

Thick-Film Odor Sensors Based on Sintered Semiconducting Oxides

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A variety of thick-film oxide sensors have been prepared on alumina substrates by sintering at 600 C° for 1 hr. It is confirmed that the resistance change of n- and p-type sensors on exposing to ethanol is opposite to each other in accordance with the model accepted so far. The temperature dependence of the rise time is governed mainly by surface reaction between odor gas molecules and adsorbed oxygen atoms, while that of the recovery time is much complicated due to the presence of residual odor gas molecules in porous structure of sintered oxide. A preliminary experiment shows the possibility of fabricating odor distinguishable detection systems in which several oxide sensors with different characteristics are unified.

1. Introduction

It is known that perfumes have begun to be used in BC 3000 to 4000. We have used various kinds of natural fragrant materials to reach mental calmness and to suppress unpleasant odors. In recent years a number of artificial fragrant chemicals have been synthesized and applied to cosmetics, bathing goods, processed foods, soft drinks and others. Moreover, our daily life can not be free from various smells due to exhaust gases, garvages or sweat in crowds. Because we live in a many kinds of pleasant and unpleasant odors, it becomes inevitable to measure a smell quantitatively or to distinguish odors. However, odor or smell has no universal physical standard as in the case of light and sound, because odor or smell is empirically sensed as a result of complex mixture of a large number of odor molecules. Thus, odor sensors are conventionally categorized as one of gas sensors, but are entirely different in the aspect mentioned above from those for inorganic gas molecules such as H₂, CO and CH₄.

Odor sensors have to learn beforehand to detect the relevant odors, because there is no physical or chemical standard on detecting odors. Furthermore, because of poor selectivity of oxide odor sensors, it is necessary to apply a set of several sensor elements with different characteristics in order to discriminate an odor among the specified odors which are previously learned.^{1,2)} This type of sensor composite has been called "electronic nose". The electronic nose can work only for the limited kinds of odors which are preliminarily experienced and calibrated.

This paper describes the fabrication process of thick film sintered oxide sensors, the fundamental

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characteristics of the sensors and the preliminary experiments on the discrimination of elemental odor molecules.

2. Sensor Preparation and Fundamental Properties

The thick film sintered oxide sensors were provided on alumina substrates onto which Pt interdigital electrodes (200 nm thick) were sputtered. The commercially available SnO_2 , ZnO , SnO_2 - ZnO , Cu_2O , NiO , Cu_2O - NiO , TiO_2 , Cr_2O_3 , Ta_2O_5 , Sb_2O_3 and WO_3 powders (their grain sizes were not specified) were milled with distilled water in alumina mortar and were slowly settled in water in a measuring cylinder. The upper portion of the sediment was dried and made into a paste with a vehicle (Tanaka Kikinzoku Kogyo Co. Ltd., TMC-10TA). The paste was hand-printed on the substrate, dried in the laboratory air and sintered in air at $600\text{ }^\circ\text{C}$ for 1 hr. The lead wires were connected with silver paste.

The sensor element was attached with silver paste on an aluminum sample holder installed with a thermocouple. The sample holder with a sensor was inserted in a pyrex glass tube (30 mm ϕ \times 400 mm long) with a wound ribbon heater by which the sample could be heated up to $340\text{ }^\circ\text{C}$. The dry air (1.0 l/min) without or with an odor gas was flowed over the sensor. The transportation of the odor gas was made by flowing the dry air over the liquid odor source which was stored at room temperature in a tiny flask. Figure 1 illustrates the diagram of the gas flow system. In the present

