Study of transient response of QCM odor/gas sensors coated with calixarene LB films

Severino Muñoz (Non member), Takamichi Nakamoto (Member), and Toyosaka Morizumi (Member)

Department of Electrical Engineering, Tokyo Institute of Technology
2-12-1 Ookayama, Meguro-ku, Tokyo 152, Japan

Abstract

The transient responses of quartz crystal microbalance (QCM) odor sensors coated with tert-butyl-calix[6]arene (calixarene) were analyzed. Calixarene is known as a molecule with a particular pot-like shape and large size. The sensor sensitivity is high because of its sensing film porous structure due to the large molecular size. The transient response, as generated by the application of a step variation in the concentration of the odor vapor, possesses useful information about the structure of the sensing film. The transient response can be modeled supposing a sum of two exponential decays with different time constants. The objective of this work is to study the relationship between the transient responses to the vapors and the sensing film structure. Calixarene was deposited as sensing film on a QCM by the Langmuir-Blodgett (LB) method at various deposition surface pressures. The deposition surface pressure modified the film structure and the transient responses. The results showed that the transient sensor response of calixarene film offers useful information for the separation and classification of odor/gas samples.

Key words: calixarene, transient response, odor sensor, LB films, QCM

1. Introduction

There have been a lot of researches in order to enhance the sensitivity and selectivity of odor/gas sensors. We focused on the QCM odor sensor since it is highly effective in the separation and discrimination of odors [1]. The sensitivity enhancement can be achieved by adopting a porous sensing film since the diffusion of the odor/gas molecules into the film occurs. By such a mechanism, the number of adsorption sites inside the film is increased [2]. The selectivity is enhanced by a modification of the adsorption site characteristics to increase the affinity of the film to certain kinds of molecules. There are a lot of methods to increase or generate special kinds of adsorption sites, such as mixed films [2,3], the introduction of molecular spacer such as fullerene [4] and molecules with molecular recognition properties, such as cyclodextrines [5] or supramolecular structures [6].

Calixarenes has a supramolecular structure, whose particular pot-like shape and big size give rise to a special kind of interactions with some small molecules [7]. Because of the large size and shape, the packing density of calixarene is not as good as that of a long chain molecule such as arachidic acid when is used for film deposition by the LB method [8]. Thus, it is used as perforated monolayer [9], which give rise to suitable porous films for gas sensors. The interest in calixarene is also increasing due to its molecular recognition property [7]. Furthermore, its cone-truncated structure with a hydrophobic rim (that with alkyl groups) and a hydrophilic one (that with hydroxyl groups), enables the monolayer formation at the water/air interface and the film can be deposited using the LB method.

In our study, the transient response of an odor/gas sensor, based on a calixarene sensing film deposited on a quartz crystal microbalance (QCM) by the LB method, was analyzed. The sensor is composed of a quartz resonator and a sensing film coated on it. The amount of the shift in frequency is proportional to the mass change due to the vapor sorption [10]. The structure of the sensing film determines the response characteristics of the odor/gas sensor and it influences the types of the sorption such as surface adsorption and penetration inside the film. The transient response has useful information about the sensing film structure and the mechanisms involved in the molecular sorption. Therefore, it can be used as a useful tool in the recognition and classification of gases and odors [11,12].

Although the transient sensor responses of QCM gas sensors have been studied [12,13,14,15], the relationship between the structure of a sensing LB film and the time constant has not been so far revealed. Such relationship is easily obtained when LB film is used. In the present study, the dependency of the deposition surface pressure upon the time constant of the vapor sorption was studied.

2. Experimental

2.1. Sensor fabrication

The molecular structure of calixarene (5,11,17,23,29,35-hexa-tert-butyl-37,38,39,40,41,42-hexa-hidroxy-calix[6]arene) purchased from Tokyo Kasei Kogyo Co., LTD. is shown in
The spreading solution was prepared in chloroform with a concentration of 0.5 mM. Y type LB films were deposited on QCM (AT-cut, 20 MHz, gold electrode) at a speed of 5 mm/min in up and down strokes [2]. The deposition temperature was 22°C and the pH of the subphase was adjusted to 9 using NaOH solution.

