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Development of SnO_2 Based Semiconductor Gas Sensor with Fe_2O_3 for Detection of Combustible Gas

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Abstract. Six kinds of SnO_2 based semiconductor gas sensors have been fabricated and investigated in the aspects of gas sensitivity to and selectivity for combustible gases. It was found that Fe_2O_3 was a more effective additive than Pd or Pt. It showed high sensitivity to and high selectivity for H_2, CH_4, C_4H_{10}, and little cross-sensitivity to ethanol and smoke.

Keywords: combustible gas sensor, tin oxide, semiconductor, ferric oxide

1. Introduction

Semiconductor gas sensors are now widely employed for protection of the environment, process control and alarm for combustible gas concentration reaching critical levels. Most sensors are based on polycrystalline SnO_2 semiconductive materials and some are based on Fe_2O_3 [1–7]. Palladium, platinum, gold, and ruthenium are often used as additives to enhance sensitivity for combustible gases [8–10]. Metal oxides such as TiO_2, Ga_2O_3, CeO_2, ZnO, CuO are also effective additives to SnO_2 or Fe_2O_3 based sensors [11–17]. But the introduction of precious metals to SnO_2 sensors was found to have some adverse effects. Sensing properties could be gradually deteriorated by exposure to atmospheres containing certain gases or water vapor [18, 19]. Furthermore Pd doped SnO_2 sensors have less selectivity for certain reducing gases or vapor, and they usually exhibit saturation at high gas concentrations [19]. These drawbacks influence seriously on reliability for long-term usage, especially under high humidity or dense smoke surroundings. On the other hand, Fe_2O_3—based sensors are commonly used for detection of combustible gases because they do not need noble metal dopants. The sensors based on Fe_2O_3 generally work at higher temperature than those based on SnO_2. They have large power consumption, usually more than one watt. Despite its better selectivity for combustible gases and stability, the application of these sensors still remains limited.

In this paper we introduce improved semiconductor gas sensors with merits of both SnO_2 and Fe_2O_3 based sensors, i.e. they possess excellent sensitivity for specific combustible gases, moderate selectivity, fast gas sensing response and recovery, high reliability, low power consumption, and resistance to saturation and poisoning. At the same time this type of sensor also possesses attractive features such as low unit cost, good consistency, and small size.

2. Experimental

2.1. Fabrication of Sensor Elements

The sensing materials were prepared by mixing SnO_2 with 1.5 wt% α-Al_2O_3, 0.3 wt% MgO, and minor additives, and then ground with an organic binder in a mortar for at least one hour to form a thick paste. Various sensing materials were prepared and are summarized in Table 1. The paste was applied to coaxial coils to form a spherical bead of the sensing body and then heat treated at 720°C for two hours.

Table 1. Compositions of various sensing materials.

	Composition (wt%)					
Sample	SnO_2	MgO	Al_2O_3	Fe_2O_3	Pt	Pd
A	98.2	0.3	1.5			
B	93.2	0.3	1.5	5.0		
C	98.0	0.3	1.5		0.2	
D	98.0	0.3	1.5			0.2
E	93.0	0.3	1.5	5.0	0.2	
F	93.0	0.3	1.5	5.0		0.2

2.2. *Methods of Measuring Electrical and Chemical Properties of Sensors*

Each sensor had three terminals. Noble metal Pt and Pt/Rh alloy wire coils were used as the sensor element's two electrodes and a heating coil of the sensor element. The operation circuit of this type sensor is rather simple as shown in Fig. 1. An arbitrary terminal of the heater coil was used as the common terminal for both heating circuit and sensor operating circuit. The sensor's resistance could be calculated from the output voltage across the load resistor R_1 connected in series with the sensor and a DC voltage of 5 V was applied to the whole operation circuit. The output voltage (V_{out}) was measured with a digital multi-meter. The gas response sensitivity was defined by the ratio of V_g to V_a. V_a and V_g were the output voltages measured across R_1 when the sensor was in clean dry air or in clean dry air (or room air when sensing responses to moisture or ethanol were examined) containing some sample gas or vapor, respectively. Gas concentration was determined by a volume mixing method. When H_2, CH_4, CO_2 etc. gases were to be examined, the sensor was placed in a quartz tube and the gas concentration was determined by the volume ratio of the test gas to the air. The static method was used for sensitivity of the sensor to alcohol vapor. The concentration of alcohol vapor was calibrated by the volume ratio (within a test chamber).

