

# Development of SnO<sub>2</sub>-based Gas Sensors for Detection of Volatile Organic Compounds

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## Summary

Recently, sick-house syndrome receive much public attention as a problem of indoor environment. Volatile organic compounds (VOCs) such as formaldehyde (HCHO) and xylene (C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub>) generated from building materials are pointed out as one of origins of sick-house syndrome. In the present work, in order to develop a semiconductor type VOC sensor, first of all, the sensitivities of several oxide semiconductor materials were studied. Among the 23 metals oxides examined, the highest sensitivity to HCHO was achieved by SnO<sub>2</sub>. Further, the sensing property of an SnO<sub>2</sub> sensor to 100 ppm HCHO was extremely improved by addition of 3 wt% Ag at 300°C, but the sensor had a short lifetime. In order to explore another additives, VOC sensing properties of SnO<sub>2</sub> loaded with several metal oxides were investigated. Among the elements loaded (5 wt%) with each of 14 metal oxides, the Mn<sub>2</sub>O<sub>3</sub>-loaded one was outstanding in sensitivity to HCHO at 200°C. However, its sensitivity of the doubly promoted sensor, Ag (1 wt%)-Mn<sub>2</sub>O<sub>3</sub> (5 wt%)-SnO<sub>2</sub> to HCHO was lower than that of each sensor loaded with one additive.

## 1. Introduction

The number of persons injured by indoor-air pollutants, especially in the new residential building, are increasing in recent years. The phenomenon is the so-called sick house syndrome or sick building syndrome [1,2]. It is mostly caused by volatile organic compounds (VOCs) emission such as formaldehyde (HCHO) and xylene (C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub>) and toluene (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>) included in adhesives or paints used for residential buildings. The resin adhesives for woods particularly need HCHO in spite of hazardous substance. However, the hazardous property of HCHO is strongly pointed out lately and WHO (World Health Organization) established the upper limit of HCHO concentration in the room to 0.08 ppm.

Over the past decade, many studies have been made on sensors concerning air pollution gases such as NO<sub>x</sub>, SO<sub>x</sub>, O<sub>3</sub>, NH<sub>3</sub> and indoor-air pollution gases such as CO<sub>2</sub>, CO. Very few studies of gas sensors for detection of VOCs in new houses, however, have been reported so far. Therefore, the development of a sensor system available to measure the indoor-air pollution level at high sensitivity is highly desired. In order to detect VOCs in new houses easily and with low cost, we have studied oxide semiconductor type gas sensors. In our previous studies, we found that SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>, ZnO, Cr<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub> showed relatively high sensitivity to HCHO, C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub>, and (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>). SnO<sub>2</sub> exhibits excellent sensitivity to HCHO, and WO<sub>3</sub> shows the highest sensitivity to C<sub>2</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub> [3].

This paper deals with the HCHO and C<sub>2</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub> sensing

properties of SnO<sub>2</sub> elements loaded with noble metals and various metal oxides, especially Ag and MnO<sub>2</sub>.

## 2. Experimental

The commercial powders (Kojundo Chemical Laboratory Co., Ltd.) of metal oxides and noble metals were used for sensor materials and additives, respectively. Several kind of metal oxides were also used for additives. All powders had an average grain size of a few μm. The sensor films of various metal oxides used throughout experiment were fabricated on a 96% alumina substrate with dimension of 12×12×0.6 mm<sup>3</sup> by screen printing with 250 mesh.

First, to make the sensor pastes, each metal oxide powder was adequately mixed with organic binder (Tanaka Kikinzoku Kogyo K.K.), which mainly includes ethyl cellulose. Also, SnO<sub>2</sub> powder was mixed well with one of 7 noble metal powders or one of 14 metal oxide powders and with organic binder. Next, a pair of parallel Pt film (Tanaka Kikinzoku Kogyo K.K.) electrodes (distance : 0.5 mm) was printed on alumina substrates and dried at 100°C, and then a Pt film heater was printed on the back surface of the substrate and dried at 100°C, followed by calcination at 900°C for 1 h in air. And then, the sensor paste was screen printed on the alumina substrate and calcined at 600°C for 1 h in air. The thickness of the sensor was about 30 μm after the calcination.

The sensitivity of the sensor to HCHO and C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub> gases was measured in a cubic test chamber which had a capacity of

about 64 liters and was made by transparent vinyl chloride. A ceramic heater and fan were set in the chamber. The heater was used to vaporize reagents (Wako Pure Chemical Industries, Ltd.) for making test gases and the fan was used to stir the gas of various VOCs. The sensitivities of 12 sensors were able to measure at once in this chamber. The sensitivity was defined as the ratio  $R_a/R_g$  for n-type semiconductor or  $R_g/R_a$  for p-type semiconductor, in which  $R_a$  and  $R_g$  stand for the electrical resistance in air and in the sample gas, respectively. X-ray diffraction (XRD) measurement was carried out using a Rigaku RAD-A with Cu-K $\alpha$  radiation. X-Ray photoelectron spectroscopy (XPS) measurement was carried out using a Shimadzu ESCA-1000 spectrometer with Al-K $\alpha$  radiation (1.486 keV). Binding energies (BEs) were referred to the Au 4f $_{7/2}$  level (84.0 eV) of sputtered gold.