In order to investigate the effects given by the structure variation of the sensing film, the depositions of LB films on QCMs at different surface pressures were performed. The pressure was varied from 10 to 35 mN/m increased by 5 mN/m per each step. Calixarene is the appropriate material for studying the dependency of the deposition surface pressure upon the sensor characteristics since it can be deposited over a wide range of surface pressures. The deposition number of layers was 20 in almost all the cases.

2.2 Measurement System

The sensor response measurements were performed in a system with a standard gas generator (Permeator PD-1B, Gas Tech.) based on diffusion method (Figure 2). The system supplies a constant concentration of the sample vapor diluted with a carrier gas, in this case dry air, to the sensor cell. The liquid sample is contained in a diffusion tube with a constant temperature and is allowed to evaporate. If the diffusion rate of the sample and the flow rate of the dilution gas are known, then the concentration can be calculated from the equation (1),

\[
C = \frac{KD_r}{F} \times 10^3
\]

where C is the concentration (ppm), D, the diffusion rate of the sample (µg/min) determined experimentally, F the flow rate of the dilution gas (ml/min) and K a conversion factor. This method has an important advantage in contrast with the bubbling method because there is not aerosol formation.

The gas samples used were benzene, toluene, xylene, ethyl benzene and propylbenzene in ascent order of molecular size. All of them are aromatic derivatives with different molecular sizes and properties due to the modification of the alkyl side chains added to the basic benzene ring. The temperature of the sensor cell was kept at 20°C, and that of the diffusion tube at 50°C. Dry air and the sample gas was alternately switched by means of electronically controlled solenoid valves to realize a step variation in the concentration. The distance between the solenoid valve and the sensor cell should be minimized since it affects the waveform of the transient response. The oscillation frequency shift of the QCM was measured as a sensor response by a frequency counter at a sampling time interval of 1 second and was stored in a personal computer. An example of sensor responses during one measurement cycle is shown in Figure 3. The sensor responses were stable enough to analyze the sensor dynamics.

2.3 Analysis method of transient sensor response

A model of the sensor dynamics is essential for the analysis. The models are considered separately for the rise and the recovery regions, since the applied stimulus is different in both cases (positive and negative steps).

To make the model of the sensor response, the following two assumptions were adopted. First, the applied stimulus, i.e. variation in the concentration of the odor/gas sample, is a pulse with a Tp duration. Since the curve could not be approximated as a first order system, it was adopted a second order one. Therefore, the second assumption is that the transient response can be represented as the sum of two exponential decays with different time constants, i.e., two different sorption mechanisms might work in the case of LB film. The exponential decay assumption can be verified solving the Fick's second law equation [13].

By the convolution of the expressions for the two assumptions [11] the resulting expressions for the response are equations (2) and (3) for the rise and recovery region, respectively.

![Figure 2. Sensor responses measurement system.](image)

![Figure 3. Sensor responses as measured from the system. The sensor film (20 layers) was deposited at 30mN/m.](image)
where \( \Delta f \) is the frequency shift of the QCM, \( c, k \) and \( b \) are constants and \( t_1 \) and \( t_2 \) are time constants. The measured data are processed by means of a computer program to fit the model into the observed data. All the parameters in equations (2) and (3) are obtained after convergence. Although the two time constants are calculated, only the second one (\( t_2 \) and \( t'2 \) in equations 2 and 3 respectively) was stably measured. The first one (\( t_1 \) and \( t'1 \)) was very large in comparison with the other one and had a large fluctuation. Therefore, it is not used and the second one (\( t_2 \) and \( t'2 \)) will be referred as the time constant in the present paper unless mentioned otherwise. The difference between the two time constants (\( t_1 \) and \( t_2 \)) will be discussed later.

