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Gas sensitivity of metal oxide mixed tin oxide films prepared by spray pyrolysis

K. NOMURA, Y. UJIHIRA, S. S. SHARMA
Faculty of Engineering, The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113, Japan
A. FUEDA, T. MURAKAMI
Kogakuin University, Nishishinjuku 1-24-2, Shinjuku-ku, Tokyo, Japan

Various kinds of SnO_2 films, modified with the addition of iron, antimony, copper, titanium, manganese, nickel, cobalt or calcium oxides, were fabricated by using the spray pyrolysis technique and their gas-sensing characteristics were studied. From electrical measurements in air, the relative sensitivity towards inflammable gas of these SnO_2-based film sensors was compared. It was observed that SnO_2-based films of higher electrical resistance had a tendency to have higher sensitivity towards ethanol than the SnO_2-based films of lower resistance. The addition of p-type metal oxides, such as NiO and MnO, to the SnO_2 matrix was found to be effective in increasing the sensitivity towards inflammable gas.

1. Introduction

Several SnO_2- and ZnO-based gas sensors have been studied for fabricating inflammable gas and vapour detectors, because the electrical resistance of these oxides varies with the concentration of the organic gas [1]. The characteristics of these gas sensors depend on many factors such as grain size, grain boundary, neck of grain, and the defects of the oxide lattice.

The mechanism of gas reaction on the oxide surface is considered as follows [2, 3, 4]. On a surface of n-type semiconductors, several tens of nanometers thick, the layers without carrier electrons are formed as the result of extraction of electrons from the matrix oxide by the adsorption of oxygen molecules, as well as the presence of lattice defects and impurities. The potential barrier at the surface causes high electrical resistance to the thin SnO_2 film. When an inflammable or reducing gas interacts with the adsorbed oxygen on the surface of SnO_2, the amount of adsorbed oxygen, which attracts carrier electrons from the matrix to yield a negative charge, decreases. The removal of adsorbed oxygen from the surface results in a reduction of the potential barrier and an increase in carrier density by releasing the carrier electrons back into the matrix. When metal ions with a valence higher than $+2$ or $+4$ are doped on to ZnO or SnO_2, respectively, these matrices gain carrier density and an increase of electrical conductivity. Precious metals such as palladium and platinum are often doped as catalysts of the oxidation reaction of inflammable gas at the gas sensing metal oxide semiconductor. Several other metal oxides are also included in ZnO or SnO_2 as binders of the polycrystalline powder. However, it is not well understood whether the higher valence dopants cause reproducible amelioration to increase the sensitivity toward inflammable gas. Therefore, a systematic investigation of the effect of addition of different valence metal ions to SnO_2 on the gas sensitivity was undertaken.

Film sensors have been developed with the purpose of miniaturization, homogenization, higher selectivity and sensitivity. Pink *et al.* [5] showed that tin oxide film prepared by the spray pyrolysis of ethyl acetate solution of $(CH_3COO)_2SnCl_2$ gave a higher sensitivity to inflammable gas. The spray pyrolysis technique is very simple and suitable for making various kinds of SnO_2 film modified with the addition of other metal oxides without using a binding reagent. The effect of the addition of other metal ions to SnO_2 on the gas sensitivity is discussed in terms of the resistance variation of SnO_2-based films in air containing inflammable gas.

2. Experimental details

2.1. Sample preparation

Chloride salts were dissolved in C_2H_5OH or CH_3OH. The ethanol or methanol solutions of 0.1 M $SnCl_2 2H_2O$ or $SnCl_4$ + $PdCl_2$ (or $H_2[PtCl_6]6H_2O$) + chloride compounds of $FeCl_3 6H_2O$, $CoCl_2$, $NiCl_2 6H_2O$, $MnCl_2 4H_2O$, $SbCl_3$, $CaCl_2 2H_2O$, or $CuCl_2 2H_2O$, were sprayed intermittently at regular time intervals of about 20 sec on to a quartz glass or an aluminium nitride ceramic sheet heated to about 300 to 400° C by a plate heater. The temperature of the substrate plate was adjusted to less than the ignition point of the solvents used (340 to 390° C for C_2H_5OH and 470° C for CH_3OH). The thickness of SnO_2 films prepared was about 200 nm.