### 3. Results and Discussion

#### 3-1 Screening test for base semiconductors

12 kinds of metal oxides including mainly transition elements were subjected to the screening test for exploring the most sensitive base semiconductor to the 3 kinds of VOCs, HCHO, C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub>, and (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>). The sensitivity of each element was measured for each VOC at 1000 ppm in air. The sensitivities of 18 metal oxides to the 3 kinds of 1000 ppm VOCs at 350°C are summarized in Fig. 1. Among the metal oxides examined, the 6 kinds of metal oxides, SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>, ZnO (n-type), and Cr<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub> (p-type) show relatively high sensitivity, as seen in the figure.

The sensitivities of these 6 kinds of metal oxides were further investigated in detail for HCHO and C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub>. Figure 2 shows the sensitivities of 6 kinds of sensors depending on HCHO concentration ranging 2.5-1000 ppm. HCHO could be detected with the excellent sensitivity by both SnO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub>. Similarly, Fig. 3 shows the dependence of the sensitivities of

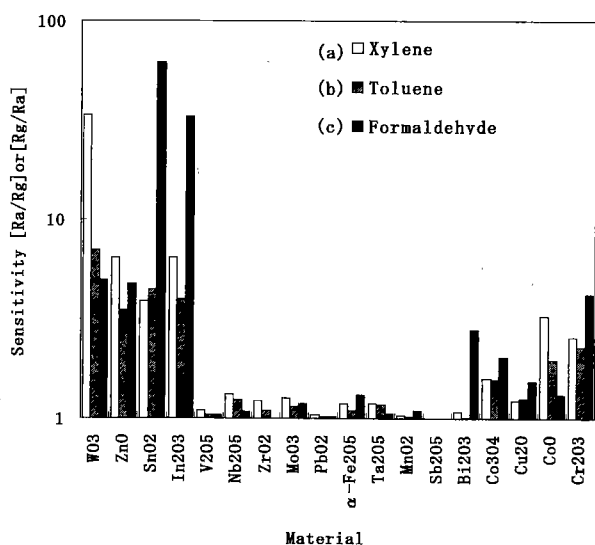


Fig.1. Sensitivities of various oxide semiconductor materials to three VOC gases, (a) xylene, (b) toluene and (a) formaldehyde.

these sensors on concentration of C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub>. Xylene was detected with the highest sensitivity by WO<sub>3</sub>. For both of Figs. 2 and 3, a good linearity isn't obtained in the log-log plot of the sensitivity and concentration. However, the detectable limits to HCHO could be roughly estimated about 1 ppm by SnO<sub>2</sub> or In<sub>2</sub>O<sub>3</sub>, as seen in Fig. 2, and that to C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub> could be estimated about a few ppm by WO<sub>3</sub>, as shown in Fig. 3. From a practical viewpoint, these sensors should be sensitive enough to sub-ppm VOCs (HCHO etc.) because concentrations of various VOCs are generally 0.1 ppm or less in a new house.

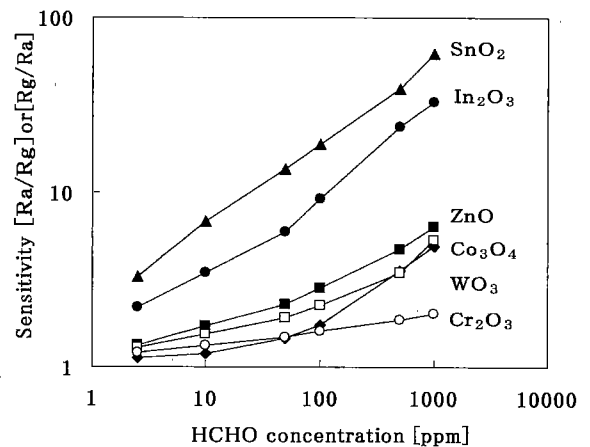


Fig.2. Dependence of sensitivities of selected sensors operated at 350°C on concentration of formaldehyde gas.

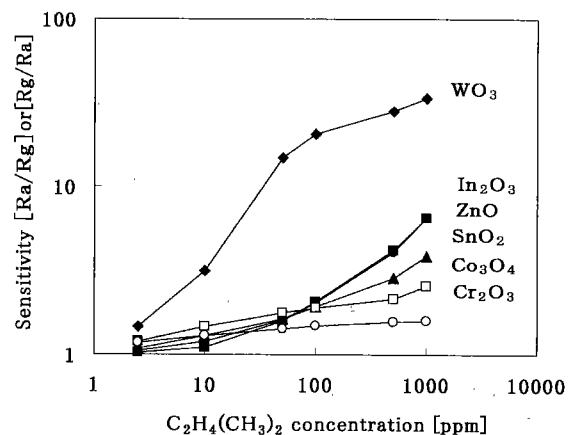


Fig.3. Dependence of sensitivities of selected sensors operated at 350°C on concentration of xylene gas.