### 3. Results and Discussion

#### 3.1. Pressure-area isotherms of calixarene monolayers

The pressure-area isotherm for a calixarene monolayer is shown in Figure 4. The curve consists of various regions, such as gas, liquid and solid-like phase regions, delimited by vertical lines. In the solid-like phase, the calixarene molecules have a parallel orientation, i.e., that with the six hydroxyl groups lying on the water surface (see Fig. 1). The region with the molecular area less than approximately 1.6 \( \text{nm}^2/\text{molecule} \) corresponds to that of the monolayer collapse, where the parallel orientation of calixarene molecules gradually shifts to a perpendicular orientation as is reported by Dei et al. [16]. The deposited mass increased when the deposition surface pressure increased owing to the increment in the packing density as is shown in Figure 5. However, it decreases at 35 mN/m, probably due to the effect of the perpendicular orientation and the decrease in the amphiphilic characteristics of the monolayer.

#### 3.2. Dependency of the transient response upon the film thickness

The curve fitting of the transient responses of QCM sensors with various numbers of LB monolayers (12, 16, 20 monolayers) to toluene in the recovering region are shown in Figure 6. From the figure, we can observe that the recovery time constant (\( t_2 \)) of the response increases with the thickness of the film. This behavior reveals the vapor penetration into the film and that the transport mechanism might be diffusion. Variations in the time constants with the concentration were negligible as it can be observed in the Figure 7, where the time constants in the recovery region obtained for the sensors with 12, 16 and 20 monolayers, respectively, are shown.

In Figure 8 is shown the relationship between the square root of the time constant (\( \tau_2 \)) and the film thickness (\( L \)). As can be seen, the behavior is linear, in concordance with the expression [17]:

\[
L = \sqrt{C \tau_2}
\]
Figure 7. The time constant ($t_2$) and its behavior with the concentration of the gas sample.

than that in the recovery one. The same phenomenon is often seen in dynamics of QCM sensors [10,11], and is a kind of non-linear characteristic, where we must divide the transient response into two phases such as rise and recovery regions, respectively. As the second time constant ($t_2$) was reliable and has the behavior shown in Figure 8, it can be said that the mechanism responsible for this constant is not surface adsorption but diffusion of the odor/gas molecules.

3.3. Dependency of the transient response upon the deposition surface pressure

The steady state responses of the sensors, as a function of the deposition surface pressure of calixarene LB films, measured for benzene, toluene, xylene, ethylbenzene and propylbenzene are shown in Figure 9. As the surface pressure becomes high, the response increases. Such kind of behavior is different from that for long molecules such as arachidic acid with a high packing density. When the surface pressure becomes higher, the number of deposited molecules, i.e. the number of adsorption sites, increase as can be seen in Figure 5. It was also observed that, as the size of the side chain added to the basic benzene ring increases, the sensitivity of the sensors becomes higher as can be seen from the steady state response magnitude in relation with the concentration (Figure 9). However, there is not enough information for discriminating vapors if only the magnitude patterns of the steady state responses output from the films deposited at different surface pressures are compared.

The time constants ($t_2$) calculated for sensors with sensing LB films deposited at different surface pressures to the organic compounds used are shown in Figure 10. From the figure it can be said that, as the size of the vapor molecule increases from benzene to propylbenzene, the time constant becomes higher. The characteristics observed in this figure can be explained taking into account the fact that calixarene is a large molecule (almost 0.9 nm of radius), compared with the odor/gas molecules, and that the space among calixarene molecules becomes smaller as the packing density increases. Then, the diffusion of the odor/gas molecules into the film bulk becomes more difficult, giving origin to an increment in the time constant.

Although the parallel orientation loss of the calixarene molecules at the water/air interface starts at approximately 25 mN/m, it appears dominant after 30 mN/m. In this region, the film is disordered and becomes more porous, making the response faster, especially for ethyl benzene, xylene and propylbenzene. At a deposition surface pressure of 30 mN/m, there is the maximum difference among the time constants. Therefore, that pres-
sure value is the most suitable packing condition for calixarene monolayers before it becomes disordered. We will focus on this point from now on.

