Paper

Removal of Ammonia Gas by using Layer-by-Layer Self-Assembly Film

Non-member Masashi Kikuchi (Keio University)

Non-member Yuji Inami (Keio University)

Member Seimei Shiratori (Keio University)

Department of Applied Physics & Physico-Informatics, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, kouhoku-ku, Yokohama 223-8522, Japan
TEL/FAX ++81-45-566-1602
shiratori@appi.keio.ac.jp

A high performance chemical filter for ammonia gas was established by forming the layer-by-layer self-assembly film on the surface of glass fiber. The filter was superior to active carbon filter in the case of removing ammonia gas. The newly developed filter showed remarkably high performance because it can adsorb large amount of odor molecules by chemical adsorption. Ammonia gas react with the polyelectrolytes in the film and was adsorbed into the multilayers of the film. In this paper, we report the high performance filter which can remove ammonia gas.

Key words: layer-by-layer, self-assembly, thin film, polyelectrolyte, ammonia, filter, glass fiber

1. Introduction

Air filter for gas molecules was required in various places, such as clean rooms for semiconductor technology, airports, stations and public transportation such as railways. The conventional air filters have high performance to dust, however, they are not superior in adsorbing toxic gas.

Recently we found that layer-by-layer self-assembly film had the property of adsorbing not only colloid aerosol such as smoke from a cigarette but also toxic gas such as ammonia. The film adsorb colloid aerosol by physical adsorption and adsorb the specific gas molecules by chemical and physical adsorption.

In this study the property of the adsorbing characteristics for ammonia gas of the thin polymer film was evaluated by using quarts crystal microbalance (QCM) method, and the filter was fabricated by depositing the layer-by-layer self-assembly film on glass fiber cloth.

Recently, we developed an automatic dipping machine for the fabrication of the mass-controlled layer-by-layer self-assembly film.[1] By using this machine, we can deposit layer-by-layer self-assembly film on QCM or glass fiber with various experimental condition, such as the composition ratio of polyelectrolyte, solution pH, and number of bilayers.[2]

By depositing the layer-by-layer sequential adsorption film on the glass fiber cloth, a high performance filter for ammonia gas was fabricated. In this study we report the initial experimental results on the performance of the newly fabricated filter.

2.Experimental Method

2-1 Absorbance spectrum using Fourier transform infrared spectroscopy (FT-IR)

Poly (acrylic acid) (PAA) cast films were formed on two Si wafer substrates, one of the PAA cast film was exposed to ammonia atmosphere for 15h. The absorbance spectrum was measured by FT-IR in order to investigate the change of the chemical bonding before and after exposing to the ammonia gas.

2-2 Measurement of frequency response of Layer-by-layer self-assembly film on QCM with various polyelectrolytes

Multilayer polyelectrolyte films were deposited on QCM. The QCM substrate was first immersed in solution of ($KOH : H_2O : C_2H_5OH = 1 : 40 : 60$) in weight. In this way, the substrate was being hydrophilic. After rinsing and drying, the substrate was immersed in a polycationic solution (10^{-2} M) for 1 min. In

this way, the substrate was covered with polycationic layer. After rinsed 3 times for 1 min each, the substrate was transferred into a polyanionic solution (10^{-2}M) for 1 min and rinsed. Thus, an alternating multiplayer film was obtained by repeating the above steps in a cyclic fashion.

The experimental setup was shown in Fig.1. As show in the figure, ammonia gas was injected in the sample bottle (55ml). The gas was kept at the concentration of 300ppm. The QCM was put into the sample bottle for 10 minutes and frequency shift for observing gas adsorption to self-assembly film was measured. Then the QCM was taken out of the sample bottle and frequency shift to measure gas desorption from self-assembly film was measured.

