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Conductivity Change of SnO_2 with CO_2 Adsorption

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Evidence for the electronic interaction of CO_2 with the SnO_2 surface has been collected for the first time. The adsorption of CO_2 at 100 °C resulted in an considerable increase in electric resistance of SnO_2, holding a quantitative relation between them. Such interaction became invisible in the presence of H_2O because of the interference.

Semiconductor gas sensors based on SnO_2 are widely used for detecting inflammable gases from a change in electric resistance.[1)] In air, oxygen is adsorbed on the SnO_2 surface to form negatively charged adsorbates (O^- or O^{2-}) which trap conduction electrons and bring about high electric resistance of the sensor element. Inflammable gases, if present, consume the adsorbed oxygen to cause lowering of the electric resistance. However, a gaseous species, which apparently has nothing to do with such a redox process, can also affects the electric resistance, as typically exemplified by the case of water vapor adsorption.[2)] It has long been assumed that CO_2 is inert for the resistance change of semiconductor gas sensors, but we have found that this is not quite true. The electric resistance of SnO_2 can in fact be significantly changed with the adsorption of CO_2 under some particular conditions, as described belows.

SnO_2 powder was prepared as follows. An aqueous solution of $SnCl_4$ was neutralized with an ammonia solution. The resulting precipitate (stannic acid) was washed thoroughly with deionized water, dried at 100 °C, and finally calcined in air at 600 °C for 5 h. The powder sample was pressed and ground to granules of 0.25-0.83 mm, and was packed in the sample cell shown in Fig. 1 for the measurements of temperature programmed desorption (TPD) chromatograms as well as changes in electric resistance of SnO_2 resulting from the adsorption of CO_2. Prior to each TPD experiment, SnO_2 sample was exposed to O_2 (100 Torr) at 700 °C for 30 min followed by cooling to room temperature in the same atmosphere to secure the oxidized surface of SnO_2. An He flow (60 cm^3/min) was then introduced and a known amount of CO_2 (99.999%) was injected as a pulse into the flow at 100

°C. At the same time, the resistance change of the sample caused by the CO_2 adsorption was measured between the platinum mesh electrodes sandwiching the sample. Finally, TPD was carried out at a heating rate of ca. 10 °C/min. The desorbed gases were monitored with a thermal conductivity detector (TCD) and a quadrupole mass spectrometer (MASS).

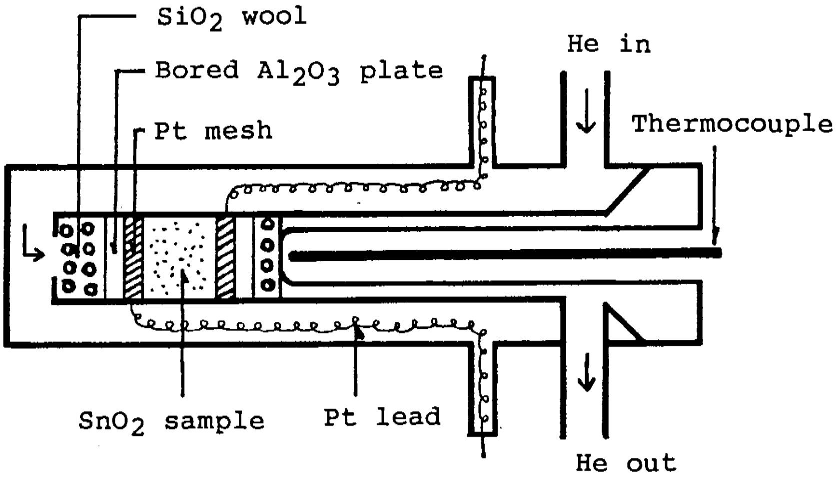

Fig. 1. Sample compartment for TPD and electric resistance measurements.

Curve (a) in Fig. 2 is a TPD chromatogram observed after SnO_2 was exposed to a CO_2 pulse (10 μmol) at 100 °C. As already reported,[3] the chromatogram from SnO_2 consists of two desorption peaks around 200 °C and above 450 °C, which are assigned to the desorptions of CO_2 (M/e= 44) and O_2 (M/e=32), respectively, by using MASS. Figure 3 shows the transient of electric resistance of SnO_2 on introduction of a CO_2 pulse (10 μmol) at 100 °C. The resistance increased sharply, followed by a gradual decrease to reach a steady value. The gradual decrease is considered to reflect that a part of adsorbed CO_2 is desorbed reversibly when the CO_2 pulse is gone, while the major part remains irreversibly adsorbed at this temperature. The steady value of the electric resistance after the CO_2 pulse is far above the original level, indicating that CO_2 adsorption causes the electric

