

# Gas sensing characteristics of tin dioxide with small crystallites

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The effect of calcining temperature on gas sensitivity and resistance in wet air was observed with elements of SnO<sub>2</sub> thick film. The results were interpreted as a function of the crystallite size. As the crystallite size reduced, the sensitivity to H<sub>2</sub> gas enhanced at temperatures lower than 300 °C, but at those higher than 350 °C it did not. The temperatures showing the minimum resistance in air and the maximum sensitivity to H<sub>2</sub> gas decreased with reduction of the crystallite size. The temperature variations were assigned to the change of the activation energies of the oxygen adsorbates. It is suggested that the decrease of activation energies is one of the reasons for the sensitivity enhancement with the fine powder.

## 1. Introduction

Tin oxide has been widely used in semiconductor gas sensors. For the improvement of the properties in SnO<sub>2</sub>-based elements, the gas sensing mechanisms have been investigated by many workers. Among the gas sensing models suggested up to now, the grain boundary model is generally accepted for porous poly-crystalline SnO<sub>2</sub> gas sensors [1]. This model illustrates that the gas sensitivity is independent of the crystallite size. However, there have been many contradictory reports [2–8].

Morrison [2] explained that, at extreme conditions in the porous pellet, the necks formed between adjacent grains can be so thin as to become the resistance-controlling feature. There can also be the mixed-case of control by both necks and grain boundaries. Xu *et al.* [5] and Yamazoe [6] reported that the sensitivity of a thick film of SnO<sub>2</sub> sensor was enhanced as the crystallite size decreased. They interpreted this phenomenon with both the two-dimensional neck model and the mixed state of grain boundary contacts and neck contacts. Clifford [7] explained that gas sensitivity changes with surface disorder, which can be altered by sample preparation processes. Harrison *et al.* [8] expounded that presintering could greatly influence the observed activation energy value of tin (IV) oxide gel samples by way of modifying the bulk properties, of changing the intergrain contact area or of altering the nature of the surface.

In this paper we observe the effect of calcining temperature on the sensitivity to 0.5 vol % H<sub>2</sub>, 0.5 vol % CO gas, and the resistance in air. For the observation of the calcining effect, as above, we should consider many different terms, such as geometrical ones and others which may properly represent the properties of the bulk and the surface. However, for consistency of view-point, the results will be interpreted only as a function of the crystallite size, by

which it is not meant that the same crystallite size generally induces the identical properties, regardless of the powder fabrication processes. For the interpretation, the two possible factors, the contact area change and the surface property alteration, will be examined, assuming constant bulk material properties.

## 2. Experimental procedure

The SnO<sub>2</sub> powder was prepared by neutralizing a cold solution of SnCl<sub>4</sub> with an aqueous ammonia solution. The resulting precipitate was washed thoroughly with distilled water, dried at 100 °C for 1 day, ground into powder under a 100 mesh size and calcined for 1 h in air at temperatures of 500–1100 °C to obtain SnO<sub>2</sub> crystallites of various sizes in the range 8–54 nm. The specific surface area of the prepared powders was measured by Brunauer, Emmett, Teller (BET), using the Micromeritics Rapid Surface Area Analyzer 2200. The average crystallite sizes of the powders were evaluated from transmission electron microscopy (TEM; Joel 200CX) images and averaged for more than 100 crystallites.

Sensor elements were fabricated into the form of a thick film. The sample powder was mixed with distilled water and the resulting paste was applied to an alumina substrate. The thickness of the resulting layer was about 0.5 mm. On the substrate the interdigitated electrode, in the shape of a 4 mm square and a 0.4 mm electrode gap, had been printed with Pt paste using the silk screen printing method. Then the elements were sintered for 1 h at 400 °C in air. The sensor elements were set in an alumina tube (inner diameter 50 mm) located inside an electrical furnace. Their electrical resistances were measured under the flow (400 cm<sup>3</sup> min<sup>-1</sup>) of air and the sample gas of 0.5 vol % H<sub>2</sub> or 0.5 vol % CO, balanced with air. The humidity

of the flows was maintained at 50% RH H<sub>2</sub>O at 20 °C in all experiments.

