CHEMISTRY LETTERS, pp. 2001-2004, 1987. © 1987 The Chemical Society of Japan

CO Sensitive Pt/SnO_2 Diode Type Gas Sensor

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A Pt(sputtered film)/SnO_2(disc) diode was found to respond to small amounts of CO in air at lower temperatures below 100 °C, while no response was observed for CH_4 and C_3H_8. The CO sensitivity of the diode gave a maximum at 90 °C, which was about three times as high as the sensitivity to H_2. The 50% response time of the sensor to 1000 ppm CO was about 1 min.

Various Schottky-diode type gas sensors using metal-semiconductor contacts have been investigated by many researchers; for example, Pd/CdS diode by Steele et al,[1] Pd(or Pt)/TiO_2 diodes by Tsubomura et al.,[2,3] Pd/ZnO diode by Ito,[4] thick film type Pd/TiO_2 diode by Harris,[5] and some Schottky diodes by Poteat et al.[6] These sensors are worthy of note for sensitivity to hydrogen at temperatures below 100 °C. However, the diode type sensors aiming at other reducing gases have been scarcely studied. The rare examples are Au/TiO_2 diode as a SiH_4 sensor[7] and Pd/TiO_2 diode with limited sensitivity to CO in addition to H_2 sensitivity.[2,8]

Selective and sensitive detection of CO is important in social life to prevent poisoning accidents. In response to a strong need for a solid-state CO sensor with simple structure and high performance, several types of CO sensors have been reported.[9-12] In the course of our investigation on the responses of various metal-semiconductor contacts to CO and H_2 in air, we have found that Pt/SnO_2 diode showed relatively high selectivity to CO at lower temperature. In this letter, we report the sensing characteristics of this Pt/SnO_2 diode.

Tin oxide (SnO_2) powder, prepared from $SnCl_4$ by a neutralization method,[13] was cold-pressed into a disc, 10 mm in diameter and 1.5 mm thick, at a pressure of 200 MPa. After sintering at 700 °C for 4 h in air, the disc was polished at both ends to 1.0 mm thick. A Pt film (ca. 0.1 μm^t x 8 $mm\phi$) was deposited on one end of the SnO_2 disc by a RF sputtering method under Ar pressure of 5.3 Pa. An ohmic back contact was made with an evaporated In film. Both the metal films were connected to electrical leads through Au plates as shown in Fig. 1. The current-voltage (I-V) characteristics were measured in a gas flowing system by using a Hokuto Denko HA-301 potentiostat over the temperature range 15 °C - 120 °C. V is an applied voltage by which Pt film was positively polarized against In film. Sample gases were prepared by mixing a small amount (usually 1000 ppm) of combustible gas (H_2, CO, CH_4 or C_3H_8) with air and passed over the sensor element at a rate of 60 cm^3/min.

Figure 2 shows the I-V curves of Pt/SnO_2 diode in air and in 1000 ppm CO

diluted in air at 90 °C. A slightly non-ohmic curve was obtained in CO, while a highly non-ohmic curve was seen in air. It is noted that both the forward and the reverse bias currents were larger in the sample gas than in air. A similar I-V curve was also found for 1000 ppm H_2 diluted in air. As also shown in Fig. 2, an element with In/SnO_2/In structure exhibited I-V characteristics which were ohmic in both air and the sample gas. This confirms an ohmic contact between In film and SnO_2 surface.

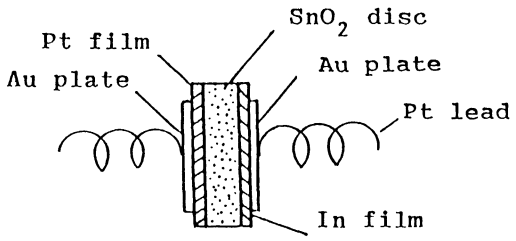

Fig. 1. Schematic view of the Pt/SnO_2 diode senser.

