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HYDROGEN SENSITIVE GAS DETECTOR USING SILVER ADDED TIN(IV) OXIDE

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A semiconductor gas sensor using silver added tin dioxide was found to exhibit high sensitivity to H_2 compared with that to C_3H_8, CH_4, or CO at RT ~ 250°C. The promoting effects of Ag for the H_2 detection was very sensitive to its loading, an optimum loading being ca. 1.5 wt%.

Since the proposal of Seiyama et al.,$^{1)}$ gas sensors using semiconductive metal oxides have experienced extensive research and developments. Nowaday semiconductor gas sensors are commercially manufactured as detectors or alarms for combustible gases such as propane, methane, and hydrogen as well as for toxic gases such as carbon monoxide and hydrogen sulfide. The current sensors mostly utilize tin(IV) oxide as the semiconductive material, to which a small amount of Pd (less than 2 wt%) is conventionally added as an activator or sensitizer.$^{2)}$ One of the problems in the SnO_2 + Pd sensors currently used is the lack of ability to detect a particular gas at high selectivity in the presence of other combustible gases. It is expected that the gas selectivity is very much dependent on the combinations of semiconductor materials and sensitizers. In the course of investigation of the effects of various additives on the SnO_2 gas sensor, we have found that the addition of small amounts of Ag greatly increases the sensitivity of the sensor to hydrogen in preference to C_3H_8, CH_4, etc., thus enabling one to detect H_2 very selectively. This letter describes some characteristics of Ag added SnO_2 sensors in the detection of H_2 and other gases.

Tin(IV) oxide was prepared by treating metallic tin (five nine) with heated nitric oxide. The precipitate (stannic acid) obtained was washed with water, dried at 100°C, and calcined at 600°C for 10 h in air. Ag was added by impregnating the above SnO_2 powder with aqueous $AgNO_3$ solution followed by evaporation to dryness at 100°C and calcination at 600°C for 10 h in air. The obtained powder, SnO_2 + Ag, was used to fabricate two types of sensor elements. In one type (type A), the powder was cold-pressed into a disc 10 mm in diameter and 1 mm in thickness at 1500 $kg \cdot cm^{-2}$, inside which the ending parts (5 mm in length) of two platinum wires (0.3 mm in diameter) were buried in parallel 4 mm apart at the symmetric positions as electrodes. In another (type B), the powder, after mixing with a small quantity of water into a paste, was applied on two platinum coil electrodes separated 2 mm apart by a tiny alumina spacer. The element completed was of a roughly spherical shape with a diameter of ca. 5mm. Both types of elements were calcined or sintered at 600°C for 5 h in air before use. The sensitivity (k) of a gas sensor to a gas is usually defined by the ratio $k = R_a/R_g$ where R_a and R_g are the electrical resistances of the sensor element in air and in the gaseous mixture of the gas and air, respectively. The gas sensitivity measurements were carried out in a flow apparatus, through which air and the gaseous mixtures were passed. To measure R_a or R_g, the sensor element was connected with a resistor of a known resistance, and under applying a controlled DC voltage to the circuit, the voltage drop at the resistor was monitored with a recorder.

The gas sensitivity are usually dependent on temperature. Figure 1 shows the sensitivities of type A sensors using SnO_2 and silver (0.5 wt%) added SnO_2 to H_2, C_3H_8, CH_4 and CO as a function of temperature. The sensitivities were measured during heating the sensors at a constant rate (5°C/min) in air and in the gaseous mixture repeatedly. As seen in Fig. 1, the sensitivities of SnO_2 sensor to the gases were all less than 70 in the temperature range tested. In marked contrast the sensitivities of SnO_2 + Ag sensor to H_2 showed a large maximum in the range room temperature ~ 400°C. Its maximum value, ca. 700 in this case, was found to be extraordinarily large, indicating that the H_2 detection was sensitized quite effectively by the addition of Ag. It is also noted that the sintization effect of Ag was observed almost exclusively in the hydrogen detection; the sensitivities to the other gases remained almost unchanged with or without the Ag addition. Such a feature seems to be favorable from a viewpoint of selective detection of H_2. With the disc type sensor (type A), however, the response time was rather large, being usually larger than a few minutes. The response time could be shortened by use of type B sensor which was apparently more porous than type A.