### 3. Results and discussion

#### 3.1. Physical state of calcined powder

Fig. 1a and b show the TEM images of the SnO<sub>2</sub> powders calcined at 500 °C and 1100 °C, respectively. The crystallites are agglomerated at the necks into large grains, which suggests the mixed-case. It was reported that grains of SnO<sub>2</sub> grow without an increase in the apparent density of the sintered body for heat treatment below 1200 °C [9]. So it can be expected that there is negligible change in porosity even after calcining at 1100 °C. Table I shows the crystallite size and the specific surface area of the SnO<sub>2</sub> powders as a function of the calcination temperature. Compared with the data of Xu *et al.* [5], the data in Table I show some deviation. However, in view of the crystallite size versus the surface area, on the whole, the geometrical relationship between the neck and the crystallite can be considered to be similar to that of Xu *et al.* [5] considered the neck size of the powder to be about 80% of the crystallite size on the basis of the relationship between crystallite size and surface area. With this relationship, the change of neck area can be represented as a function of crystallite size.

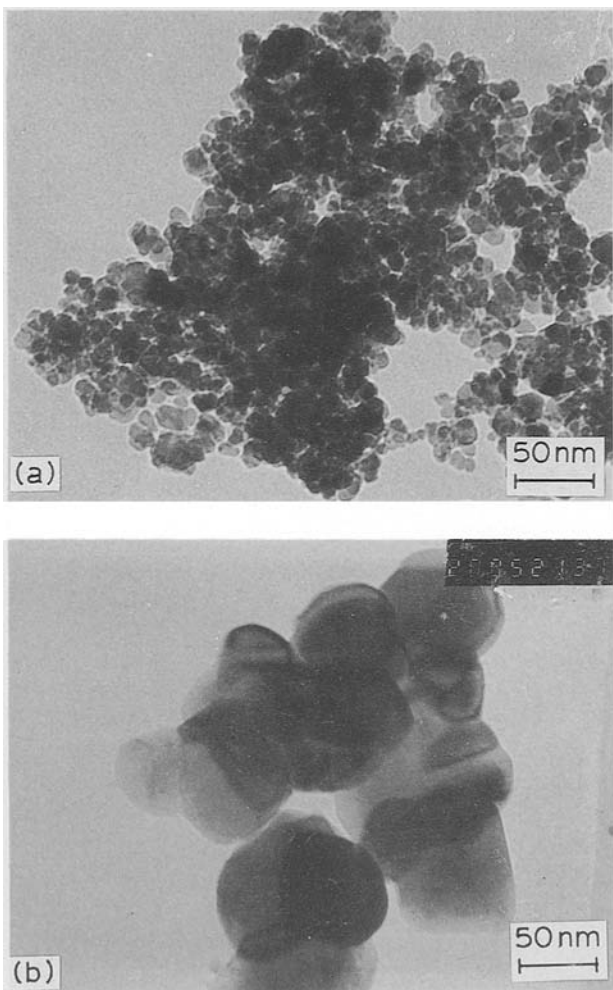


Figure 1 TEM micrographs of SnO<sub>2</sub> powders calcined for 1 h in air at (a) 500 °C and (b) 1100 °C.

#### 3.2. Gas sensitivity

Fig. 2 shows the sensitivities of sintered thick films of SnO<sub>2</sub> with various crystallite sizes to 0.5 vol % H<sub>2</sub> and 0.5 vol % CO gases at 300 °C. The sensitivity (*S*) is defined as  $S = R_{\text{air}}/R_{\text{gas}}$ , where *R*<sub>air</sub> and *R*<sub>gas</sub> stand for the resistance of elements in air and in the sample gas, respectively.

The sensitivities increase with a decrease of the crystallite size in both gases, which is similar to the results of Xu *et al.* They explained the results using the sensitivity equation of the two-dimensional neck model for the elements of the small crystallites, and the mixed state of grain boundary contacts and neck contacts for the large crystallites. The sensitivity equations for the neck model (*S*<sub>n</sub>) [5] and the grain boundary model (*S*<sub>gb</sub>) [1] can be expressed as Equations 1 and 2, respectively.

$$S_n = \frac{(x - 1)^2 + n_L(\text{g})/n_0 [x^2 - (x - 1)^2]}{(x - 1)^2 + n_L(\text{a})/n_0 [x^2 - (x - 1)^2]} \quad (1)$$

where  $x = X/2L$ , and *X* is the neck size and *L* the length of the depletion layer, *n*<sub>0</sub> is the carrier density in the bulk material, *n*<sub>L</sub>(g) and *n*<sub>L</sub>(a) are the carrier densities in depletion layer in the gas and air, respectively.

$$S_{\text{gb}} = \exp(q\Delta V_s/kT) \quad (2)$$

$\Delta V_s$  is the difference in the surface potential barriers at the grain boundary as the atmosphere changes from