It is well known that a Schottky barrier is formed when an n-type semiconductor is contacted with a metal, work function of which is larger than the electron affinity of the semiconductor, as is the case for Pt/SnO_2. The observed non-ohmic behavior of Pt/SnO_2 diode is thus considered to be caused by a Schottky barrier, while the I-V curve in air is not a typical one of metal/n-type semiconductor diode as observed for Pt/TiO_2 contact.[2] As for the I-V curve of Pt/SnO_2 in the reverse bias region, it is suspected at the present stage that a leakage current (tunneling current) seems to be responsible for the extraordinary

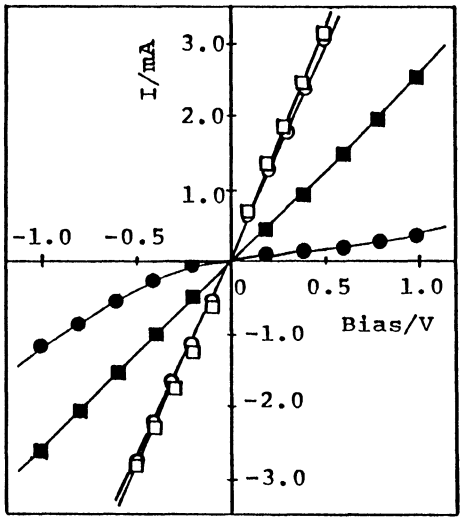

Fig. 2. I-V curves of the Pt/SnO_2 (In/SnO_2) contact at 90 °C.
●: Pt/SnO_2 in air
■: Pt/SnO_2 in 1000 ppm CO
○: In/SnO_2 in air
□: In/SnO_2 in 1000 ppm CO

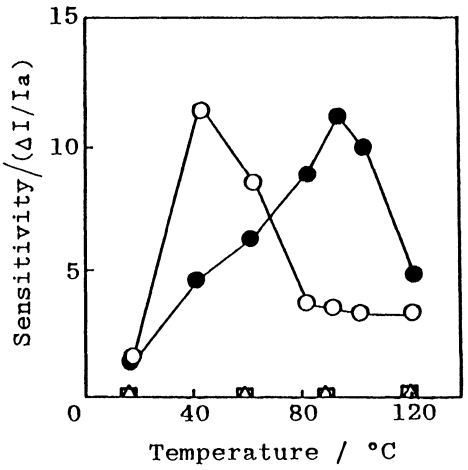

Fig. 3. Temperature dependence of sensitivities of the Pt/SnO_2 diode sensor. Gas concentration: 1000 ppm in air, bias: +0.6 V.
○: H_2, ●: CO, □: CH_4, △: C_3H_8

behavior. The Schottky barrier height is known to change with the adsorption of gases at the metal-semiconducter interface. The increase in forward bias current with a change of atmosphere from air to the CO-containing air in Fig. 2 is considered to result dominantly from the decrease of the barrier height.

The gas sensitivity of diode sensor is defined in terms of $(I_s-I_a)/I_a=\Delta I/I_a$, where I_s and I_a are the currents in a sample gas and in air, respectively, at a fixed bias voltage. Figure 3 shows the sensitivity of the diode biased at +0.6 V to 1000 ppm CO diluted in air as a function of temperature, together with the sensitivities to H_2, CH_4, and C_3H_8. The sensitivities to H_2 and CO were found to give a maximum at about 40 °C and about 90 °C, respectively, while the diode had no sensitivities to CH_4 and C_3H_8 over the temperature range examined. Thus, the sensor exhibited relatively high sensitivity and selectivity to CO at 90 °C: the sensitivity to 1000 ppm CO was about three times as high as that to 1000 ppm H_2 at 90 °C. This is in good contrast to the case of Pd/TiO_2 diode,[2] whose sensitivity to CO at the optimum temperature (about 70 °C) was less than one tenth of that to H_2. It is considered that the observed temperature dependences of the gas sensitivities were mainly associated with a change in adsorbed oxygen concentration at the Pt-SnO_2 semiconductor interface. The adsorbed oxygen concentration at a steady state is determined by the rate of oxygen adsorption from gas phase and the rate of adsorbed oxygen consumption for reactions with reducing gases. It is inferred that, in the lower temperature region, the oxygen consumption rate increases faster with a rise in temperature than the oxygen