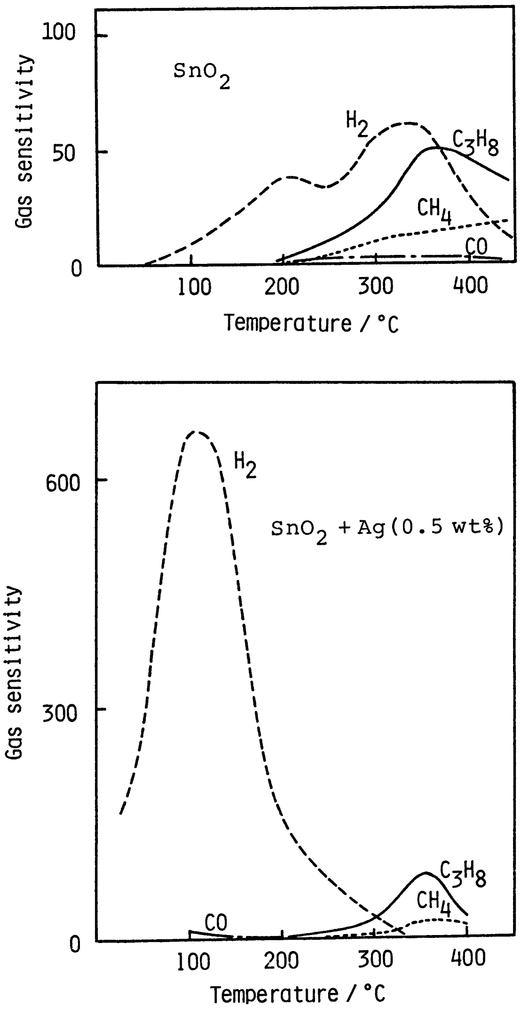

Fig. 1 Gas sensitivities of SnO_2 sensor (upper) and SnO_2 + Ag sensor (lower). (type A)
Gas concentration (in air); H_2 0.8 %, CH_4 0.5 %, C_3H_8 0.2 % and CO 0.02 %

With type B sensor, the effects of Ag on the sensitivity and response time for hydrogen detection were investigated as a function of Ag loading. The results at 200°C are

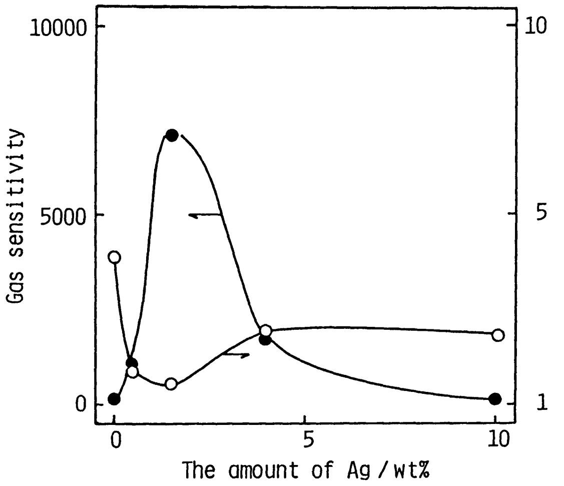

Fig. 2 Effects of Ag loading on the gas sensitivity and the 90 % response time of Ag added SnO_2 sensors (type B) at 200 °C.
Gas, a flow (150 cm^3/min.) of 0.8 % H_2 (diluted in air)

shown in Fig. 2. Quite notably both the gas sensitivity and response time were very sensitive to the Ag loading. The promotion effects of Ag appeared in a narrow range of Ag loading below ca. 5 wt%, and became optimum at ca. 1.5 wt% where the sensitivity to 0.8 % H_2 was as high as 7000 with the time for 90 % response being ca. 20 s at 200 °C. This again confirms the high sensitivity of SnO_2 + Ag sensor to H_2. The marked dependences of the sensitivity and response time on Ag loading suggests the importance of the dispersion of Ag on the SnO_2 surface, although the phenomenon seems to be fairly complex.

Figure 3 shows the sensitivities of SnO_2 + Ag sensor (type B) to several gases at 250 °C as a function of gas concentration together with an example of its response to a 0.8 % H_2 stream. At this temperature, the response time is seen to be further shortened to 12 s or 26 s for 90 % or 100 % response, respectively. The figure shows that the sensor can detect H_2 at high sensitivities while the sensitivities to CO, C_3H_8, and CH_4 are very low. This assures that highly selective detection of H_2 in the presence of these gases is possible with this sensor. It was found, however, that C_2H_5OH vapor interfered