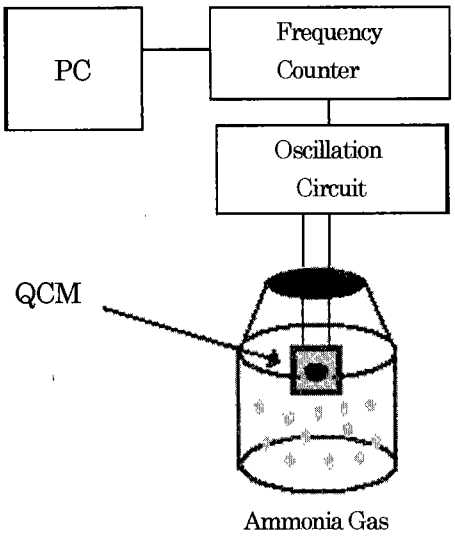

Fig.1 Experimental setup

In this experiment the following polymers were used. Poly (allylamine hydrochloride)(PAH), Poly (acrylic acid)(PAA), (poly (sodium 4-stylenesulfonate)(SPS), (poly (bis (2-chloroethyl) ether-alt-1,3 –bis[3-(dimethylamino)propyl] urea (PBCE). PAH and PBCE are polycation, PAA and SPS are polyanion.

Layer-by-layer self-assembly films of PAH/PAA, PBCE/PAA, and PAH/SPS were deposited on the electrode of QCM and the frequency shift of these were compared. The pH of polycationic solution and polyanionic solution was adjusted to 3.5.

2-3 Evaluation of performance of the filter for ammonia by flowing gas system

The performance of the filter was evaluated by using flow experimental system. The experimental setup was shown in Fig.2 and Fig.3. Fig.2 is the flow system of permeater to produce the ammonia gas with a constant concentration. As show in the Fig.3, the ammonia filter was fabricated by depositing the film on glass fiber. The gas after passing through the filter was gathered in a sampling bag. After filling ammonia gas in vinyl bag gas concentration was measured by using a gas detector (Gastec No.3L).

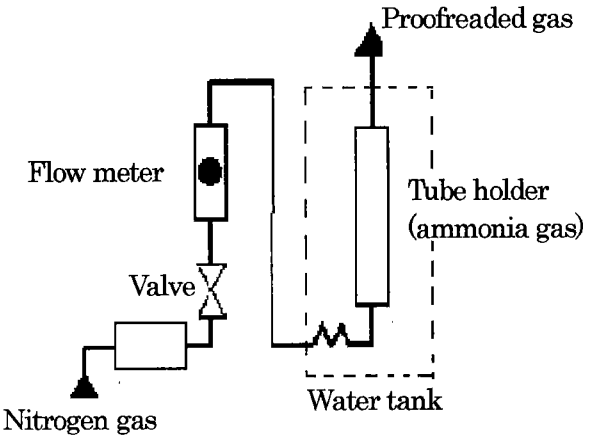

Fig.2 Gas proofreading device

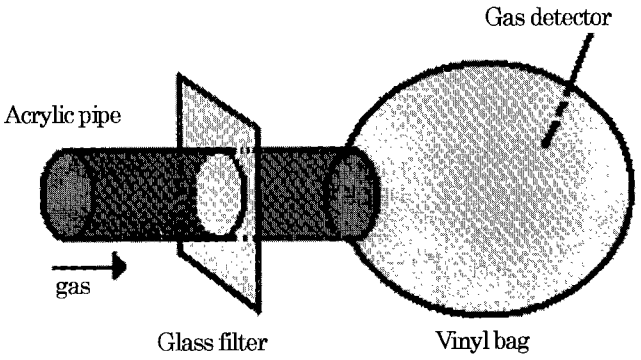

Fig.3 Experimental setup

2-4 Evaluation of connection of gas velocity and performance of the filter

Performance of the filter was measured in various velocity of the ammonia gas. Gas velocity was controlled by adjusting the diameter of the acrylic pipe.

2-5 Evaluation of durability of the filter

Durability of this filter was compared with that on the market. This comparison was performed by using the flow experimental system. The ammonia filter and active carbon filter was set on experimental equipment. The velocity of ammonia gas was fixed on 30 [cm/sec], and the concentration was fixed on 8 [ppm]. The concentration of ammonia gas after passing through the filter was measured by using a gas detector every one hour.

