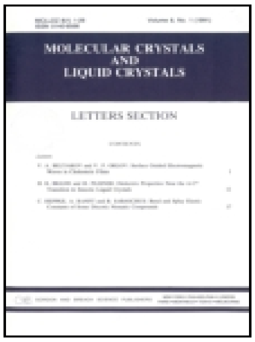


Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Vapor Sorption to Polyvinyl Alcohol Thin Film Observed Using a Hybrid Sensor of Quartz-Crystal-Microbalance and Surface-Plasmon-Resonance

Kazunari Shinbo, Yasuo Ohdaira, Akira Baba, Keizo Kato & Futao Kaneko

To cite this article: Kazunari Shinbo, Yasuo Ohdaira, Akira Baba, Keizo Kato & Futao Kaneko (2015) Vapor Sorption to Polyvinyl Alcohol Thin Film Observed Using a Hybrid Sensor of Quartz-Crystal-Microbalance and Surface-Plasmon-Resonance, Molecular Crystals and Liquid Crystals, 622:1, 67-73, DOI: 10.1080/15421406.2015.1097002

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1097002

Published online: 16 Dec 2015.

Mol. Cryst. Liq. Cryst., Vol. 622: pp. 67–73, 2015

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2015.1097002

Vapor Sorption to Polyvinyl Alcohol Thin Film Observed Using a Hybrid Sensor of Quartz-Crystal-Microbalance and Surface-Plasmon-Resonance

KAZUNARI SHINBO,* YASUO OHDAIRA, AKIRA BABA, KEIZO KATO, AND FUTAO KANEKO

Graduate School of Science and Technology and Center for Transdisciplinary Research, Niigata University, Ikarashi, Nishi-ku, Niigata, Japan

A quartz-crystal-microbalance (QCM) and surface-plasmon-resonance (SPR) hybrid sensor was prepared, and the sorptions of water and ethanol vapors to polyvinyl alcohol (PVA) films were observed in situ. The shift of the SPR wavelength depended on the PVA film thickness as well as the sorbed vapor. It was estimated to be due to the film swelling induced by the vapor sorption and the relationship between the film thickness and the penetration depth of evanescent wave.

Keywords quartz crystal microbalance; surface plasmon resonance; hybrid sensor; gas sorption; polyvinyl alcohol

Introduction

Recently we reported on a hybrid sensor of surface plasmon resonance (SPR) and quartz crystal microbalance (QCM) [1, 2]. SPR condition depends on the thicknesses and refractive indices of the metal film and adjacent media; therefore, the SPR method is known as a powerful technique for detecting molecular adsorption and for investigating thin film deposition [3, 4]. The QCM technique is another useful method for detecting adsorbed mass on the electrode based on the frequency shift [5]. In this study, the QCM substrate was used as an optical waveguide and QCM metal electrode was used for surface plasmon excitation. Other combination measurements using QCM and SPR methods using different structures have been reported previously. For example, QCM with metal grating structures or metal particles were prepared to induce propagating or localized surface plasmon [6–9]. In contrast, the structure in this study does not need grating or particle structure, and simple and low-cost sensor can be developed.

The SPR and QCM methods are using different laws of nature, and there are differences in the properties for sensing properties. For example, the SPR method exhibits high sensitivity for thin films deposited within the penetration depth of the evanescent wave,

*Address correspondence to Kazunari Shinbo, Graduate School of Science and Technology and Center for Transdisciplinary Research, Niigata University, 2-8050 Ikarashi, Nishi-ku, Niigata 950-2181, Japan. E-mail: kshinbo@eng.niigata-u.ac.jp

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

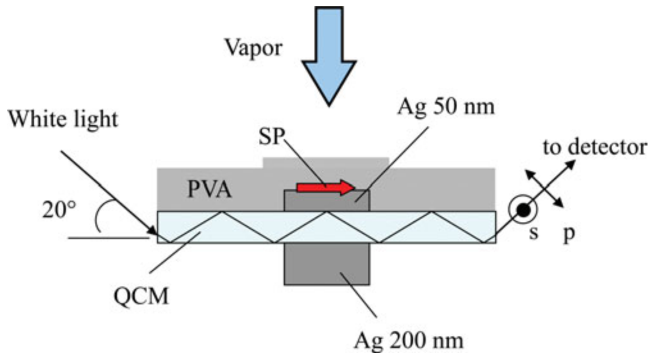


Figure 1. Schematic structure of the prepared sensor. (The thickness is not to scale.)

