Characteristics of the TiO2/SnO2 thick film semiconductor gas sensor to determine fish freshness

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ABSTRACT

This study is to investigate the use of TiO2, Pd, Pt, In, Ru, and Rh in a gas sensor material, which greatly improves the sensitivity of detecting trimethylamine gas. The metal-SnO2 thick films are prepared by screen-printing method onto Al2O3 substrates with platinum electrode. The sensing characteristics are investigated by measuring the electrical resistance of each sensor in a test box as a function of gas concentration. This is then used to detect trimethylamine, dimethylamine and ammonia gases within a concentration range of 100–1000 ppm. The gas sensing properties of metal-SnO2 thick films depend on the kind and the amount of metal added. The sensor material of SnO2 containing 1 wt.% Pd and 10 wt.% TiO2 shows the best sensitivity to TMA gas and good selectivity to dimethylamine and ammonia gases with respect to TMA gas at 250°C.

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1. Introduction

Nowadays, with the enforcement of ISO 9000 system, people are concerned more about the safety problem of their foods so that the scientific system of a safety inspection of foods is required. Especially, the freshness of fishes needs to be determined correctly in terms of the quality of raw material and the safety and sanitary conditions of processing function. As the decomposition fashion of fishes varies a lot depending on the kinds of fishes, the condition of muscle of fishes, and also the condition of preservation, it is important to develop a method of testing the freshness of fishes rapidly before they are destroyed.

The methods used to test fish freshness so far include sensory evaluation, measurement of specific gravity, pH test, ammonia test, protein precipitation, measurement of volatile basic nitrogen (VBN), the chemical change in the reaction of ATP decomposition, and quantitative measurement of trimethylamine. Among these methods, sensory evaluation and measurements of specific gravity and pH do not give clear accuracy to determine the freshness of fishes since the measurement is basically based on the kind, odor, and color change of fishes, while protein precipitation, measurement of VBN, and chemical change in ATP decomposition can only be carried out by specialized investigators by use of high technical equipments and facilities, take long time and destroy sample in a way for a measurement. Quantitative measurement of trimethylamine is most widely used method to test the fish freshness. As the fishes lose freshness, they begin to generate volatile basic nitrogen gases such as trimethylamine, dimethylamine, and ammonia. Trimethylamine gas in particular is known to increase rapidly as the freshness of fishes begins to deteriorate. The amount of trimethylamine in fish and seafood products can be measured to tell the degree of spoilage, and various techniques have been employed for that purpose. A titration method[1] using standard HCl solution is known to give accurate result but is destructive and time consuming. Application of gas chromatography[2] method to trimethylamine vapor can be another way. The natural fluorescence of fish muscle was also studied as a rapid and non-destructive method for monitoring fish freshness, but the structure of device prevents its use on individual packed food products[3]. Using semiconductor gas sensor is another method to measure the quantity of TMA, where the conductivity of sensor materials is changed with changes in the resistance caused by gas adsorption, which offers cost effective, rapid, reliable, non-destructive, and is a method of on-site and a real time analysis[4–12]. As materials of these semiconductor gas sensors, SnO2, ZnO, WO3 and TiO2 have been widely used.

In this study, we manufactured a thick film gas sensor by screen method using SnO2 as main sensor material. In order to stabilize the electric characteristics, small amount of TiO2 is added to pure SnO2, to increase the selectivity and sensitivity, Pd, Pt, In, Ru, and Rh are also added with given weight ratios. Using this thick film gas
sensor, we measured and analyzed the sensitivity and selectivity of gas in accordance with the operating temperature and gas concentration.

2. Experimental

2.1. Reagents and materials

In this study, we obtained the main sensor material SnO$_2$ by precipitating tin(IV) chloride (SnCl$_4$·H$_2$O) using wet chemical process [13]. In addition, to stabilize the electric characteristics of main sensor material, TiO$_2$ dissolved in deionized water at various composition ratios is added to SnO$_2$ while rotating the liquid solution in a magnetic stirrer.

To improve the sensitivity and selectivity, which are the essential functions for a gas sensor, metal catalysts were added using the infiltration method presented in Fig. 1 [14–16].

In infiltration method, homogenous solution of 1–3 wt.% of transition metals of Pd, Pt, Ru, Rh was made in deionized water by adding 1 ml of hydrochloric acid. After infiltrating the transition metal by adding SnO$_2$ or TiO$_2$/SnO$_2$ powder, SnO$_2$ powder or TiO$_2$/SnO$_2$ powder containing transition metal was obtained by gradually heating the infiltrated metal while rotating the solution in a magnetic stirrer. The powder obtained was dried at 110 °C for 12 h and calcinated at 600 °C for 2 h, followed by crushing to powder. The components and ratios of the sensor materials are shown in Table 1.

