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Sensing Behavior of CuO-Loaded SnO_2 Element for H_2S Detection

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CuO-loaded SnO_2 element was found to show extraordinary sensing properties to H_2S in air, with such high sensitivity as ca. 35 000 to 50 ppm H_2S at 200 °C and switching-like recovery on turning off H_2S. The change of state between CuO and CuS on the surface of SnO_2 seems to be responsible for such unique sensing properties.

Semiconductor gas sensor, now widely used as a gas leak alarm, detects gases in air from a change in electric resistance of an element made of an n-type semiconductive oxide. For usual objective gases, such as H_2, propane, and iso-butane (inflammable gases), limiting gas concentrations are well above several hundreds ppm. With the recent development in living environment and industrial technology, however, objectives have been expanding to include toxic gases, pollutant gases, IC process gases, odors, and so on, some of which exist in air even at sub-ppm levels. For these new objectives, the gas sensor should be promoted in both sensitivity and selectivity to much higher levels than it is. From this motivation, we have been trying to promote SnO_2 gas sensor with various additives.[1-3] Among various smelling compounds, volatile sulfides are typical components of bad smell generated from human mouth, toilet or dump. A useful sensor for them is highly requested for dentistry and auto-ventilation of toilet or kitchen. Detection of the simplest volatile sulfide, H_2S, with semiconductor sensors has been attempted in a few reports so far. However, the sensitivity and selectivity to H_2S, though somewhat improved by adopting a quick cooling method[4] or by adding hydrophobic silica[5] or basic oxide to the elements,[6] never seem to have been promoted to sufficient levels. In the course of our investigation, CuO was found to be a very unique and excellent promoter of SnO_2 sensor for H_2S detection, as described below.

SnO_2 powder was prepared from $SnCl_4$ as follows. An aqueous solution of $SnCl_4$ was neutralized with an aqueous solution of ammonia. The precipitate obtained (stannic acid) was thoroughly washed with deionized water, dried at 100 °C, and calcined at 600 °C for 5 h in air. To be loaded with metal-oxides, SnO_2 powder was impregnated with aqueous solutions of respective metal salts (acetates if available), followed by drying, and calcining at 600 °C for 5 h. The loading was fixed to 5 wt% for each metal oxide unless noted otherwise. The powder, after being mixed with water into a paste, was applied on an alumina tube substrate having two Pt-wire electrodes, and calcined at 700 °C for 4 h. The resulting sensor element was subjected to

the measurements of electric resistance in a flow (200 cm^3/min) of air or the sample gas (50 ppm H_2S in dry air). Gas sensitivity was defined as the ratio (R_a/R_g) of the electric resistance in air (R_a) to that in the sample gas (R_g).

The gas sensitivity to 50 ppm H_2S was examined for the SnO_2 elements loaded with various metal oxides at 200 °C. Figure 1 shows the sensitivity as a function of the electronegativity of the loaded metal cations. The sensitivity of all loaded elements except for Cu^{2+} tended to increase with a decrease in electronegativity of the cations added. This tendency is consistent with the report by Nakahara et al.,[6] who have suggested that, as an acidic gas, H_2S is adsorbed on the element more favorably and hence detected at higher sensitivity as the surface becomes more basic with basic additives. It is quite noteworthy that the sensitivity of CuO-SnO_2 element is extraordinarily high, far deviating from this general tendency. This suggests that the combination of CuO and SnO_2 is quite unique among those investigated.

Figure 2 shows response transients to 50 ppm H_2S at 200 °C for the SnO_2 elements with and without loaded CuO. On turning on H_2S flow, pure SnO_2 element responded very slowly, being unable to reach a steady state even in 40 min. The sensitivity at the steady state was about 8 and the resistance could not recover the initial level when air flow was resumed. On the other hand, the sensitivity of CuO-SnO_2 element was as extremely high as 35000 to 50 ppm H_2S. Although the response to turning-on H_2S was not so quick (70% response time of about 7 min), the response on turning-off could recover the initial level completely in 1 min, showing a switching-like characteristic. These remarkable sensing properties to H_2S, i.e., quite high sensitivity and surprisingly fast recovery response at as low temperature as 200 °C, are quite unique to CuO-SnO_2 element and there seems to be no precedent for such properties. The highly