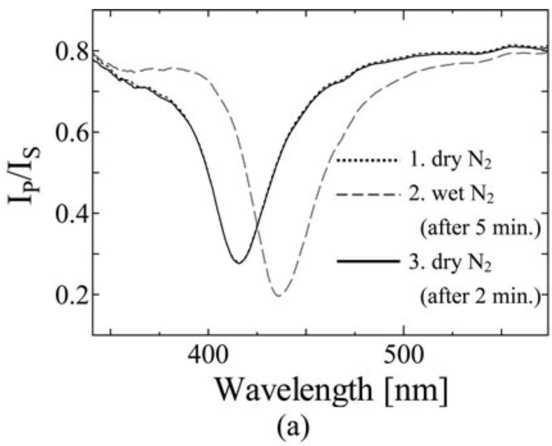
approximately half the wavelength of incident light [3]. Furthermore, the SPR property depends on refractive indices, as well as thicknesses of the media; therefore complicated response would be observed for gas sorption for films, especially including film swelling. The QCM method detects the adsorbed or deposited mass for a wide range of several hundred nanometers [10, 11], however, film structure change (swelling or shrinking) cannot be detected. The proposed hybrid sensor is suitable for investigating vapor sorption phenomena because the SPR method offers information that cannot be obtained by using only QCM method, and vice versa. Accurate relationship between optical property and sorbed mass would be observed using the proposed sensor. A previous study reported on thin-film evaluation in air and fundamental vapor sorption sensing [1]. In this study, water and ethanol vapor sorptions to polyvinyl alcohol (PVA) thin films were observed using the sensor, and kinetic responses and SPR wavelength shift properties were investigated.

Experimental

The structure of the proposed sensor is shown in Fig. 1. An AT-cut quartz substrate with fundamental frequency of 5 MHz was used in this study. 5-mm-width silver films with 50- and 200-nm-thick were vacuum evaporated on the front and back QCM surfaces, respectively. The silver films work as the QCM electrodes. Then, a transparent PVA (Aldrich) film was spin-coated on the 50-nm-thick Ag by using an aqueous solution. In this study, samples A – D with 30.5, 65.9, 200.8 and 344.5 nm-thick PVA films were prepared, respectively. The SPR wavelength qualitatively red shifts with PVA thickness.

A white light was input from the edge of the substrate to observe SPR properties [1], and the incident angle was 20 deg. in this study. The evanescent wave was produced by the total reflection and induced SPR at the 50-nm-thick Ag surface. We observed the output light from the opposite side edge of the substrate. It is known that SPR can be induced by p-polarized light. Therefore, we measured output-light spectra under two conditions: s-polarized light (I_S) for a reference and p-polarized light (I_P) for an SPR measurement. SPR property was obtained as I_P/I_S, and attenuation of the curve can be observed when SPR occurs in the sensor.

A cell (not shown in the figure) was set on the sensor, and N_2 gas without water vapor (relative humidity of 0%, dry N_2), that with water vapor (relative humidity of 95%, wet N_2), and that with saturated ethanol vapor were alternately introduced to the cell.



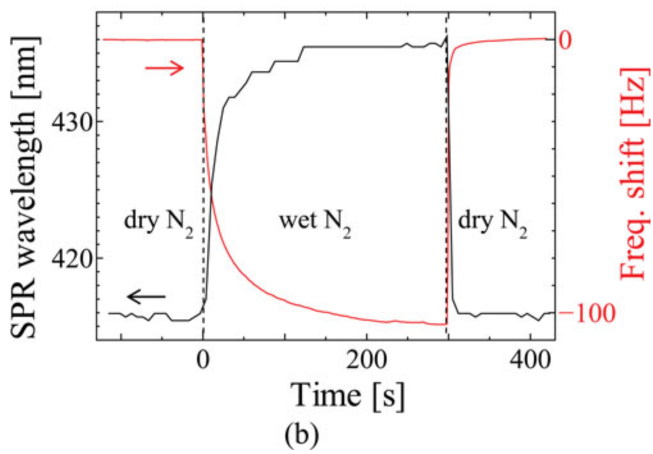


Figure 2. SPR properties of 30.5-nm-thick PVA film for water vapor sorption: (a) SPR curves before and after the vapor sorption and (b) kinetic curves.

