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A Smart Ammonia Gas Sensor Using QCM with Plasma-Polymerized Membrane

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Quartz resonator gas sensors coated with films of styrene, allylamine, acrylic acid or methacrolein as the molecular recognition membrane are prepared using plasma-polymerized CVD. The sensor coated with acrylic acid film exhibits an excellent selectivity and a high sensitivity for ammonia gas. This sensor is useful in a sensor array in conjunction with pattern recognition analysis for identification of gases and odors.

1. Introduction

A quartz crystal resonator provides a very sensitive mass-measuring device at nanogram levels because of the resonance frequency changes caused by the deposition of a given mass of a material on the electrode of the quartz crystal. Synthetic polymer-film-coated quartz resonators have been studied as sensors for various gases, because a quartz resonator coated with a sensing membrane works as a gas sensor. In recent years, considerable interest has arisen in the use of arrays of quartz resonator gas sensors in conjunction with associated pattern recognition analysis for the identification of odors, fragrances and aromas.[1–8)]

We have previously reported that quartz resonator gas sensors coated with propylene-butyl, polycarbonate and acrylic-resin film exhibit high sensitivity for toluene, dimethylamine

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and acetaldehyde gas, respectively.[9] The objective of this paper is to demonstrate a plasma-polymerized-film-coated sensor with excellent selectivity and high sensitivity for ammonia gas.

2. Experimental

Commercially available AT-cut 9 MHz quartz resonators with Au electrodes, which were coated with plasma-polymerized membranes such as styrene, allylamine, acrylic-acid or methacrolein films, were prepared using a plasma chemical vapor deposition (CVD) apparatus (Samco International Co., LTD. : Model BP-1) as shown in Fig. 1. The membrane film was deposited on the electrode of the quartz resonator by a plasma polymerization of a monomer such as styrene (boiling point: 145.1°C), allylamine (b.p.: 53.0°C), acrylic acid (b.p.: 146.1°C) or methacrolein (b.p.: 69°C) at a pressure of 100 Pa with an rf power of 100 W. The chemical structure of each monomer is shown in Fig. 2. The monomers styrene, allyamine, acrilic acid and methacrolein were vaporized at 60°C, 20°C, 30°C and 20°C, respectively, and supplied to the CVD chamber. The thickness of each film can be controlled by the temperature and the deposition time. It was confirmed that the film thickness increased monotonically with increasing deposition time under a constant vaporizing temperature for each monomer. The film was coated on the quartz resonator until the frequency was changed to 6 kHz.

The frequency of the vibrating quartz resonator gas sensor, which decreases with increasing gas adsorbed on the sensing membrane, was measured using a frequency counter connected to a personal computer. A constant amount of a gas such as acetaldehyde, benzaldehyde, ammonia, trimethylamine, propionaldehyde, ethylacetate, xylene, toluene, aceton, chloroform, diethylether, dimethylamine, ethanol, methanol, methane,

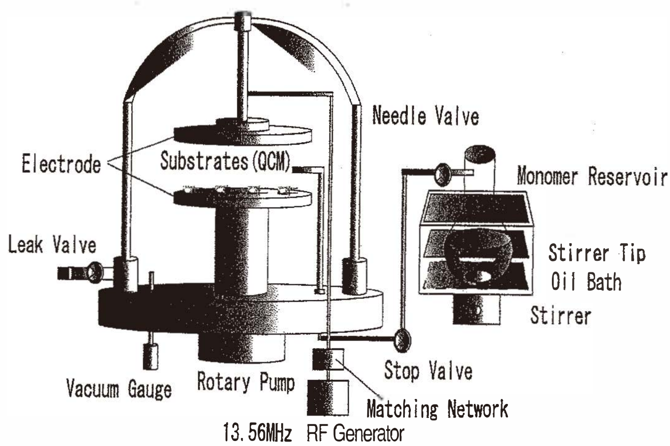
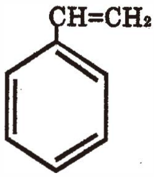


Fig. 1. Schematic diagram of plasma CVD apparatus.



styrene b.p. : 145.1℃

$CH_2{=}CH{-}CH_2NH_2$

allylamine b.p. : 53.0℃

$CH_2{=}CH{-}COOH$

acrylic-acid b.p. : 141.6℃

$CH{=}C(CH_3)CHO$

methacrolein b.p. : 69℃

Fig. 2. Chemical structure of each monomer.

propane, hydrogen, 2-propyl alcohol, butane or octane was injected into the sensing chamber as shown in Fig. 3. The frequency change Δf of the sensor as a function of time was measured immediately after the gas was injected into the chamber.