TABLE I Crystallite size and surface area of powder calcined at different temperatures

Calcining condition	Crystallite size (nm)	Surface area (m <sup>2</sup> g <sup>-1</sup> )
500 °C – 1 h	8.2	48.5
700 °C – 1 h	17.7	18.6
900 °C – 1 h	23.8	8.7
1100 °C – 1 h	54.4	3.2

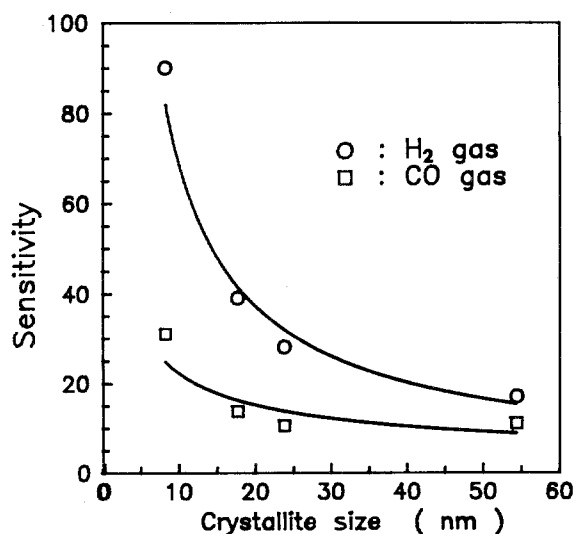


Figure 2 Effect of crystallite size on gas sensitivity to 0.5 vol % H<sub>2</sub> and 0.5 vol % CO balanced with air at 300 °C.

gas to air. The potential barrier  $V_s$  can be expressed as  $V_s = qN_s^2/2\kappa\epsilon_0N_D$  [1]. Where  $q$  is the effective charge of adsorbates,  $N_s$  is the density of charged surface states of grain.  $\kappa$ ,  $\epsilon_0$  and  $N_D$  represent dielectric constant, permittivity in vacuum and density of donor in grain, respectively.

Xu *et al.* formulated Equation 1 assuming that the resistance of elements is controlled by the number of carriers within one neck having a diameter  $X$ . They assumed the depletion layer length  $L$  to be about 3 nm. They also assumed the carrier densities in the depletion layer to be constant, being  $n_L(a)$  in air and  $n_L(g)$  in the gas. According to Equation 1 for the neck model, the sensitivity increases as the crystallite size decreases, while for Equation 2 for the grain boundary model, the sensitivity is independent of crystallite size.

Fig. 3 shows the sensitivities to 0.5 vol %  $H_2$  gas as a function of the crystallite size at various measuring temperatures. The relationship between sensitivities and crystallite size changes with the measuring temperatures. At low measuring temperatures below 300 °C, the sensitivity increases with a reduction of crystallite size. The sensitivities of the element fabricated with small crystallites of average size 8 nm, show maximum values at a temperature of 300 °C and decrease at temperatures above 350 °C. The sensitivities of the element fabricated from crystallites of average size 18 nm show maximum values at 350 °C and decrease above 400 °C. Those averaged about 24 nm and 54 nm show a maximum value at 400 °C. Neither Equation 2 for the grain boundary model nor Equation 1 for the neck model can interpret this behaviour. There seems to be factors other than the geometrical ones which have an effect on the sensitivity with change of crystallite size. The possible reasons for this temperature dependency of the sensitivity need to be ascertained.

### 3.3. Temperature dependency of sensitivity

It is known that the sensitivity of a gas sensor to a given gas varies with the change of measuring temper-

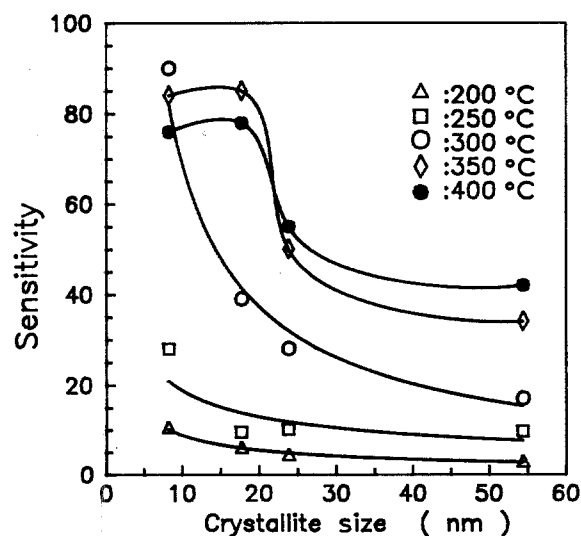


Figure 3 Effect of crystallite size on gas sensitivity to 0.5 vol %  $H_2$  balanced with air at various measuring temperatures.