2.2. Fabrication of thick film sensor

The process of manufacturing thick film screen is composed of two stages: the stage of printing thick film sensor and that of forming the electrode and heater of sensing film. The commercial product of plate installed with electrode of sensing film and a heater is used in this work. In the front part of the alumina plate with the dimension of 13 mm × 8 mm × 0.67 mm, the electrode of three pairs of Pt is located, while in the back part, the heater of Ni–Cr is placed. Fig. 2 represents the composition of thick film sensor.

The thick film corresponding to each sensor material was manufactured by screen-printing paste with suitable viscosity on alumina plate holding an electrode, where paste was made by mixing powder of sensor material with 10 wt.% of ethylene glycol as a binder in 30 wt.% of deionized water. The thick film device was dried at room temperature for 24 h, dried at 110 °C for 12 h in a temperature-programmed convective dryer at a rate of 5 °C/10 min, and then calcinated at 600 °C for 1 h.

The gas sensor manufactured is fixed in a 10 l volume container with a dimension of 250 mm × 200 mm × 200 mm at 50 mm height, and then a stabilization process was carried out to remove the electrons contained in a thick film device at same temperature as used in measurements for 12 h. After the sensor gas is introduced into the container with the fan on, the resistance was measured with electrometer when the equilibrium concentration is reached. The sensitivity of sensor indicates the ratio of change in resistance based on gas flow against the resistance to gas in the air, and is defined as the following equation:

\[ S = \frac{R_a}{R_g} \]

where \( R_a \) and \( R_g \) are the resistance before and after the injection of sensor gas. Generally, if reducing gas is sensed with an n-type semiconductor sensor as is in this study, the resistance is decreased, the sensitivity of sensor is enhanced as the value of \( S \) increases [17,18]. Fig. 3 exhibits a diagram of the gas measurement device.

3. Results and discussion

3.1. Analysis of the characteristics of sensor materials

In this study, we manufactured a sensor material for gas sensing by making different ratios of SnO$_2$ to mixing powder of TiO$_2$ and transition metals, and obtained main sensor material of SnO$_2$ via
precipitation process in a solution of pH 9.5. The XRD method was used to analyze the crystallization and phase identification of sensor materials and main material SnO\textsubscript{2} manufactured via a wet chemical process. The results of XRD analysis are presented in Fig. 4. As shown in Fig. 4, the degree of TiO\textsubscript{2} crystallization is increased as the amount of TiO\textsubscript{2} increased. In addition, the phase change is observed as a rutile structure.

The results of analysis of particles of manufactured sensor materials are written in Table 2. We obtained the average size of SnO\textsubscript{2} particles to be 132.2 nm and the surface area to be 7.16 m\textsuperscript{2}/g. Moreover, as the amount of TiO\textsubscript{2} increased, the size of SnO\textsubscript{2} particles decreased and the surface area increased. In that case 10 wt.% TiO\textsubscript{2} was added to SnO\textsubscript{2}, we found the size of SnO\textsubscript{2} particles to be 80.3 nm while the surface area measured as 8.38 m\textsuperscript{2}/g.

### 3.2. Gas sensing characteristics of SnO\textsubscript{2} sensor containing TiO\textsubscript{2}

SnO\textsubscript{2} being able to be commercialized as a sensor material of detecting gases, both high degree of sensitivity and long-term stability must be offered. The analysis result of gas sensing characteristics of SnO\textsubscript{2} sensor with various weight percentage of TiO\textsubscript{2} is drawn in Fig. 5. It is shown that the sensitivity of SnO\textsubscript{2} sensor does not change much with gas concentration, for example, 1 wt.% and 5 wt.% of TiO\textsubscript{2} does not affect much in sensitivity difference.

![Fig. 4. XRD patterns of SnO\textsubscript{2} mixed with various ratios of TiO\textsubscript{2} calcined at 600 °C.](image)

![Fig. 5. Sensitivity curves with various weight percentages of TiO\textsubscript{2} as a function of concentration of TMA gas at 250 °C.](image)

### Table 2
Crystallite size, d-spacing and surface area of SnO\textsubscript{2} containing TiO\textsubscript{2}.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SnO\textsubscript{2}</th>
<th>1 wt.%-TiO\textsubscript{2}/SnO\textsubscript{2}</th>
<th>5 wt.%-TiO\textsubscript{2}/SnO\textsubscript{2}</th>
<th>10 wt.%-TiO\textsubscript{2}/SnO\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-spacing ((\theta))</td>
<td>2.9140</td>
<td>2.9192</td>
<td>2.9189</td>
<td>2.9208</td>
</tr>
<tr>
<td>Crystallite size (nm)</td>
<td>132.2</td>
<td>110.2</td>
<td>100.2</td>
<td>80.3</td>
</tr>
<tr>
<td>Surface area (m\textsuperscript{2}/g)</td>
<td>7.16</td>
<td>8.03</td>
<td>8.01</td>
<td>8.38</td>
</tr>
</tbody>
</table>
However, a significant difference in sensitivity was observed at different gas concentrations when 10 wt.% TiO$_2$ is added to SnO$_2$.

