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Correlation between Gas Sensitivity and Crystallite Size in Porous SnO_2-Based Sensors

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The gas sensing properties of SnO_2-based sensors in which the size of SnO_2 crystallites was controlled by various dopants were investigated. It was found that the gas sensitivity to H_2, CO or i-C_4H_{10} increased as the SnO_2 crystallite size decreased in the range below 10 nm. Quite high gas sensitivity was achieved at a crystallite size of ca. 5 nm.

Semiconductor gas sensors based on tin dioxide detect reducing gases from a change in conductivity. It is generally accepted that the chemisorption of oxygen on the surface of SnO_2 particles creates a high electric resistance layer in the depth of Debye length (L). Consumption of chemisorbed oxygen by reducing gases results in an increase in conductivity. The Hall effect measurement by Ogawa et al.[1)] has revealed that L for a porous thin film of SnO_2 is as small as about 3 nm at 300 °C. On the other hand, the crystallite size of SnO_2 particles (D) in conventional sensor elements is usually in the order of a few tens nanometer. If it is possible to decrease D to a sufficiently small value comparable to 2L, the gas sensitivity would become highly increased than the present level. Recently we have found that the microstructure of SnO_2 sensor elements can be controlled in a wide range by the addition of a small amount of foreign oxides. Some of the additives are effective to maintain fine SnO_2 particles having a high surface area up to 40 m^2/g and a small D value down to 6 nm even after calcination at 900 °C.[2,3)] In other words, the D value can be controlled by the choice of additive and/or calcination temperature. In this paper, we have prepared SnO_2 sensor elements in which D is varied in the range of 5-32 nm to investigate the influence of D on the gas sensing properties, as described below.

SnO_2 powder was prepared by neutralizing a cold solution of $SnCl_4$ with an aqueous ammonia solution followed by washing, drying and grinding. Metal oxide-doped samples were obtained by impregnating the hydrous SnO_2 with an aqueous solution of metal salts (mainly acetates) followed by drying and calcining at temperature above 600 °C. The amount of a dopant (M) was fixed to 5% in atomic composition (M/(Sn+M)). The specific surface area was measured by B.E.T. method using N_2 adsorption. The average crystallite size of SnO_2 was evaluated from the X-ray diffraction (XRD) line (101) based on the Scherrer's equation. For comparison the crystallite size was also investigated by transmission electron microscopy

(TEM) on a JEM-2000EX for same cases. To fabricate a sensor element, the powder sample calcined at 600 °C for 1 h in air was mixed with water, and the resulting paste was applied on an alumina tube attached with two Pt coil electrodes 1.5 mm apart from each other. The element was then sintered at 700 °C for 4 h in air before electric measurements. The gas sensing property was investigated in a heated chamber through which air or a sample gas was let to flow at a rate of 150 cm^3/min.

Figure 1 shows the average size (D) of SnO_2 crystallites for undoped as well as doped SnO_2 samples as a function of calcination temperature (calcination time, 1 h). For the undoped samples, D grew steeply from 3 nm at 400 °C to 13.8 and 27.2 nm at 600 and 900 °C, respectively. In this way, it is difficult to keep the size of SnO_2 crystallites below 10 nm in the sensors made with the undoped SnO_2 powder, because calcination (sintering) at 600 °C or above is required for obtaining sufficient mechanical strength of the sensor elements. On the other hand, the SnO_2 crystallites could often be kept at much smaller sizes in the doped samples, while some dopants promoted grain growth of SnO_2. At sintering temperature of 700 °C, D could be controlled in the range of 5-32 nm by selecting proper dopants. It should be stated that the D values evaluated from XRD were well coincident with those obtained from TEM observation.

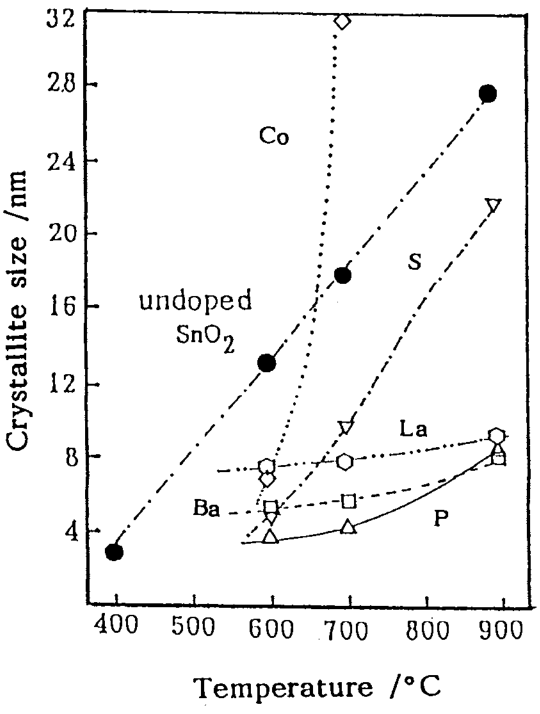

Fig. 1. Dependence of SnO_2 crystallite size for various samples on the calcination temperature.