3. Results and Discussions

3-1 Absorbance spectrum using Fourier transform infrared spectroscopy (FT-IR)

The peak of absorbance spectrum exists in the range of 1600~1680 [cm^{-1}] in PAA casting film after exposed to ammonia atmosphere. Otherwise, the peak was not observed in PAA cast film.

Ammonia gas (NH_3) reacts with PAA as shown in the following reaction formula (A)

$$R\text{-}COOH + NH_3 \Leftrightarrow R\text{-}COO^-NH_4^+ \quad (A)$$

This result shows that PAA react with ammonia. In this experiment, we found that PAA adsorb with ammonia molecules chemically.

3-2 Measurement of frequency response of Layer-by-layer self-assembly film on QCM with various polyelectrolytes

The results of the frequency response of layer-by-layer self-assembly film on QCM with various polyelectrolytes are shown in Fig.5. Frequency shift between before and after being fabricated film was shown in Table 1.

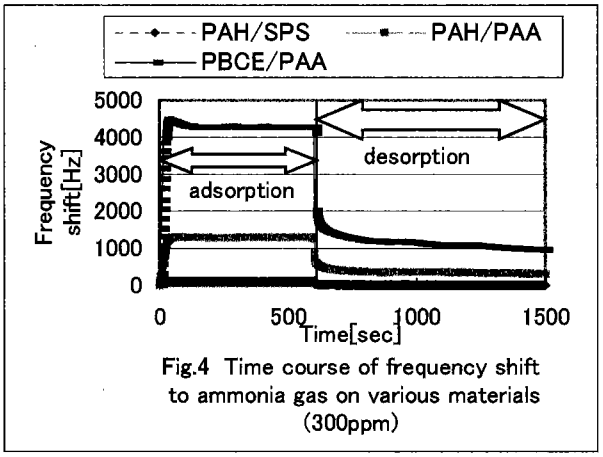

Fig.4 Time course of frequency shift to ammonia gas on various materials (300ppm)

Table 1 Mass of polymer films

Polycation / Polyanion	Frequency shift[Hz]
PBCE/PAA	19200
PAH/PAA	4550
PAH/SPS	1590

As shown in Fig.4, the multilayer film on QCM substrate responded ammonia gas molecules. The frequency shift was the same as in the order of the quantity of the polymer films, PBCE/PAA (4280Hz), PAH/PAA (1230Hz), PAH/SPS (110Hz). PAH/SPS film showed little response to ammonia. It is considered that SPS doesn't adsorb ammonia, because PAH/SPS layer-by-layer self-assembly film thickness was relatively small compared with the other samples. On the other hand, PBCE/PAA film showed very large response to ammonia. It is considered that, almost all the PBCE (strong base) was electrically dissociated, the large electric charge adsorb the large quantity of PAA molecules as adsorbing layer above PBCE layer. Consequently, the thickness of the layer-by-layer self-assembly film of PBCE/PAA film was very large and as the result, the large quantity of ammonia gas was adsorbed in the PAA layer. Since the PAA polyelectrolyte is water soluble, it cannot form a stable coating film on glass fiber cloth, however, by using the alternate deposition technique, thick and stable PAA layer was coated on the surface of glass fiber cloth.

Frequency shift of the QCM was decrease in the desorption process. The reason was considered that the film absorb ammonia molecules not only by chemically but also by physically, and the physically adsorbed gas molecules was removed easily.

3-3 Evaluation of performance of the filter for ammonia and acetaldehyde flowing gas system

Ammonia gas concentration after passing through the filter as a function of number of bilayers is measured and shown in Fig.5. The measurement result without filter was the same to result of the bare glass filter (0 bilayer). As shown in this figure, ammonia filter with 100bilayers removed 96% of ammonia gas. It is considered that the since the carboxylic acid of each PAA layer adsorb ammonia gas effectively, the layer-by-layer self-assembled filter successfully worked in the condition of gas flowing system.

