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Preparation of a Hybrid Sensor of Surface Plasmon Resonance and Quartz Crystal Micorobalance by Using Imprinted Grating Structure

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1. Introduction

The quartz crystal microbalance (QCM) technique is known to be an useful and reasonable way to detect small mass of deposited molecules. However, the QCM signal is not enough to identify the chemical species of analyte. Needless to say, other measurement should be performed for evaluation of optical and electrical properties for the deposited film. The surface plasmon resonance (SPR) technique is recognized as a powerful optical method for thin film evaluation.[1)] Furthermore, many studies of of gas- and bio- sensors have been reported utilizing QCM and SPR methods up to now.[2-4)]

In this study, a hybrid sensor of QCM and SPR methods was prepared and its fundamental property was investigated.[5-7)] Grating structure of CD-R was imprinted on the QCM electrode, and the QCM frequency and grating-coupled SPR property were observed simultaneously. The relationship between the QCM and SPR signals should enable to identify the chemical species of analyte and/or detecting non-specific adsorption. Although simultaneous observation can be carried out using SPR and QCM method individually, the hybrid method can give more accurate signal. Furthermore, imprinted grating allows us to prepare devices quite reasonably. The evaluation of polymer film deposition and humidity sorption were demonstrated in order to investigate the effectiveness of the proposed sensor.

2. Experimental details

Figure 1 shows the structure of the hybrid sensor in this study. The grating was prepared as follows. A fluoropolymer film was spin-coated on a commercially available AT-cut QCM substrate (5 MHz, 1 inch φ). The mold of CD-R surface was attached to the fluoropolymer film, and then the sample was pressed and cured at 373 K for 60min. Successively, Ag thin film with 130 nm thickness was thermally deposited for SP excitation. The grating structure of CD-R was imprinted on the film, as shown in Fig. 2. The reflectivity curve of p-polarized light laser beam of 632.8 nm was observed. The SP excitation is possible under the following condition,

$$k_{SP} = k_{px} + \frac{2\pi}{\lambda}\sqrt{\varepsilon_m(\omega)}\sin\theta + \frac{2\pi}{\Lambda}m \qquad (1)$$

where, k_{SP} is the wavenumber of SP, k_{px} is the wavenumber of incident light along the metal surface, Λ is the diffraction grating pitch, λ is the wavelength, m is the diffraction order, and $\varepsilon_m(\omega)$ is the wavelength dependent dielectric constant of silver. The SP excitation induces the attenuation of reflected light.

Cationic poly(diallyl dimethyl ammonium chloride) (PDDA) and anionic poly(sodium 4-styrene-sulfonate) (PSS) were used, and the electrostatic layer-by-layer (LbL) deposited film of PDDA and PSS was prepared on the device. The concentration of the aqueous solutions of PDDA and PSS was 1wt% for the deposition. The changes

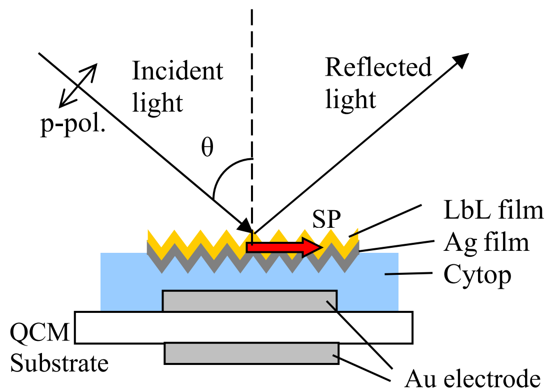

Fig. 1. The sample structure prepared in this study.

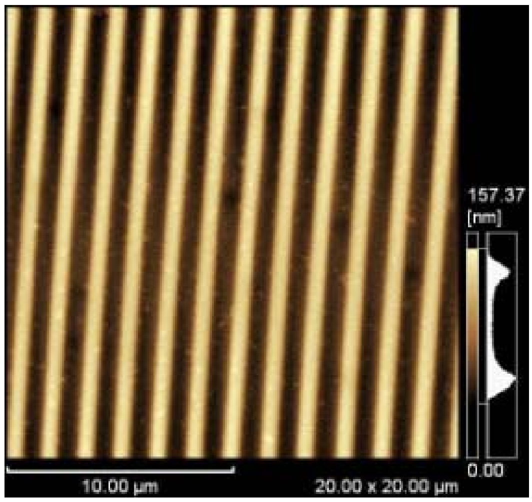

Fig. 2. An AFM image of Ag film (130 nm)/ imprinted grating structure on a QCM electrode.

of the QCM frequency and the reflectivity curve for the film deposition and humidity sorption of the film were simultaneously observed.