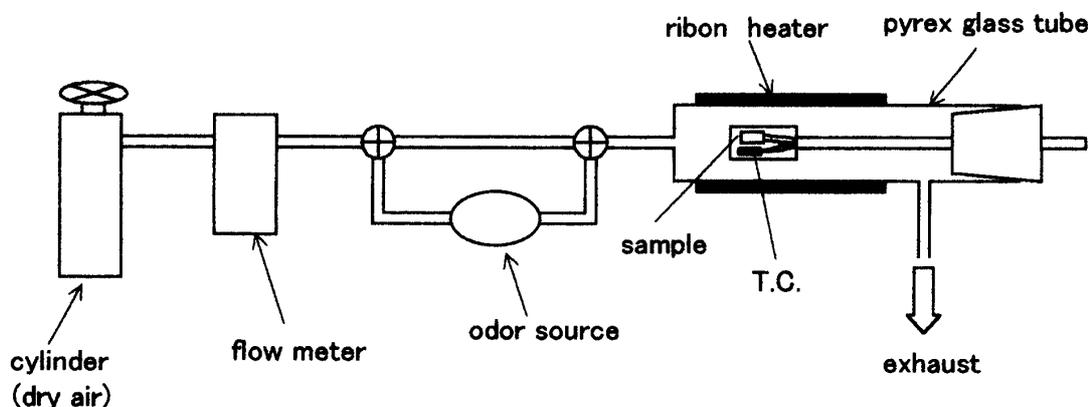


Fig.1 Gas flow system.

preliminary experiment on odor discrimination, the liquid odor sources (ethanol, 2-heptanone, α -pinene, ethyl-formate and ethyl-benzoate) were conventionally kept at room temperature; the odor concentration transported by dry air was different from each other. The detection sensitivity S was usually defined as the ratio of the sensor resistance in dry air to that in odor-incorporated dry air. The sensitivity S thus defined is only relative, because it depends on the odor gas concentration in dry air. Moreover, the magnitude of S is generally larger than unity for n-type oxides, but is smaller than unity for p-type materials. In the present experiment the odor source was held at

room temperature in the same flask and transported by dry air at the same flow rate, allowing relative comparison between the sensor characteristics.

3. Results and Discussion

3.1 Temperature dependence of sensor resistance

The electric resistance of various sensors was measured in flowing dry air with and without ethanol. After the sensor to be measured was held at 330 C° for 30 min to stabilize the surface condition, the sensor temperature was lowered down to room temperature and then the resistance was measured first in dry air during the temperature-raising step. After the measurement in dry air was finished, the sensor temperature was lowered again down to room temperature. The resistance in flowing dry air with ethanol was measured also during the temperature-raising run.

Figures 2 and 3 show the temperature dependence of the resistance in dry air without and with ethanol for SnO₂ and Cu₂O sensors, respectively. These materials were chosen as typical n- and p-

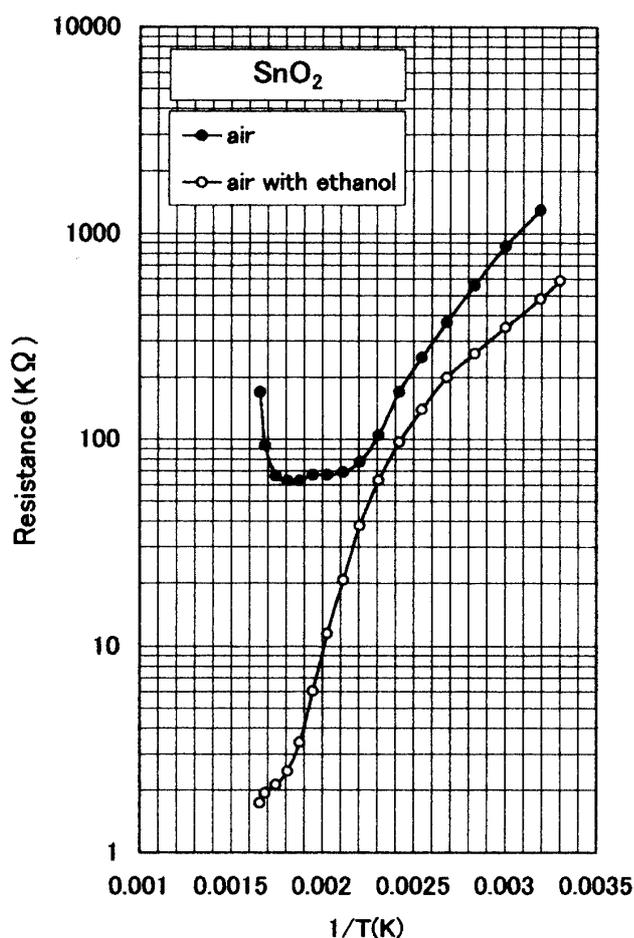


Fig.2 Temperature dependence of resistance for SnO₂ sensor in dry air with and without ethanol.