#### 3-2 Sensing properties of SnO<sub>2</sub> sensors loaded with noble metals

One of the purpose of our study is to develop the sensor which is capable of detecting 0.01 ppm HCHO. Generally, as the means of sensitization, the grain-size control, valency control, addition of another material (chemical or electronic sensitization) and sensor configuration are well known [4-6]. The present work is intended as an investigation of promoting effect of noble metals and metal oxides.

Figure 4 shows the sensitivities of SnO<sub>2</sub>-based sensors loaded

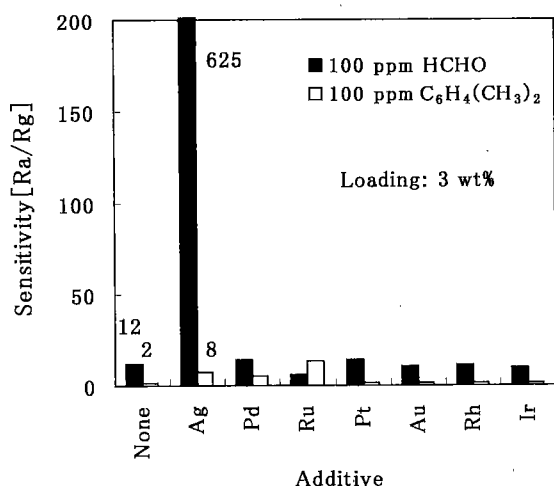


Fig.4. Sensitivities to formaldehyde (■) and xylene (□) of SnO<sub>2</sub> based sensors loaded with various noble metals (3 wt%) operated at 300°C.

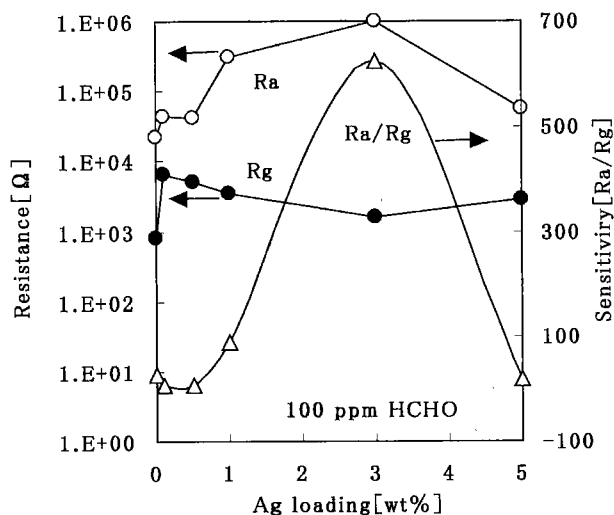


Fig.5. Effects of Ag loading on electrical resistances in air (Ra) and in 100 ppm HCHO (Rg) as well as resulting gas sensitivity (Ra/Rg) for Ag-SnO<sub>2</sub> sensors operated at 300°C.

with 7 kinds of noble metals to 100 ppm HCHO and C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub> at 300°C. It is found that Ag greatly enhanced the sensitivity of SnO<sub>2</sub> to HCHO as much as about 40 times larger than that without Ag.

Figure 5 shows the electrical resistance in air (Ra) and in 100 ppm HCHO (Rg) as well as the resulting gas sensitivity for each Ag-SnO<sub>2</sub> sensor at 300°C as a function of Ag loading. Ra increases with increasing Ag content up to 3 weight percent (wt%) and beyond that decreases gradually. On the other hand, at first Rg increases up to 0.1 wt% and then decreases with Ag content up to 3 wt% and increases again. As a cause of the sensitization, an electronic interaction between Ag and SnO<sub>2</sub> which has been indicated by Yamazoe et al., seems to be concerned [7-8]. That is, in air, an Ag particle dispersed on

SnO<sub>2</sub> surface may be covered by Ag<sub>2</sub>O, forms a redox couple of Ag<sup>+</sup>/Ag<sup>0</sup>, the electronic potential of which is located at 5.3 eV below the vacuum level (0.79 eV vs NHE; NHE potential is located at 4.5 eV below the vacuum level). Also, the electron affinity of SnO<sub>2</sub> is taken to be 4.49 eV, and the Fermi level (E<sub>F</sub>) of SnO<sub>2</sub> is assumed to be 0.1~0.2 eV below the conduction band, and the work function of SnO<sub>2</sub> is thus estimated at 4.59~4.69 eV. Therefore, to attain electronic equilibrium, the migration of electron from the surface of SnO<sub>2</sub> to that of Ag takes place, producing an electron depleted space-charge layer, resulting in the increase of resistance of SnO<sub>2</sub>. In contrast, in formaldehyde gas which causes the reduction of Ag<sup>+</sup> to Ag<sup>0</sup>, the E<sub>F</sub> of SnO<sub>2</sub> shifts upward to be pinned at the work function of Ag (4.49 eV), resulting in a decrease of resistance of SnO<sub>2</sub>. As the electron affinity of Ag<sub>2</sub>O is eventually much stronger than that of the adsorbed oxygen, leading to the much higher gas sensitivity.