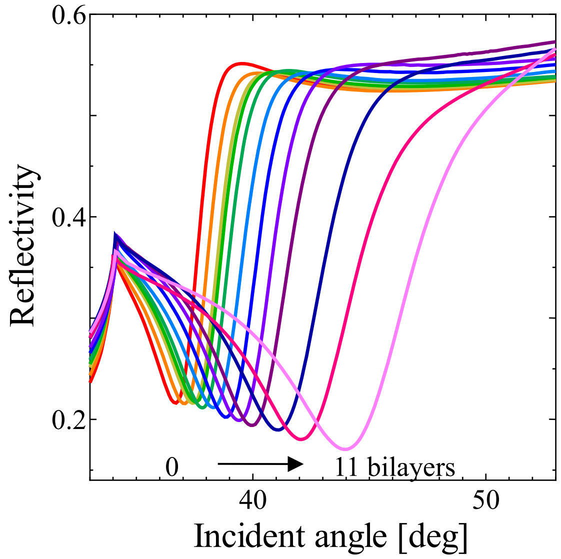

Fig. 3. Reflectivity curves for LbL film/ grating Ag on the QCM sensor.

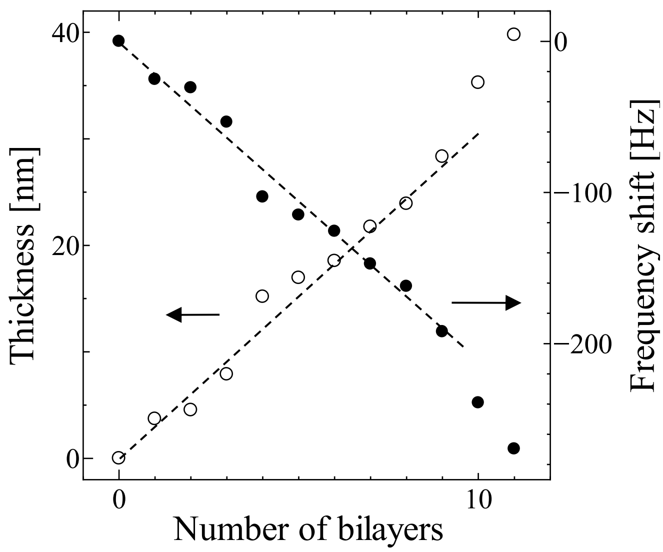

Fig. 4. Relationship between the estimated thickness of LbL film (QCM frequency shift) vs. number of bilayers.

3. Results and discussion

Figure 3 shows the reflectivity curves for PDDA/PSS LbL films on the hybrid sensor. The reflectivity dips are considered to be due to the SP excitation, and shifted to higher angle side with the film deposition. The reflectivity curves were also observed for Ag (130 nm) on CD-R substrate (data not shown). Narrower dip width and lower dip angle for the imprinted grating were observed compared to those of the CD-R substrate. The depth of the imprinted grating is shallower than the original one, and it seems to induce the difference of the SPR property. The detail is now under investigation.

Figure 4 shows the QCM frequency change for LbL film deposition onto the sensor. The thickness of the film, calculated by assuming the film density of 1.2 g/cm^3, is also shown. The thicknesses for 10th and 11th bilayer are a little larger than those of others, and large dip angle shift is also observed for the films in Fig. 3. Furthermore, the SPR dip width tends to be large with the number of bilayer,and it suggests the surface roughness increases with the deposition. It is estimated that the surface condition (roughness and charge density) changes with the number of layers and it induces thick film adsorption.

The responses against humidity sorptions were also investigated for the PDDA/PSS LbL film (Data not shown). Both of the reflectivity dip shift to higher angle and the QCM frequency decrease were repeatedly observed with humidity sorption. The relationship between the QCM and SPR signals can be precisely observed, so that this sensor should be used for identifying chemical species. It is also considered that the sensor is useful for evaluating molecular orientation and crystal formation, which affect to the refractive index.

3. Conclusions

The grating structure of CD-R substrate was imprinted for a fluoropolymer film on a QCM, and a hybrid sensor utilizing SPR and QCM methods was prepared. The dips of reflectivity curves indicated the SP excitation due to grating coupling, and the shift of the dip angle was observed with the deposition of PDDA/PSS film. The QCM frequency was also monitored using the sensor, and the tendency was almost similar to the SPR result Moreover, the relationship between the SPR and QCM response was investigated for humidity sorption. By using the imprinting method to obtain grating structure, the hybrid sensor can be prepared quite reasonably. It is also expected that the sensor in this study enables detailed film evaluation and discrimination of adsorbed molecular species.

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