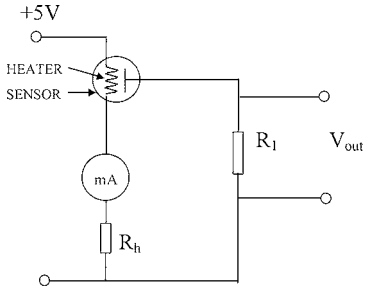

Fig. 1. Measuring circuit diagram: R_1: sensor resistor, R_h: variable resistor, mA: ammeter, V_{out}: sensor output.

3. Results and Discussion

The sensor's conductance is approximately proportional to the output voltage in the above measuring circuit and the sensor's temperature is also proportional to square of the current passing through the sensor. Therefore, the engineering parameters such as output voltage and heating current were used throughout the experiments instead of sensor conductance and operating temperature. For the sake of easy comparison, the electrical response characteristics of various sensor elements are shown in Figs. 2 and 3 for systems

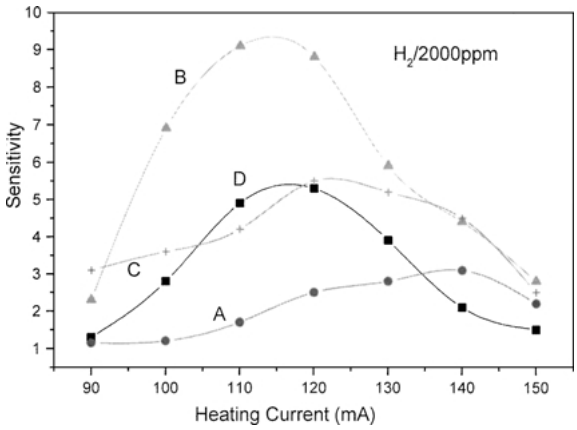

Fig. 2. Sensitivities of sensors A, B, C, and D to 2000 ppm H_2 in dry air for different operating currents.

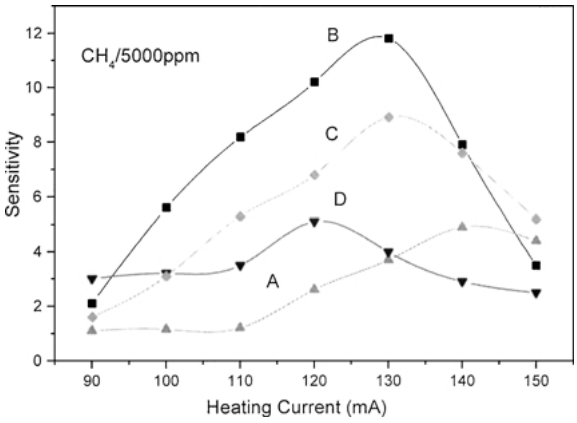

Fig. 3. Sensitivities of sensors A, B, C and D to 5000 ppm CH_4 in dry air for different operating currents.

of 2000 ppm H_2 and 5000 ppm CH_4 in clean dry air. Based on these preliminary experimental results, our initial prediction that the sensor C and D with Pt or Pd additive, respectively should have higher sensitivities to CH_4 and H_2 gases was not satisfied. Unexpectedly, the sensor B containing Fe_2O_3 exhibited excellent sensitivity to both gases. Thus, more attention was paid to the sensing characteristics of sensor B. It is worth noting that the addition of Pt, Pd, or Fe_2O_3 significantly lowered the peak sensing temperature of the SnO_2 sensors. This can be seen by comparing optimum heating currents for sensors B, C, and D with that of sensor A. This is most obvious for sensor D. This implies that the addition of certain additives to SnO_2 based sensors can achieve dual advantages, i.e. they can not only enhance sensitivity but also reduce power consumption.