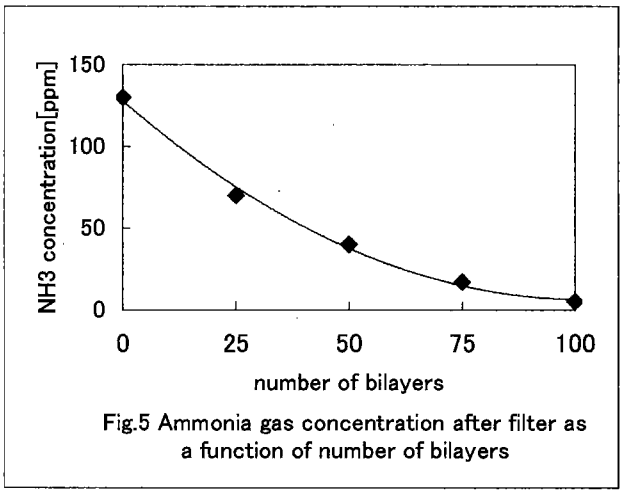

Fig.5 Ammonia gas concentration after filter as a function of number of bilayers

3-4 Evaluation of connection of gas velocity and performance of the filter

Ammonia gas concentration after passing through the filter as a function of gas velocity is shown in Fig.6.

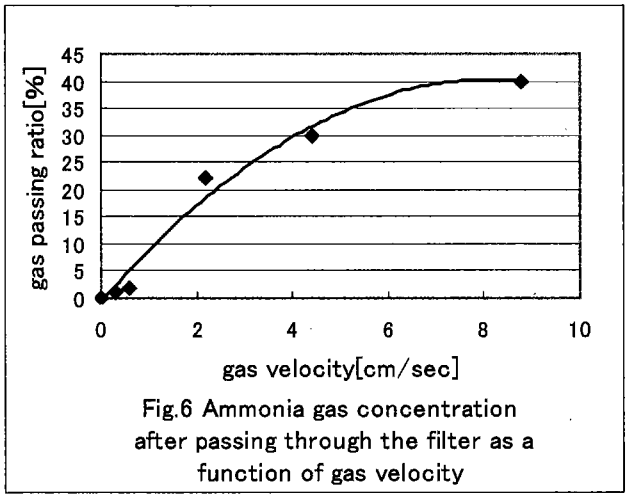

Fig.6 Ammonia gas concentration after passing through the filter as a function of gas velocity

The filter showed high performance in lower gas flowing velocity, however, in higher gas flowing velocity, the performance of this filter was not so high. We consider that since it takes time for chemical adsorption, the polyelectrolytes of the filter could adsorb ammonia gas much effectively when the gas flowing velocity was lower.

3-5 Evaluation of durability of the filter

Durability of the newly fabricated filter was examined by measuring the transient characteristics of the ammonia gas concentration after passing through the filter. The result was compared with the commercially available active carbon filter and shown in Fig.7.

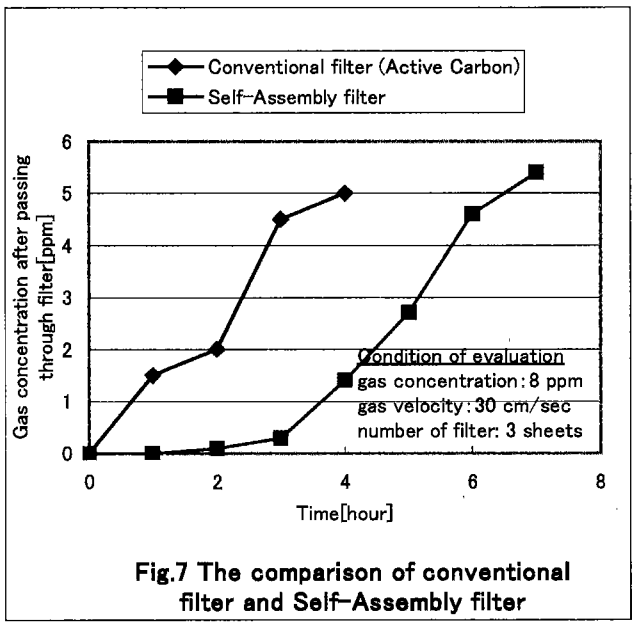

Fig.7 The comparison of conventional filter and Self-Assembly filter

In the aspect of the durability of these filters, the ammonia filter showed much superior performance to the active carbon filter. The breakthrough time was 6 hours for the newly fabricated filter. On the other hand, it was 3 hours for the active carbon filter on the market. It was shown that chemical adsorption is more effective than physical adsorption for removing ammonia gas.

