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Enhancement of Trimethylamine Sensitivity of Semiconductor Gas Sensors by Ruthenium

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The gas sensitivities to trimethylamine (TMA) of semiconductor gas sensors with several additives have been investigated to develop a new type of sensor capable of detecting freshness of fishes. Among the additives studied, ruthenium was the most suitable sensitizer to enhance the gas sensitivity to TMA. Furthermore, the TiO_2 + Ru elements exhibited the highest sensitivity at about 560 °C. The role of the ruthenium supported on semiconductors was briefly described.

It is well-known that freshness of fish can be expressed by K value which is defined as the percentage of inosine and hypoxanthine among the adenosine triphosphate (ATP) related compounds in fish muscle. Usually, the freshness index is calculated from results of separation and quantitative analysis of the ATP related compounds, but the method is accompanied by much efforts as well as much time. It is worth noting that a freshness sensor utilizing a multisensor system consisting of three enzyme sensors, microcomputer, and so on has been developed by Karube et al.[1] This system enables us to obtain a freshness index of fish within 20 min. But fish samples have to be destructed for extraction of ATP related compounds.

On the other hand, many investigations have so far been directed to identifying gaseous species, which come out during deterioration of fishes after death, and also to clarifying their concentration changes. For example, Miwa et al.[2] reported that concentrations of the evolved gases such as thrimethylamine (TMA), dimethylamine (DMA), and ammonia in the dry odor from raw Alaska pollack waste increased after storage at about 20 °C for 4 d. Katayama et al.[3] also reported that the amount of TMA in the distillate obtained by steam distillation of Japanese saurel significantly increased with lowering of the freshness. These results suggest a possibility to determine freshness of fishes by detecting concentration changes of gaseous TMA evolved from fishes. These consideration prompted us to investigate and develop semiconductor gas sensors highly sensitive to TMA. In the present paper, enhancement of the TMA sensitivity of n-type semiconductor gas sensor materials by ruthenium catalyst has been demonstrated.

First, a typical semiconductive metal oxide, SnO_2, was employed as a sensor material. The powder of the oxide was mixed with an appropriate amount of $RuCl_3$ in ethanol. The mixture was dried, and then treated in the stream of hydrogen at 400 °C for 5 h. In addition, other SnO_2-based sensor materials were also prepared

by impregnating the SnO_2 powder with an aqueous solution of $HAuCl_4$ or $PdCl_2$, followed by drying and heating at 800 °C for 5 h or at 1000 °C for 1 h, respectively, in air. Furthermore, other three kinds of sensor materials, ZnO, WO_3, and TiO_2, doped with ruthenium were prepared in the similar manner mentioned above. In all cases, the amounts of the metals added were 0.5 wt%. Each of the sensor material thus obtained was mixed with a small amount of water and the resulting paste was applied on the surface of an alumina tube (1.2 mm in diameter and 3.5 mm in length), on which two Au electrodes (distance : 0.5 mm) were printed. A small nichrome heater was inserted inside of the alumina tube. The construction of the sensor element was shown in Fig. 1. The operating temperatures of the sensor elements were controlled by voltage applied to the heater. The elements were calcined or sintered at 600 °C for 10 d in air before use. The elements thus prepared were subjected to measurement of gas sensitivity to TMA in the temperature range of 300 to 650 °C.

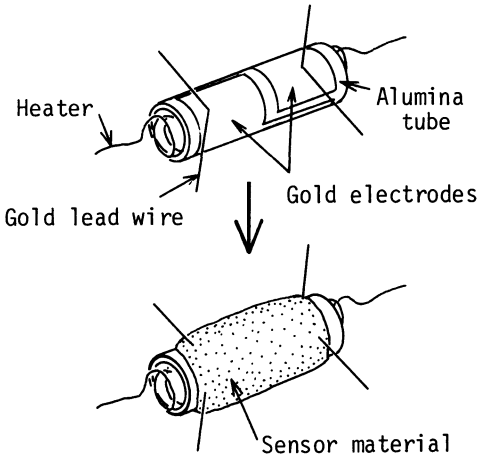

Fig. 1. Structure of sensor element.