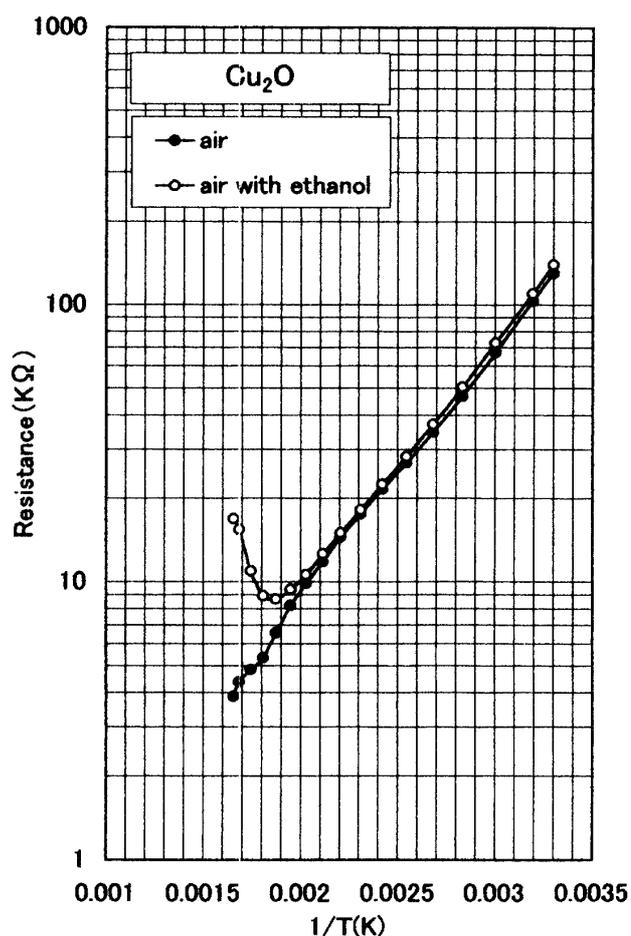


Fig.3 Temperature dependence of resistance for Cu₂O sensor in dry air with and without ethanol.

type oxides. The characteristic features in the SnO_2 sensor in Fig. 2 are a decrease in the resistance in ethanol-added air in comparison to that in air and an appearance of the positive temperature coefficient of the resistance at high temperatures.

The opposite change in the resistance between SnO_2 and Cu_2O sensors under the influence of ethanol vapor has been understood qualitatively in terms of the oxidation-reduction reaction between ethanol and oxygen adsorbed on the oxide surface³⁾ which causes an opposite change in the surface space-charge layer of n- and p-type oxides.

As to the appearance of the positive temperature coefficient of the resistance, the chemical reaction of oxygen in air with the oxide surface should be considered. In an n-type oxide such as SnO_2 , the oxygen adsorption causes a surface depletion layer, leading to an increase in the resistance of the sintered film. Because the oxygen adsorption is activated with temperature, an increase in the resistivity due to an enhancement of the depletion layer formation can be competitive with a resistivity decrease due to an increase in the electron density. When the effect of the oxygen adsorption becomes dominant over that of the electron density increase, an appearance of the positive temperature coefficient of the resistance can occur.

In order to obtain an evidence for the incorporation of oxygen adsorption in the temperature range of the positive temperature coefficient of the resistance, we made the same measurements in flowing dry nitrogen instead of dry air. The sample was heated to $330\text{ }^\circ\text{C}$ in dry air and then the ambient gas was switched to nitrogen with ethanol to react sufficiently with surface oxygen atoms. After that the sample temperature was reduced in dry nitrogen to room temperature and then the resistance was measured during temperature-raising run. Moreover, the similar measurement was carried out in dry nitrogen with ethanol. It was clearly observed that the positive temperature coefficient of the resistance disappeared entirely. Figure 4 shows the temperature dependence of the resistance in dry nitrogen without and with ethanol. It is evident in Fig. 4 that the temperature

