CHEMISTRY LETTERS, pp. 335-338, 1994. © 1994 The Chemical Society of Japan

H_2S and CH_3SH Sensor Using a Thick Film of Gold-Loaded Tungsten Oxide

Masami ANDO,* Seiichi SUTO, Takahiro SUZUKI, Takashi TSUCHIDA, Chiaki NAKAYAMA, Norio MIURA,† and Noboru YAMAZOE†

R & D Division, TOTO Ltd., 2-1-1 Nakashima, Kokurakita-ku, Kitakyushu 802

†Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816

A thick film sensor element fabricated with 0.5 wt% Au-loaded WO_3 was found to exhibit excellent sensing properties to H_2S and CH_3SH in air at 300 °C. The element was sensitive to very dilute H_2S and CH_3SH, the detection limits of the gases being 20 ppb and 30 ppb, respectively.

Gas sensors using semiconducting oxides are now used extensively for gas leakage alarms for usual inflammable gases such as H_2, CH_4 and C_3H_8. Recently much attention is being paid on the development of those semiconductor sensors that detect various smells or, more precisely, typical constituents of smells. For example, sensor elements sensitive to trimethylamine[1] and CH_3SH[2] have been investigated for the purposes of checking the freshness of fishes and a breath odor, respectively. Detection of odors is also important for our civil life. Volatile sulfides such as H_2S and CH_3SH are typical odorous components in living environments, which produce a sick odor even at a very low concentration, and their detection is requested for realizing an auto-ventilation system. For this purpose, the relevant sensor should be at least as sensitive as human noses, to which the threshold concentrations of H_2S and CH_3SH are as low as a few tens ppb. So far attempts have been made for H_2S-sensitive elements,[3-7] but none seems to be able to detect such dilute H_2S satisfactorily. We have found that a thin film SnO_2 element fabricated by using hydrothermally synthesized SnO_2 sol shows fairly good sensing properties to dilute H_2S.[8] Subsequently it has been found that a thick film element using Au-loaded WO_3 shows far better properties, being able to detect H_2S and CH_3SH of 20 - 30 ppb levels satisfactorily, as described below.

The powder of WO_3 was prepared by pyrolyzing ammonium paratungustate ($(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$) at 600 °C for 5 h in air, followed by milling the product in a zirconia-ball mill for 1 day. The powder was loaded with Au by mixing it with an aqueous dispersion of colloidal Au particles (colloid concentration : 0.5×10^{-3} $mol\cdot dm^{-3}$) for 5 h under agitation, followed by filtration, washing with deionized water, drying at 110 °C, and calcination at 600 °C for 5 h. Each powder sample was mixed with an organic binder (a mixture of ethyl cellulose and α-terpineol), and the resulting paste was applied on an alumina substrate (5.0 mm x 6.0 mm), on which comb type Au electrodes were printed, and calcined at 700 °C for 4 h. The sensor films thus obtained were about 20 μm thick. Each element was put inside a conventional flow cell for exposure to the flow (500 cm^3/min) of air or H_2S (or CH_3SH)-air mixtures. Both of air and the gas mixtures were humidified to 60% RH at 25 °C. The electrical resistance of the element was measured under the applied voltage of dc 5V. From the resistance values in air (Ra) and in the gas mixtures (Rg), the gas sensitivity was obtained as Ra/Rg as usual. The sensor temperature was

controlled by means of a Pt heater, printed on the back of the alumina substrate.

The influences of Au loadings on the H_2S sensing characteristics of WO_3-based elements were first investigated. Figure 1 shows the gas sensitivity to 1 ppm H_2S at 300 °C as a function of Au loading. The sensitivity, starting from a small value of about 2 for the pure WO_3 element, increased with an increase in Au loading, and reached a maximum value of 11 at 0.5 wt% Au, whereas it decreased to lower values at 0.8 and 1.0 % Au. From these results, an optimum Au loading is judged to be 0.5 wt%. The corresponding element will be abbreviated as Au(0.5 wt%)-WO_3 hereafter.