3. Results and Discussion

It was found that an acrylic-acid-film-coated sensor exhibited an excellent selectivity for ammonia gas while the other three sensors coated with styrene film, allylamine film and methacrolein film exhibited no selectivity for any gas. Figures 4 (a) and 4(b) show a typical transient response of the acrylic-acid-film-coated sensor for ammonia (10,000 ppm) and other gases, respectively. The acrylic-acid-film-coated sensor exhibited no response to gases such as benzaldehyde, trimethylamine, propionaldehyde, ethylacetate, xylene, toluene, acetone, chloroform, diethylether, dimethylamine, ethanol, methane, propane, hydrogen 2-propyl alcohol, butane and octane but did respond to ammonia, methanol and acetaldehyde. Figure 5 shows a typical transient response of the styrene-film-coated sensor for various gases, indicating that the sensor exhibits no selectivity for a specific gas. It was confirmed that the methacrolein-film-coated sensor and the allylamine-film-coated sensor exhibited low sensitivity for all gases tested. Since the acrylic-acid-film-coated sensor exhibited good selectivity for ammonia gas as shown in Fig. 3, we measured the responses of this sensor for ammonia gas in detail.

Figure 6 shows typical responses of the acrylic-acid-film-coated sensor for ammonia gas at various concentrations. It can be seen that the sensor responses were saturated at about 2 min after the gas was injected into the sensing chamber. Figure 7 shows the sensitivity of the sensors as a function of ammonia gas concentration, indicating that the

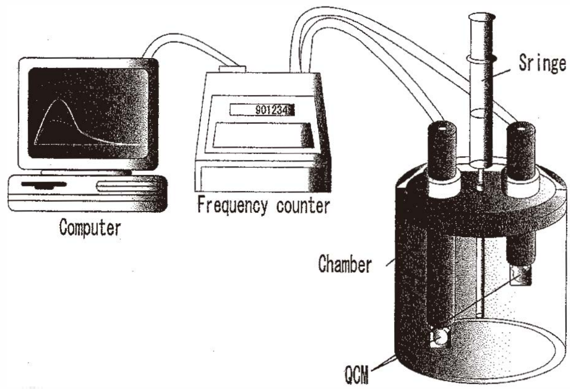


Fig. 3. Schematic diagram of the sensing chamber.

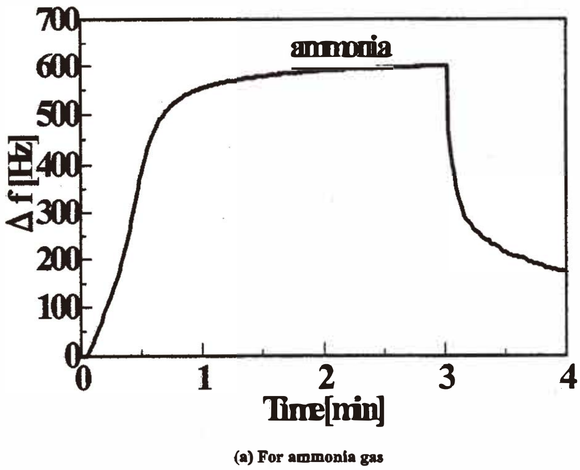


Fig. 4(a). Transient responses of the acrylic-acid-film-coated sensor for various gases: ammonia gas.

sensitivity of the sensor for ammonia gas increases with increasing ammonia concentration. It was confirmed that the sensor responded to the ammonia gas at a concentration of about 1 ppm. This is not sufficient for the technological application of our sensor in environmental monitoring. Further studies on the development of a sensor with higher sensitivity for ammonia gas have to be carried out. The results described above, however, suggest that the acrylic-acid-film-coated quartz resonator sensor with excellent selectivity for ammonia gas is useful for the detection of ammonia gas. These results can be explained by considering that polymer membranes with carboxyl radicals such as acrylic acid have a tendency to chemically adsorb ammonia.[10]

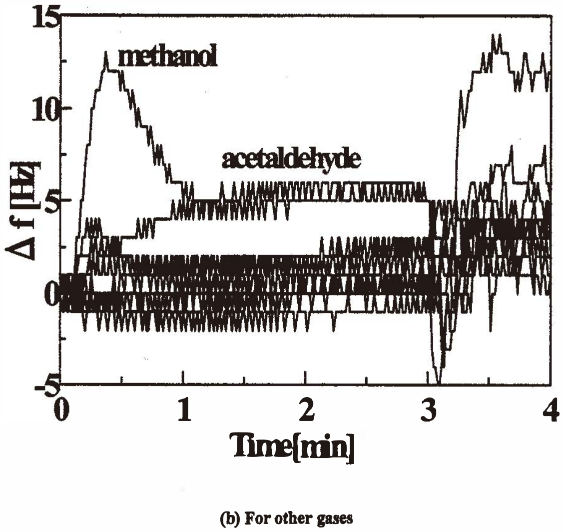


Fig. 4(b). (continued) Transient responses of the acrylic-acid-film-coated sensor for various gases: other gases.

