Development of SnO₂-based Gas Sensors for Detection of Volatile Organic Compounds

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Keyword: gas sensor, oxide semiconductor, volatile organic compounds, sick-house syndrome, formaldehyde

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 (C₆H₄(CH₃)₂) 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 SnO₂. Further, the sensing property of an SnO₂ 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 SnO₂ loaded with several metal oxides were investigated. Among the elements loaded (5 wt%) with each of 14 metal oxides, the Mn₂O₃-loaded one was outstanding in sensitivity to HCHO at 200°C. However, its sensitivity of the doubly promoted sensor, Ag (1 wt%)-Mn₂O₃ (5 wt%)-SnO₂ 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 (C₆H₄(CH₃)₂) and toluene (C₆H₅CH₃) 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_x, SO_x, O₃, NH₃ and indoor-air pollution gases such as CO₂, 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 SnO₂, In₂O₃, WO₃, ZnO, Cr₂O₃, Co₃O₄ showed relatively high sensitivity to HCHO, C₆H₄(CH₃)₂, and (C₆H₅CH₃). SnO₂ exhibits excellent sensitivity to HCHO, and WO₃ shows the highest sensitivity to C₆H₄(CH₃)₂ [3].

This paper deals with the HCHO and C₆H₄(CH₃)₂ sensing

properties of SnO₂ elements loaded with noble metals and various metal oxides, especially Ag and MnO₂.

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 mm³ 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, SnO₂ 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 C₆H₄(CH₃)₂ 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 $\text{Cu-K}\alpha$ radiation. X-Ray photoelectron spectroscopy (XPS) measurement was carried out using a Shimadzu ESCA-1000 spectrometer with $\text{Al-K}\alpha$ 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, $\text{C}_6\text{H}_4(\text{CH}_3)_2$, and $(\text{C}_2\text{H}_5)_2$. 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_2 , In_2O_3 , WO_3 , ZnO (n-type), and Cr_2O_3 , Co_3O_4 (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 $\text{C}_6\text{H}_4(\text{CH}_3)_2$. 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_2 and In_2O_3 . 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 (c) formaldehyde.

these sensors on concentration of $\text{C}_6\text{H}_4(\text{CH}_3)_2$. Xylene was detected with the highest sensitivity by WO_3 . 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_2 or In_2O_3 , as seen in Fig. 2, and that to $\text{C}_6\text{H}_4(\text{CH}_3)_2$ could be estimated about a few ppm by WO_3 , 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_2 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_2 -based sensors loaded

Fig.4. Sensitivities to formaldehyde (■) and xylene (□) of SnO₂ 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-SnO₂ sensors operated at 300°C.

with 7 kinds of noble metals to 100 ppm HCHO and C₆H₄(CH₃)₂ at 300°C. It is found that Ag greatly enhanced the sensitivity of SnO₂ 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-SnO₂ 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 SnO₂ which has been indicated by Yamazoe et al., seems to be concerned [7-8]. That is, in air, an Ag particle dispersed on

SnO₂ surface may be covered by Ag₂O, forms a redox couple of Ag⁺/Ag⁰, 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 SnO₂ is taken to be 4.49 eV, and the Fermi level (E_F) of SnO₂ is assumed to be 0.1~0.2 eV below the conduction band, and the work function of SnO₂ is thus estimated at 4.59~4.69 eV. Therefore, to attain electronic equilibrium, the migration of electron from the surface of SnO₂ to that of Ag takes place, producing an electron depleted space-charge layer, resulting in the increase of resistance of SnO₂. In contrast, in formaldehyde gas which causes the reduction of Ag⁺ to Ag⁰, the E_F of SnO₂ shifts upward to be pinned at the work function of Ag (4.49 eV), resulting in a decrease of resistance of SnO₂. As the electron affinity of Ag₂O 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 SnO₂ particles promotes extremely the HCHO sensitivity. However, Ag-SnO₂ 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 SnO₂ sensor loaded with Ag.