Figure 2 shows the gas sensitivity of Au(0.5 wt%)-WO_3 element to 1 ppm H_2S as a function of operating temperature. With a rise in temperature, the sensitivity increased up to 300 °C, and exhibited a maximum value of 11 at 300 °C. Then it showed a plateau value of *ca.* 10 at 350 and 400 °C before going down sharply to no more than 3 at 450 °C and above. These results indicate an optimum operating temperature of 300 °C.

The gas sensitivity of the same element to varying concentrations of H_2S was examined at 300 °C. Figure 3 shows the resulting data together with those of the pure WO_3 element. It is noteworthy that Au(0.5 wt%)-WO_3 element can respond to as dilute as 10 ppb H_2S in air with a sensitivity value of 1.7, giving an almost linear relationship between the logarithm of the gas sensitivity and that of the H_2S concentrations of the range 10 - 1000 ppb. In contrast, the pure WO_3 element is seen to be far less sensitive to H_2S, responding to H_2S at a level of 500 ppb or above. For a practical semiconductor gas sensor combined with ordinary circuitry, the lower detection limit is often assumed to be the gas concentration to which the sensor exhibits a sensitivity value of 2. According to this criterion, the limiting H_2S concentration for the Au(0.5 wt%)-WO_3 element is estimated to be 20 ppb, to be compared with the corresponding value of 1000 ppb for the pure WO_3 element.

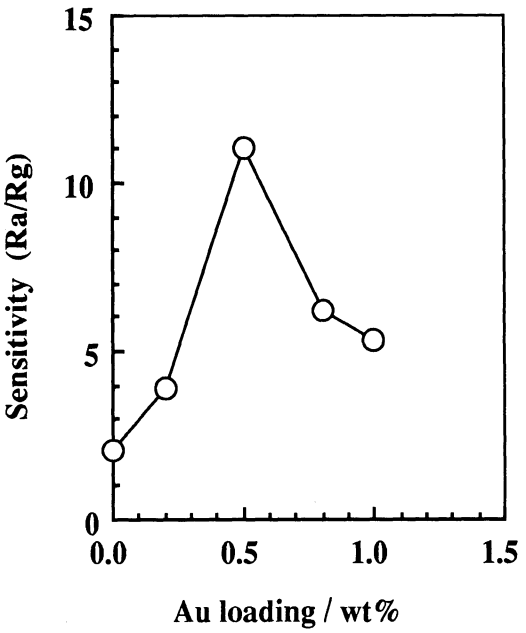

Fig.1. Sensitivity of Au-loaded WO_3 elements to 1 ppm H_2S at 300 °C as a function of Au loading.

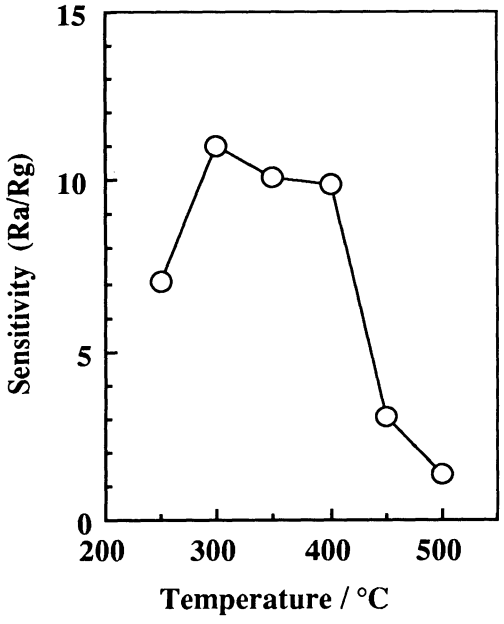

Fig.2. Sensitivity of 0.5 wt% Au-loaded WO_3 element to 1 ppm H_2S at various operating temperatures.