SPR and QCM properties were simultaneously observed at room temperature by using a multichannel spectrophotometer (HR4000HC, Ocean Optics) and a frequency counter (RQCM, Maxtek), respectively.

Results and Discussion

Figure 2(a) shows SPR properties of 30.5-nm-thick PVA film for water vapor sorption (sample A). Before vapor sorption (curve 1), a dip was observed at 416 nm due to SPR. After vapor sorption for 5 min (curve 2), the dip wavelength, that is, SPR wavelength, red shifted. The redshift of SPR wavelength qualitatively suggests increase of thickness or refractive index, and it was considered that the water vapor sorption induced increase in thickness. After desorption for 2 min (curve 3), the curve almost recovered. Kinetic responses of SPR wavelength and QCM frequency shifts during the sorption are shown in Fig. 2(b). The curves exhibit very similar profile, since they were observed on the same substrate. The curves seem to change exponentially; however, they cannot be fitted to a

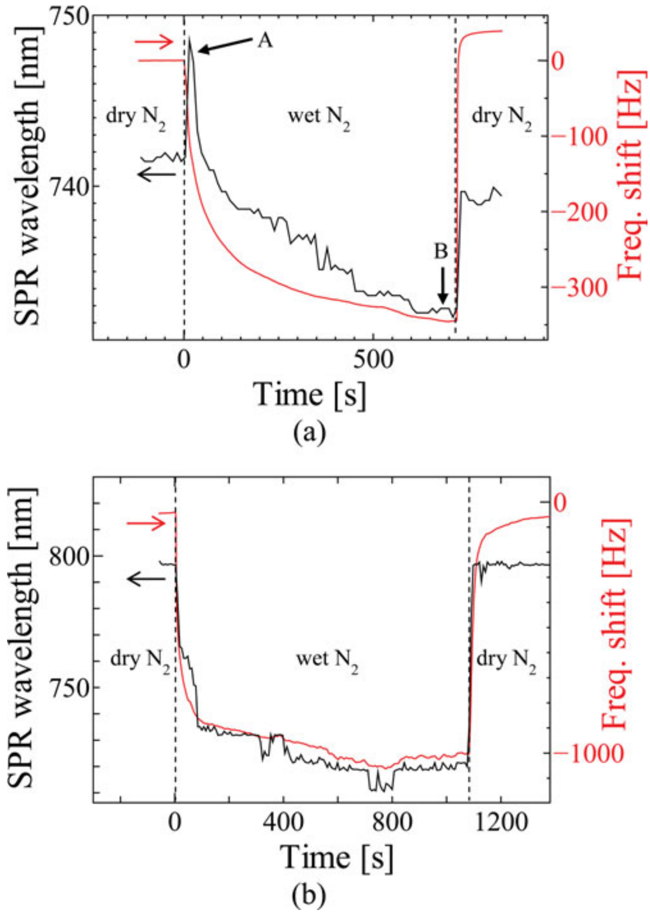


Figure 3. Kinetic curves of (a) 200.8-nm-thick and (b) 344.5-nm-thick PVA films for water vapor sorption.

single exponential curve. After the water vapor introduction, the curve responded fast (time constant obtained from QCM by curve-fitting, $\tau_{QCM} = 12.6$ s and that from SPR, $\tau_{SPR} = 15.5$ s for $t = 0 \sim 10$ s) and then gradually responded ($\tau_{QCM} = 80.6$ s and $\tau_{SPR} = 96.3$ s for $t = 60 \sim 120$ s). The process would reflect the attachment of water molecule to the PVA surface at early stage and successive penetration of water molecule into the PVA film. The water desorption processes were very fast and the time constant could not be obtained in this study. Similar tendency has been reported in the previous study [12].