3-3 Sensing properties of SnO₂ sensors loaded with metal oxides

As we mentioned in the previous section, owing to the instability of Ag-SnO₂ sensor, metal oxides were looked for new modifier instead of Ag. Figure 6 summarizes the sensitivities of SnO₂ elements loaded with various metal oxides (5 wt%) to HCHO and C₆H₄(CH₃)₂ at 280°C and 200°C. Although most of additives are little effective, the MnO₂ (5 wt%)-SnO₂ sensor shows extremely high sensitivity as high as 161 to 100 ppm HCHO and 97 to 100 ppm C₆H₄(CH₃)₂ 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 SnO₂ without MnO₂. In contrast, the sensitivity of the sensor shows as low as 16 to 100 ppm C₆H₄(CH₃)₂ and largely falls at 200°C.

Generally, C₆H₄(CH₃)₂ and C₆H₅CH₃, 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 MnO₂ to SnO₂ markedly promotes the sensitivity to HCHO at 200°C without increasing the sensitivity to C₆H₄(CH₃)₂ and C₆H₅CH₃.

Figure 7 shows the electrical resistance of MnO₂-SnO₂ sensors in air (Ra) and in 100 ppm HCHO (Rg) as well as the resulting HCHO sensitivity at 200°C as a function of MnO₂ loading. Ra increases steeply with an increase in MnO₂ 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 MnO₂ loading in the range between 0 and 20 wt%.

Fig.6. Sensitivity of SnO₂-based sensors with various additives to 100 ppm HCHO and 100 ppm C₆H₄(CH₃)₂ at (a) 280°C and (b) 200°C.

Fig.7. Effects of MnO₂ loading on the electrical resistances (Ra) in air and in 100 ppm HCHO (Rg) as well as resulting gas sensitivity (Ra/Rg) for MnO₂-SnO₂ 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% MnO₂. The Ra of MnO₂-SnO₂ 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-SnO₂ sensor in Fig. 5 decrease after the sensitivity reaches a maximum value (about 600). Since the resistance of MnO₂ is larger than that of SnO₂, the resistance of MnO₂-SnO₂ sensors is likely to increase toward the MnO₂ resistance with increasing MnO₂ content.

We examined the reason why sensitivity of SnO₂ sensor is increased with MnO₂ loading. First, XRD pattern was measured to examine the crystalline state of the sensor. Figure 8 shows XRD pattern of SnO₂ loaded with MnO₂. It is found that MnO₂ changed into Mn₂O₃ through calcining, and also no other complex oxides are observed except Mn₂O₃ and SnO₂. Therefore, as for the crystalline state of Mn-oxide, Mn₂O₃ is used instead of MnO₂ from now on.

Fig.8. X-ray diffraction patterns for the MnO₂-SnO₂ sensors calcined at 600 °C.

Figure 9 shows the sensitivities to 100 ppm HCHO of SnO₂ sensors variously loaded with Mn₂O₃ 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 Mn₂O₃ 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-SnO₂ [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 CeO₂-SnO₂ [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 $1\ \mu\text{m}$) 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) $\text{Sn } 3d_{5/2}$, (b) $\text{O } 1s$, and (c) $\text{Mn } 2p_{3/2}$ levels for Mn_2O_3 - SnO_2 as a function of the amount of Mn_2O_3 .

[11] and Au-WO₃ [12] systems, were investigated by XPS, and also as for p-n junction type sensors, CuO-SnO₂ [13,14] and Rb₂CO₃-In₂O₃ [15] systems were reported. Therefore, we tried to investigate the surface state of the Mn₂O₃-SnO₂ system by XPS.

Figure 11 shows the change in the binding energies (BEs) of Sn 3d, O 1s and Mn 2p levels of Mn₂O₃-SnO₂ sensors as a function of Mn₂O₃ loading. The BE value (641.7) of Mn 2p_{3/2} of Mn₂O₃ was used instead of that of MnO₂. As shown in Fig.11, Sn 3d_{5/2} and O 1s levels shift downward sharply with an increase in MnO₂ loading (up to about 10 wt%), while the BE of Mn 2p_{3/2} shifts downward to that of pure Mn₂O₃. These BE shifts are similar to what has been reported with CuO-SnO₂ [13,14] and Rb₂CO₃-In₂O₃ [15] systems, accounted for by assuming the formation of a p-n junction between p-type (CuO) and n-type (SnO₂) or p-type (Rb₂CO₃) and n-type (In₂O₃).