Thus, the addition of Ag particles of about 3 wt% in SnO<sub>2</sub> particles promotes extremely the HCHO sensitivity. However, Ag-SnO<sub>2</sub> sensor had a very short lifetime. The resistance of its sensor began to vibrate up and down in air as if it resonates, and the vibrations of its resistance became more and more large with time. At the present stage, we have no clear explanations for such instability of the resistance. Further investigations are necessary on the SnO<sub>2</sub> sensor loaded with Ag.

### 3-3 Sensing properties of SnO<sub>2</sub> sensors loaded with metal oxides

As we mentioned in the previous section, owing to the instability of Ag-SnO<sub>2</sub> sensor, metal oxides were looked for new modifier instead of Ag. Figure 6 summarizes the sensitivities of SnO<sub>2</sub> elements loaded with various metal oxides (5 wt%) to HCHO and C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub> at 280°C and 200°C. Although most of additives are little effective, the MnO<sub>2</sub> (5 wt%)-SnO<sub>2</sub> sensor shows extremely high sensitivity as high as 161 to 100 ppm HCHO and 97 to 100 ppm C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub> at 280°C. Moreover, the sensitivity of the sensor marks as high as 883 to 100 ppm HCHO at 200°C, which is about 100 times larger than that of SnO<sub>2</sub> without MnO<sub>2</sub>. In contrast, the sensitivity of the sensor shows as low as 16 to 100 ppm C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub> and largely falls at 200°C.

Generally, C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, which are usually used as the solvent of paint, are highly contained in indoor air pollutants in new houses and therefore these gases may interfere with the detection of HCHO in coexisting gases. According to the present experiment, it is found that the addition of MnO<sub>2</sub> to SnO<sub>2</sub> markedly promotes the sensitivity to HCHO at 200°C without increasing the sensitivity to C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>.

Figure 7 shows the electrical resistance of MnO<sub>2</sub>-SnO<sub>2</sub> sensors in air (Ra) and in 100 ppm HCHO (Rg) as well as the resulting HCHO sensitivity at 200°C as a function of MnO<sub>2</sub> loading. Ra increases steeply with an increase in MnO<sub>2</sub> loading up to about 5 wt% and then still increases gradually for more loading. On the other hand, Rg increases gradually with an increase in MnO<sub>2</sub> loading in the range between 0 and 20 wt%.

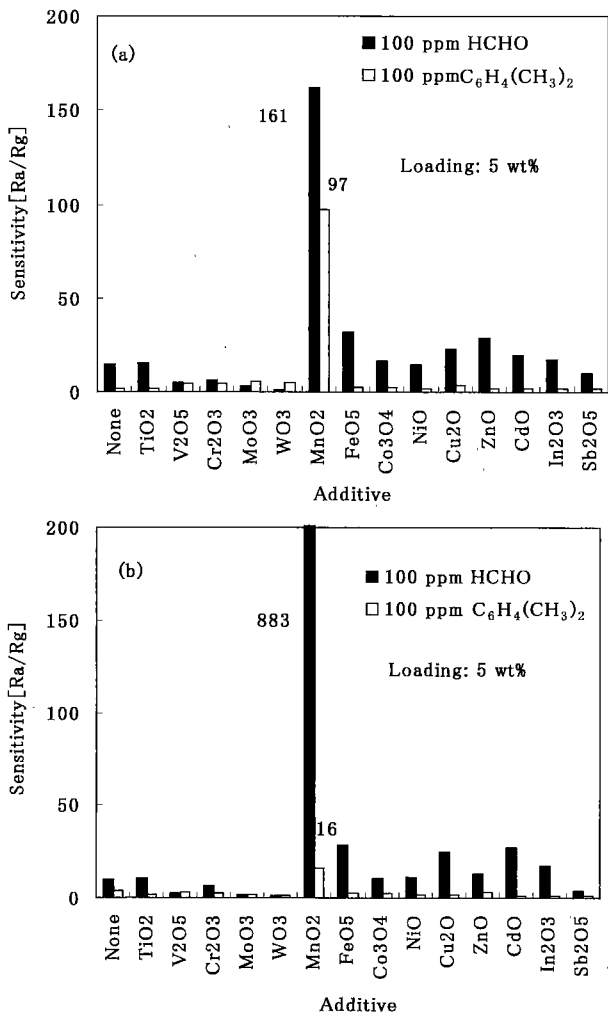


Fig.6. Sensitivity of SnO<sub>2</sub>-based sensors with various additives to 100 ppm HCHO and 100 ppm C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub> at (a) 280°C and (b) 200°C.

