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MULTI-CHANNEL SAW CHEMICAL SENSOR USING 90MHz SAW RESONATOR AND MOLECULAR FILMS DEPOSITED BY DROPLET-SURFACE CASTING METHOD

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Abstract

The objective of the present study is to build a chemical sensor utilizing the feature of a high frequency SAW device for enhansing the sensor sensitivity and the feasibility of making a multi-channel structure on the substrate for integration of plural sensors. We developed the fine casting method (which was named as "droplet - surface casting method"), and deposited several kinds of adsorption films on the channels of a SAW device. The device was ST cut Quartz 90MHz SAW resonator chips, each of which has 2 resonators on a substrate. We constructed 4-channel odor sensing system that have one reference channel and three sensing channels using the two chips, and measured the response patterns of the organic solvents which have same carbon number and different atomic groups.

INTRODUCTION

Chemical sensors using mass loading effect on piezoelectric devices and reversible adsorption have been studied by many researchers. Those devices are quartz crystal microbalance (QCM) or surface acoustic wave (SAW) devices, which are coated with adsorption films. The sensor output is caused by the mass change of the film due to the adsorption of molecules in the vapor or liquid phase onto the films.

In those chemical sensors, a higher frequency response enhances the sensitivity [1][2]. In a QCM, the frequency characteristic is determined by the thickness of the quartz crystal plate. To obtain a high frequency response, the plate must be made thin. So far, the upper frequency limit of the devices are about 60MHz. Molecular or odor recognition using plural sensors with different adsorption films have been studied[3], but it is generally difficult for QCM sensors to be miniaturized

and integrated. As a result, the sensing system is large and complex, and the system property is influenced by the inhomogeneity of gas or liquid flow and temperature ditribution.

In contrast, the frequency response of a SAW device is determined by the period and pair number of an interdigital transducer (IDT), and plural devices can be integrated to compose a multi channel structure. This advantage realizes a multi - channel sensor. However, there exist several difficulties for realizing it. One of them is a film coating method. Adsorption films are deposited on SAW devices by various methods such as casting method, PVD method, etc. Although molecular films such as LB films are appropriate for realizing sensors with quick responses and with biomimetic properties, there are no smart and efficient ways for depositing different LB films on the plural and small SAW channels. In the previous report, we proposed a new coating method which was called "partial casting method", and prepared multi - channel SAW chemical sensors[4].

In this paper, we report the results of a multi-channel SAW chemical sensor system. The sensor comprises four resonators of 90MHz and three kinds of sensing films on ST cut quartz substrates. The films were deposited by the second generation of the method named as "droplet - surface casting method", which was device for coating molecular films on the small area of SAW propagation paths. We measured the output patterns from those resonators to various organic vapors, and found that they can be used for discriminating the vapros.

DROPLET - SURFACE CASTING METHOD AND CASTING SYSTEM

The precise casting method developde in this study is shown schematically in Fig.1. The system consists of a shank pipette for coating the films, another glass tube for adjusting the height of water surface, a lift with speed adjustment, and an X-Y-Z manipulator for positioning the substrate above the pipette.

The method makes use of the water surface segmented by a circular frame of the pippet, and the molecules spread on the surface in the pipette are compressed by the vertical movement of the surface. The compression ratio of the surface area was about 16. The film with a circular shape is finally deposited on the substrate placed on the frame top, though some part of the deposited molecular film is peeled to go back onto the water surface. The serial phenomena during the deposition process

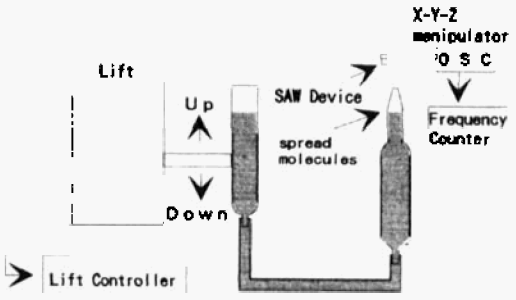

Figure 1. Shematic diagram of the compact casting system in the present study.

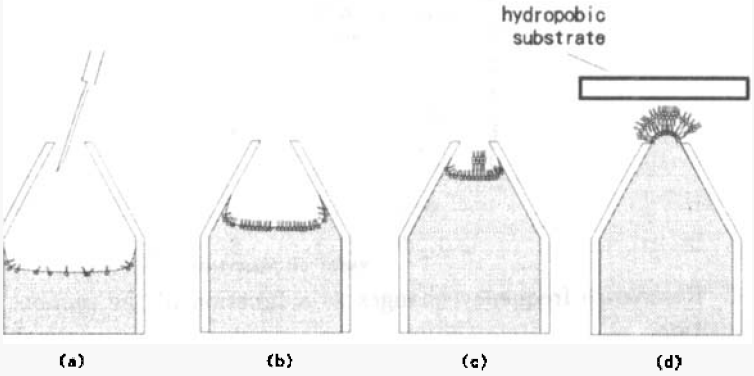

Figure 2. Schematic diagram of the molecular model predicted in the present method.

are illustrated schematically in Figs. 2 (a) to (d).