The electrical resistance change of a sensor element was calculated from the output voltage change across a load resistor connected in series with it under the applied voltage of dc 2.0 V. Gas sensitivity (k), defined as the ratio of the electrical resistance in dry air (R_a) to that in a sample gas (R_g), was measured in a flow apparatus. The sample gas was prepared by the following procedure. Aqueous solutions of TMA with different concentrations were injected at a constant rate by a microfeeder into the hot zone of the gas line, which was located before the test chamber. The vaporized TMA was mixed with dry air flowing at 100 ml/min, and then was introduced into the test chamber where the sensor elements had been mounted. Concentrations of TMA in the sample gas was varied from 10 to 300 ppm. In spite of the different concentration of TMA, the content of water vapor in the sample gas was maitained approximately constant (about 1.89 vol%).

Figure 2 shows temperature dependences of the gas sensitivities of SnO_2-based sensor elements to 300 ppm TMA. Resistance of a pure SnO_2 element was 3.50 kΩ in air and 0.180 kΩ in 300 ppm TMA at 420 °C, and hence it exhibited its maximum sensitivity $K_M \simeq 20$ at this temperature. This value would not be high enough to detect freshness of fishes. The sensitivity to TMA and the temperature (T_M) at the maximum sensitivity varied with additives. Similar phenomena have been found for many other sample gases.[4,5] As

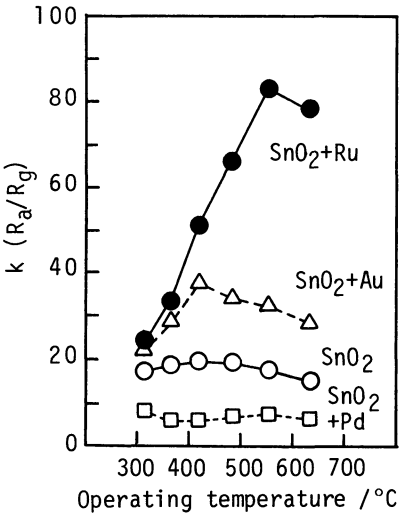

Fig. 2. Sensitivities of SnO_2-based sensor elements to 300 ppm TMA.

seen in Fig. 2, the k_M is approximately doubled by the addition of Au. More remarkable is that the maximum sensitivity is achieved by the addition of Ru among the additives studied. Resistance of the element at 555 °C was 31.1 kΩ in air and 0.374 kΩ in 300 ppm TMA. On the other hand, the sensitivity of SnO_2 + Pd element is smaller than that of the pure SnO_2 in the whole temperature range studied. The reason of this phenomenon is not clear at present.

The SnO_2 + Ru element responsed to very low concentration of TMA in the sample gas, as shown in Fig. 3. The T_M was almost unchanged with the variation of the concentration of TMA, suggesting that the activation of TMA and/or reaction of TMA with chemisorbed oxygen on the element was dominant in this temperature region. Since it is thus indicated that ruthenium is useful as a sensitizer for TMA detection in the case of SnO_2, further investigations were performed on other semiconducting oxides to develop more sensitive sensor materials.

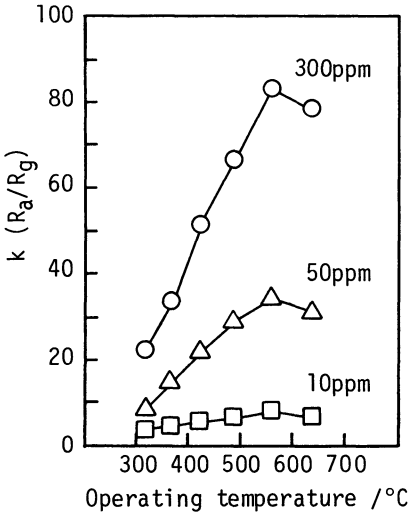

Fig. 3. Sensitivities of a SnO_2 + Ru sensor element as a function of TMA concentration.

Temperature dependences of gas sensitivity to 300 ppm TMA of ZnO, WO_3, and TiO_2 with and without 0.5 wt% Ru are shown in Fig. 4. In all cases, significant enhancement of the sensitivity to TMA was achieved by addition of the Ru catalyst, whereas the T_M is dependent upon the species of oxides. From these results, it seems that the TiO_2 + Ru element is one of the most suitable sensor materials to detect TMA by means of gas-sensing.

