

EFFECT OF CATALYST ON DETECTION CHARACTERISTICS OF SEMICONDUCTING OXIDE ODOR SENSORS

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It has been well known that addition of small amount of catalyst can induce a considerable improvement of the detection sensitivity of oxide gas sensors. The catalyst has usually been added to oxides in the form of gas or liquid phase. In this paper a conventional method of adding catalyst in the form of powder of catalytic metal oxides has been satisfactorily used for oxide odor sensors.

Ag₂O, PdO and PtO₂ powders are employed to investigate the effect of Ag, Pd and Pt as catalyst on the detection sensitivity of SnO₂ thick film sensors. It is observed that the addition of Ag₂O and PdO shows a remarkable enhancement of the detection sensitivity in comparison with the case of PtO₂.

1. Introduction

Semiconducting oxide SnO₂ has been widely used for fabricating a variety of gas sensors. SnO₂ thick film sensors are also useful for detecting various kinds of odors. In order to improve detection abilities of SnO₂ sensors, an addition of Pt, Pd or Ag has been known to be successful^{1,2)}. These catalytic metals have usually been introduced initially in the form of their solution³⁾. After sintering process these catalytic metals segregate on the surface of mother oxide particles, and can enhance the oxidation of reductive gas molecules by spill-over¹⁾ or by electronic²⁾ mechanism.

In this article metallic catalysts, Ag, Pt and Pd, are introduced in the form of their oxides powder. These oxides can decompose in a high temperature environment into oxygen and metals which segregate on the surface of semiconducting oxide particles. It is revealed that this conventional way of introducing catalytic metals in the form of their oxides is quite effective to improve the detection characteristics of SnO₂ thick film odor sensors.

2. Experimentals

Metallic catalysts, Ag, Pt and Pd, were introduced into semiconducting oxide sensors by adding Ag₂O, PtO₂ or PdO powder which was decomposed into metal and oxygen during heat-treatment in laboratory air for making sintered films of oxide odor sensors. The decomposition temperature of Ag₂O, PdO and PtO₂ are reported to be 200, 875 and ca 400 °C. respectively. These decomposition temperatures are practically low enough to decompose into metal and oxygen gas during the sintering process of sensors

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at 700 °C. The typical semiconducting oxide SnO₂ was chosen for a host oxide material. The catalyst metals decomposed during the sintering treatment were supposed to be segregated on the surface of SnO₂ particles.

SnO₂ and catalyst oxide powders were fully mixed and were then made to paste-like with a dilution vehicle (Tanaka Kikinzoku Kogyo Co. Ltd., TMC-10T). The paste-like mixed powder was hand-printed on alumina substrates onto which interdigital platinum electrodes were patterned in the spacing of 300 μm by sputtering and etching processes (Toyo Seimitsu Kogyo Co. Ltd.). The printed oxide paste was then dried in laboratory air and finally sintered in air at 700 °C for 1 hr to form thick-film sensor elements. By the way silver lead-wires were fixed in advance on the connecting pads of the interdigital electrodes on the alumina substrate by sintering in air with silver paste (Tanaka Kikinzoku Kogyo Co. Ltd., MH-406A).

The compositions of Ag₂O, PtO₂ and PdO were varied in the range from 2.4 to 66.7 weight % to the mother material SnO₂. A SEM observation in X-ray microanalysis mode showed that in the case of small composition of catalyst there was no indication of the existence of segregated catalytic metal, but at medium compositions a small number of segregates were observed. However, when the composition of catalytic metal oxide was close to or over 50 weight %, the resistance of the sintered films was found in some cases to be significantly low indicating the formation of percolation paths between the electrodes because of too many metallic segregates.

The odor sensor thus obtained was mounted on a metal holder installed with a thermo-couple for ambient temperature control and was then inserted into a glass tube wound with a tape-shaped heater. The temperature dependence of the resistance of the sensors was measured from 40 to 330 °C in a flowing dry air or in a flowing ethanol-carrying air. Ethanol-carrying air was provided by passing dry air on ethanol stored in a tiny flask. The saturated vapor of ethanol was transported with dry air at the flowing rate of 0.5 l/min. Ethanol was chosen because it is a typical smell commonly encountered and can be easily handled.