3.1. *Response to Combustible Gases*

Sensor B was found to be very sensitive to some inflammable gases, such as H_2, CH_4, C_4H_{10}; but less sensitive to alcohol vapor as shown in Fig. 4. The experimental results indicated that different gases require different heating currents to obtain maximum sensitivities. The optimum heating current was about 130 mA for CH_4, 120 mA for C_4H_{10}, and 110 mA for H_2, and the largest sensitivity to alcohol vapor appeared below 100 mA. It is known that maghemite (γ-Fe_3O_4) exhibits good sensitivity to hydrocarbon gases, but hematite (α-Fe_2O_3) shows poor sensitivity. But according to our results, adding small amount of α-Fe_2O_3 to SnO_2 with MgO and Al_2O_3 enhanced sensitivity to a large extent even though the pathway is not known.

Gas sensors sometimes need to be exposed to very high concentrations of combustible gases, such as in coal mines to monitor methane of concentration above its LEL (lower explosive limit). In this case, it is required that the sensors should be resistant to saturation. Their sensing response should show proper resolving power even though they are exposed to high concentration. Most known SnO_2 or Fe_2O_3 based sensors exhibit saturation phenomena above 4000 ppm C_4H_{10}. But our test results shown in Fig. 5 demonstrated that sensor B did not exhibit saturation phenomena even at 60000 ppm H_2 or CH_4.

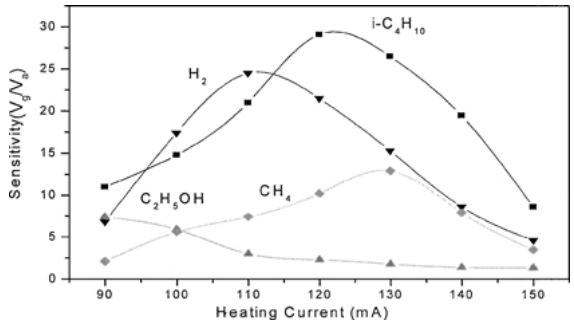

Fig. 4. Relation between sensitivity and heating current for sensor B at concentrations of 5000 ppm C_2H_5OH, 5000 ppm CO_2, 5000 ppm C_4H_{10}, 4000 ppm CH_4, and 4000 ppm H_2.

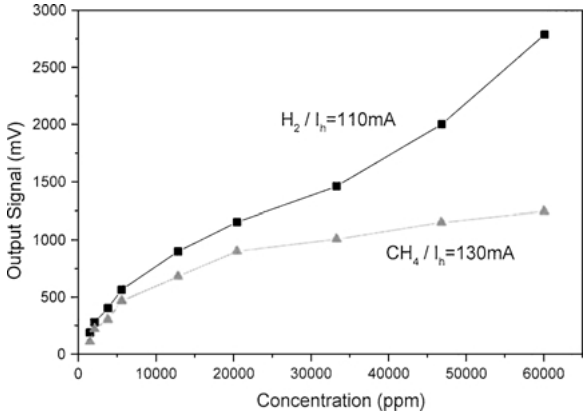

Fig. 5. Output signal of sensor B to CH_4 and H_2 at various gas concentrations.

3.2. *Effect of Amount of α-Fe_2O_3*

The amount of additive to SnO_2 based sensors had a remarkable effect on its sensitivity as shown in Fig. 6.

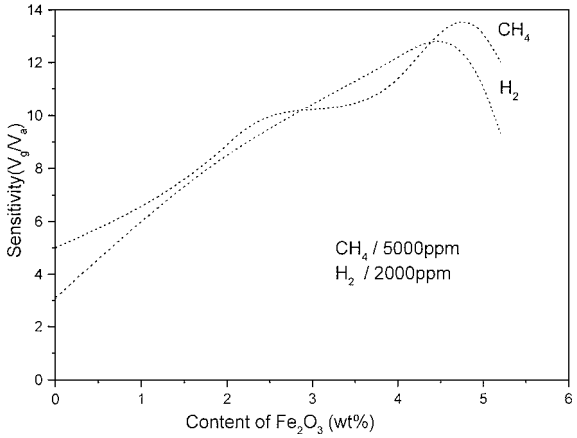

Fig. 6. Sensitivity versus amount of Fe_2O_3 additive.

