Extended Abstracts of the 2008 International Conference on Solid State Devices and Materials, Tsukuba, 2008, pp. 814-815

I-6-3

A Hybrid Sensing Method Utilizing Surface Plasmon Resonance and Quartz Crystal Microbalance

Kazunari Shinbo[1,2], Yoshinori Tsurugai[1], Kazuya Aida[1], Yasuo Ohdaira[1,2], Akira Baba[2], Keizo Kato[1,2], Futao Kaneko[1,2] and Nobuo Miyadera[3]

[1]Niigata University, Department of Electrical and Electronic Engineering
2-8050, Ikarashi, Nishi-ku, Niigata 950-2181, Japan
Phone: +81-25-262-7543 E-mail: kshinbo@eng.niigata-u.ac.jp
[2] Niigata University, Center for Transdisciplinary Research
2-8050, Ikarashi, Nishi-ku, Niigata 950-2181, Japan
[3]Hitachi Chemical Co. Ltd.,
8 Wadai, Tsukuba, Ibaraki 300-4247, Japan

1. Introduction

Attenuated total reflection (ATR) technique utilizing surface plasmon (SP) excitation is recognized as a useful optical method for thin film evaluation, sensing and so forth[1)]. The thickness and dielectric constants can be obtained by the ATR method. Moreover, quartz crystal microbalance (QCM) is known as a sensitive technique for detecting deposited mass. Many studies of film evaluation and sensors of gas- and bio- molecules have been reported utilizing ATR and QCM methods up to now[2-5)].

In this study, a hybrid sensor of ATR and QCM methods was prepared and its fundamental property was investigated. Advantages of the ATR and QCM methods were combined and the hybrid detection should be useful for detailed evaluation of thin films and/or sensing. For example, optical property of dielectric film depends on its structure, so that accurate relationship between the optical property and the deposited mass is important for obtaining desired dielectric films. The hybrid detection should be also useful to discriminate adsorbed specie in sensors. Although simultaneous observation can be carried out using ATR and QCM method individually, the hybrid method can give more accurate signal.

2. Experimental details

Figure 1 shows the configuration for the hybrid sensor. An AT-cut QCM substrate (5 MHz) was used in this study. Ag films with 50 and 200 nm thickness were thermally deposited as QCM electrodes. Then, poly(vinylalcohol) (PVA) films were deposited by dip-coating using PVA aqueous solutions with appropriate concentrations. White light was applied to the substrate from the edge and the light is guided in the quartz substrate. SPs were excited at certain wavelength at the interface of Ag (50 nm) and PVA films, and output light intensity from the other side of the edge was attenuated at the wavelength. The results observed for incident angle θ = 60° were shown in this paper. The output light was observed by a multi-channel photodetector (Ocean Optics, USB-2000) and the QCM frequency was simultaneously obtained (MAXTEK, RQCM). In this study, the relationship between the QCM frequency (PVA film thickness) and the SP excitation was observed. Moreover, the responses against gas adsorption were investigated. The PVA film was used to facilitate gas adsorption and to improve gas sensitivity. Furthermore, the PVA film was used to control the SP excitation condition at the Ag surface.

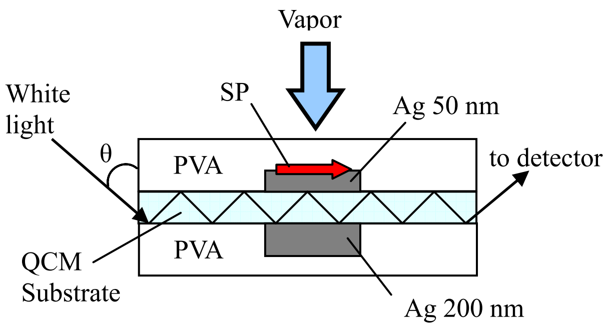

Fig. 1. The sample configuration.

3. Results and discussion

Figure 2 shows the optical absorption spectra of PVA/Ag films. Guided light was also observed at area without Ag films and were used as a reference light. By assuming the film density was 1.2 g/cm^3, the thicknesses of deposited PVA films were calculated as 25, 74, 250 nm for used PVA aqueous solutions of 10, 20, 30 mg/ml from the QCM frequency shifts. Absorption peaks were observed for the p-polarized light components and were considered to be due to the SP excitation. As the film thickness increased, the absorption peak shifted to the longer wavelength side. The result qualitatively corresponds with the nature of SP dispersion relation, and the peak wavelength shifts with the thickness and real part of the dielectric constant of the deposited film. The absorption spectra were also observed at various incident angles and the peak shifted to the shorter wavelength as the incident angle increased.

The responses against gas adsorptions were also investigated for the PVA film (thickness: 74 nm). Figure 3 shows the absorption spectra change and the peak shifted to the higher angle side with humidity adsorption. It is considered that the real part of the PVA film decreased with the humidity adsorption[6)], but the effective thickness increased and the contribution of the thickness increase was large in this case. The responses of QCM and absorption properties were repeatedly observed and the result is shown in Fig. 4. The change of absorption intensity at 528 nm is plotted in the figure. When the device was exposed to N_2 gas with high humidity, the QCM frequency and absorption intensity decreased. The responses were repeatedly observed and it suggests the device can be used as a humidity sensor. The responses against gas adsorptions were also observed for ethanol and acetone gases. The absorption spectra change against the QCM frequency shift depended on the adsorbed gas, and was the largest for the ethanol. It was considered to be due to the dielectric constant of the adsorbed gas molecule as well as the swelling of the PVA film. When the swelling and the dielectric constant decrease of the PVA films are small, absorption change should be large.