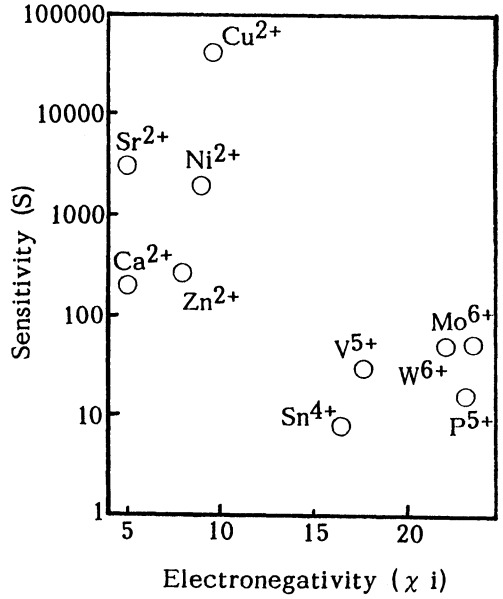

Fig.1. Gas sensitivity of metal oxide loaded-SnO_2 elements to 50 ppm H_2S at 200 °C as a function of electronegativity of loaded metal cations.

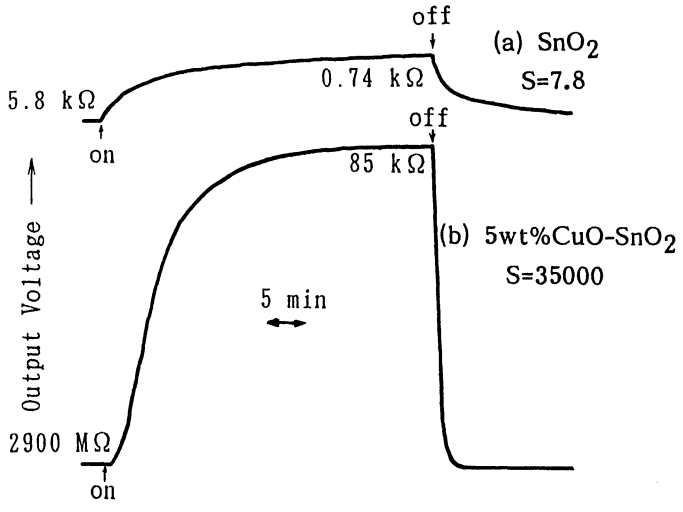

Fig.2. Response transients of CuO-loaded(5 wt%) and unloaded SnO_2 elements to 50 ppm H_2S at 200 °C.

Table 1. Sensitivity of CuO(5 wt%)-SnO_2 element to various gases

Gas	H_2S	CO	i-C_4H_{10}	C_2H_5OH	H_2
Conc. /ppm	50	1000	1000	1000	800
Sensitivity	35000	1.3	1.2	1.9	1.0

selective nature of the element to H_2S is well demonstrated in Table 1. As compared with the extremely high sensitivity to 50 ppm H_2S, the sensitivity levels to CO, i-C_4H_{10}, C_2H_5OH, and H_2 at a 1000 or 800 ppm concentration are negligibly low.

Figure 3 shows the electric resistances in air (R_a) and in 50 ppm H_2S (R_g) as well as the resulting gas sensitivity for CuO-SnO_2 element as a function of temperature. R_a was very high ($3\times10^9\ \Omega$) up to 300 °C and decreased gradually at higher temperatures. In constant, R_g was low (ca. $10^5\ \Omega$) up to 200 °C but then began to increase drastically to high values ($10^8\ \Omega$) at 250 °C and above. Because of such properties, the gas sensitivity was as high as 35000 - 40000 up to 200 °C, but decreased to no more than 10 above 300 °C. Apparently the unique properties of the element are associated with its extremely low resistance in the H_2S atmosphere below 200 °C.

All the data above were obtained for a CuO loading of 5 wt%. It was found that variations in CuO loading (0.1 - 20 wt%) affected the response transients considerably, as shown in Fig. 4. Generally speaking, both the response rate on turning on H_2S and the H_2S sensitivity tended to decrease with an increase in CuO loading, while the switching-like recovery was observed at a CuO loading of 3 wt% or above. An optimum CuO loading seems to be 3 - 5 wt%.