3.3. Effect of temperature on sensor materials

Fig. 6 exhibits the sensitivity of sensors when the temperature is changed in accordance with the amount of metal oxides added to SnO$_2$ sensor and the kinds of metal catalysts used. The sensitivity of SnO$_2$ sensor was found to be good at 250 °C at all concentration range, while 1 wt.% TiO$_2$ was added to SnO$_2$ sensor, the sensing temperature is lowered down to 200 °C. In the case of 10 wt.% TiO$_2$ or 1 wt.% Pt plus 10 wt.% TiO$_2$ added to SnO$_2$ sensor, the best sensitivity was achieved. This result can be explained as follows, the amount of metal oxides and the kind of metal catalysts affect on the activation energy rapidly at suitable temperatures.

3.4. Catalytic effects on sensor materials

We added transition metals to sensor materials in order to improve the sensitivity and selectivity to trimethylamine gas even if it does not directly affect stability, which is one of the essential functions of gas sensors. The analysis results show that the electrons are activated when transition metals are added to TiO$_2$/SnO$_2$, which result in the increase in the amount of adsorbed species, which consequently increase the change in electric conductivity. It was reported that increasing the contact area of catalysts with specific gas changes the sensitivity, selectivity, and operating temperature of sensor greatly [16].

Fig. 7 exhibits sensitivity of gas sensor with various kinds of transition metal added. To a system of 10 wt.%-TiO$_2$/SnO$_2$ of metal oxide as a basic sensor, we added various kinds of metal catalysts. As we can see from Fig. 7, when In or Pt are added as a metal catalyst, the sensitivity become even worse. However, when Pd is added, the sensitivity is found to be better than adding any other metal catalysts and even the case of 10 wt.%-TiO$_2$/SnO$_2$ sensor. Consequently, 1 wt.%-Pd plus 10 wt.%-TiO$_2$/SnO$_2$ sensor material is found to oxidize reducing gas of TMA more rapidly than any other sensor materials, that, offers best sensitivity.

Fig. 8 exhibits that the sensitivity of sensor to gas depending on the amounts of Pd and Ru employed. Using a system with 10 wt.%-TiO$_2$/SnO$_2$ of metal oxide as a basic sensor, 0–3 wt.% of Pd and Ru catalysts are added. As we can see from Fig. 8, the best sensitivity is obtained when 1 wt.% of Pd is added as a catalyst.

3.5. Selectivity of various sensor materials to TMA gas

Fig. 9 exhibits the sensitivity of various sensor materials to gases of trimethylamine, dimethylamine, and ammonia as a function of concentration at temperature of 250 °C when different amount of TiO$_2$ and various kinds of catalysts are added to SnO$_2$. Because the sensitivity to trimethylamine gas is found to be best at the temperature of 250 °C, the sensitivities to all other gases are also measured at same temperature for a comparison. As we can see from Fig. 9, while the difference in sensitivity to be less than 0.5 in the case of 1 wt.%-TiO$_2$/SnO$_2$, it is more than 2 in the case of 10 wt.%-TiO$_2$/SnO$_2$, although the selectivity is not as good as when metal catalysts are added.

Fig. 10 exhibits the selectivity to gases when the sensor materials are composed of 1 wt.%Pd/10 wt.%-TiO$_2$/SnO$_2$. As we can see from Fig. 10, the sensitivity difference between trimethylamine and other gases is more than 6, so that the selectivity to trimethylamine gas is in fact the best. This indicates that sensor material consisting of 1 wt.%Pd/10 wt.%-TiO$_2$/SnO$_2$ decompose trimethylamine gas and activate a reaction greater than dimethylamine or ammonia gas, which results in the improvement of selectivity.
4. Conclusions

In this study, we manufactured a SnO₂ type thick film sensor to which TiO₂ and various kinds of transition metals are added to improve the sensitivity and selectivity to TMA gas, and also analyzed the characteristics of SnO₂ type sensor. Based on the experimental data with various amount of metal oxides and the kind, amount, thickness, and operating temperature of transition metals, which affect the physical properties of thick film sensor, the following conclusions are deduced.

1. The sensitivity to TMA gas increased with increasing the amount of TiO₂ added to main material SnO₂ within the experimental range and reached the highest at 10 wt.% of TiO₂.
2. The sensitivity depended on the kinds and amounts of transition metal used and showed the best when 1 wt.% Pd was added.
3. As the thickness of sensor material decreased, the sensitivity was increased. The best operating temperature for sensitivity was found to be 250°C with small difference in various sensor material.
4. The sensor material composed of 1 wt.%Pd/10 wt.%-TiO₂/SnO₂ showed the best sensitivity to TMA gas and good selectivity to dimethylamine and ammonia gases with respect to TMA gas.

References