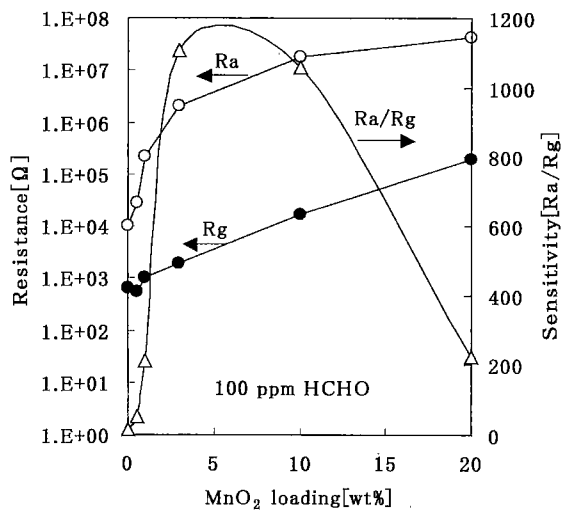


Fig.7. Effects of MnO<sub>2</sub> loading on the electrical resistances (Ra) in air and in 100 ppm HCHO (Rg) as well as resulting gas sensitivity (Ra/Rg) for MnO<sub>2</sub>-SnO<sub>2</sub> sensors at 200°C.

As a result of such behavior of Ra and Rg, the HCHO sensitivity reached a maximum value of about 1200 at 5 wt% MnO<sub>2</sub>. The Ra of MnO<sub>2</sub>-SnO<sub>2</sub> sensors in Fig. 7 tends to increase further after the sensitivity reached a maximum value (about 1200). On the other hand, the Ra of Ag-SnO<sub>2</sub> sensor in Fig. 5 decrease after the sensitivity reaches a maximum value (about 600). Since the resistance of MnO<sub>2</sub> is larger than that of SnO<sub>2</sub>, the resistance of MnO<sub>2</sub>-SnO<sub>2</sub> sensors is likely to increase toward the MnO<sub>2</sub> resistance with increasing MnO<sub>2</sub> content.

We examined the reason why sensitivity of SnO<sub>2</sub> sensor is increased with MnO<sub>2</sub> loading. First, XRD pattern was measured to examine the crystalline state of the sensor. Figure 8 shows XRD pattern of SnO<sub>2</sub> loaded with MnO<sub>2</sub>. It is found that MnO<sub>2</sub> changed into Mn<sub>2</sub>O<sub>3</sub> through calcining, and also no other complex oxides are observed except Mn<sub>2</sub>O<sub>3</sub> and SnO<sub>2</sub>. Therefore, as for the crystalline state of Mn-oxide, Mn<sub>2</sub>O<sub>3</sub> is used instead of MnO<sub>2</sub> from now on.

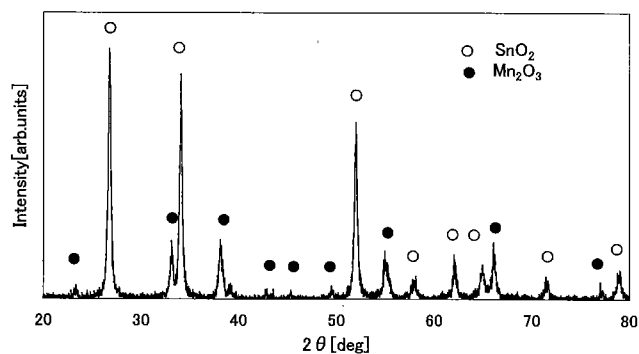


Fig.8. X-ray diffraction patterns for the MnO<sub>2</sub>-SnO<sub>2</sub> sensors calcined at 600°C.

Figure 9 shows the sensitivities to 100 ppm HCHO of SnO<sub>2</sub> sensors variously loaded with Mn<sub>2</sub>O<sub>3</sub> as a function of operating temperature. As shown in the figure, the maximum value of HCHO sensitivity is likely to be obtained in the range between 3 wt% and 10 wt% loadings. The temperature of maximum sensitivity ( $T_{max}$ ) is plotted against Mn<sub>2</sub>O<sub>3</sub> loading in Fig. 10. The  $T_{max}$  shifts to low operation temperature with an increase in the loading amount. This result indicates that a cause of this sensitization may be related with what is called chemical sensitization [7]. A chemical sensitization is mediated by both activation and spill over effect, and also two types of the chemical sensitization may exist. As for first type, a test gas is activated on the surface of the additives, followed by spillover to the semiconductor surface, and the activated gas react with the surface oxygen, resulting in a decrease in the surface resistance of the n-type semiconductor as an example of Pt-SnO<sub>2</sub> [7]. As for second type, the oxygen is activated on the surface of the additive, followed by spillover to the semiconductor surface, leading to increase in activated oxygen for reacting with the test gas in air, resulting in an increase in the surface resistance as an example of CeO<sub>2</sub>-SnO<sub>2</sub> [9]. The maximum sensitivity of the sensors loaded with additive will be observed at the lower temperatures than that for additive free due to the chemical