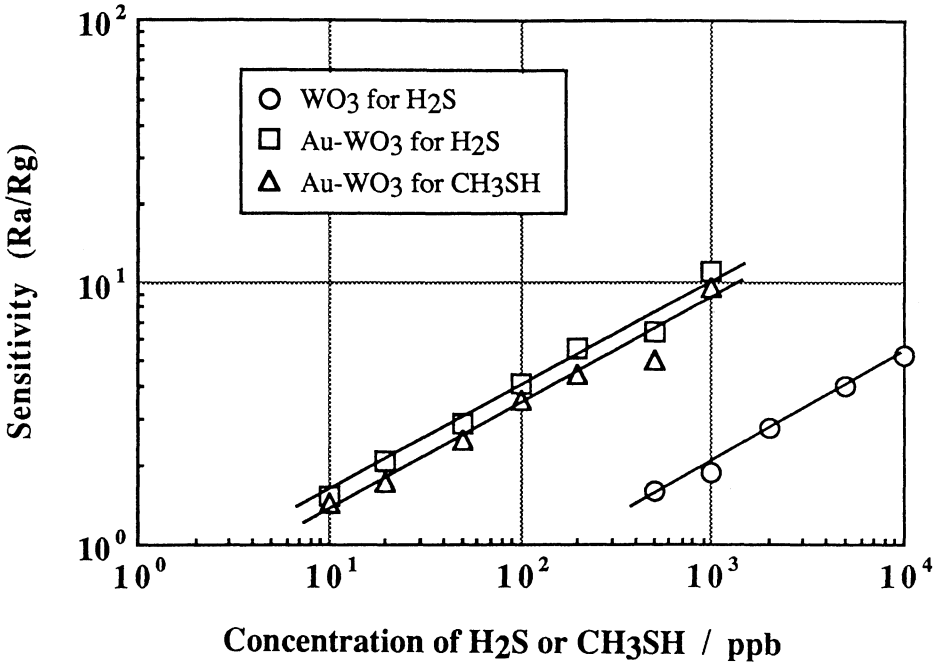

Fig.3. Sensitivity to H_2S or CH_3SH for the sensor element using pure or 0.5 wt% Au-loaded WO_3 as a function of gas concentration (300 °C).

Figure 4 shows the response transient of Au(0.5 wt%)-WO_3 element to 100 ppb H_2S in air at 300 °C. On turning-on H_2S the sensor resistance decreased rapidly, reaching a steady state in about 2 min, and on turning-off it recovered the initial value in about 3 min. The response rate became somewhat slower as the concentration of H_2S decreased, but the 90% response time to 20 ppb H_2S was still 2.5 min. This assures that the present element has practically acceptable transient characteristics to dilute H_2S.

It was further found that the Au(0.5 wt%)-WO_3 element was also very sensitive to CH_3SH at 300 °C. As seen from the gas sensitivity vs. CH_3SH concentration correlation over a range of 10 - 1000 ppb indicated in Fig. 3, the detection limit of the element was again as low as 30 ppb CH_3SH. The response rates to CH_3SH were much the same as those to H_2S.

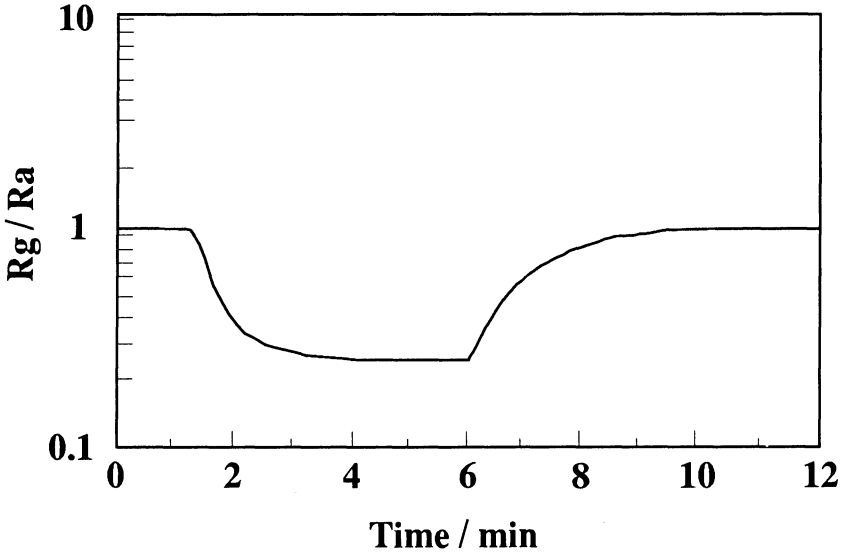

Fig.4. Response transient of 0.5 wt% Au-loaded WO_3 element to 100 ppb H_2S at 300 °C.