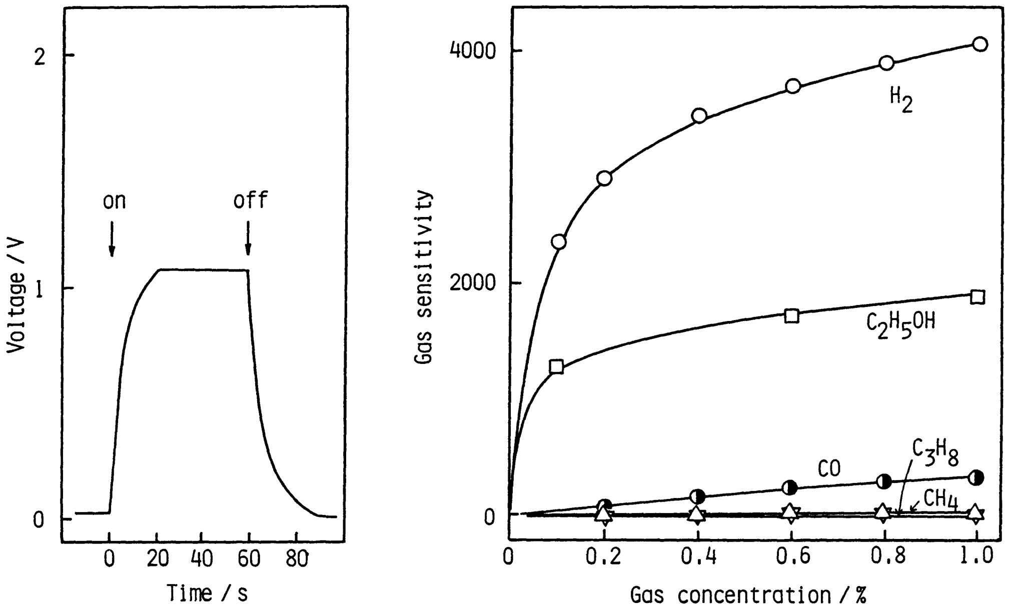

Fig. 3 Response of Ag (1.5 wt%) added SnO_2 sensor (type B) to a flow of 0.8 % H_2 (left), and its sensitivities to several gases (right), at 250 °C.

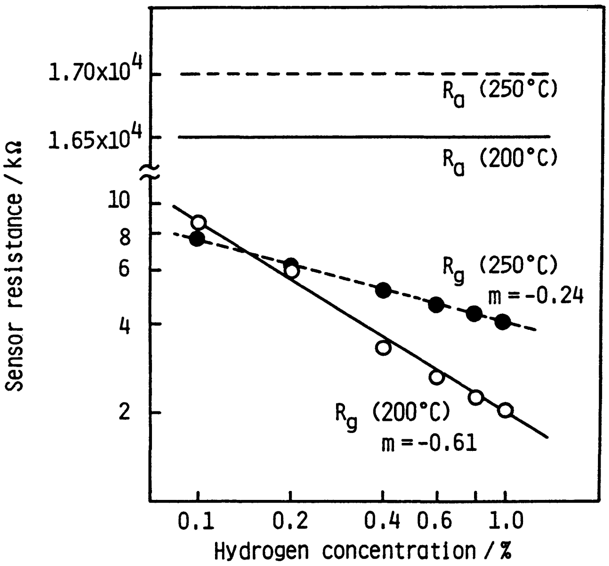

Fig. 4 The dependences of resistance of SnO_2 + Ag sensors on H_2 concentration
SnO_2 + Ag (1.5 wt%) (type B)

the H_2 detection. It is known that, in the catalytic oxidation of C_2H_5OH on metal oxides, hydrogen is often produced as a partial oxidation product.3) Therefore we suspect that the high sensitivity to C_2H_5OH may be ascribed to the presence of H_2 formed in this way. As seen in Fig. 3, the hydrogen sensitivity (k) tended to saturate when H_2 concentration (c) increased. It was found that k was expressed by an emperical function of c in the following form.

$$\log k = m \log c + n$$

$$\text{or} \quad \log R_g = -m \log c + \log R_a - n$$

where m and n are constants at given temperatures. The adaptability of the equation at 200 and 250°C is exemplified in Fig. 4.

As mentioned above, the Ag added SnO_2 sensor shows extraordinarily high sensitivity to hydrogen and is considered to be promising as a hydrogen selective gas sensor which is workable in the presence of C_3H_8, CH_4 or CO. For the promoting effect the dispersion state of Ag is likely to be very important. Egashira et al. have suggested a strong interaction between SnO_2 and Ag from TPD studies4). The strong interaction is also suggested from XPS studies which we are now carrying out. The promoting effect appears to be associated with the modification of O_2-adsorptive properties of the SnO_2 surface.

References
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