2.2. Electric conductivity measurements

Silver was evaporated as two squares at 1 cm spacing on SnO_2 films in order to plant electrical contacts which connected the SnO_2 film to the platinum wire. Then, the prepared samples were annealed at 600° C

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for 3 h. The response of the fabricated gas sensor to inflammable gas with temperature was observed by adopting the two-point electrical measuring technique while heating the samples to 500° C at a rate of about 10° C min^{-1}. In this measurement system, a protection resistor (R_p) was connected to the sensor in series and a d.c. voltage of 10 V was applied. The electrical resistance of the film sensor was calculated by measuring the change of the d.c. voltage across the protection resistors, the value of which was replaceable according to the resistance of the sample. An aliquot of C_2H_5OH was introduced by microsyringe into the 10 litre chamber and evaporated in it by stirring with a fan. The standard air balance gas of CO, H_2 or CH_4 was passed at a rate of 20 ml min^{-1} into the 500 ml chamber. To ensure ohmic contacts in the arrangement, preliminary experiments had been carried out until precise results were obtained. The gas sensitivity was defined by the ratio of the electrical resistances measured in dry air with and without inflammable gas.

3. Results

The variation of electric resistance and the sensitivity of SnO_2 films containing various metal oxides towards 1000 p.p.m. C_2H_5OH confined in the 10 litre chamber are summarized in Table I. SnO_2 film and palladium-doped SnO_2 film showed almost the same sensitivity to ethanol. The addition of only palladium to the SnO_2 matrix did not enhance the sensitivity, although palladium had been considered to play basically a role of catalyst and might increase the sensitivity. On doping various metal ions together with Pd^{2+} in the SnO_2 matrix, the electrical resistance increased remarkably and the gas sensitivity also increased. Manganese ion-doped SnO_2 and nickel ion-doped SnO_2, in particular, into which palladium ions were also added, showed a high resistance and high sensitivity to ethanol.

3.1. Antimony(V) ion-doped tin oxide films

Electrical resistance of Sn–Sb–Pd oxide films with the mole ratios of Sn : Sb : Pd = 100 : 10 : 1, 100 : 100 : 1 and 100 : 400 : 1 decreased to 18, 3 and 0.4 kΩ cm^{-2} in this order. An increase in the antimony ratio decreased the resistance of the film. The response of Sn–Sb–Pd oxide films was too unstable to detect the inflammable gas because the relative standard deviation for repeated measurements in air increased to 20, 30, and 50%, respectively. This phenomenon suggested that higher electrically conductive film is not always suitable as a gas sensing material.

TABLE I Gas sensitivity of tin oxide-based semiconductor for 1000 p.p.m. ethanol

Materials	Mole ratio	Temp. (° C)	Resistance (kΩ cm^{-2})	Sensitivity, R_{air}/R_{gas}
Sn		350	10	2
Sn : Pd	100 : 1	350	10	2
Sn : Ca : Pd	100 : 500 : 1	350	100	3
Sn : Ti : Pd	100 : 100 : 1	350	100	6
Sn : Cu : Pd	100 : 100 : 1	375	100	3.2
Sn : Fe : Pd	100 : 100 : 1	350	100	6.4
Sn : Co : Pd	100 : 100 : 1	350	10	3.4
Sn : Mn : Pd	100 : 1000 : 1	350	2×10^5	43
Sn : Ni : Pd	100 : 1000 : 1	350	10^5	33