The responses against humidity adsorptions were also investigated for 250 nm thick PVA film (Data not shown). The absorption peak shifted to the shorter wavelength with humidity adsorption and the result was opposite to that of Fig.3. The sensitivity of the ATR method is largest near the metal surface and becomes small with the distance from the metal surface. It was considered that the contribution of thickness change was small and that of dielectric constant change was large in this case.

3. Conclusions

Hybrid sensors utilizing ATR and QCM methods were prepared, and PVA film deposition and gas adsorption to the PVA films were investigated. The optical absorption properties due to SP excitation depended on the PVA film thickness (QCM frequency). Furthermore, the adsorptions of humidity, ethanol and acetone gases were investigated and responses were repeatedly observed. The humidity response depended on the PVA thickness and it was considered to be due to the sensitive area difference between ATR and QCM methods. The hybrid sensors in this study were quite easy to fabricate and useful for various film evaluation and sensors.

References

[1] *Surface Polaritons*, eds. V. M. Agranovich and D. L. Mills (North-Holland, Amsterdam, 1982).

[2] K. Kato , C. M. Dooling, K. Shinbo, T. H. Richardson, F. Kaneko, R. Tregonning, M. O. Vysotsky, C. A. Hunter, Colloids and Surfaces A: Physicochem. Eng. Aspects, 198–200 (2002) 811–816.

[3] K. Shinbo, H. Furukawa, Y. Ohdaira, K. Kato, F. Kaneko, Thin Solid Films, accepted.

[4] X. Su, Y-J. Wu, W. Knoll, Biosensors and Bioelectronics 21 (2005) 719–726.

[5] L. E. Bailey, D. Kambhampati, K. K. Kanazawa, W. Knoll, and C. W. Frank, Langmuir, 18 (2002) 479-489.

[6] M. Biesalski and J. Rühe, Langmuir, 16 (2000) 1943-1950.

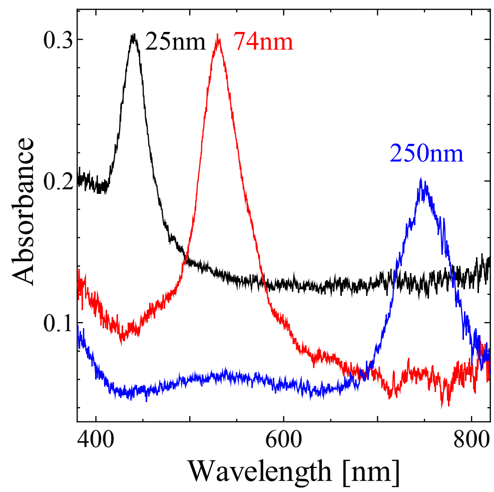

Fig. 2. The optical absorption spectra of PVA/Ag films.

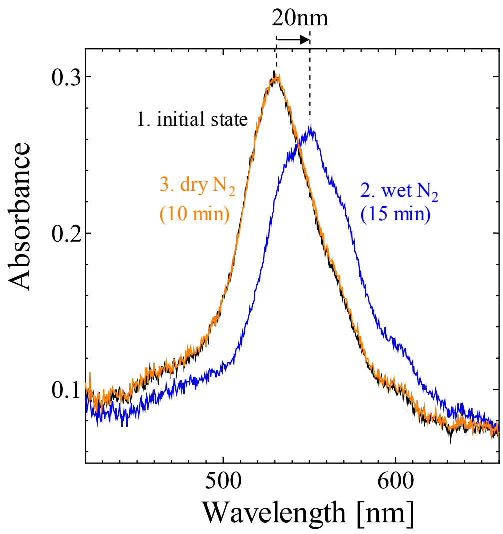

Fig. 3. The optical absorption change of PVA (74 nm)/Ag due to humidity adsorption.

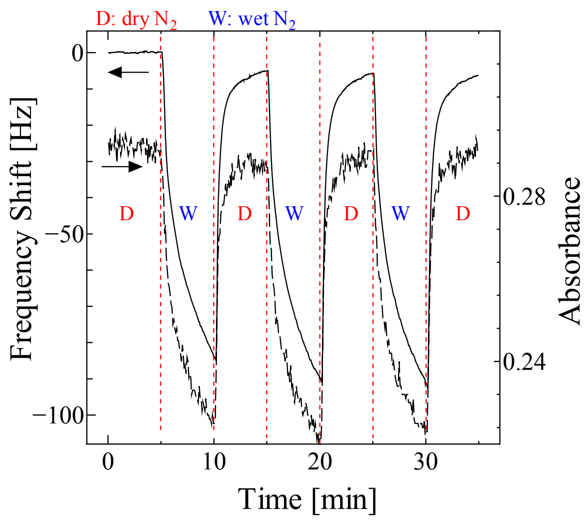

Fig. 4. The responses of QCM frequency and optical absorption due to SP excitation.