sensitization. It is suspected that a cause of sensitization of  $Mn_2O_3$ - $SnO_2$  sensor is the latter because the resistance of  $Mn_2O_3$ - $SnO_2$  sensor in air ( $R_a$ ) increased steeply with an increase in  $Mn_2O_3$  loading up to about 10 wt% in the Fig.7.

$MnO_2$  ( $Mn_2O_3$ ) is the high ability material to catalytic oxidation [10,16]. So far, it has been pointed out that  $MnO_2$  ( $Mn_2O_3$ ) tend to activate most of test gas at only the surface of sensor because of its superior oxidation activity [10]. Therefore, in the test gas atmosphere, the resistance of the sensor does not vary much, and the sensitivity as well. On the contrary, in our experiment,  $SnO_2$  loaded with  $Mn_2O_3$  showed very excellent sensitivity to HCHO.

We suppose the enhancement of the sensitivity achieved by means of  $Mn_2O_3$  loading in the present experiment as follows: The size (diameter: about  $1 \mu m$ ) of  $Mn_2O_3$  particles used in these sensors are as large as the one of  $SnO_2$  particles, hence, the

total percent of the surface of  $MnO_2$  particles is small compared to that of the usually used  $Mn_2O_3$  particles. Consequently, the test gas is oxidized moderately over the whole of sensor, resulting in the great change of the resistance of the sensor, leading to increase of the sensitivity. However, the details of causes should be confirmed in further studies.

### 3-4 XPS study of $Mn_2O_3$ - $SnO_2$ sensor

We also suspected that the marked sensitization result from not only the chemical interaction but also the electronic interaction, because the resistance of  $Mn_2O_3$ - $SnO_2$  sensor in air increased steeply with an increase in the amount of  $Mn_2O_3$  loaded. Furthermore,  $Mn_2O_3$  and  $SnO_2$  were p-type and n-type semiconductor, respectively. In the past, as for the change of oxidation state of noble metals, such as Ag- $SnO_2$  [7,8], Pd- $SnO_2$

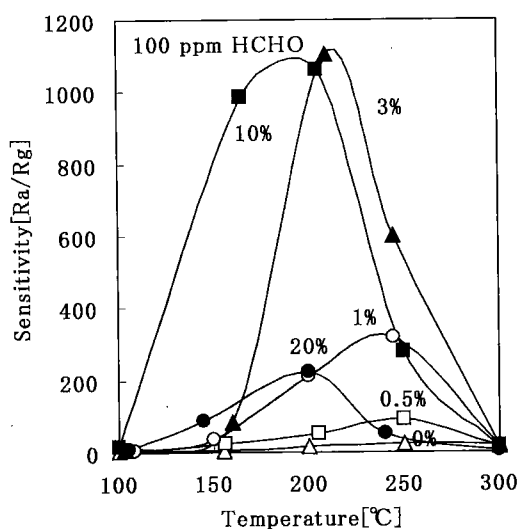


Fig.9. Operation temperature dependence of 100 ppm HCHO sensitivity of  $Mn_2O_3$ - $SnO_2$  sensors loaded with various contents of  $Mn_2O_3$  (shown in wt%).

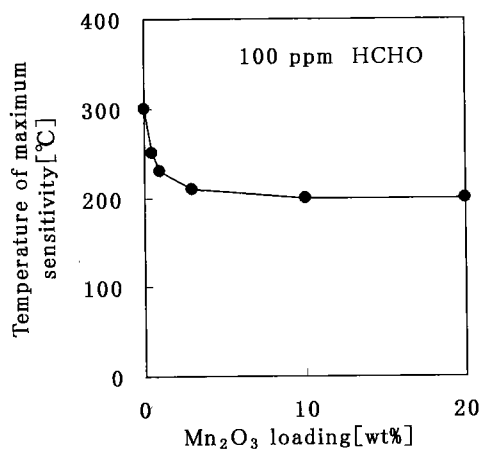


Fig.10. Variation in operation temperature showing maximum sensitivity of  $SnO_2$  sensors loaded with different amounts of  $Mn_2O_3$  to 100 ppm HCHO.