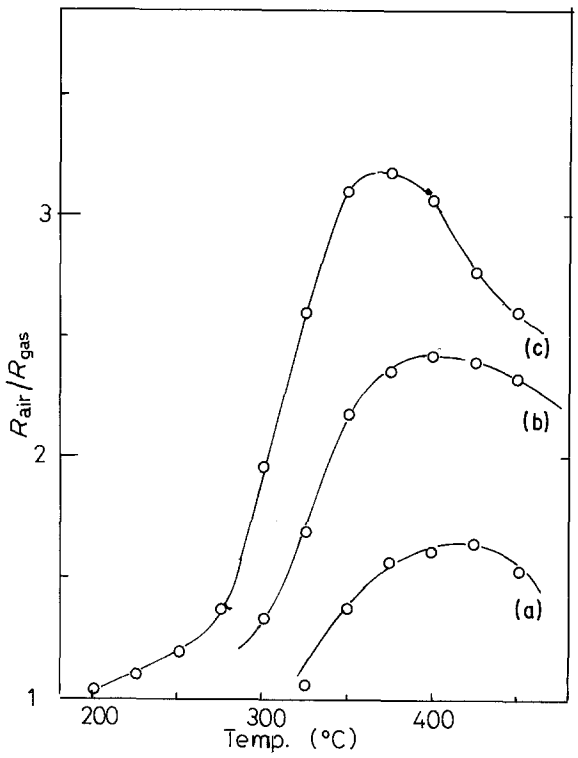

Figure 1 Effect of the addition of copper ion into tin oxide films on the sensitivity to 1000 p.p.m. ethanol. Mole ratio of Sn : Cu : Pd: (a) 100 : 10 : 1, (b) 100 : 100 : 1, (c) 100 : 400 : 1.

3.2. Copper(II) ion-doped tin oxide films

The electrical characteristics of Sn–Cu–Pd oxide films are shown in Fig. 1. The addition of copper enhanced the sensitivity to ethanol and contributed to lowering the optimum working temperature for the measurement, whereas the resistance increased from 16 to 180 kΩ cm^{-2} at 280° C for the samples with Sn : Cu : Pd ratios of 100 : 10 : 1, 100 : 100 : 1 and 100 : 400 : 1. The electrical resistance of Sn–Cu–Pd oxide films decreased in the ethanol gas and increased in the methane gas in the temperature range 280 to 400° C. In Sn–Cu–Pd oxide film with the ratio of 100 : 100 : 1, the resistance decreased in air containing methane at a temperature higher than 400° C. The reason for this was considered to be due to the decomposition of methane. The film which contained 40 times more copper than tin resulted in a difficulty in obtaining electrical resistance measurements.

3.3. Iron(III) ion-doped tin oxide films

In Sn–Fe–Pd oxide films, the change in resistance on increasing the doped iron was relatively small. The oxide film with an Sn : Fe : Pd ratio of 100 : 100 : 1 had a resistance of 60 kΩ cm^{-2}. The film showed the highest sensitivity of 6.3 to ethanol but showed a very low sensitivity of 1.1 and 1.2 towards methane and carbon monoxide, respectively. The film with Sn : Fe : Pd = 100 : 1000 : 1 gave a lower resistance of 2.5 kΩ cm^{-2} and a lower sensitivity of 1.3 at 400° C. It is considered that iron(III) and iron(II) oxides, which might be produced by reduction, contributed to the electrical conductivity of the film and decreased the electrical resistance. This analogy also confirmed the fact that the film with lower electrical resistance has a lower sensitivity in the series of iron mixed