ature [10]. The temperature dependency of sensitivity is also known to be modified by the composition of the element. These phenomena can be explained by the facts that, with the change of temperature, both the adsorbed species on the element and the reaction mechanism of a particular gas may alter [4, 8, 10, 11], and that some adsorbed species are dominantly participating in a certain reaction mechanism [12, 13].

The most reactive species to  $H_2$  gas was reported to be  $O^{2-}$  [12]. The temperature showing the maximum sensitivity to  $H_2$  was reported to be room temperature for the element Pt/ $SnO_2$ , and to be about 150 °C for Pd/ $SnO_2$  [10]. The starting temperature for the transformation from  $O_2^-$  to  $O^-$  and  $O^{2-}$  was interpreted to be about 230 °C on porous pellets of pure  $SnO_2$ , which were made from meta-stannic acid followed by heat treatment at 1000 °C for 16 h. At 400 °C the major adsorbed oxygen species was reported to be  $O^{2-}$ . It was also suggested that the combustible gas reacts with the adsorbed oxygen species and establishes a changed steady-state occupancy of the surface states. The sensitivity to  $H_2$  on these pellets was reported to increase rapidly with an increase in temperature from 300 °C, but to decrease above 380 °C [4]. It was stated that the sensitivity enhancement can be related to the activity increase on the surface, and the catalytic oxidation can be accelerated with the rise of temperature. The temperature above which the sensitivity decreases was defined as the cut-off temperature [14]. The cut-off temperature was explained to be caused by the fact that above the cut-off temperature the reaction between the gas and adsorbates could become so fast that the gas is mainly consumed near the surface of the porous pellet, with the result that little un-consumed gas is able to penetrate into the centre of the pellet [14].

From the above considerations, it is remarkable that the surface activity could be enhanced by the activation of either the combustible gas or the adsorbed species [13]. For convenience of interpretation, the activation process of the gas is termed the activation process and that of the adsorbed species is called the transition process. It is also remarkable that the change in the steady-state occupancy of the surface states and the increase of the surface activity may mean fast desorption and re-adsorption of surface adsorbates, especially  $O^{2-}$  in an  $H_2$  gas atmosphere near the cut-off temperature [4, 12, 14]. The surface adsorbate of  $O^{2-}$  would be produced by the transition processes  $O_2 \rightarrow O_2^- \rightarrow O^- \rightarrow O^{2-}$  on the element rather than directly from  $O_2$  in air [4, 12, 13], because the latter needs a large activation energy. The hydroxide radical was also postulated to participate in the transition processes, as  $OH^- \rightarrow O^-$  [4]. The high sensitivity and low cut-off temperature with the element Pt/ $SnO_2$  were explained by the fact that Pt, as a catalyst, causes the easy adsorption and spill-over of the active species at low temperatures by its activation energy lowering [13, 14].

As shown in Fig. 3, the maximum sensitivity temperature, the so-called cut-off temperature, becomes lower with the smaller crystallite size. The activation processes of the gases and the transition processes of

the adsorbates are thermally activated. Thus the reduction of the cut-off temperature can be explained by the decrease in the activation energies of the processes. Therefore it may be inferred that the activation energies of the transition processes reduce with the diminution of the crystallite size. On the other hand, the surface activity of the fine crystallite may be higher than that of the coarse one at the same measuring temperature. Now the sensitivity variation with change of measuring temperature in Fig. 3 may be interpreted to be partly due to the modification of the activation energies on the transition processes at the surface. The sensitivity enhancement with the smaller crystallites in Fig. 2 may be due to both the easy formation of the active adsorbate, i.e.  $O^{2-}$ , and the decrease of the crystallite neck area. Before the modification of surface nature is suggested, it is necessary to differentiate the sensitivity increase caused by the modification of the transition process of the adsorbates from that caused by the change of the activation process of the gas on the surface.