The role of the Ru catalyst in enhancing the sensitivity to TMA may be ex-

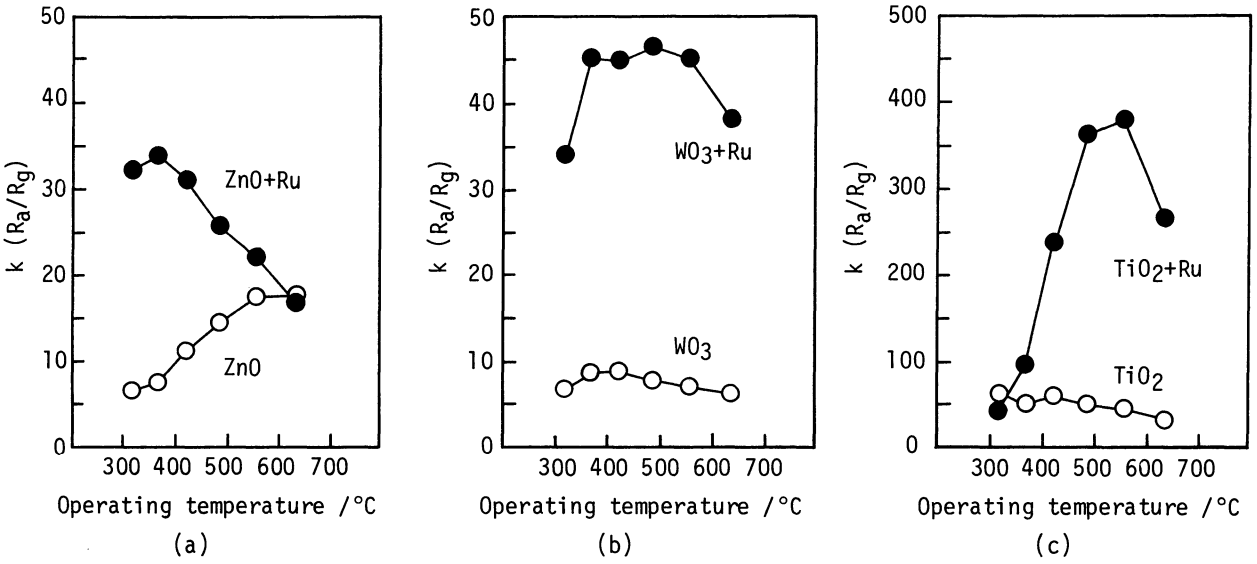

Fig. 4. Sensitivities of (a) ZnO-based, (b) WO_3-based, and (c) TiO_2-based sensor elements to 300 ppm TMA.

plained by either one of the following two ways or by both, though the details are not clear at present. It is well-known that ruthenium metal exhibits a remarkably high activity to decompose ammonia.[6] Therefore, it is considered that the metal is also active for decomposition of TMA. Hydrogen atoms or molecules produced by the decomposition may be detected by the sensor element. Another explanation is that the increased sensitivity arose from the electronic interaction between ruthenium metal and a semiconductor, which had been pointed by Yamazoe et al. for the Ag-doped SnO_2 sensor.[4,7] It is anticipated that the difference between the work function of Ru (4.71 eV) and the electron affinity of SnO_2 (4.49 eV) induces transfer of electrons from the oxide to the metal, and also that the ruthenium added are partially oxidized and covered with chemisorbed oxygen, whose negative charge comes from the oxide, at elevated temperatures in air. Thus, the electron concentration in the positively charged space region of the semiconductor would be lower in the Ru-doped SnO_2 element than in the pure SnO_2. In fact, electrical resistance in air was larger for the Ru-doped element. The electron transfer thus enhanced may result in the enhancement of the sensitivity to TMA.

The observed TMA sensitivities are the sum of the sensitivity to TMA and that to water vapor, since the sample gas contained 1.89 vol% of water vapor. However, it has been found that the sensitivity of oxide semiconductors to water vapor (humidity sensitivity) is less than 10 at elevated temperatures even for the most excellent one.[8,9] As for the TiO_2 + Ru element, therefore, the sensitivity to water vapor is considered negligibly small compared with that to TMA.

From the results mentioned above, the present method monitoring gaseous TMA by semiconductor gas sensors is promising for the detection of freshness of fishes. This method has a potential to realize a rapid nondestructive analysis of the freshness. Further investigations are now directed to establishing a multisensor system consisting of several sensor elements presented here, to detect freshness of fishes by the patern recognition method utilizing differences in the TMA sensitivity of the multisensors.

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