Evaluation of Polyvinylalcohol:Rhodamine Film Deposition Using Optical Waveguide and Surface Plasmon Resonance Spectroscopies

Shinji Yokoyama¹, Kazunari Shinbo¹,², Yasuo Ohdaira¹,², Akira Baba², Keizo Kato¹,², and Futao Kaneko¹,²

¹ Department of Electrical and Electronic Engineering, Niigata University
2-8050, Ikarashi, Nishi-ku, Niigata 950-2181, Japan
Phone: +81-25-262-7543, E-mail: kshinbo@eng.niigata-u.ac.jp
² Center for Transdisciplinary Research, Niigata University
2-8050, Ikarashi, Nishi-ku, Niigata 950-2181, Japan

1. Introduction
The optical waveguide (OWG) spectroscopy [1-3] is a powerful method to observe optical absorption properties of thin films. The OWG spectroscopy is quite sensitive because the evanescent field of a guided light is absorbed many times 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 the OWG method. 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. The thickness should be obtained from other measurement, such as quartz-crystal microbalance (QCM) [3,4].

The surface plasmon resonance (SPR) spectroscopy [5,6] 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 evanescent field of a totally reflected light can excite SPs, and the SPR measurement can be carried out using an OWG with a metal film on the core. The attenuation of the guided light (optical absorption) can be observed when the SPs are excited.

In this study, polyvinylalcohol (PVA) mixed with rhodamine 6G (R6G) dye films (PVA:R6G films) were deposited on a waveguide with a silver film. We attempted to carry out a hybrid observation using the OWG and SPR spectroscopies for the film. By measuring the output light from the single waveguide, the optical absorption spectrum and the film thickness were obtained simultaneously.

2. Experimental details
Figure 1 shows the structure of the sensor in this study. A BK-7 slide glass was used as the substrate, and a silver film with 50-nm-thick and a polyvinylcarbazole (PVK) film with 73-nm-thick were deposited. Finally, PVA:R6G films were deposited by the spin-coating method using aqueous solutions with various concentrations. R6G is used because it is transparent in a red light region, which is used for SPR observation. PVK is almost transparent in visible region and it does not solve in water, which is used for the fabrication of PVA:R6G films. Transverse electric (TE) and transverse magnetic (TM) mode white lights were used for the measurements. A TE mode light was entered to the substrate from the edge before the deposition of PVA:R6G film, and the output light was used as the reference. Then, the optical absorption spectra of the PVA:R6G film were observed by the OWG spectroscopy, using the evanescent wave of the TE and TM mode lights. Furthermore, the evanescent wave of the TM mode light can excite SPs on the silver film. The SP resonant wavelength depends on the incident angle, thicknesses and dielectric constants of the silver and the PVK films. By controlling the thickness of the PVK film to excite SPs at longer wavelength than the R6G absorption band, the optical absorption of the PVA:R6G film and the SP excitation can be separately observed.
3. Results and discussion

Figure 2 shows examples of theoretical curves for a BK-7/Ag/PVK/air structure for the incident angle $\theta = 50^\circ$. The y-axis shows the ratio of the TE and TM mode output light intensities. The dielectric constant of the PVK was assumed to be 2.86, and the dielectric constants of Ag film for various wavelength were obtained from a literature [7]. Sharp dips due to SP excitation can be observed and the dip wavelength depends on the PVK thickness shown in the figure. R6G dye exhibits optical absorption in the range from 400 to 600 nm, so that the PVK thickness should be 70 nm or more to observe the absorptions of R6G dye and SPR separately.

Figure 3 shows the experimental output light spectra for the spin-coated R6G:PVA (weight ratio was 1:10) films on the BK-7 waveguide with Ag and PVK. The y-axis value was obtained from the following equation in the similar manner with the calculation of the usual absorption,

\[
\text{Abs} = - \log_{10}(I_{\text{TM}}/I_{\text{TE}})
\]  

where $I_{\text{TM}}$ is the intensity of the TM mode output light, and $I_{\text{TE}}$ is the reference light intensity of the TE mode output light before the PVA:R6G film deposition. Curve 1 shows the spectra before the PVA:R6G film deposition, and clear peak is observed at 650 nm which is due to the SP excitation. After the film deposition (curve 2), a peak at 520 nm is observed due to the absorption of R6G dyes. At the same time, the SPR wavelength shifted to the longer wavelength side. The thickness of the deposited R6G:PVA film was calculated to be 4.8 nm by assuming the dielectric constant to be 2.25. The optical absorptions of R6G and SP excitation can be separately observed as shown here.

The PVA:R6G films with several thicknesses were prepared using the aqueous solutions of PVA and R6G with various concentrations and with the same ratio. The output light spectra are also shown in curves 3-6 in Fig. 3. Using the proposed method in this study, the thickness and the optical property of a deposited film can be obtained easily. The relationship between the intensity of the peak at 520 nm and the estimated thickness of the spin-coated film is shown in Fig. 4. The relationship was almost linear in the observed region.

3. Conclusions

In this study, simultaneous measurements of optical property and thickness for PVA:R6G film were carried out by optical waveguide and surface plasmon resonance spectroscopies. In-situ measurements can be carried out in vacuum, in air, and in solution using this method. It is easy and reasonable to prepare, and should be useful for practical use.

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References