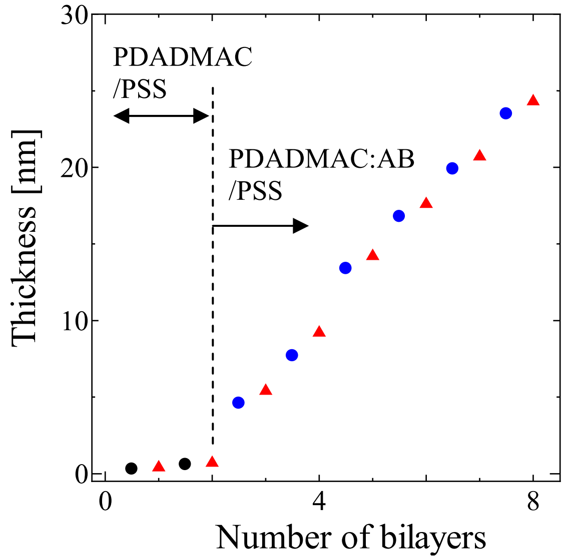

Fig. 4. Relationship between thickness and number of bilayers (circle: PDADMAC or PDADMAC:AB, triangle: PSS).

The amount of PDADMAC and AB in the mixed layer was estimated. Similar measurement was performed for AB/PSS film (without PDADMAC) and relationship between optical absorption and thickness was obtained. Using the result, the average thickness ratio of AB:PDADMAC ≅ 1:4 was obtained for the mixed layer in Figs. 2 ~ 4. Further study of LbL film depositions under different mixture condition is now being carried out.

3. Conclusions

In this study, an evaluation of LbL deposited film was performed using an OWG sensor with SPR method. It enables to obtain optical absorption property and thickness simultaneously. The novel sensor in this study should be useful for investigating various molecular adsorptions

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