Increasing the amount of Fe_2O_3, the sensitivities of the sensor increased to maximum values, such as 4.5 wt% for H_2 and 5.0 wt% for CH_4, and then starts to decrease as the amount of Fe_2O_3 increased. The optimum amount of α-Fe_2O_3 in sensor B seemed to depend slightly on its detecting gases. Therefore 5 wt% of Fe_2O_3 was chosen for sensor B.

3.3. Effect of Noble Metals

Effects of addition of Pd or Pt to sensor B were studied. Sensitivity to various H_2 concentrations are shown in Fig. 7. The heating current was 110 mA for the sensors. The results demonstrated that all three sensors showed very high sensitivity to H_2 gas; among them sensor F was the most sensitive, followed by sensor B, and then sensor E. It also indicates that the addition of Pd to the sensor B enhances the sensitivity to some reducing gases and reduces its optimum operating temperature (heating current), but Pt seemed to deteriorate the sensitivity. As shown in Fig. 8, the sensors also showed excellent sensing response to CH_4 at various concentrations, and the heating currents of sensor E and sensor F were lowered from 130 mA to 120 mA. But it should be also noted that sensor F showed some saturation tendency at high CH_4 gas concentrations. The experimental results of the transient response for sensors B, E and F showed that the response to and recovery from test gases H_2 and CH_4 was rapid. The time was within 10 seconds for response, less than 30 seconds for recovery even at high gas concentrations.

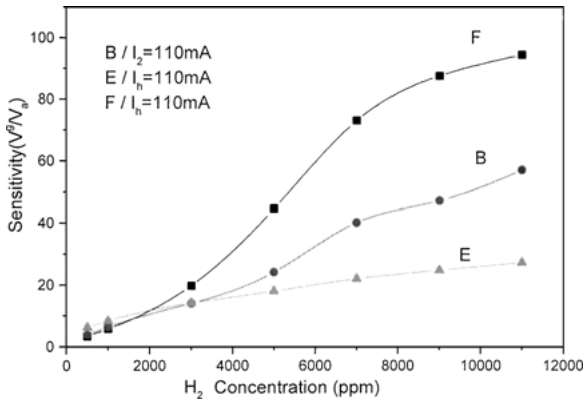

Fig. 7. Sensitivities of sensors B, E, and F to various H_2 concentrations at a heating current of 110 mA.

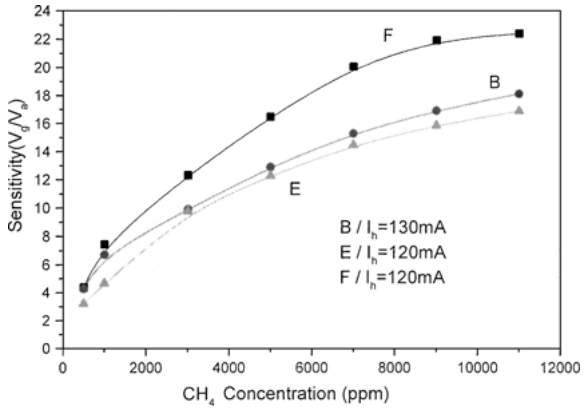

Fig. 8. Sensitivity of sensors B, E, and F to CH_4. The heating currents of the sensors were 130, 120, and 120 mA, respectively.

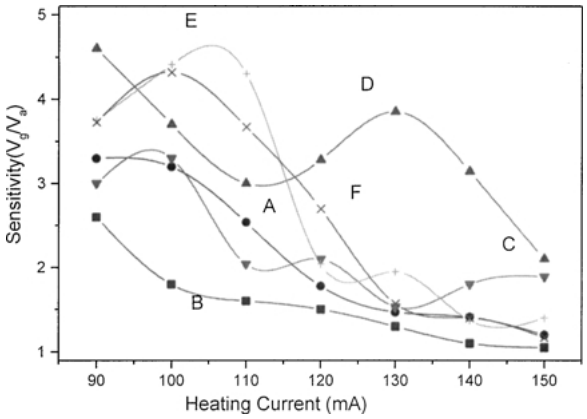

Fig. 9. Sensitivities of sensors A, B, C, D, E and F to 200 ppm C_2H_5OH as a function of heating current.