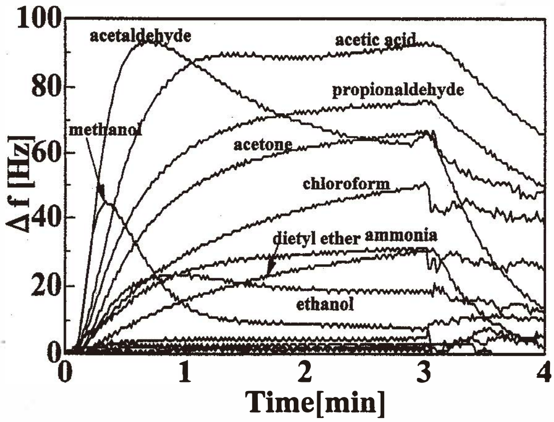


Fig. 5. Transient responses of the styrene-film-coated sensor for various gases.

In order to study why the QCM sensor coated with acrylic-acid film has excellent selectivity and high sensitivity, we fabricated sensors coated with thin films of methyl acrylate, vinyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, tert-butyl acrylate, iso-butyl acrylate, n-hexyl acrylate and 2, 2, 2-trifluoroethyl acrylate and measured the responses of these sensors to various gases.

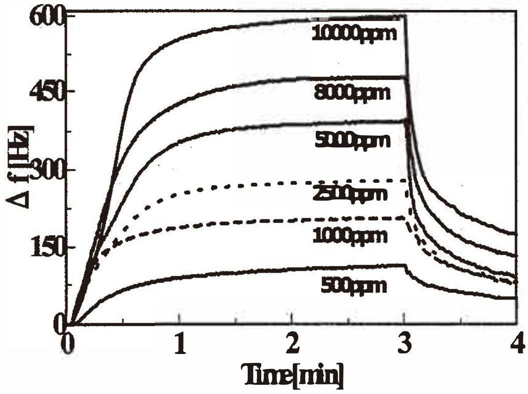


Fig. 6. Transient responses of the acrylic-acid-film-coated sensor for ammonia gas at various concentrations.

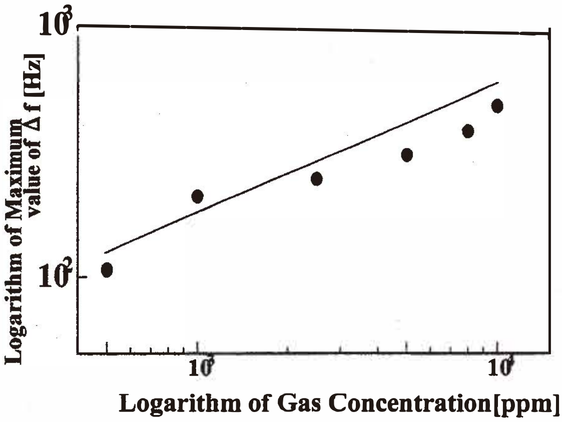


Fig. 7. Frequency change Δf of the acrylic-acid-film-coated sensor as a function of ammonia gas concentration.

The sensors coated with thin films of vinyl acrylate, ethyl acrylate, n-propyl acrylate, and tert-butyl acrylate exhibited an excellent selectivity and high sensitivity for ammonia. Sensors coated with thin films of n-butyl acrylate and n-hexyl acrylate responded to acetic acid gas, although the sensors also exhibited high sensitivity for ammonia gas. The sensor coated with 2, 2, 2,-trifluoroethyl acrylate which does not have excellent selectivity for ammonia exhibited high sensitivity for acetaldehyde, ammonia and ethanol gas. The responses of the sensors coated with acrylate films for various gases are listed in Table 1. The study to clarify the mechanism which accounts for the acrylic-acid-film-coated sensor's excellent selectivity for ammonia gas is now underway.

Table 1
Responses of sensors coated with acrylate films for various gases. ◎: highly sensitive, ○: relatively highly sensitive, △: sensitive and ×: not sensitive.

	ammonia	acetic acid	acetaldehyde	ethanol	others
Acrylic acid	◎	×	×	×	×
Methyl acrylate	◎	△	×	×	×
Vinyl acrylate	◎	×	×	×	×
Ethyl acrylate	◎	×	×	×	×
n-Propyl acrylate	◎	×	×	×	×
n-Butyl acrylate	○	◎	×	×	×
tert-Butyl acrylate	◎	×	×	×	×
iso-Butyl acrylate	○	○	×	×	×
n-Hexyl acrylate	○	○	×	△	×
2,2,2-Triflouroethyl acrylate	○	×	◎	×	×

4. Conclusions

Four gas sensors using quartz resonators coated with a thin film of styrene, allylamine, acrylic acid or methacrolein as the molecular recognition membrane were prepared using plasma CVD. The transient responses of each sensor were measured during exposure to various gases. The acrylic-acid-film-coated sensor exhibited excellent selectivity for ammonia gas, indicating that this sensor may be useful as a gas sensor in conjunction with pattern recognition analysis for identification of odors, fragrances or aromas.

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