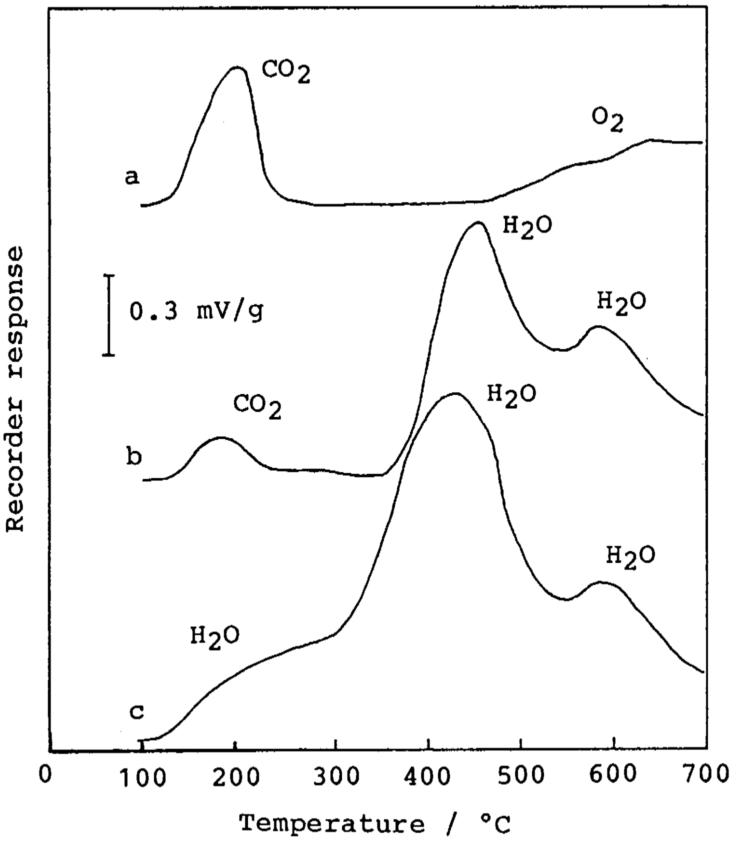

Fig. 2. TPD chromatograms after exposure to a CO_2 pulse at 100 °C.
(a): SnO_2 without H_2O preadsorption, (b) and (c): SnO_2 preadsorbed with water vapor by 40 μmol (b) and 65 μmol (c), respectively.

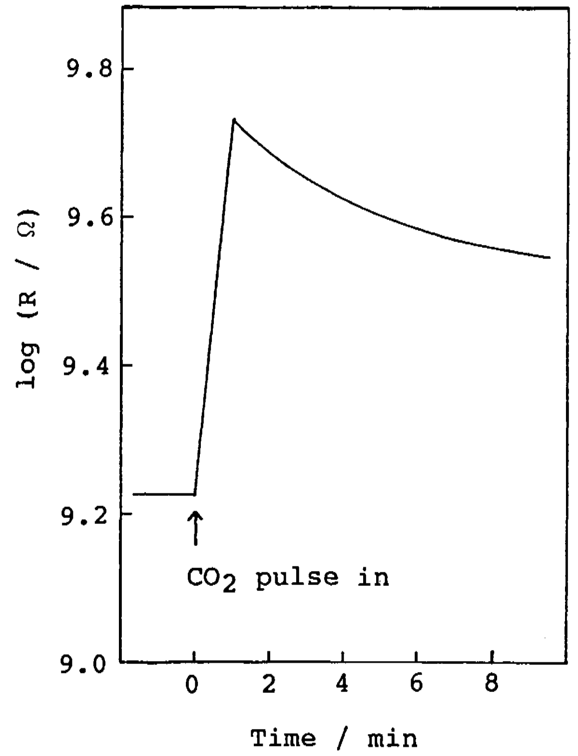

Fig. 3. Resistance change of SnO_2 on exposure to a CO_2 pulse at 100 °C.