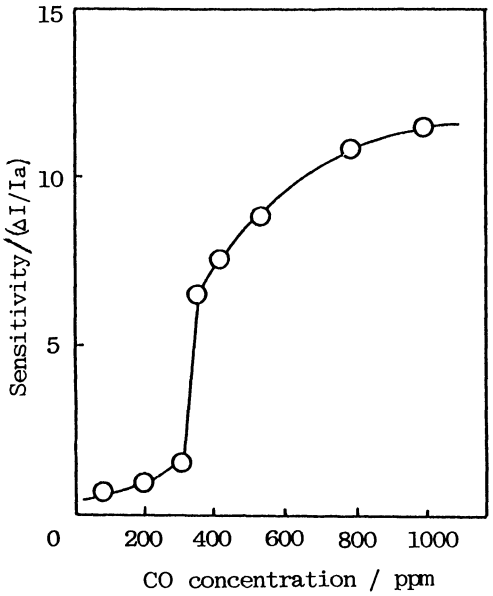

Fig. 4. Dependence of sensitivity of the Pt/SnO_2 diode on CO concentration in air. Temperature: 90 °C, bias: +0.6 V.

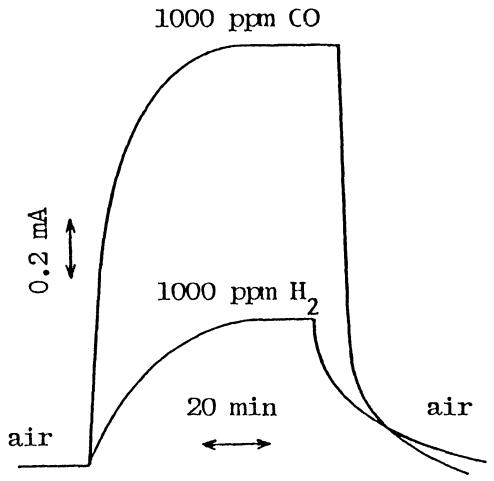

Fig. 5. Response curves of the Pt/SnO_2 diode to both 1000 ppm CO and 1000 ppm H_2 at 90 °C in air. Bias: +0.6 V.

adsorption rate, giving rise to an increase in gas sensitivity. At higher temperatures above the sensitivity maximum, however, two factors which suppress the sensitivity become increasingly significant. First, I_a becomes larger which tends to diminish the term $\Delta I/I_a$. Second, the probability for CO (or H_2) molecules to reach the metal-semiconductor interface decreases because of increased combustion rate on the outer metal surface.

Figure 4 shows the sensitivity ($\Delta I/I_a$) of the Pt/SnO_2 diode as a function of CO concentration in the range from 100 ppm to 1000 ppm at the bias voltage +0.6 V and 90 °C. The sensitivity increased abruptly as the CO concentration exceeded ca. 300 ppm. This behavior seems to imply that the concentration of adsorbed oxygen at the interface decreases in an effective way around this CO concentration region. Such a highly non-linearity is again indicative of complex nature of the reactions taking place at the interface. It is suggested that the abrupt increase of sensitivity around 300 ppm CO may be advantageous for making an alarming device which raises an alarm when CO exceeds this concentration.

The response curves to 1000 ppm CO and 1000 ppm H_2 at 90 °C are shown in Fig. 5. The responses were rather slow, with the 90% response time (t_{90}) being about 20 min. However, the initial response rate was relatively fast, e.g., the 50% response time (t_{50}) for 1000 ppm CO was about 1 min. Therefore, a far shorter response time may be possible, if the initial response can be properly utilized.

Further investigations on the sensing characteristics and the sensing mechanism are now in progress.

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(Received July 2, 1987)