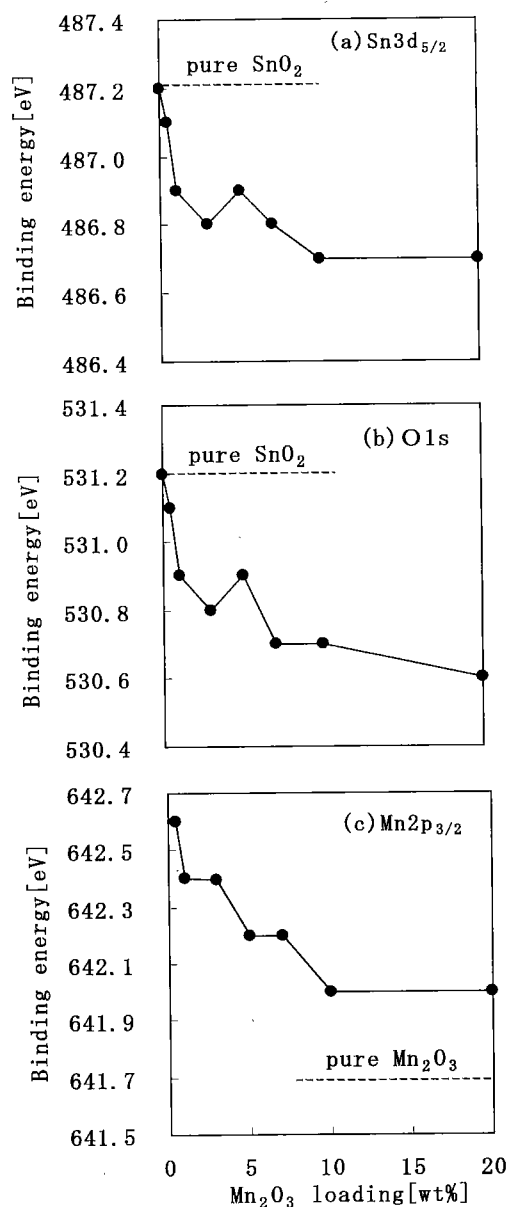
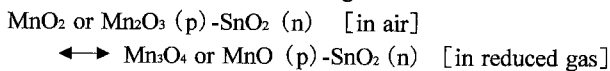


Fig.11. Changes in binding energies of (a)Sn 3d<sub>5/2</sub>, (b)O 1s, and (c)Mn 2p<sub>3/2</sub> levels for  $Mn_2O_3$ - $SnO_2$  as a function of the amount of  $Mn_2O_3$ .

[11] and Au-WO<sub>3</sub> [12] systems, were investigated by XPS, and also as for p-n junction type sensors, CuO-SnO<sub>2</sub> [13,14] and Rb<sub>2</sub>CO<sub>3</sub>-In<sub>2</sub>O<sub>3</sub> [15] systems were reported. Therefore, we tried to investigate the surface state of the Mn<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub> system by XPS.

Figure 11 shows the change in the binding energies (BEs) of Sn 3d, O 1s and Mn 2p levels of Mn<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub> sensors as a function of Mn<sub>2</sub>O<sub>3</sub> loading. The BE value (641.7) of Mn 2p<sub>3/2</sub> of Mn<sub>2</sub>O<sub>3</sub> was used instead of that of MnO<sub>2</sub>. As shown in Fig.11, Sn 3d<sub>5/2</sub> and O 1s levels shift downward sharply with an increase in MnO<sub>2</sub> loading (up to about 10 wt%), while the BE of Mn 2p<sub>3/2</sub> shifts downward to that of pure Mn<sub>2</sub>O<sub>3</sub>. These BE shifts are similar to what has been reported with CuO-SnO<sub>2</sub> [13,14] and Rb<sub>2</sub>CO<sub>3</sub>-In<sub>2</sub>O<sub>3</sub> [15] systems, accounted for by assuming the formation of a p-n junction between p-type (CuO) and n-type (SnO<sub>2</sub>) or p-type (Rb<sub>2</sub>CO<sub>3</sub>) and n-type (In<sub>2</sub>O<sub>3</sub>).

The present result seems to confirm that p-n junction is formed at the interface between Mn<sub>2</sub>O<sub>3</sub> (p type) and SnO<sub>2</sub> (n type) in Mn<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub> system. That is, in air the electron transfer from SnO<sub>2</sub> (work function; 4.69 eV) into Mn<sub>2</sub>O<sub>3</sub> (electronic potential of Mn<sup>3+</sup>/Mn<sup>2+</sup>; 5.95 eV) may occur at the SnO<sub>2</sub>-Mn<sub>2</sub>O<sub>3</sub> interface. This electron transfer causes the upward band bending of SnO<sub>2</sub> surface, resulting in an increase of the resistance of SnO<sub>2</sub>. From the charge transfer consideration, the BE of Sn 3d<sub>5/2</sub> and O 1s may shift to higher energy side due to the contact with Mn<sub>2</sub>O<sub>3</sub>. However, the BE rather shifts to lower energy side due to the upward band bending of n-type SnO<sub>2</sub> surface. In the same way, the energy band of Mn<sub>2</sub>O<sub>3</sub> will be bent in the opposite direction, resulting in an upward shift of Mn 2p<sub>3/2</sub> level from the Mn 2p<sub>3/2</sub> state of pure Mn<sub>2</sub>O<sub>3</sub>. On the other hand, in the HCHO, the Mn<sub>2</sub>O<sub>3</sub> state may change to Mn<sub>3</sub>O<sub>4</sub> or MnO with lower work functions than SnO<sub>2</sub>. So, the electron transfer from Mn<sub>3</sub>O<sub>4</sub> or MnO to SnO<sub>2</sub> occurs at the interface of Mn<sub>2</sub>O<sub>3</sub> and SnO<sub>2</sub>, resulting in the decrease in the resistance of SnO<sub>2</sub>. A p-n junction outline could be the following:



We note here that the higher oxide state of Mn changes easily to lower oxide state under the reduced atmosphere as follows [16]:

$\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4 \rightarrow \text{MnO} \rightarrow \text{Mn}$   
As the electron affinity of Mn<sub>2</sub>O<sub>3</sub> is also much stronger than that of the adsorbed oxygen, which leads to an enhancement of the gas sensitivity. As a result, the sensing properties of Mn<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub> systems to HCHO might be extremely improved.

In addition, as we mentioned before, it seems that the chemical sensitization operated largely upon the sensitivities of these sensors to HCHO gases, too.

### 3-5 Sensing properties of SnO<sub>2</sub> sensors loaded with both Ag and Mn<sub>2</sub>O<sub>3</sub>

As shown in the above sections, it is found that Ag and MnO<sub>2</sub> are effective to detect the low concentration HCHO as additives for SnO<sub>2</sub>. In order to further increase sensitivity of SnO<sub>2</sub> sensor, SnO<sub>2</sub> doubly promoted by Ag and Mn<sub>2</sub>O<sub>3</sub> was investigated.

The result of the measurement at 300 °C is shown in Fig. 12. The loading amount of Ag was 1 wt% and that of Mn<sub>2</sub>O<sub>3</sub> was 5

wt%. The Ag (1 wt%)-SnO<sub>2</sub> sensor is superior to Mn<sub>2</sub>O<sub>3</sub> (5 wt%)-SnO<sub>2</sub> sensor as for the sensitivity to HCHO at 300°C. It is found in Fig.12 that the sensitivity of Ag (1 wt%)-MnO<sub>2</sub> (5 wt%)-SnO<sub>2</sub> sensor is as low as additive free SnO<sub>2</sub> sensor against expectation. It is suspected that the doubly promotion to SnO<sub>2</sub> sensor heighten too much oxidation activity to HCHO.

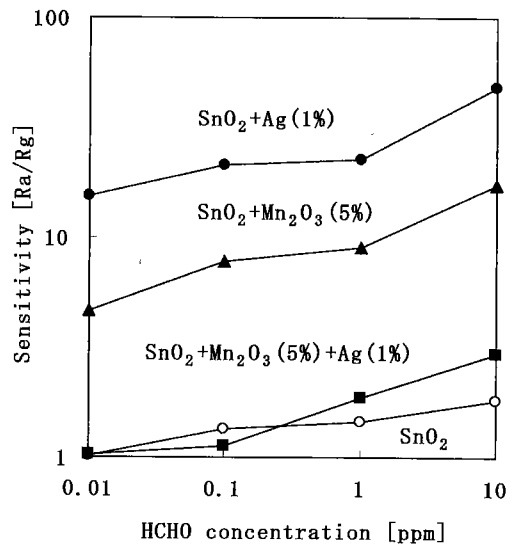


Fig.12 Sensitivities of SnO<sub>2</sub> sensors loaded with Mn<sub>2</sub>O<sub>3</sub>, Ag and Mn<sub>2</sub>O<sub>3</sub>+Ag as a function of HCHO concentration at 300°C.

### 4. Conclusions

Among various metal oxides, SnO<sub>2</sub> is the most attractive for the detection of HCHO. Further research has shown that both Ag (1~3 wt%) and Mn<sub>2</sub>O<sub>3</sub> (3~10 wt%) are excellent promoters to SnO<sub>2</sub> for increasing the sensitivity to HCHO. However, Ag-SnO<sub>2</sub> sensor have the very short lifetime, further investigation are necessary for this reason. It was found that Mn<sub>2</sub>O<sub>3</sub> is the best promoter to SnO<sub>2</sub> for increasing the sensitivity to HCHO. The doubly promoted Ag (1 wt%)-Mn<sub>2</sub>O<sub>3</sub> (5 wt%)-SnO<sub>2</sub> sensor showed low sensitivity to 100 ppm HCHO against expectation.

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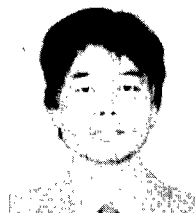
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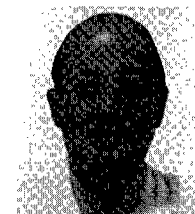
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