The detection sensitivity S was defined conventionally as the ratio of the resistance in dry air to that in ethanol-carrying air; that is

$$S = R_{\text{air}} / R_{\text{ethanol}},$$

where R_{air} is the resistance in dry air and R_{ethanol} the resistance in ethanol-carrying air. Because of n-type nature of SnO₂ the sensor resistance becomes lower in ethanol ambient, yielding always the sensitivity S larger than unity.

3. Experimental Results and Discussion

The electrical properties and the detection characteristics in the sensors were not similar and scattered sample to sample. Only the typical and promising results are

described in this section. The observed scattering in the experimental data among samples may be related closely to dissimilar granular and porous structures of the sintered oxide films. However, the porous nature of the oxide films is essential to enlarge the effective surface area of the films, which is necessary for obtaining high detection sensitivity.

Figure 1 shows an example of the temperature dependence of the detection sensitivity in a Ag-added sensor in which the composition of Ag oxide is 4.8 weight %. A significant increase in the sensitivity is clearly seen in the Ag-added SnO_2 sensor in comparison to the case of the pure SnO_2 sensor, indicating a large catalytic role of Ag on detecting odor gas although what happens on segregated Ag fine particles is not clear yet. In the case of Fig. 1, the sensitivity of the Ag-added sensor reaches to a value as high as an excess of 10000 at about 300 °C, about 10 times higher than that of the pure SnO_2 sensor. Although the enhancement of the sensitivity due to catalytic Ag was observed to differ sample to sample, the highest sensitivity enhancement of 20000 was achieved in a sample added with 66.7 weight % Ag_2O . The observed scattering in the sensitivity in Ag-added sensors may be associated with the sensor fabrication process. In the present experiment the raw materials of SnO_2 and Ag_2O were powders prepared for conventional chemical use and the particle size was not specified (presumably to be several micrometers in average). This may cause a large fluctuation in the distribution of size and location of segregated Ag particles, inducing a scattering in the effectiveness of catalytic activity of Ag. The application of fine powder of Ag_2O hope-

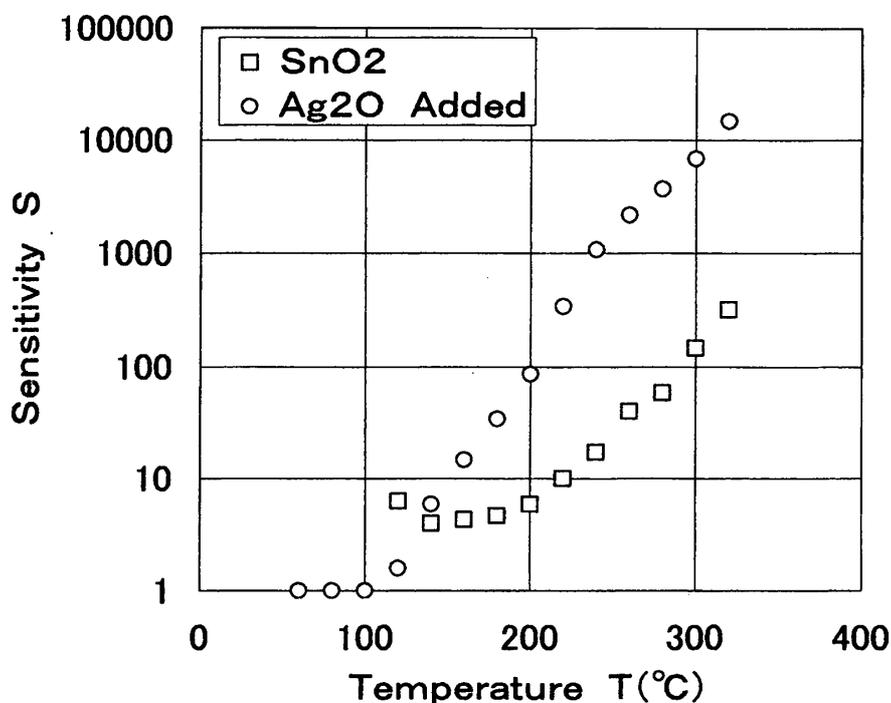


Fig.1 Temperature dependence of sensitivities in pure and Ag_2O -added SnO_2 sensors.

fully in nanometer-size as well as SnO₂ fine powder is promising to improve the scattering of the detection sensitivity.