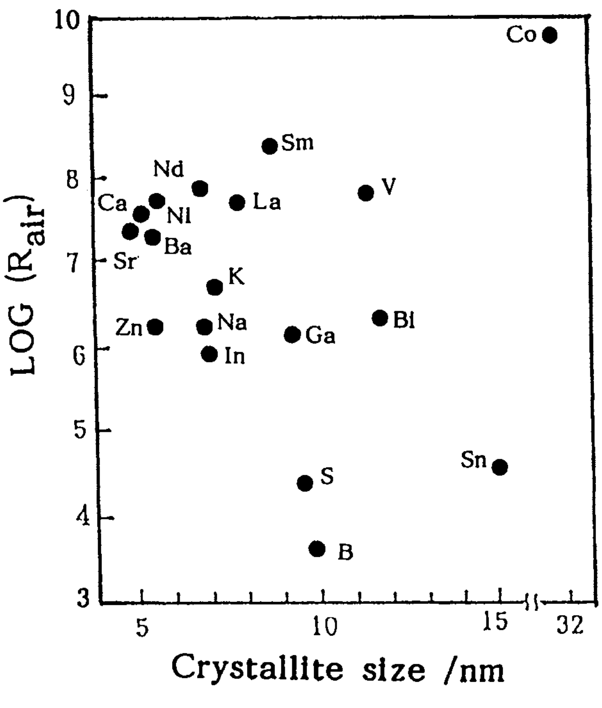

Fig. 2. Electric resistance of SnO_2-based sensors doped 5 at% additives in dry air at 300 °C.

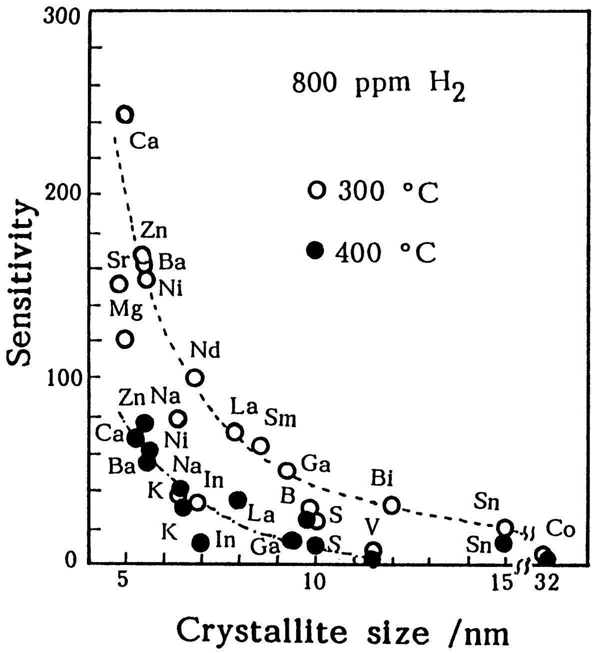

Fig. 3. Gas sensitivity of the SnO_2 sensors doped with 5 at% additives to 800 ppm H_2.

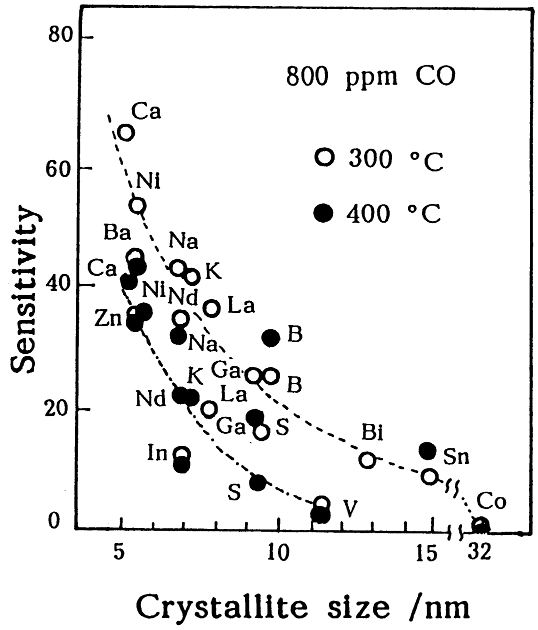

Fig. 4. Gas sensitivity of the sensors doped with 5 at% additives to 8000 ppm CO.