As mentioned above, a thick film element using WO_3 becomes very sensitive to H_2S and CH_3SH when loaded with Au. In the case of a thin film element using SnO_2 previously reported,[8] rather high sensitivity to H_2S is obtained without the addition of such a promoter. It appears that WO_3 is less reactive to H_2S than SnO_2 so that it needs an assistance of a weak promoter like Au. We have reported that a sintered block type element using Au-WO_3 is highly sensitive to NH_3 and that the high sensitivity benefits from an electronic interaction between Au and WO_3[9] ; The interaction presumably takes place through the formation of adsorbed oxygen at the Au/WO_3 interface and decreases the conduction electrons of WO_3. A similar mechanism can be operative in the present case. That is, the electrical resistance of the element decreases from a very high level in air to a level comparable to that of a pure WO_3 element when the adsorbed oxygen at the interface is consumed upon exposure to H_2S, giving rise to the high gas sensitivity of the Au-loaded WO_3 element. It should be pointed out, however, that a structural factor is also involved in the high H_2S sensitivity of the present thick film element, since the block type element using the same material has been confirmed to be hardly sensitive to H_2S despite its high sensitivity to NH_3 as mentioned. This seems to be ascribed to the differences in gas diffusivity and reactivity between H_2S and NH_3. Assuming Knudsen diffusion through the pores of the element, the rates of gas diffusion are in the order $H_2S \approx O_2 < NH_3$. It has been pointed out by Egashira *et al.*[10] that the thickness of the gas sensing layer affects the gas sensitivity differently depending on the diffusivity of the gas in problem relative to that of O_2. It is considered that the sensitivity to H_2S (or CH_3SH) becomes more favorable with a thinner sensing layer, while the reverse is true for that to NH_3. In addition, H_2S appears to be more reactive on the oxide surface than NH_3, making the thinner sensing layer even more favorable for the H_2S detection. These would explain why the high sensitivity to H_2S (or CH_3SH) was attained only with the present thick film element using Au-WO_3.

In conclusion, the thick film using Au-loaded WO_3 exhibited excellent sensing properties to H_2S and CH_3SH in air at 300 °C. The detection limit of the film was as low as 20 ppb for H_2S and 30 ppb for CH_3SH.

References

1) M. Egashira, Y. Shimizu, and Y. Takao, *Chem. Lett.*, **1988**, 389.
2) T. Nakahara and H. Koda, *Chemical Sensor Technology*, **3**, 19 (1991).
3) V. Lantto and P. Romppainen, *J. Electrochem. Soc.*, **135**, 2550 (1988).
4) S. Kanefusa, M. Nitta, and M. Haradome, *J. Electrochem. Soc.*, **132**, 1770 (1985).
5) S. Kanefusa, M. Nitta, and M. Haradome, Tech. Digest, 7th Chemical Sensor Symp., Saitama, Japan, 1988, p.145.
6) T. Nakahara, K. Takahata, and S. Matsuura, Proc. Symp. on Chemical Sensors, ECS, Honolulu, 1987, p.55.
7) J. Tamaki, T. Maekawa, N. Miura and N. Yamazoe, *Sens. Actuators B*, **9**, 197 (1992).
8) M. Ando, S. Suto, T. Suzuki, T. Tsuchida, C. Nakayama, N. Miura, and N. Yamazoe, submitted.
9) T. Maekawa, J. Tamaki, N. Miura, and N. Yamazoe, *Hyomen kagaku*, **13**, 254 (1992).
10) Y. Shimizu, Y. Nakamura, and M. Egashira, *Sens. Actuators B*, **13-14**, 128 (1993).

(Received November 8, 1993)