As stated above, CuO-loaded SnO_2 element has extraordinary properties for H_2S sensing. From the unusual behavior on changing temperature, we speculate the following sensing mechanism, although it is to be verified with further investigation. In the calcined element, CuO exists as fine particles dispersed on the SnO_2 surface. Since CuO and SnO_2 are p- and n-type semiconductors, respectively, a p-n junction can possibly be formed at each interface between CuO and SnO_2, inducing an electrons-depleted space charge layer at the surface of SnO_2. This ex-

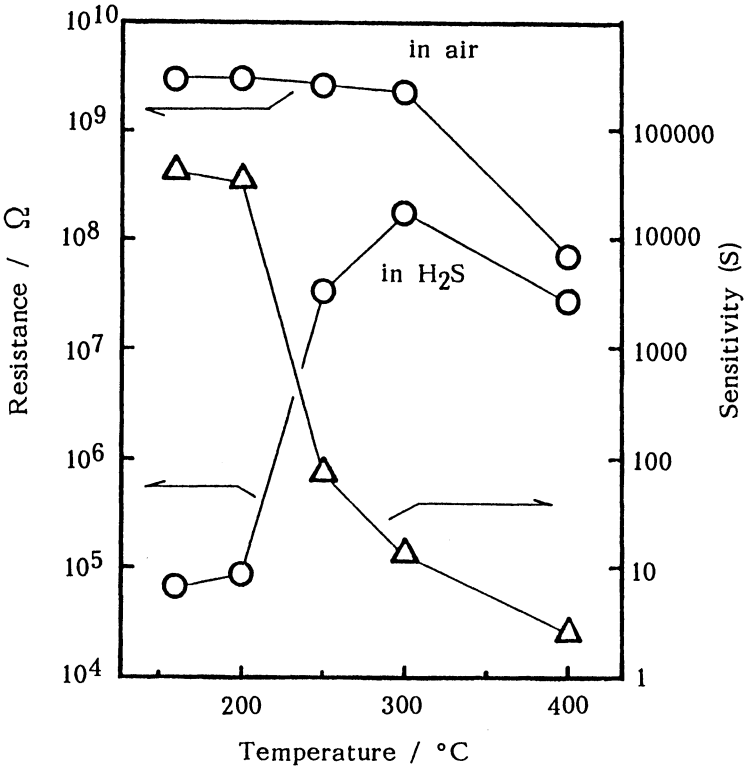

Fig.3. Temperature dependence of the resistances and the H_2S sensitivity of CuO-SnO_2 element (H_2S : 50 ppm).

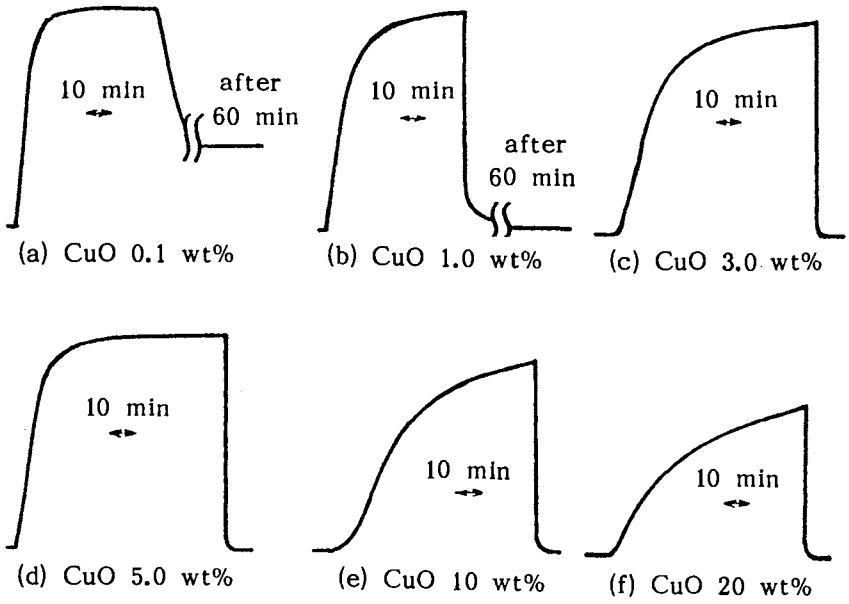

Fig.4. Response transients of various CuO-SnO_2 elements to 50 ppm H_2S in air at 200 °C.

plains high resistance (R_a) of the element in air. In the presence of H_2S which is very reactive with CuO, on the other hand, CuO is easily converted to CuS which is a good electronic conductor.

$$CuO + H_2S \longrightarrow CuS + H_2O \qquad (1)$$

This reaction will destroy the p-n junction and bring about a large drop in resistance of the element and hence extremely high sensitivity to H_2S as observed. When air flow is resumed, CuS is transformed back into CuO to recover the p-n junctions.

$$CuS + 3/2O_2 \longrightarrow CuO + SO_2 \qquad (2)$$

If this reaction is very fast, the recovery response can be very quick as observed.

In conclusion, the SnO_2 element loaded with CuO shows excellent and unique sensing properties to H_2S, i.e., high sensitivity, high selectivity and quick recovery response.

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