Kinetic curves of 200.8-nm-thick (sample C) and 344.5-nm-thick (sample D) PVA films for water vapor adsorptions are shown in Fig. 3 (a) and (b), respectively. The QCM curves in Fig. 3 were similar to that in Fig. 2, and $\tau_{QCM} = 29.7$ s for $t = 0 \sim 10$ s and 276 s for $t = 180 \sim 420$ s in Fig. 3(a) and $\tau_{QCM} = 8.5$ s for $t = 0 \sim 10$ s and 718 s for $t = 300 \sim 540$ s in Fig. 3(b). It suggests that the water molecule attachment to PVA film surface barely depends on the film thickness; however, the penetration into film inside tends to take longer time with film thickness. SPR response for sample C was also shown in Fig. 3(a), and the original SPR wavelength was 741.7 nm because of the PVA thickness (200.8 nm). The SPR response in Fig. 3(a) exhibits complicated behavior. After the vapor introduction,

Table 1. Estimated thicknesses and refractive indices before and after the vapor sorption. The values under saturated state are shown, except for a) and b): a) and b) shows the values after 15 and 63 s after the vapor introduction, respectively

	Before sorption			After sorption			
Sample	λ_{SPR} [nm]	d [nm]	n	λ_{SPR} [nm]	d [nm]	n	vapor
A	415.8	30.5	1.578	435.5	49.0	1.469	water
B	495.0	65.9	1.546	508.5	84.0	1.495	
C	741.7	200.8	1.508	748.5[a)]	220.1	1.496	
				732.5	262.2	1.470	
D	797.0	344.5	1.470	720.0	521.5	1.454	
B	495.0	65.9	1.546	507.8	78.1	1.499	ethanol
C	741.7	200.8	1.508	753.0[b)]	218.3	1.499	
				749.3	229.1	1.491	
D	797.0	344.5	1.470	797.0	386.7	1.464	

[a]after 13 s, [b]after 63 s

the SPR wavelength in Fig. 3(a) rapidly red shifted and successively blue shifted, that is, the direction of the shift changed at 13 s. Simultaneously observed QCM frequency indicated that the water vapor continuously sorbed to PVA film during the time. It was estimated that swelling of the PVA film induced the SPR result. It is known that PVA film swells and the refractive index reduces with water vapor adsorption [1]. Just after the exposure to wet N_2 gas, water molecules adsorbed onto the PVA film surface, and the SPR wavelength red shifted due to thickness increase. Then, the water molecules penetrated into the PVA film and it induced swelling of the film and the reduction of refractive index. The contribution of the reduction of refractive index became dominant and caused the blue-shift of the SPR wavelength. The time constant for SPR wavelength could not be calculated because of this phenomenon.

SPR response for sample D (344.5-nm-thick PVA film) was shown in Fig. 3(b), and the SPR wavelength was originally 797.0 nm. The SPR curve exhibited only blue-shift against the water vapor sorption. In SPR measurement, the evanescent wave decays exponentially along the distance from the metal surface (the penetration depth was calculated to be 194 nm for sample D), and SPR property is sensitive for thin film existing in the penetration depth. Therefore, SPR is not so sensitive for thickness increase (molecular adsorption on the surface) in sample D. The contribution of the reduction of refractive index due to swelling would be large and the blue-shift of the SPR wavelength was observed. $\tau_{SPR} = 33.7$ s for $t = 0 \sim 6$ s and 612 s for $t = 90 \sim 240$ s in Fig. 3(b). τ_{SPR} is larger than τ_{QCM} for $t = 0 \sim 10$ s, and the difference would be due to the complicated SPR property (the opposite contributions of thickness increase and refractive index reduction).

Similar measurements for ethanol vapor sorption were conducted for samples B - D. Table 1 summarizes the SPR wavelength, estimated thickness and refractive index in this study. The ethanol vapor sorption for sample C induced a red-shift of the SPR wavelength and a successive weak blue-shift (the direction changed at 63 s). The weak blue-shift suggests the swelling and refractive index change of PVA film are not remarkable for ethanol vapor. Furthermore, the SPR wavelength barely responded to ethanol vapor in sample D, and it would be due to weak sensitivity for adsorption on the film surface (since it existed outside of the penetration depth) and small refractive index change after ethanol sorption. The thicknesses and refractive indices in Table 1 were estimated from the QCM and SPR results, respectively. The density of PVA is set as 1.27 g/cm^3 from the material safety data sheet. The estimated refractive indices of PVA before the vapor sorption are close to those reported before [13]. The thickness after sorption was nominally calculated using density of water (1.0 g/cm^3) or ethanol (0.789 g/cm^3). The refractive indices were calculated from the SPR wavelength assuming the film structures were uniform. The refractive indices after water sorption are smaller than those after ethanol sorption, and it suggests the large film swelling for water sorption.