The sensor elements fabricated with these doped samples were subjected to measurements of electric resistance in air (R_{air}) and in sample gases (R_s). After these measurements, each element was destroyed to evaluate the average size (D) of SnO_2 crystallites by XRD. As shown in Fig. 2, R_{air} scattered widely depending on the samples and could hardly be correlated well with D. The same situation also resulted for R_s. Very interestingly, however, the ratio of R_{air} to R_s, which was defined as gas sensitivity here, was found to be well correlated with D as follows.

The gas sensitivity values of various doped elements to 800 ppm H_2 diluted with air at 300 and 400 °C are plotted against the crystallite size of SnO_2 in Fig. 3. Obviously the gas sensitivity tended to increase enormously as D decreased below 10 nm; it increased from 25 of the undoped SnO_2 element (D=15 nm) up to 246 of the Ca-doped element (D=5.4 nm) at 300 °C. The gas sensitivity is seen to follow a monotonous function of D through all the doped samples at a fixed temperature. Such a correlation is rather striking when one considers the wide variety of dopants used. This seems to imply that the sensitivity to H_2 is dependent exclusively on D under these conditions. Similar correlation between gas sensitivity and D was also obtained for 800 ppm CO as shown in Fig. 4. For 1000 ppm i-C_4H_{10}, however, the data scattered more widely, although a general tendency of increasing gas sensitivity with decreasing D could still be observed clearly as shown in Fig. 5. In the last case, the gas sensitivity was higher at 400 °C than at 300 °C, being opposite to those of H_2 and CO. Since i-C_4H_{10} is usually less reactive than H_2 or CO, it is speculated that its oxidation in sensor elements becomes more dependent on the catalytic properties of dopants, leading to the wider scattering of the data.

As mentioned above, the gas sensitivity of SnO_2-based elements to H_2, CO and i-C_4H_{10} depends on the size of SnO_2 crystallites, and it can be promoted enormously at a D value around 5 nm. So far such a striking correlation between gas sensitivity and D has not been found because conventional sensor elements usually consist of SnO_2 crystallites having far larger sizes. It is quite probable that the observed correlation results from the relative size between D and Debye length (L). As D decrease to come closer to 2L, the space charge region becomes more dominant in each SnO_2 crystallite, and thus the electric resistance would become more sensitive to objective gases. The fact that the gas sensitivity increases sharply as D decreased down to 5 nm is in rather good coincidence with the reported L value (3 nm) for SnO_2. Theoretical analyses of these correlations are under way.

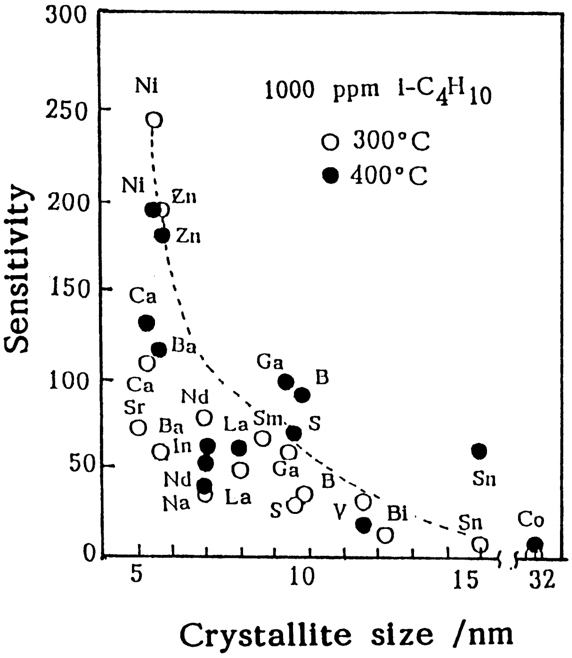

Fig. 5. Gas sensitivity of the sensors doped with 5 at% additives to 1000 ppm i-C_4H_{10}.

In conclusion, the gas sensitivity of SnO_2-based elements is strongly dependent on the crystallite size of SnO_2 when the crystallite size becomes smaller than 10 nm. Very high sensitivity can be achieved when D is controlled to ca. 5 nm by the addition of proper dopants.

References
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