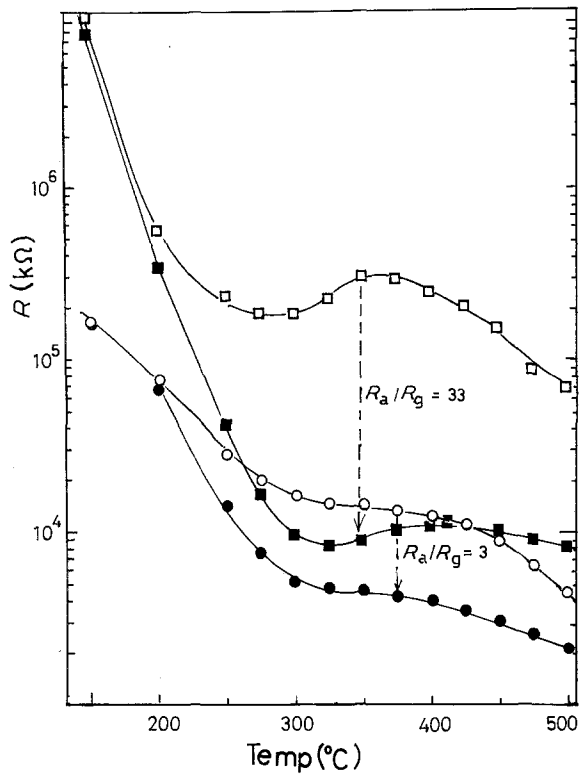

Figure 2 Effect of heating temperature on the resistance of nickel ion-doped tin oxide in (□, ○) air and in (■, ●) 1000 p.p.m. ethanol atmosphere. Mole ratio of Sn : Ni : Pd: (■, □) 100 : 1000 : 1, (●, ○) 1 : 10.

samples. The Sn–Fe–Pd oxide film did not improve the sensitivity to methane and carbon monoxide so much. The highest sensitivity of 1.3 was observed for the film with Sn : Fe : Pd = 100 : 1000 : 1.

3.4. Cobalt(III) ion-doped tin oxide films

The cobalt-doped tin oxide film with Sn : Co : Pd = 100 : 10 : 1 showed a resistance of 0.52 kΩ cm^{-2} and a sensitivity of 1.6 for 1000 p.p.m. ethanol, while the oxide film with Sn : Co : Pd = 100 : 100 : 1 gave 14 kΩ cm^{-1} and 3.3 for 1000 p.p.m. ethanol at 350° C.

3.5. Titanium(IV) ion-doped tin oxide films

The oxide film with Sn : Ti : Pd = 100 : 100 : 1 showed a sensitivity of 6 for 1000 p.p.m. ethanol. The addition of titanium caused the increase in sensitivity through the increase of the electrical resistance.

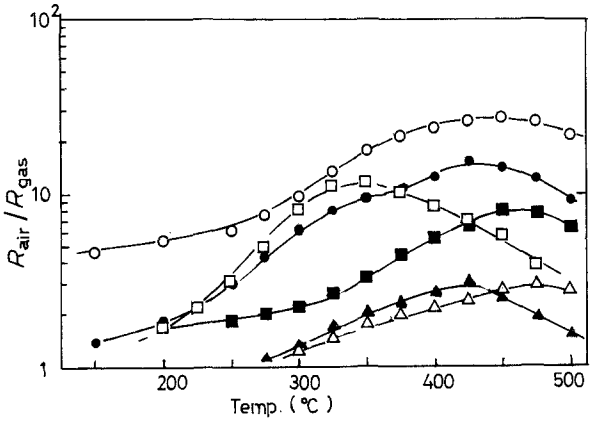

Figure 3 The sensitivity of nickel ion-doped tin oxide films to 5000 p.p.m. H_2, 1000 p.p.m. C_2H_5OH, and 1000 p.p.m. CH_4. Mole ratio: Sn : Ni : Pd = 100 : 500 : 6 (○) H_2, (□) C_2H_5OH, (△) CH_4; Sn : Ni : Pt = 100 : 500 : 6 (●) H_2, (■) C_2H_5OH, (▲) CH_4.

3.6. Nickel(II) ion-doped tin oxide film

Because measurement of the electrical conductivity of tin oxide films containing various amounts of nickel(II) ion at room temperature was difficult due to the very high electrical resistance, the initial measurements were carried out at a temperature higher than 150° C.