The hybrid sensor in this study can obtain accurate relationship between the mass and optical property and enables to investigate sorption phenomena in detail. The combination measurement offers information which cannot be obtained by only QCM or SPR method and it would be a powerful tool to investigate thin film structure.

The QCM and SPR methods are promising for vapor sensing, and the hybrid sensor in this study would be also useful for developing vapor sensors such as hygrometer and alcohol sensor. Furthermore, the relationship between SPR and QCM results would be useful for identification of sorbed vapor. For example, SPR wavelengths in sample B of Table 1 were similar for water and ethanol vapor sorption, however, clear difference was observed in thickness (QCM frequency). It was estimated to be due to the difference of refractive index of sorbed molecules and film swelling. Additionally, the combination measurement would allow us to detect mixing of foreign vapor from the relationship between SPR and QCM results. The hybrid sensing in this study would be a convenient technique which is widely used.

Conclusion

In-situ observations of the sorptions of water and ethanol vapors to PVA films were conducted using a hybrid sensor of SPR and QCM methods. The SPR wavelength shift exhibited complicated behavior, due to film swelling. An accurate relationship between the SPR and QCM responses can be obtained by using the sensor, since the properties are observed on the same metal film on the single QCM substrate. The hybrid sensor should be useful for investigating sorption phenomena in thin films and developing functional vapor sensors.

Acknowledgments

This work was supported by JSPS KAKENHI Grant Number 23560362.

References

[1] Shinbo, K., Ishikawa, H., Baba, A., Ohdaira, Y., Kato, K., & Kaneko, F. (2012). *Appl. Phys.* Express 5, 036603.
[2] Kawachi, K., Shinbo, K., Ohdaira, Y., Baba, A., Kato, K., & Kaneko, F. (2014). *IEICE Trans. Electron. (2015)*. E98-C, 136.
[3] Agranovich, V. M., & Mills, D. L. (Eds.). (1982). *Surface Polaritons*, Elsevir, Amsterdam.
[4] Kawata, S. (Ed.). (2001). *Near-Field Optics and Surface Plasmon Polaritons*, Springer: Berlin.
[5] Sauerbery, G., (1959). *Z. Phys. 155*, 206. [in German].
[6] Bund, A., Baba, A., Berg, S., Johannsmann, D., Lübben, J., Wang, Z., and Knoll, W. (2003). *J. Phys. Chem. B*, *107*, 6743.
[7] Shinbo, K., Kuroki, K., Tesuma, Y., Ohdaira, Y., Baba, A., Kato, K., and Kaneko, F. (2010) *the 2010 International Conference on Solid State Devices and Materials*, A-5-3, 661.

[8] Nagasaki, H., Iwami, K., Tanahashi, T., & Umeda, N. (2010). Proc. SPIE 7544, Sixth International Symposium on Precision Engineering Measurements and Instrumentation, 75442O; doi:10.1117/12.885191
[9] Shinbo, K., Furukawa, H., Ohdaira, Y., Kato, K., & Kaneko, F. (2008). *Thin Solid Films*, *516*, 9020.
[10] Shinbo, K., Otuki, S., Kanbayashi, Y., Ohdaira, Y., Baba, A., Kato, K., Kaneko, F., & Miyadera, N., (2009). *Thin Solid Films*, *518*, 629.
[11] Shinbo, K., Iwasaki, M., Ohdaira, Y., Baba, A., Kato, K., & Kaneko, F. (2011). *IEICE TRANS ELECTRON*, *E94-C*, 1851.
[12] Shinbo, K., Mizusawa, K., Takahashi, H., Ohdaira, Y., Baba, A., Kato, K., Kaneko, F., & Miyadera N., (2011). *Jpn. J. Appl. Phys.*, *50*, 01BC15.
[13] Álvarez, A. L., Tito, J., Vaello, M. B., Velásquez, P., Mallavia, R., Sánchez-López, M. M., Fernández de Ávila, S., (2003). *Thin Solid Films*, *433*, 277.