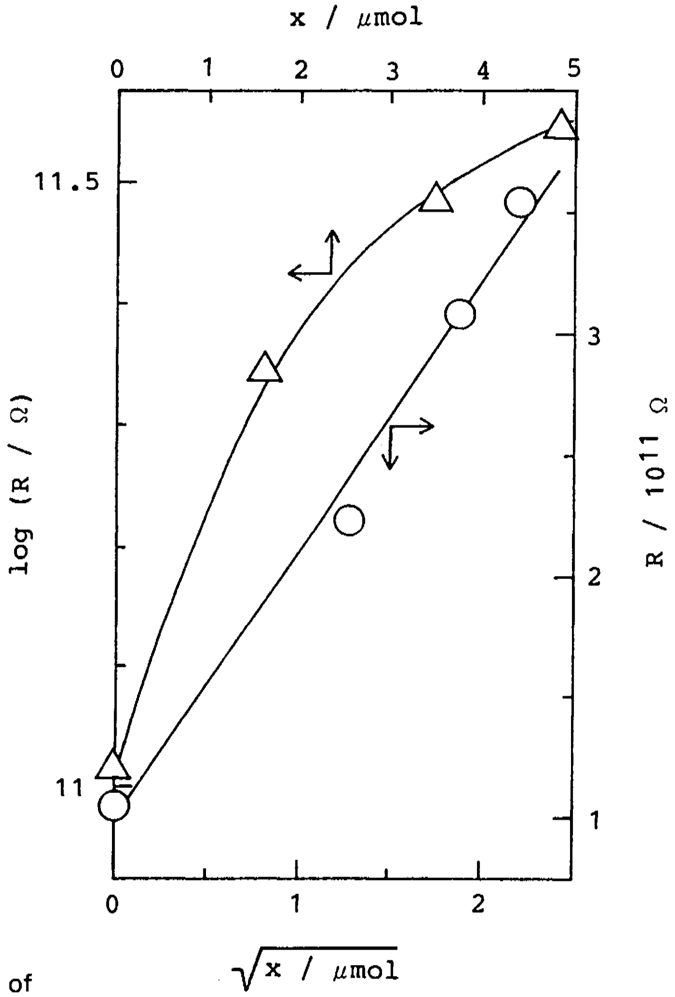

Fig. 4. Relationship between amount of adsorbed CO_2 (x) and resistance of SnO_2 (R).

resistance to increase.

To elucidate the electronic interaction of CO_2 in more detail, CO_2 was successively introduced as small pulses, whereas the electric resistance of SnO_2 (R) was pursued as a function of the amount of adsorbed CO_2 (x). As shown in Fig. 4, R was a monotonic function of x, being expressed rather well by an empirical equation, $R = R_0 + c \cdot x^{1/2}$, where R_0 and c are constants. Thus there is no doubt the electronic interaction of CO_2. The mechanism of the interaction, however, is still open to question at this stage. The adsorbed CO_2 probably forms a carbonate species (CO_3^{2-}) on the surface as reported by Thornton and Harrison.[4] This process requires the participation of a surface oxide ion: $O^{2-} + CO_2 \longrightarrow CO_3^{2-}$. If the oxide ion is less negatively charged for some reason, the formation of the carbonate species further requires the participation of conduction electrons, as indicated by the following equation, for example: $O^- + CO_2 + e \longrightarrow CO_3^{2-}$. Thus we assume tentatively that the adsorption of CO_2 involving such a less negatively charged oxide ion should bring about the increase of electric resistance.

All the above experiments were carried out in an He atmosphere. In order to examine the possibility of a CO_2 sensor based on such a resistance change, a conventional type sintered SnO_2

element was exposed to CO_2 in air. Figure 5 shows the response curves of the SnO_2 element to 0.8% CO_2 in dry air at 165 °C (a) and in wet air at 120 °C (b). In dry air, the electric resistance increased on introducing CO_2, and went back on cutting it out. This indicates that the element responds to CO_2 under these conditions although response rates are rather slow. In wet air, however, no response to CO_2 was observed as shown. This suggests that water vapor interferes the adsorption of CO_2. To confirm this, the SnO_2 samples on which prescribed amounts of water vapor had been preadsorbed were exposed to CO_2 at 100 °C and subjected to TPD experiments. The resulting chromatograms are curves (b) and (c) in Fig. 2. As compared with curve (a), the desorption of CO_2 decreased drastically by the preadsorption of 40 μmol H_2O (b) and totally disappeared when 65μmol H_2O was preadsorbed (c). In the last chromatogram, H_2O desorption commenced at ca. 120 °C and the absence of CO_2 was confirmed with MASS. These results confirm that H_2O adsorption strongly hinders the CO_2 adsorption, and this is a reason why SnO_2 element was insensitive to CO_2 in wet air.

In conclusion, the adsorption of CO_2 has been found to increase the electric resistance of SnO_2. However, such a change can be observed only with the clean surface. When the SnO_2 surface is contaminated with H_2O adsorbates, the sensitivity to CO_2 disappears because of a strong interfering effect of H_2O.

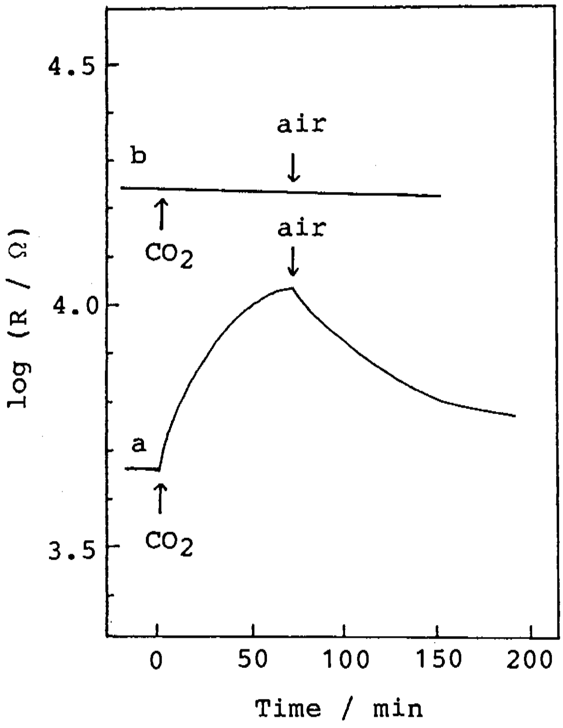

Fig. 5. Response curves of the SnO_2 element to 0.8% CO_2
(a) in dry air at 165 °C and
(b) in wet air at 120 °C.

References

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