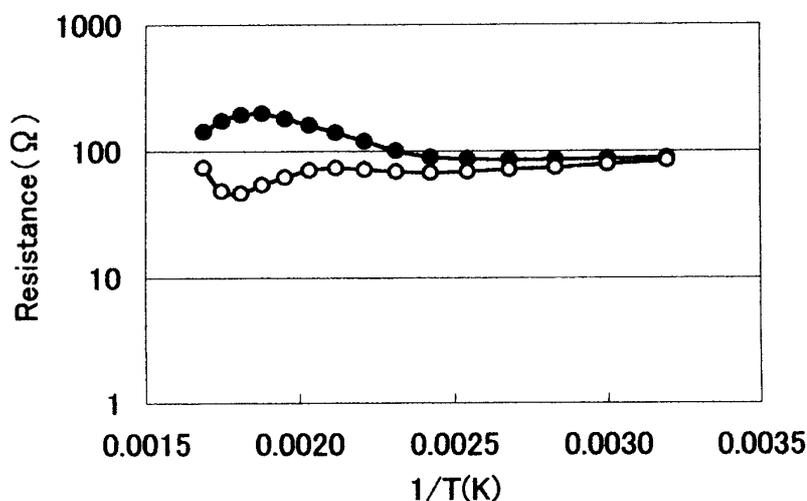


Fig4. Temperature dependence of SnO_2 sensor resistance in flowing dry nitrogen with (○) and without (●) ethanol.

dependence of the sensor resistance measured in nitrogen is entirely different from those measured in dry air. This result suggests that oxygen-oxide surface reaction dominates the oxide film resistance in dry air through formation of the surface depletion layer.

3.2 Temperature dependence of response time

Figures 5 and 6 show the rise and recovery times, respectively, of a SnO_2 sensor for ethanol as function of temperature. The rise time was defined as the time at which the change in the

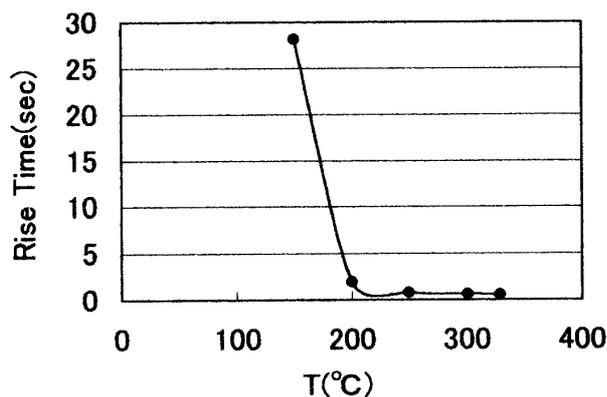


Fig.5 Temperature dependence of rise time in SnO_2 sensor for ethanol.

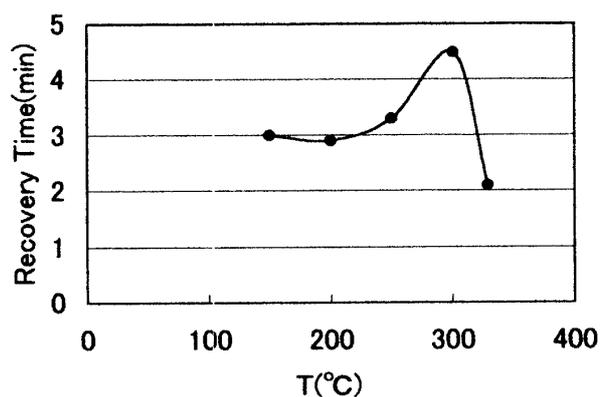


Fig.6 Temperature dependence of recovery time in SnO_2 sensor for ethanol.

resistance reached 90 % of the saturation value after commencing ethanol gas supply. On the other hand, the recovery time was conventionally determined as the time when the resistance change recovered to 50 % of the saturation value after the stop of the ethanol gas flow. It is worth to notice that the time scale on the vertical axis is remarkably different between rise and recovery times. The rise time is mainly governed by the chemical reaction of ethanol with oxygen adsorbed on the oxide surface. When the temperature is raised above 200 C°, the reaction of surface oxygen with ethanol is largely enhanced, causing a rapid decrease in the rise time down to 1 sec with increasing temperature. The behavior of the rise time approaching a constant value of about 1 sec above 200° is probably apparent, not reflecting intrinsic property of the chemical reaction between ethanol and oxygen adsorbed on the oxide surface, but rather relating to a time delay of ethanol gas transportation. On the other hand, the recovery of the sensor resistance after switch-off of ethanol in dry air is not only associated with re-adsorption of oxygen onto the oxide surface, but with residual ethanol trapped in porous structure of the sintered oxide film. A competitive process between oxygen adsorption and reduction of surface oxygen by ethanol left in the porous structure can lead to a rather complicated behavior of the recovery time on temperature.