But the selectivity of a sensor is another very important parameter for its actual application. Figure 9 show that all the sensors were sensitive to alcohol vapor, but there were big differences in their sensitivities as well as for their working temperatures. Noble metal doped sensors, D, E, and F, were much more sensitive to alcohol vapor than those of the others. It could be explained that the doped noble metal as a promoter in metal oxide semiconductor had almost no selectivity for special gas or vapor. Whereas, the sensor B exhibited better selectivity and had small cross-sensitivities to alcohol vapor. It should be also mentioned that these sensors responded slowly to both alcohol and water vapors at all operating currents. The recovery was also slow.

4. Conclusion

Addition of foreign species to polycrystalline tin dioxide improves gas sensing response (sensitivity and selectivity) and reduces operating temperature. The experimental results indicated the following;

1. Addition of α-Fe_2O_3 to SnO_2 together with small amounts of Al_2O_3 and MgO (Sensor B) improved sensitivity to H_2 and CH_4 dramatically.
2. The optimum amount of Fe_2O_3 is about 4.5–5 wt%.
3. The required heating current was lowered in Sensor B almost as much as those with Pd or Pt.
4. Sensor B did not show saturation phenomena even for 60000 ppm of H_2 and CH_4.
5. Small amounts of Pd enhanced Sensor B's performance but Pt did not.
6. α-Fe_2O_3 seemed more effective as an additive than precious metal catalysts such as Pd or Pt.
7. Sensor B exhibited little cross-sensitivity to ethanol and smoke.

References

1. W. Göpel and K.D. Schierbaum, *Sensors and Actuators B*, **26**, 1 (1995).
2. N. Yamazoe and N. Miura, *Sensors and Actuators B*, **20**, 95 (1994).
3. F. Lu, Y. Liu, M. Dong, and X. Wang, *Sensors and Actuators B*, **66**, 225 (2000).
4. L. Barbosa, J. Herguido, and J. Santamaria, *Catalysis Today*, **64**, 43 (2001).
5. K.R. Han, C.S. Kim, K.T. Kang, H.J. Joo, D.I. Kang, and J. He, *Sensors and Actuators B*, **81**, 182 (2002).
6. X.Q. Liu, S.W. Tao, and Y.S. Shen, *Sensors and Actuators B*, **40**, 161 (1997).
7. M. Schweizer-Berberich, S. Strathmann, U. Weimar, R. Sharma, A. Seube, A. Peyre-Lavigne, and W. Göpel, *Sensors and Actuators B*, **58**, 318 (1999).
8. G. Tournier, C. Pijolat, R. Lalauze, and B. Patissier, *Sensors and Actuators B*, **26**, 24 (1995).
9. A. Cabot, J. Arbiol, J.R. Morante, U. Weimer, N. Barsan, and W. Gopel, *Sensors and Actuators B*, **70**, 87 (2000).
10. R.S. Niranjan, S.R. Sainkar, K. Vijayamohanan, and I.S. Mulla, *Sensors and Actuators B*, **82**, 82 (2002).
11. T. Kobayashi, M. Haruta, H. Sano, and M. Nakane, *Sensors and Actuators B*, **13**, 339 (1988).
12. J. Yu and G.M. Choi, *Sensors and Actuators B*, **75**, 56 (2001).
13. A. Khodadadi, S.S. Mohajerzadeh, Y. Mortazavi, and A.M. Miri, *Sensors and Actuators B*, **80**, 267 (2001).
14. U. Hoefer, J. Frank, and M. Fleischer, *Sensors and Actuators B*, **78**, 6 (2001).
15. V.A. Chaudhary, I.S. Mulla, and K. Vijayamohanan, *Sensors and Actuators B*, **55**, 127 (1999).
16. K. Fukui and M. Nakane, *Sensors and Actuators B*, 25, 486 (1995).
17. Delmastro, D. Mazza, S. Ronchetti, M. Vallino, R. Spinicci, P. Brovetto, and M. Salis, *Mater. Sci, and Eng. B*, **79**, 1405 (2001).
18. Fukui and A. Katsuki, *Sensors and Actuators B*, **65**, 316 (2000).
19. J.C. Kim, H.K. Jun, J.S. Huh, and D.D. Lee, *Sensors and Actuators B*, **45**, 271 (1997).