20 monolayers of calixarene were deposited on QCM at the surface pressure of 30 mN/m (occupied area, 1.2 nm²/molecule) and the normalized transient responses to benzene, toluene, xylene, ethyl benzene and propylbenzene in the rise and recovery regions are shown in Figures 11 (a) and (b), respectively. The solid lines indicate the results of the curve fitting. As can be observed from the graphs, the time constants (τ₂) for the various samples were different, indicating the different diffusion coefficients of the gas molecules into the films. From this result it can be said that the time constants provide useful information for recognition and classification of odor and gas samples, since the molecular size corresponds to the time constants.

In Figure 12, the values of the parameter b and b' in equations (2) and (3), respectively, are shown. This parameter is the contribution ratio of the term containing τ₂ to that of the term containing τ₁. Since τ₁ is typically much larger than τ₂ and its fluctuation is often large, we do not focus on that value. However, the value of the parameter b was more stable, since the maximum deviation was within 12% of the mean value. The value of

![Figure 11. Comparison between the responses to different samples τ₂. The concentrations are the same as those in Figure 9 and 10. a) Rise region and b) recovery region (Deposition surface pressure 30 mN/m).](image)

![Figure 12. The parameter b calculated from the model equation for different samples in the rise and recovery region, respectively.](image)

4. Conclusions

The transient response analysis of calixarene odor/gas sensors was carried out. A model with two exponential decays with different time constants was used, and there was a good fitting between the experimental data and the calculated values. The results from the time constant study showed that there is almost no effect of surface adsorption and the dynamic behavior in odor vapor sorption seems to be dominated by diffusion. Furthermore, when the appropriate deposition surface pressure is selected, a difference among the time constants for different samples is obtained. Therefore, the time constants can be used for separation and classification of odor/gas samples. Such classification is in relation with the size and probably the shape of the sample molecules. Likewise, the parameter b, the contribution ratio of τ₂ term to that of τ₁, changed remarkably from sample to sample, indicating that it can be also used for separation and classification of odor/gas samples.

A further study of transient analysis for various types of sensing films and gas samples will be performed in the future.

5. References


QCM 旬い/ガスセンサの過去応答

Severino Muñoz Aguirre (non member)
received his B.E. in Electronics Instrumentation from the Veracruz University (Mexico) in 1991 and his M.E from the Center of Research and Advanced Studies (Cinvestav) of the Polytechnic National Institute (Mexico). He was a research assistant at the Department of Electrical Engineering (Cinvestav, Mexico) from 1994 to 1995. Currently, he is studying for the Ph. D. at the Department of Electrical and Electronics Engineering, Tokyo Institute of Technology. He has been working on solid state electronics and his present interest are gas sensors.

Takamichi Nakamoto (Member)

Takamichi Nakamoto received B.E., M.E. and Ph.D degrees from Tokyo Institute of Technology, Tokyo, Japan, in 1982, 1984 and 1991, respectively.

He worked for Hitachi Ltd. from 1984 to 1987. In 1987, he joined Tokyo Institute of Technology as a research associate. He has been an associate professor with the Department of Electrical and Electronic Engineering, Tokyo Institute of Technology since 1993. From 1996 to 1997, he was a visiting scientist at Pacific Northwest Laboratories, Richland, WA. His research interests cover chemical sensing system, neural network and ASIC chip design.

Toyosaka Morizumi (Member)

Toyosaka Morizumi was born in Gunma Prefecture, Japan, on February 19, 1942. He received the B.E., M.E. and Ph.D degrees all in electronics, from Tokyo Institute of Technology, Tokyo, Japan, in 1964, 1966 and 1969, respectively. From 1973 to 1985, he was an Associate Professor of the Department of Electrical and Electronics Engineering, a Professor at the International Cooperation Center for Science and Technology from 1986 to 1988, and he is now a Professor at the Department of Electrical and Electronic Engineering, Tokyo Institute of Technology. He is currently in charge of Institute Senator, Tokyo Institute of Technology. From 1978 to 1979, he was at Carnegie-Mellon University, Pittsburgh, Pennsylvania, U.S.A. as a visiting Associate Professor. He has been engaged in research in the fields of semiconductor thin films, heterojunctions and surface acoustic wave devices. His present interest is bioelectronics and biomimetics; i.e., odor identification systems and gas/odor searching robot systems.