

Development of a Highly Sensitive Sensing Film of a Gas Sensor by Molecular Arrangement Control of Self-assembled Film

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Summary

We have found that the spatially controlled LB films with polymer backbone were fit for a sensing film of the novel gas sensor using a quartz crystal microbalance with molecular sifter function and high durability. By the systematic optimization of the film fabrication condition such as polymer concentration, number of layers and the dipping conditions of LB films, the sensor sensitivity reached 70 to 100 times of the sensor response of the conventional QCM type gas sensor. The maximum sensor response showed 7000 Hz frequency shift for the small hydrophilic gas molecules such as α -pinene. The QCM type sensor using the newly developed highly organized sensing film would be promising as a high sensitivity gas sensor because of its high S/N characteristics.

Key words: LB film, gas sensor, polymer, quartz crystal microbalance, sensing film, smell

1. Introduction

Nowadays, people tend to yearn for refreshing or something fresh. For instance, where you walk into woods and take a deep breath, you may feel relieved. This is known as "Phytoncid Effect"[1], caused by breathing Terpen-related ingredients emitted by trees. With a high-sensitivity odor sensor imitating human sense of smell and monitoring the surroundings, comfortable environment could be possible.

For this purpose, LB film is one of the best choices. Former study of LB films has made it clear that the molecular area of arachidic acid(C_{20}), the host molecule of the LB film, could be controlled by introducing Fullulene(C_{60}) as a spacer molecule between them[2-6]. With this method, larger odor molecules can be caught by this LB film, which means the higher sensitivity as odor sensor[6-8].

However, the absolute sensitivity and the durability of conventional LB films are still poor and hardly fit for practical use. In order to solve these problems, we added PAH(poly(allylamine hydrochloride)) as a polymer backbone to strengthen the LB film. As a result, the sensitivity and the durability of the sensor using a quartz crystal microbalance have been improved.

Recently, the gas or smell sensor using a quartz crystal microbalance (QCM) [9] increase its importance because it measures the mass of the chemical substance with 1-ng order accuracy, as studied by many researchers [10-12]. These sensors are formed by coating the electrodes with sensing thin films. These sensing films are empirically chosen and there are few reports on the optimum conditions for the fabrication of the structure of sensing films. The new fabrication method that we reported recently for the highly sensitive sensing films with molecular sifter function would be promising for increasing the sensitivity of the QCM type gas sensor because the molecular arrangement of the organized film can be well organized by the LB technique with spacer molecules and the polymer backbone[8].

In this study, we moved on further and have succeeded in depositing 200-Layer LB film, which was impossible to deposit without the help of polymer backbone. The sensitivity of the 200-Layer LB film was improved drastically compared with that of conventional 20-Layer LB film. It has shown great response toward odor gas molecules such as α -Pinene and Citral with different degrees of frequency shift.

2. Experimental Method

All LB films consisted of 20 or 200 monolayers containing spacer molecules (C_{60}) and were deposited on a QCM silver electrode (AT-cut, 10MHz), which was hydrophobically treated with hexamethyldisilazane. The transfer of the monolayers to the substrate was made with a moving-wall type LB trough (Nippon Laser and Electronics Lab., NL-LB240-MWC). The resistivity of the subphase pure water was $18M \Omega \text{ cm}$ and the temperature was kept at 14°C . When the polymer backbone was added to the LB films, 10^{-2} M water solution of poly(allylaminehydrochloride)(PAH) was used as the subphase. The surface pressure during the transfer was 25mN/m . The schematic illustrations of a molecular sifter by LB films containing spacer molecules are shown in Fig.1.

As shown in this figure, polymer backbones were added to the LB films with spacer molecules just like the cytoskeleton in the biological cell membrane. These backbones are introduced by adding the polyelectrolyte, PAH, into the water subphase during the deposition of the LB films. The backbone polymers are added to every bilayer through electrostatic interactions between negative charge in the carboxyl group (COO^-) and the positive charge in the amine (NH_3^+).

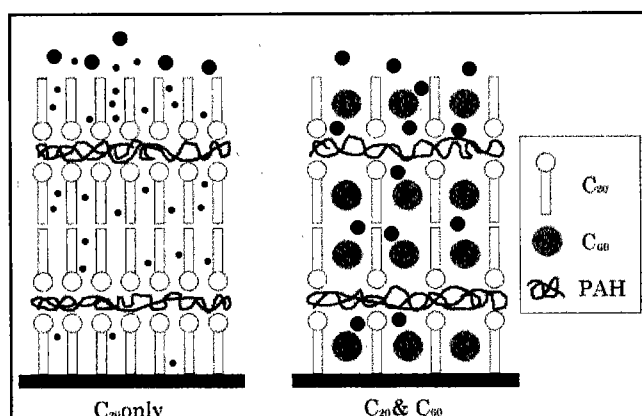


Fig.1 Schematic illustrations of the LB films with polymer backbones between bilayers.