Typical electrical characteristics of these films are shown in Figs 2 and 3. The results obtained are summarized in Table II. Whereas nickel-doped tin oxide film gave a sensitivity of only 3.1 for 1000 p.p.m. ethanol without the doping of palladium, the films which were added with a small amount of palladium were ten times more sensitive to methanol compared to Sn–Ni oxide without palladium. The gas sensitivity of the film with Sn : Ni : Pd = 100 : 500 : 1 decreased to one-sixth of that of the film with Sn : Ni : Pd = 100 : 1000 : 1. The addition of palladium to Sn–Ni oxide film was found to be more effective for improving the sensitivity toward hydrogen and ethanol, than the addition of platinum.

3.7. Manganese(II) ion-doped tin oxide films

The electrical resistance change of manganese(II) ion-doped tin oxide film with Sn : Mn : Pd = 100 : 1000 : 1 with working temperature is shown in Figs 4 and 5. The sensitivity to inflammable gas and the electrical resistance of the Sn–Mn oxide films are summarized

TABLE II Gas sensitivity of Ni–Sn oxide films

Materials	Mole ratio	Temp. (° C)	Resistance (kΩ cm^{-2})	Gas conc. (p.p.m.)		Sensitivity, R_{air}/R_{gas}
Sn : Ni	1 : 10	350	10^5	C_2H_5OH	1000	3.1
Sn : Ni : Pd	100 : 1000 : 1	350	3×10^5	C_2H_5OH	1000	33
Sn : Ni : Pd	100 : 500 : 1	450	600	H_2	5000	21
		350	400	C_2H_5OH	1000	5.6
		425	600	CO	1000	3.9
Sn : Ni : Pd	100 : 500 : 6	450	1000	H_2	5000	27
		350	800	C_2H_5OH	1000	11
		475	1000	CO	1000	3
Sn : Ni : Pt	100 : 500 : 6	425	4000	H_2	5000	15
		450	4000	C_2H_5OH	1000	8
		425	4000	CO	1000	3.2
Sn : Ni : Pd	100 : 100 : 1	400	10	C_2H_2OH	1000	2.3
		500	20	CH_4	1000	2.9
Sn : Ni : Pd	100 : 10 : 1	400	6	C_2H_5OH	1000	3.2
		500	8	CH_4	1000	1.7

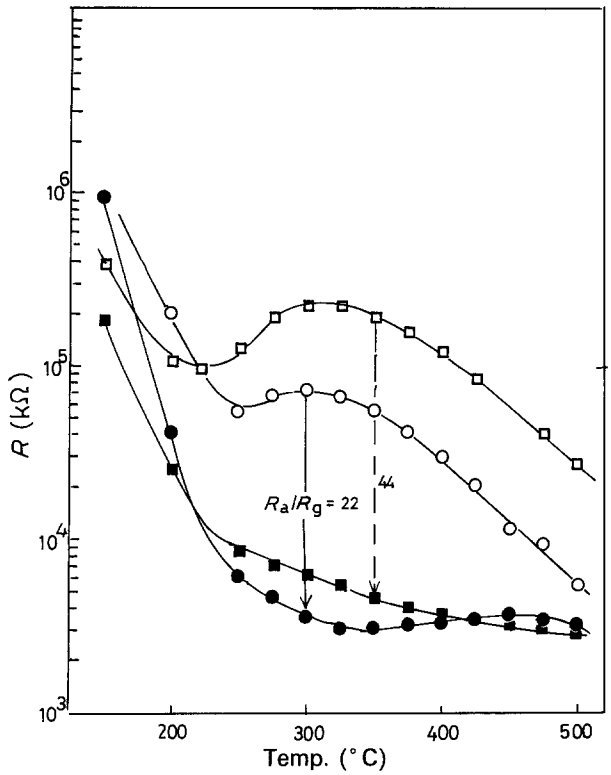

Figure 4 The effect of heating temperature on resistance of manganese ion-doped tin oxides in (□, ○) air and in (■, ●) 1000 p.p.m. ethanol atmosphere. Mole ratio of Sn:Mn:Pd: (□, ■) 100:1000:1, (○, ●) 1:10.