The similar measurements of the rise and recovery times were carried out on WO_3 , Cu_2O and NiO sensors. The rise and recovery times in p-type Cu_2O and NiO were determined in the same manner as in the case of n-type SnO_2 and WO_3 , although the resistance change between n- and p-type materials were opposite. The rise time of these three sensors decreased rapidly with increasing

temperature and reached about 1 sec above 200 C° similar to the case of SnO₂ sensor. This fact may support the speculation mentioned above that the nearly constant rise time above 200 C° is due to time delay of ethanol gas supply. In contrast to the similar trend of the rise time with temperature in all samples examined, the temperature dependence of the recovery time was considerably different from each other.

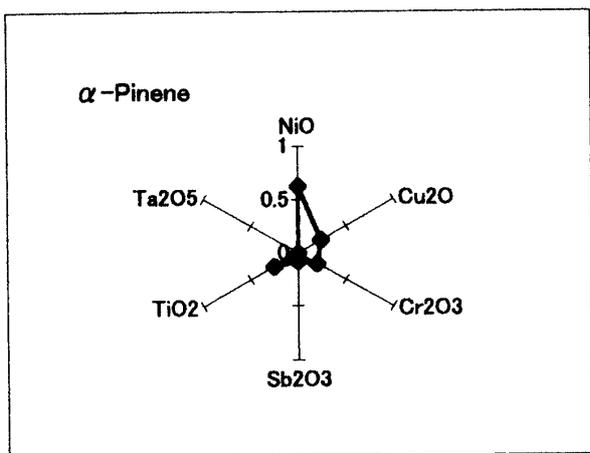
3.3 Discrimination of odor gases (a preliminary experiment)

Because of poor selectivity of oxide sensors, the use of a single sensor element is not enough to distinguish an odor among a group of odor gases. It is necessary for detecting selectively a relevant odor that one has to employ a combined-sensor system in which several oxide sensors with different characteristics are unified into a single set. In order to examine the possibility of discriminating between several kinds of odor gas molecules, we measured the detection characteristics of various oxide sensors including SnO₂, NiO, Cu₂O, Sb₂O₃, Ta₂O₅, TiO₂, Cr₂O₃ and WO₃ sensors at 300 C° for ethanol, 2-heptanone, α -pinene, ethyl-formate and ethyl-benzoate. Among these oxides, SnO₂, TiO₂, Ta₂O₅ and WO₃ are n-type, and NiO, Cu₂O and Cr₂O₃ are p-type oxides. These odor molecules were chosen because ethanol is a main constituent of men's cosmetics and liquors, and others are typical artificial fragrant odors which have different molecular structures each other. The measurements were carried out on individual oxide sensors at 300 C° for each of six odor gases. The sensor temperature of 300 C° was not optimal for attaining the highest detection performance of individual sensors, but was sufficient to utilize their distinctive detection ability. When appropriate combination of six oxide sensors was chosen, it was found that the detection sensitivity pattern shown on the radar chart with six axes were clearly different from each other for five kinds of elemental odor gases as shown in Figs. 7 (a)–(e). This result suggests strongly the possibility of discriminating odor gases which are previously learned.

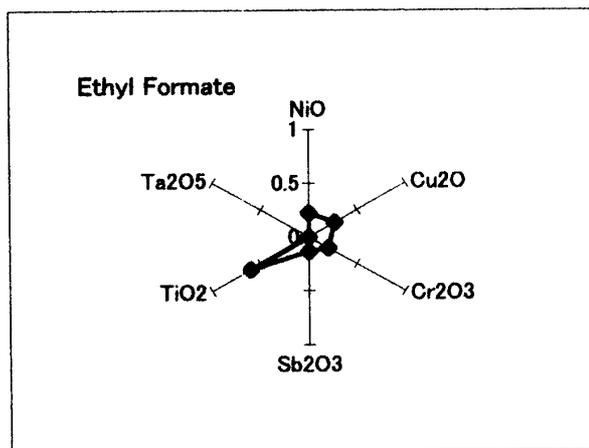
4. Summary

An opposite response is observed in n- and p-type oxide sensors for reductive odor gases typically such as ethanol. This confirms the validity of the model in which reductive gas molecules react chemically with oxygen atoms adsorbed on the oxide surface to modify the surface space-charge layer of the semiconducting oxide.