The concentration of the spread solution and the compression ratio make a significant influence on the uniformity of the film thickness. If the concentration was high and the ratio low, some part of the spread material crystallized on the subphase, giving rise to a very rough film surface. Hence, it is required that the spread film in the stage of Fig. 2 (a) is in a gas or liquid phase on the subphase, and is compressed by the movement of the subphase surface to have the structures of mono-molecular to several-molecular layers in the stage of Fig. 2 (c). For another requirement, the inside surface of the frame must be made hydrophilic in order to keep the contact angle so small and prevent the spread material from attaching to the frame wall. That condition was satisfied by making use of a glass pipette.

The lipid materials used in the present study were polyion complex synthesized by Y.Okahata's lab. and DMPE (dimyristoil phosphortidyl ethanolamine) produced by Tokyo Kasei Co and squalyrium(SQ) synthesized by Dr. L.S.Pu of Fuji Zerox Co. All the molecular scheme are shown in Fig. 3.

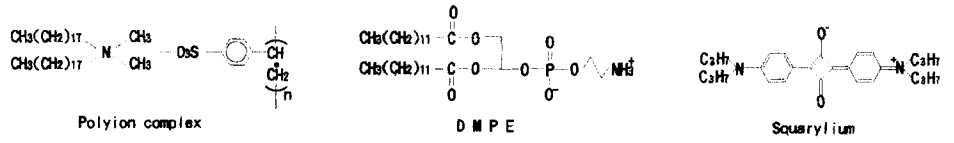

Figure 3. Molecular structures of lipid materials used in the present study.

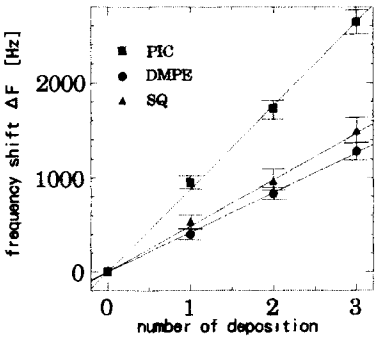

Figure 4. Resonance frequency changes as a function of the number of molecular film deposition.

We studied the deposition properties of the respective lipid materials from the resonant frequency shifts of the SAW devices mentioned below. The result is shown in Fig. 4, and the shifts are found proportional to the deposition number. We confirmed from these results that 2 monolayers in the cases of DMPE and SQ and 3 monolayers in the case of polyion complex were deposited by each deposition.

MULTI-CHANNEL SAW ODOR SENSOR FABRICATION AND PROPERTIES

We prepared sensors using the SAW devices with the configuration shown in Fig. 5. The device has 2 resonators on a ST cut quartz crystal substrate. Since the SAW energy within the cavity concentrates at the center of the resonator, the influence by mass loading is remarkable there. Hence, each of the sensing films was deposited on the IDT within the resonator. The device has a resonance frequency of 90MHz. The sensor system has two chips of the resonators, and three sensing channels with different adsorption films and one reference channel without any film on the device. Each of the channels was connected with a vector impedance meter(HP 4193A), and the frequency property was measured.

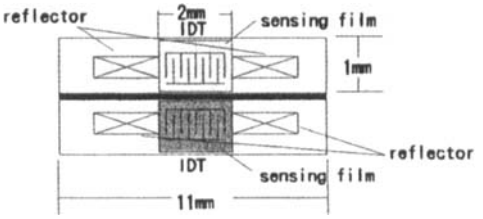

Figure 5. Configuration of SAW chemical sensor used for odor detection. The film was deposited on the IDT within the resorators.

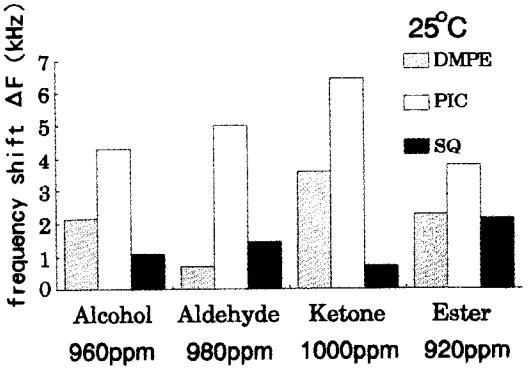

Figure 6. Sensor output pattern (frequency changes of resonance frequency) for different odorant molecules.

The 4 - channel sensor system was installed in the temperature-stabilized (at 25°C) vessel with a volume of 1.1L, and liquid odorant samples were injected into it. The samples are 4 kinds of odors with same number of carbon atoms and with different odorous atomic groups (alcohol, aldehyde, ketone and ester). After vaporization of the samples and confirming the output stabilization, the sensor outputs were taken from the differences between the reference signal and those of the sensing channels. The result is shown in Fig. 6. It is found that different odors gave different output patterns from the sensors. Considering the stability of the present system, the lower limit of the detection was 1.6 $\sim$ 2.5 ppm.

CONCLUSION

In the present study, we developed a compact and precise casting system called "droplet - surface casting method" for deposition of molecular films on a small area of a device surface, and prepared the 4 - channel SAW sensor that had three sensing

channels and one reference one. Each channel had a SAW resonator on a ST cut quartz chip. The sensor gave the output patterns depending upon odorous samples, which showed the possibility of realization of intelligent odor or gas sensors.

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