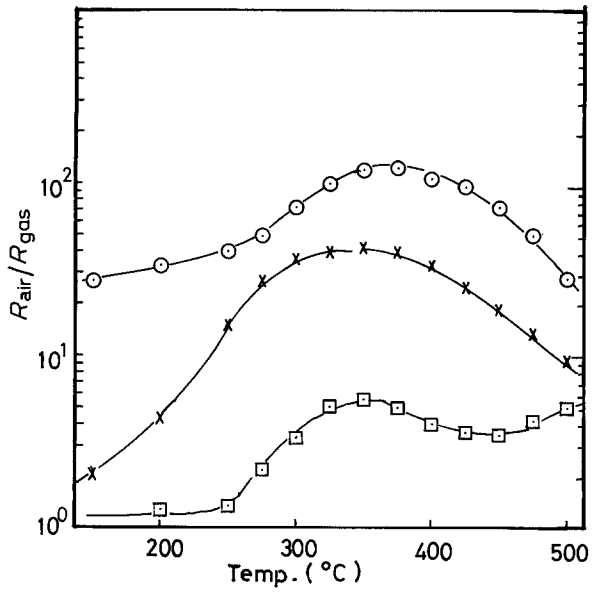

Figure 5 The sensitivity of manganese ion-doped tin oxide film (Sn:Mn:Pd = 100:1000:1) to (○) 5000 p.p.m. H_2, (×) 1000 p.p.m. C_2H_5OH, and (□) 1000 p.p.m. CH_4.

in Table III. Even the Sn–Mn oxide film without palladium gave a high sensitivity of 22 for 1000 p.p.m. ethanol at 300° C. On addition of palladium the sensitivity was increased further to 43. When the amount of Mn(II) ion added to SnO_2 was reduced, both the sensitivity and the resistance decreased. The addition of platinum was not so effective in improving the sensitivity to inflammable gas as was the addition of palladium.

4. Discussion

Mn(II) ion-doped and Ni(II) ion-doped tin oxide films showed a high sensitivity to inflammable gas.

The measurement of electrical characteristics of tin oxide-based films showed that both the resistance of n-type tin oxide-based films and the sensitivity to inflammable gas increased remarkably on addition of 3d transition metal ions, the oxides of which are known as p-type semiconductors (MnO, NiO, CoO and CuO). The resistance of Mn(II) ion-doped tin oxide film was lower than that of Mn(II) ion-doped tin(II) oxide film containing palladium as a catalyst in air, but was almost the same in ethanol gas. These phenomena were also observed for Ni–Sn and Ni–Sn–Pd oxide films. The electrical conductivity of an n-type tin oxide semiconductor was considered as the sum of the electrical conductivity due to the surface, bulk and grain boundary. The conductivity due to the bulk of tin oxide was considered to be reduced by mixing a large amount of hetero metal oxide into the matrix, because the carrier electrons of n-type semiconductors were absorbed into the p-type semiconductor at the interface of the hetero crystals. As gas sensitivity is due to the change of conductivity at the surface exposed to air and inflammable gas, the tin oxide mixed with p-type metal oxide will give a relatively high sensitivity, though the conduction mechanism of the n-type semiconductor is not inherently different from the known mechanism [3, 4]. If palladium was widely and uniformly dispersed on and in the oxides,