The present result seems to confirm that p-n junction is formed at the interface between Mn₂O₃ (p type) and SnO₂ (n type) in Mn₂O₃-SnO₂ system. That is, in air the electron transfer from SnO₂ (work function; 4.69 eV) into Mn₂O₃ (electronic potential of Mn³⁺/Mn²⁺; 5.95 eV) may occur at the SnO₂-Mn₂O₃ interface. This electron transfer causes the upward band bending of SnO₂ surface, resulting in an increase of the resistance of SnO₂. From the charge transfer consideration, the BE of Sn 3d_{5/2} and O 1s may shift to higher energy side due to the contact with Mn₂O₃. However, the BE rather shifts to lower energy side due to the upward band bending of n-type SnO₂ surface. In the same way, the energy band of Mn₂O₃ will be bent in the opposite direction, resulting in an upward shift of Mn 2p_{3/2} level from the Mn 2p_{3/2} state of pure Mn₂O₃. On the other hand, in the HCHO, the Mn₂O₃ state may change to Mn₃O₄ or MnO with lower work functions than SnO₂. So, the electron transfer from Mn₃O₄ or MnO to SnO₂ occurs at the interface of Mn₂O₃ and SnO₂, resulting in the decrease in the resistance of SnO₂. A p-n junction outline could be the following:

MnO₂ or Mn₂O₃ (p)-SnO₂ (n) [in air]

↔ Mn₃O₄ or MnO (p)-SnO₂ (n) [in reduced gas]

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

MnO₂ → Mn₂O₃ → Mn₃O₄ → MnO → Mn

As the electron affinity of Mn₂O₃ 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 Mn₂O₃-SnO₂ 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 SnO₂ sensors loaded with both Ag and Mn₂O₃

As shown in the above sections, it is found that Ag and MnO₂ are effective to detect the low concentration HCHO as additives for SnO₂. In order to further increase sensitivity of SnO₂ sensor, SnO₂ doubly promoted by Ag and Mn₂O₃ 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 Mn₂O₃ was 5

wt%. The Ag (1 wt%)-SnO₂ sensor is superior to Mn₂O₃ (5 wt%)-SnO₂ sensor as for the sensitivity to HCHO at 300°C. It is found in Fig.12 that the sensitivity of Ag (1 wt%)-MnO₂ (5 wt%)-SnO₂ sensor is as low as additive free SnO₂ sensor against expectation. It is suspected that the doubly promotion to SnO₂ sensor heighten too much oxidation activity to HCHO.

Fig.12 Sensitivities of SnO₂ sensors loaded with Mn₂O₃, Ag and Mn₂O₃+Ag as a function of HCHO concentration at 300°C.

4. Conclusions

Among various metal oxides, SnO₂ is the most attractive for the detection of HCHO. Further research has shown that both Ag (1~3 wt%) and Mn₂O₃ (3~10 wt%) are excellent promoters to SnO₂ for increasing the sensitivity to HCHO. However, Ag-SnO₂ sensor have the very short lifetime, further investigation are necessary for this reason. It was found that Mn₂O₃ is the best promoter to SnO₂ for increasing the sensitivity to HCHO. The doubly promoted Ag (1 wt%)-Mn₂O₃ (5 wt%)-SnO₂ sensor showed low sensitivity to 100 ppm HCHO against expectation.

Acknowledgments

The authors are grateful to Mr. Masanori Hoshino (Cosel Co., Ltd.), Mr. Masayoshi Minami (Hokuriku Electric Ind. Co., Ltd.) and Miss Hiromi Yamada (Toyo Kako Co., Ltd.) for experimental assistance and discussing the results.

A part of this work was financially supported by a grant from Japan Science and Technology Corporation.

(Manuscript received September 11, 2000, revised March 22, 2001)

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