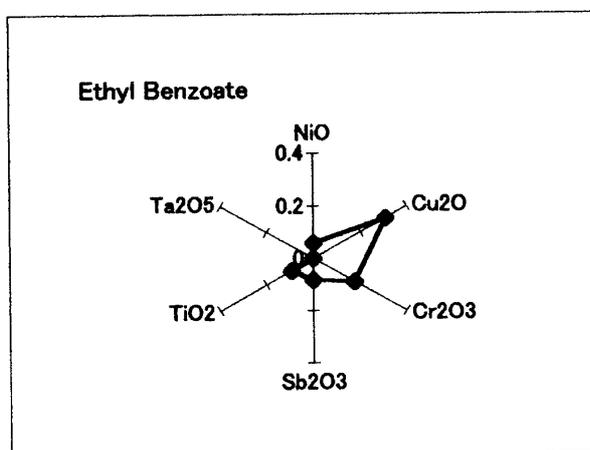
The temperature dependence of the response time (rise and recovery times) is found also to be governed by odor gas-surface oxygen reaction. The rise time decreases steeply with increasing temperature, reaching the order of 1 sec at temperatures above 200 C°, although this value of the minimum rise time may be limited by time delay of odor transportation. On the other hand, the behavior of the recovery time with temperature is more complicated because of the presence of competitive processes between re-adsorption of oxygen at vacant sites on the oxide surface, evolution of odor gas left in the porous structure of the sintered oxide and reaction of the residual odor gas with surface oxygen atoms.



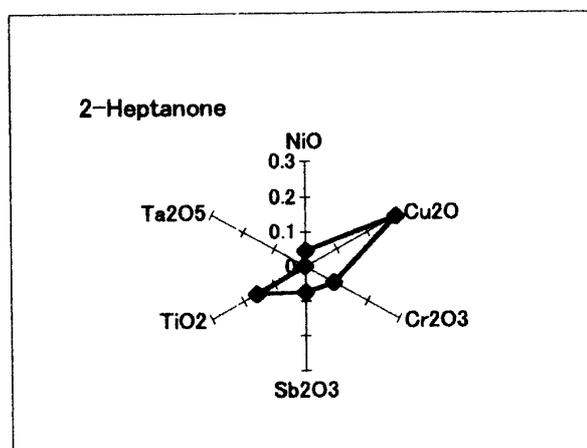
(a)



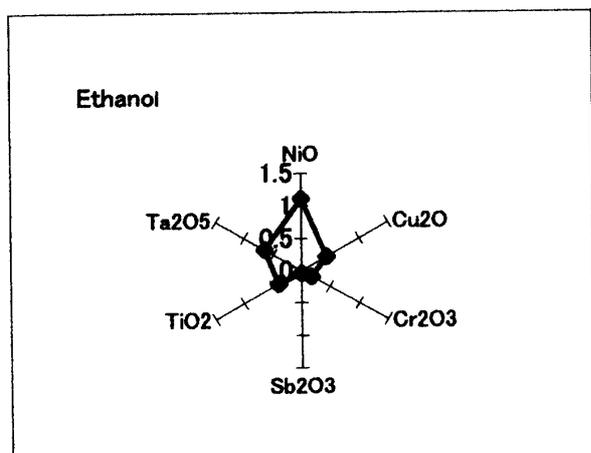
(b)



(c)



(d)



(e)

Fig.7 Sensitivity radar chart for five odor gases.

The preliminary experiment on detecting five kinds of elemental odor gases by a variety of oxide sensors suggests the possibility of realizing an odor detection system which can discriminate odor gases if the detection sensitivity patterns are learned beforehand.

Acknowledgement

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References

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