The relationship between the highest detection sensitivity observed and the weight % of the added Ag₂O is shown in Fig. 2. The high detection sensitivity in Fig. 2 can be compared to the average value of the maximum sensitivity of pure SnO₂ sensors which was 20000 reached at about 300 °C. This highest sensitivity of 20000 was achieved at the weight % of 66.7. This value can be compared to those reported for the case of the liquid phase processes.³⁾ The experimental facts shown in this figure suggest that the addition of catalytic metals in the form of oxide powder is a potential method for improving the detection sensitivity of SnO₂ sensors.

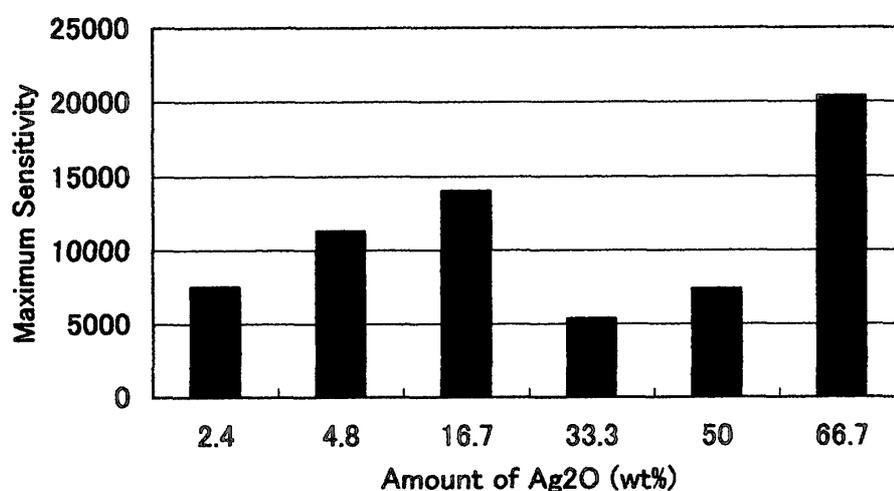


Fig. 2 Relationship between maximum sensitivity and added amount of Ag₂O for SnO₂ sensor.

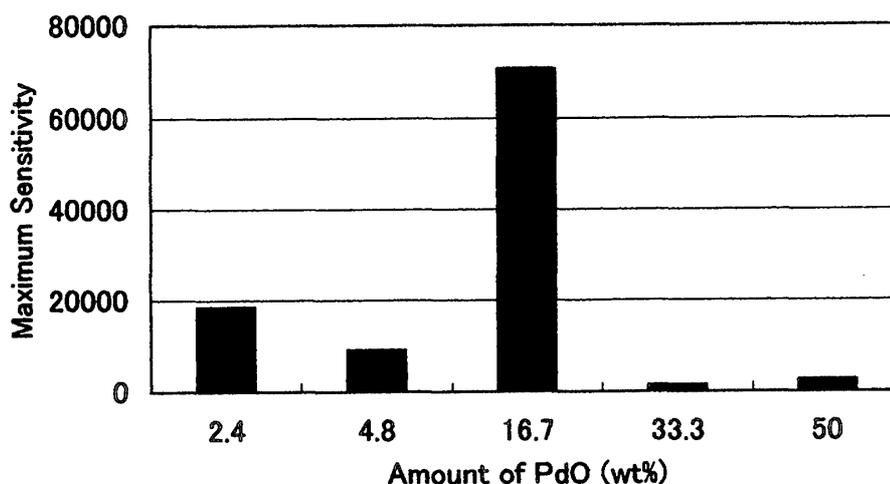


Fig. 3 Maximum sensitivity as a function of amount of PdO introduced in SnO₂ sensor.

Figure 3 illustrates the relationship of the maximum sensitivity attained to the amount of the added PdO in SnO₂ sensors. A remarkable sensitivity as high as 70000 is achieved at the PdO fraction of 16.7 weight %. It is supposed to be the first time that the tremendous enhancement of the detection sensitivity by PdO addition to SnO₂ sensors was experimentally confirmed.