The amount of gas molecules adsorbed on the LB films were measured at room temperature, in a closed glass cell, according to the reported method[10,11]. All the gases examined in this experiment were adjusted to approximately 0.2 vol.%. Gas molecules with different molecular sizes, such as benzene, 2-pentanone,

ethylbutylate, α -pinene, linalool, and citral were used in this study.

3. Results and Discussion

The frequency shift of the QCM to α -pinene gas for the sample of 20 layers of LB films with C_{60} spacer molecules is shown in Fig.2. In this experiment, the sensor was inserted in the sample bottle at the time indicated as 0 sec, and it was removed from the bottle after 6 min. As shown in the figure, for the LB films which did not contain PAH, the sensor response was 80Hz. On the other hand, for the LB films which contained PAH, it was increased up to 200Hz. We consider that this was because the intermolecular distance of the film was controlled well by using the polyelectrolyte as the polymer backbone.

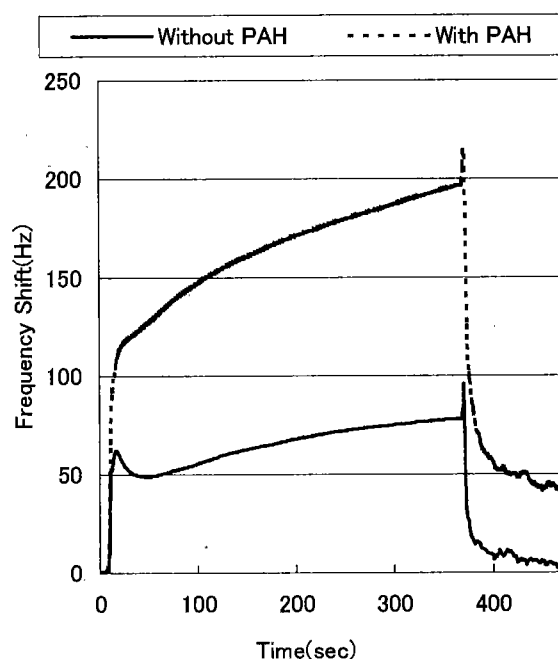


Fig.2 Comparison of the sensor response to α -pinene gas for the sensing films with and without the polymer backbone.

When the LB film contain C_{60} as the spacer molecules, we could not succeed in depositing more than 60 layers. However, when the polycation such as PAH was melted in the water subphase, it was very easy to deposit LB films up to 200 bilayers. The two results are shown in Fig.3 for comparison. In this figure, two quartz crystals were used as the substrates for LB films and the frequency shift for the film with PAH was compared with that without PAH.

These results indicate that the molecular arrangement of the LB films including spacer molecules is highly organized by introducing the polymer backbone in each layer. We consider that this organization was caused by the phenomenon that the C_{20} molecules in the LB films was anchored with each other to polymer thread introduced from water subphase.

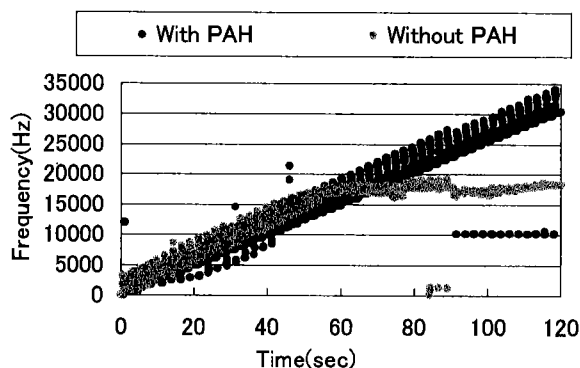


Fig.3 Difference in weight increase of LB film deposited with and without PAH. (straight line: deposition with PAH, curve line: deposition without PAH)

The changes of the sensor responses in a static system with the increase of the number of layers are shown in Fig.4. With the increase of the number of layers, the sensor response increased drastically. Since it was confirmed that the QCM showed linear relationship up

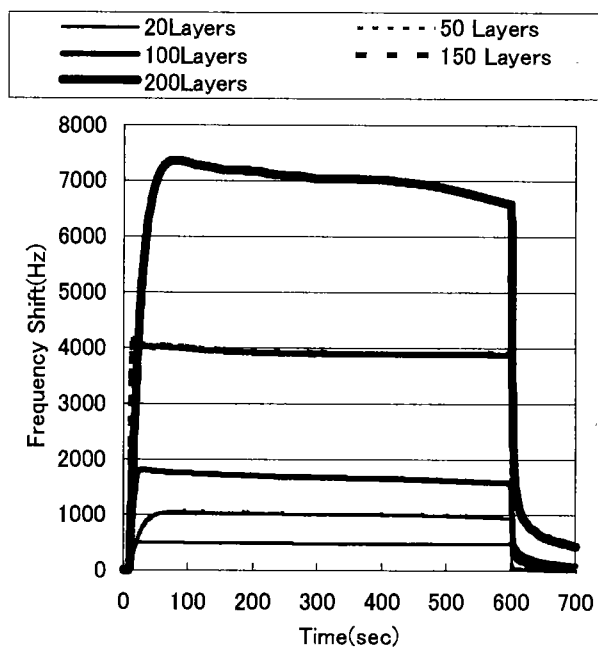


Fig.4 The changes of the sensor responses with the increase of the number of layers of LB films (static system).

to the frequency shift of 30000Hz, the measured value of the sensors are good enough within the range of the instrumentation.