TABLE III Gas sensitivity of Mn–Sn oxide films

Materials	Mole ratio	Temp. (°C)	Resistance ($k\Omega\,cm^{-2}$)	Gas conc. (p.p.m.)		Sensitivity, R_{air}/R_{gas}
Sn:Mn	1:10	350	6×10^4	C_2H_5OH	1000	22
Sn:Mn:Pd	100:1000:1	375	2×10^5	H_2	5000	123
		350	2×10^5	C_2H_5OH	1000	43
		375	2×10^5	CH_4	1000	5
Sn:Mn:Pd	100:500:1	450	400	H_2	5000	23
		425	400	CO	1000	4.5
Sn:Mn:Pd	100:500:6	425	4000	H_2	5000	43
		350	2000	C_2H_5OH	1000	12
		400	4000	CO	1000	9
Sn:Mn:Pt	100:500:6	450	2000	H_2	5000	13
		475	2000	CO	1000	1.6
Sn:Mn:Pd	100:100:1	400	20	C_2H_5OH	1000	3.0
		450	30	Co	1000	2.2
Sn:Mn:Pd	100:10:1	450	5	C_2H_5OH	1000	2.0

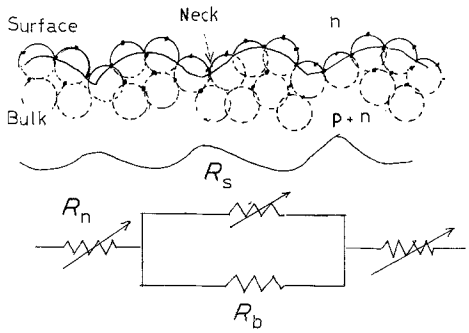

Figure 6 Ideal schematic diagram of cross-section of the gas-sensing material and the corresponding circuit. (●) Catalyst dispersed; n and p, n-type and p-type semiconductive materials; R_s, surface resistance; R_b, bulk (inner film) resistance; R_n, the neck resistance of the grain.

it is little expected that its addition would cause a change in the electrical resistance of SnO_2 film in air. When palladium was effectively dispersed at the neck of the grain boundary of the oxides, a high resistance was obtained. When the amount of palladium was added about six times greater, the sensitivity increased only by 2, as is known from comparison of the gas sensitivity of Sn : Ni : Pd = 100 : 500 : 1 and 100 : 500 : 6. It suggested that the dispersion state of palladium is important in increasing the gas sensitivity of SnO_2 sensors. It was found that palladium played an effective role in increasing the electrical conductivity of the film when coexisting with manganese and nickel oxides to oxidize an inflammable gas, especially at the neck of the grain boundary, according to the spillover mechanism or Fermi energy control [6].

The ideal model of the circuit corresponding to the conductivity of these oxide materials due to the interaction of gas and oxide films is thought to be as shown in Fig. 6. Although it is hard to estimate how much the conductivity of bulk, surface and grain boundary contributed to the total electrical conductivity of the film, it is easy to understand how to increase the gas sensitivity from the following relation of the resistance

$$R = 1/(1/R_s + 1/R_b) + R_n,$$

where R_s, R_b, and R_n are the resistance of surface, bulk (inner film), and neck of grain, respectively. When the electrical resistance of inner film is very large, i.e. $R_s \ll R_b$

$$R = R_s + R_n$$

It is very important to make a thinner sensing film or to make a thick film in which the inner layer can have a very high resistance by mixing hetero materials, and to control the electrical resistance in the neck of the grain boundary by the dispersion of catalyst in order to increase the sensitivity towards inflammable gas.

References

1. T. SEIYAMA, A. KATO, K. FUJIISHI and M. NAGATANI, *Anal. Chem.* **34** (1962) 1502.
2. N. YAMAZOE, J. FUCHIGAMI, M. KISHIKAWA and T. SEIYAMA, *Surf. Sci.* **86** (1979) 335.
3. S. R. MORRISON, *Sensors and Actuators* **2** (1982) 329.
4. Y. TAKUMA, M. MIYAYAMA and H. YANAGIDA, *Chem. Lett.* **1982** (1982) 345.
5. H. PINK, L. TREITINGER and L. VITE, *Jpn. J. Appl. Phys.* **19** (1980) 513.
6. S. R. MORRISON, *Sensors and Actuators* **12** (1987) 425.

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