4. Conclusion

High performance filter for ammonia gas was fabricated by depositing layer-by-layer self-assembly film on glass fiber cloths. PAA layer in the thin film chemically adsorb ammonia gas. By using the alternate deposition of layer-by-layer self-assembly technique, the multi layers of the PAA in the filter adsorb ammonia gas effectively. We consider that this technique was very promising for constructing the high performance filter to remove toxic gas such as ammonia.

Acknowledgements

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References

[1] Seimei S. Shiratori and Masayoshi Yamada, "Nano-scale Control of Composite Polymer Films by Mass-controlled Layer-by-Layer Sequential Adsorption of Polyelectrolytes", to be published in Polymers for Advanced Technologies, 2000

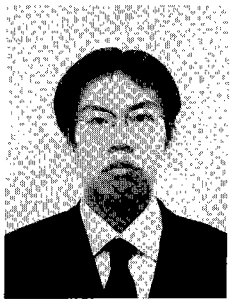
[2] Seimei S. Shiratori, Yuji Inami, Masashi Kikuchi and Takeshi Yamada "Thin Polymer Films for the Filter of an Air cleaner Fabricated by Mass-controlled Layer-by-Layer Adsorption of polyelectrolytes" The 5th International Symposium on Polymers for Advanced echnologies, PAT-99-Tokyo, Abstracts p.253, August 31-September 1999

[3] G.Sauerbrey "Verwendung von Schwingquartzen zur Wagung dunner Schichten und zur Mikrowagung", Zeitschrift fur physik, Vol.155, p.206-222, 1959

[4] K. Kenji Kanazawa and Joseph G. Gordon II "The oscillation frequency of a quartz resonator in contact with a liquid" Analytica Chimica Acta 175 (1985) 99-105

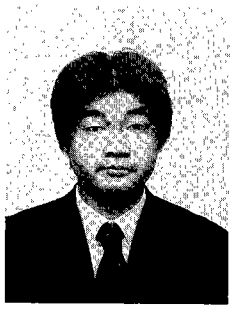
[5] S. Bruckenstein and M. Shay "Experimental aspects of use of the quarts crystal microbalance in solution" Electrochimica Acta Vol.30 No.10 p.1295-1300, 1985

Masashi Kikuchi



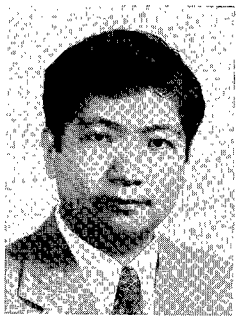
(nonmember) Masashi Kikuchi is a graduate student of department of Applied Physics and Physico-informatics of Keio University. He is engaged in the research on fabrication and evaluations of gas sensors and chemical gas filters.

Yuji Inami



(nonmember) Yuji Inami is a graduate student of department of Applied Physics and Physico-informatics of Keio University. He is engaged in the research on thin film fabrication and the evaluation.

Seimei Shiratori



(Member) Seimei Shiratori was born in Yokohama, Japan in 1963. He graduated from Waseda University in 1987. He received a Master of Engineering degree and a Ph.D. from Tokyo Institute of Technology in 1989 and 1992, respectively. He was appointed an instructor in the Department of Instrumentation Engineering at Keio University in 1994 and assistant professor in the Department of Applied Physics and Physico-informatics in 1997. Until March 1998, he stayed at Massachusetts Institute of Technology as a visiting scientist for one year. He is now an associate professor of the Department of Applied Physics and Physico-informatics of Keio University. He is engaged in research on electronics using organic thin films.