Therefore, we consider that the sensor response increased drastically because the intermolecular space, the path for the gas molecules into the LB films, was secured with the increase of the number of layers.

Another possible reason for the drastic sensitivity improvement of the sensing film with the increase of the number of layers is that the gas molecules can stay longer in a very stable state at the deep part in the sensing film. Generally, the molecules near the surface of the sensing film are considered to be very unstable and occasionally repeat adsorption and desorption. On the other hand, however, the gas molecules inside the sensing film can stay longer in the sensing film because they strongly trapped to the film molecules by the obstacles of the other trapped gas molecules.

Nevertheless, the very quick recovery characteristics of the sensors also can be seen in Fig.4.

These experimental facts of the quick responses of the sensors support the model of the highly organized molecular arrangement of the molecules in the sensing films as shown in Fig.1.

Next, the 3-D chemical structures of the gas molecules used in this study are shown in Fig.5. The molecular weights are also shown in the same figure.

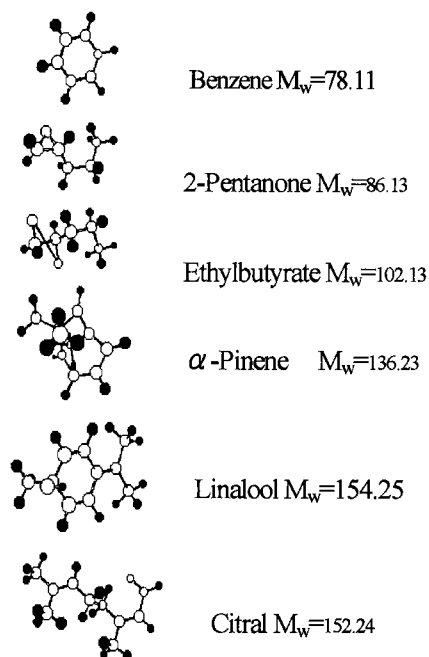


Fig.5 Chemical structure of the gas molecules

The sensor response to various gas molecules was examined in a gas flow system. The results are shown in Fig.6. In this measurement, the flow rate of the carrier gas was 120ml/min, sample quantity was 4ml, smell supplying time was 30 sec.

In this figure, the sensor showed the highest response to benzene, the smallest gas molecule in this experiment. And the order of the sensor responses was exactly in accordance with that of the size of the gas molecules shown in Fig.5.

Consequently, high selectivity of the newly developed sensing film was clearly demonstrated in a gas flow system.

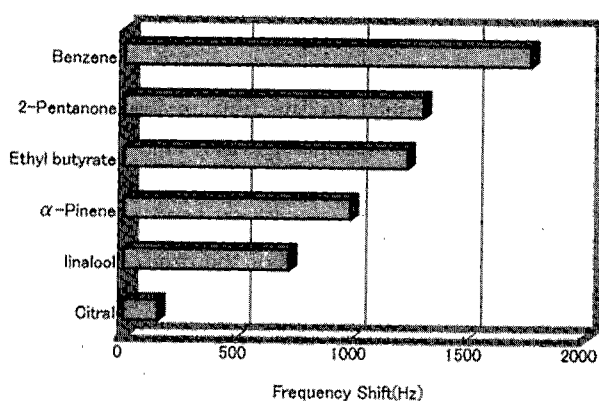


Fig.6 Sensor responses in gas flow system

Though the data is not shown here, the highly ordered molecular arrangements were also confirmed by the microscopic observation of the cross-sectional image of LB film using an atomic force microscopy. Therefore, we consider that by the systematic optimization of the sensing film structure, a novel smell sensor with molecular sifter function and remarkably high sensitivity was established.

Conclusions

It was demonstrated that by controlling the molecular organization in the sensing film using spacer molecules and polyelectrolytes, high performance sensing film with high sensitivity and molecular sifter function for gas or smell sensor was established. The molecular arrangement design in the self assembled film would be very promising for the construction of a high performance gas sensor.

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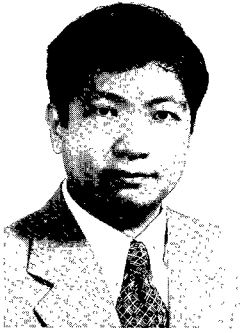
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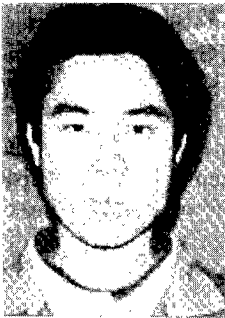
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