### 3.4. Temperature-resistance curves in air

Fig. 4 shows the temperature-resistance curves under wet air flow as the temperature was increased at a rate of  $15^\circ\text{C h}^{-1}$ . The element with crystallites of 8 nm diameter in Fig. 4 shows the minimum resistance point at about  $160^\circ\text{C}$  and the maximum resistance point at about  $310^\circ\text{C}$ . The temperatures at the turning points, where the slope of the curves changes sign, are shown to increase as the crystallite size increases. This sigmoid or anomalous curve is well known for  $\text{SnO}_2$  and  $\text{ZnO}$ . The temperature-resistance curves in wet air represent only the transition properties of the adsorbates of oxygen and hydroxide radicals, while the sensitivity curves show the properties including the activation process of the reducing gasses [4, 10, 13, 15, 16].

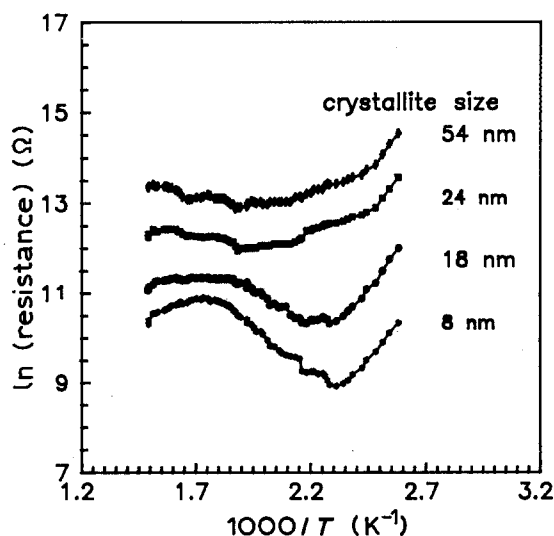


Figure 4 Temperature-resistance relationship for a thick film of  $\text{SnO}_2$  in RH 50% air flow. Temperature was increased at a rate of  $15^\circ\text{C h}^{-1}$ . The crystallite sizes of elements are marked at the right side of each curve.

Saito *et al.* [15] suggested that the sigmoid curve is related with the transitions of the adsorbed oxygen species such as  $O_2^-$ ,  $O^-$ ,  $O^{2-}$  on  $\text{ZnO}$ . With the  $\text{SnO}_2$  element, Chang [11] found the transition of  $O_2^-$  to  $O^-$  at  $150^\circ\text{C}$  by electron paramagnetic resonance measurement. Chang used powder made from the hydrolysis of  $\text{SnCl}_2$  followed by calcination at  $550^\circ\text{C}$  for 2 h. McAleer *et al.* [4] reported the minimum resistance point at  $280^\circ\text{C}$  and the maximum resistance point at  $460^\circ\text{C}$  with the pellet heat-treated at  $1000^\circ\text{C}$  for 16 h. They explained that the sigmoid curve is caused by the moisture in air, while near the low turning point (about  $230^\circ\text{C}$ ) the transition from  $O_2^-$  to  $O^-$  and  $O^{2-}$  occurs. According to Harrison *et al.* [16], the turning points of the elements without heat treatment at the minimum and the maximum resistance points are at  $147 \pm 20^\circ\text{C}$  and  $247 \pm 20^\circ\text{C}$ , respectively.

In the above citations, the crystallite size of the elements would be smaller as the temperatures of the heat treatment became lower. Therefore it can be inferred that the turning temperatures become lower [11, 16], and that the transition temperatures of  $O_2^-$  to  $O^-$  and  $O^{2-}$  decrease with reduction of the crystallite size [4, 11]. The decrease of transition temperatures explains the diminution of the activation energies of the transition processes; it also explains the increase of sensitivity measured at temperatures below the cut-off temperature. However, it is reasonable to think that there is still a possibility of sensitivity increase by the activation of gas on the fine crystallite. The change of the turning temperatures in Fig. 4 is consistent with the former inference. The latter inference also accords with the data in Fig. 4, if the transition temperatures are shown to be intimately related with the temperatures at the turning points.

## 4. Conclusion

With elements of crystallites sized in a range 8–54 nm, the sensitivities to 0.5 vol%  $\text{H}_2$  gas increased with decrease of crystallite size at temperatures lower than  $300^\circ\text{C}$ , but did not at temperatures above  $350^\circ\text{C}$ . The temperatures showing the maximum sensitivity and the minimum resistance in air reduced as the crystallites diminished in size. From these results, it can be concluded that the activation energies of the adsorbed oxygen species reduce with decrease of crystallite size. It can also be suggested that the sensitivity enhancement with the fine crystallites is partly due to the easy formation of active oxygen adsorbates.

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