The improvement of the detection sensitivity by the incorporation with catalytic metals, Ag, Pd and Pt, is compared in Fig. 4 where the average maximum sensitivity of pure SnO₂ sensors of 2000 is to be compared. The maximum sensitivities in Fig. 3 are attained at the amount of 66.7, 16.7 and 4.8 weight %, respectively, for Ag₂O, PdO and PtO₂. The highest detection sensitivities in whole samples were achieved in the temperature range between 250 and 330 °C. The addition of PdO is most effective to improve the detection sensitivity, reaching 70000, although the full decomposition temperature of PdO is as high as 875 °C. However, this experimental fact may indicate that only a small incorporation of Pd metal is effective to improve the detection sensitivity. On the other hand, the improvement of the sensitivity by the addition of PtO₂ was rather poor in comparison with the cases of Ag₂O and PdO. The decomposition temperature of PtO₂ is about 400 °C which is well lower than the sintering temperature of 700 °C. Thus the whole of added PtO₂ powder is supposed to be fully decomposed to give Pt metal segregates on the surface of SnO₂ particles. Therefore, less sensitivity improvement in the case of Pt may be due to a low measuring temperature of about 300 °C which is not satisfactory for Pt to catalyze the oxidation of reductive gas molecules.

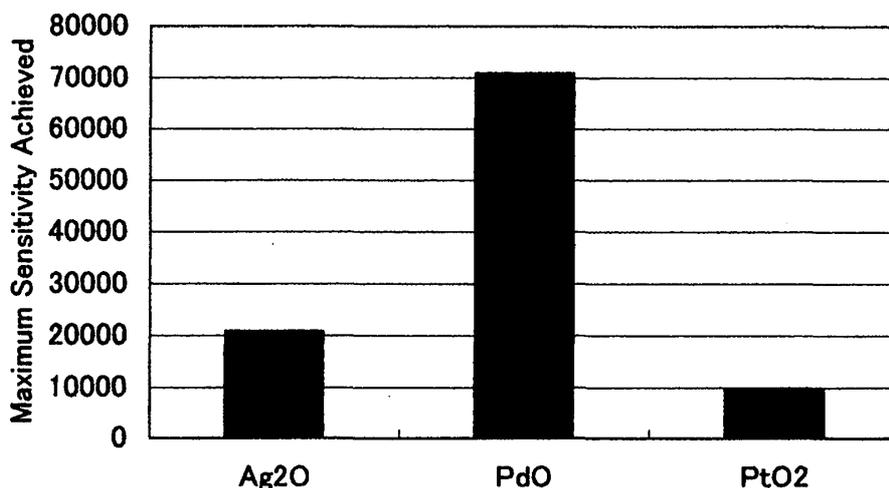


Fig. 4 Comparison of maximum sensitivities achieved in SnO₂ sensors added with Ag₂O, PdO and PtO₂.

4. Summaries and Comments

It is demonstrated in this article that the catalytic metals introduced in the form of

their oxide powders have a potential role for improving the detection sensitivity of SnO₂ odor sensors. In the present experiment the effectiveness of the catalytic metal addition is observed for Ag, Pd and Pt, although their effectiveness is different. The addition of PtO₂ is observed to be less effective in contrast to the fact that its decomposition temperature is as low as about 400 °C. The reason for the less catalytic activity of Pt observed in the present experiment is presumably due to less suitable condition that the measuring temperature of the sensitivity at 300 °C is lower for Pt catalyst to give a high catalytic reaction.

The methods of the incorporation of catalytic metals into oxide films have usually been made in liquid phase because uniform distribution of segregated fine grains of catalytic metals on the surface of oxide particles is reasonably expected. In contrast to this usual method, the conventional way of adding catalytic metals in the form of oxide powder has been thought to be not recommended. However, the results of the present experiment can offer a new route for introducing catalytic metals into oxide sensors.

The significant scattering in the observed detection sensitivity of SnO₂ sensors added with catalytic metals is strongly associated with the use of conventional chemical agents of not-specified grain size. Nano-scale fine particles of catalytic metal oxides, if available, would bring much satisfied results.

The effect of catalytic metals on the detection sensitivity has been the main target of the present study. However, high detection sensitivity means high oxidation rate of reductive gas molecules; this indicates the possibility of fast transient response of odor sensing. The transient performance of catalyst-loaded oxide sensors is remained for future studies.

References

- 1) P.A.Serman et al., *Catalysis Rev.* **8** (1973) 221.
- 2) M.Nitta et al., *J. Electron. Mater.* **9** (1980) 727.
- 3) T.Shirasaki "Preparation of Catalyst" (Kodansha-Scientific, 1974) in Japanese.
- 4) Tokyo Kagaku-Dojin ed. "Encyclopedic Dictionary of Chemistry" (Tokyo Kagaku-Dojin, 1989) in Japanese.

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