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Relationship between Gas Sensitivity and Film Structure of SnO_2 Thin Film Gas Sensor by Sol-Gel Method

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Gas sensing properties of SnO_2 films prepared by sol-gel method are investigated to be strongly dependent on the firing temperature conditions. The films obtained at 400 °C have much higher sensitivity than those at 800 °C, being attributed to the fact that the crystallite size of the films linearly increased with the firing temperature. Probable mechanisms to explain the sensing properties are discussed.

Tin dioxide is one of typical n-type oxide semiconductors which has been extensively used as a gas sensor to detect various flammable gases. The sensing is described by the conductivity change in air and a flammable gas. Oxygen gas adsorbed on SnO_2 surface lowering the free carrier concentrations in SnO_2 surface layer called as the depletion layer is the cause of the electrical conductivity reduction in air.[1,2] On exposing the SnO_2 surface to a reducing atmosphere containing a flammable gas, the gas reacts with the adsorbed oxygen molecules to release the electrons which have been trapped as negatively charged O_2^- ions. Three important gas sensing models have been proposed for the polycrystalline devices: (1) double Schottky model,[3,4] (2) neck model[5-7] and (3) ultra fine particle model.[8,9]

Examining the relationship between gas sensitivity and crystallite size (4-27 nm) of SnO_2 fine powders prepared by hydrolysis of tin tetrachloride ($SnCl_4 \cdot 5H_2O$), Xu et al.[10] concluded that the gas sensing mechanism could be described by a combination of double Schottky model and neck model. Based on the measurements of Hall effect, Ogawa et al.[7] reported that gas sensing of gas evaporated films which consist of fine particles (5-20 nm) could be explained by the neck model. In this paper, gas sensitivities of sol-gel SnO_2 thin films with various crystallite sizes were measured to elucidate the sensing mechanism.

SnO_2 thin films were prepared on a glass (# 7059, Corning Co.) or quartz glass substrate by the dip-coating method reported previously.[12] Isopropanol solution of tin tetra(isopropoxide) $Sn(O\text{-}i\text{-}C_3H_7)_4$ (99.9% purity; High Purity Chemicals Co. Ltd.) was used as the dip-solution. Triethanolamine equimolar to the alkoxide was added to stabilize the solution. In this study, the substrate pulling-rate was fixed at 6 $cm \cdot min^{-1}$. After coating by dipping, the gel films were dried at 110 °C for 10 min and subsequently heated at 400-800 °C for 30 min in air. SnO_2 thin films were obtained by repeating the cycle of dippingdrying-firing: 7 times for 520-440 nm thickness. The crystallite size was calculated from the width of X-ray diffraction peak (110) based on Scherrer's equation. And the particle size which build the films was evaluated from TEM images. The resistivity of SnO_2 thin films was measured by conventional two terminal method and van der Pauw method in dry air and in test gas containing a flammable gas (2-methyl-2-butene balanced by dry air, 2000 ppm) at 350 °C. Gas sensitivity is defined as R_{air}/R_{gas} in which R_{air} and R_{gas} are resistivities in air and in test gas, respectively. In order to evaluate carrier concentrations and mobilities in both concditions, Hall coefficients were measured under the applied field of 0.5 T.

Figure 1 shows the effect of firing temperature on the responses of gas sensing of SnO_2 thin film sensors for 2-methyl-2-butene test gas, measured by two terminal method. As clearly shown from this figure, the sensing behaviors strongly depend on the firing temperatures, while time constants of response remained almost unchanged. Firing temperature may affect the film properties such as film porosity or pore size, crystallite size and stoichiometry (ratio of oxygen vacancies). In order to clarify which of these caused the sensitivity change, the basic data for the films was examined including film thickness, refractive index, crystallite size, which are summarized in Table 1. As shown in Table 1, the crystallite size of the films increases with the firing temperatures from 6 nm at 400 °C to 22 nm at 800 °C. A typical TEM image of the cross section of SnO_2 thin films with 280 nm thickness is depicted in Fig. 2, suggesting that the film consists of spherical particles, the primary particle size being equal to crystallite size evaluated from XRD. These facts hint that the primary particle size of SnO_2 thin films can be easily controlled by changing the firing temperature.

Figure 3 shows relationship between gas sensitivity and crystallite size of the films. Gas sensitivity decreases gradually by increasing crystallite size. But the tendency deviates from that expected by neck model,[5-7] where gas sensitivity increases steeply when the diameter of the neck part is smaller than twice the Debye length. Debye length of SnO_2 films fired at 600 °C in this study was evaluated to be about 6 nm from observed carrier concentration of 10^{18} cm^{-3} at 350 °C. Fig. 4 exhibits variations of the resistivities of SnO_2 thin films at 350 °C with crystallite size both in, dry air and test gas. The resistivity in test gas remained almost constant irrespective of crystallite size. On the other hand, the resistivity in dry air decreased greatly with increasing crystallite size. From these results, it can be easily concluded that the increase in gas sensitivity depends exclusively on the increase in the resistivity in dry air caused by decrease in crystallite size. This fact reflects the limitation of explaining the sensing behaviors by double Schottky model or neck model. Further ultra fine particle model[8,9] proposed by Ipponmatsu and his coworkers can partly explain the tendency shown in Fig. 4. In this model, for SnO_2 with fine particle, which is much smaller than the width of space-charge layer, its electrical conductivity would be determined only by the number of electrons which are released by the reaction of adsorbed oxygen O_2^- with flammable gas.

In order to quantitatively investigate the effect of crystallite size on the carrier concentration and mobility, van der Pauw and Hall coefficients measurements for the SnO_2 films were made at 350 °C in air and test gas. The results obtained are compiled in Table 2. This table manifests that carrier concentrations exponentially decrease in air with the decrease in the crystallite size but remains almost constant in test gas at a value of 10^{19} cm^{-3} order. This is the tendency expected from ultra fine particle model.[8,9,13] On comparing Table 2 and Fig. 3, however, it is important to note that there is a great difference between the sensitivity data obtained by van der Pauw (virtually four probe) method and by two terminal method, being due to the resistivity difference in air. This might be attributed to Schottky barrier formed between SnO_2

Table 1. Effect of firing temperature on film thickness, refractive index, and crystallite size

Firing Temperature/°C	400	500	600	700	800
Film Thickness/nm	520	500	460	450	440
Refractive Index	1.7	1.7	1.8	1.8	1.8
Crystallite Size/nm	6	8	10	19	22

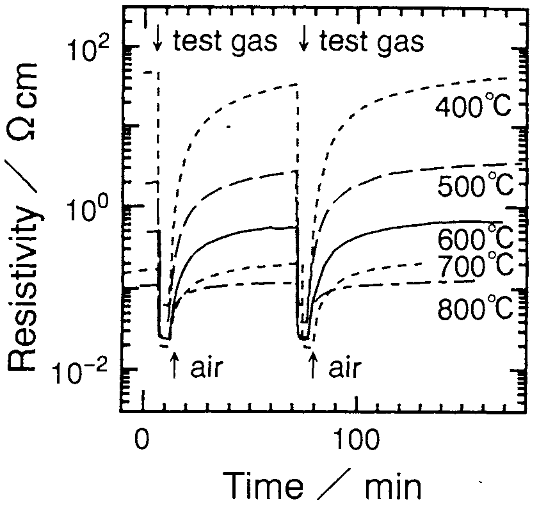

Fig. 1. The effect of firing temperature on the responses of gas sensing (for 2-methyl-2-butene).

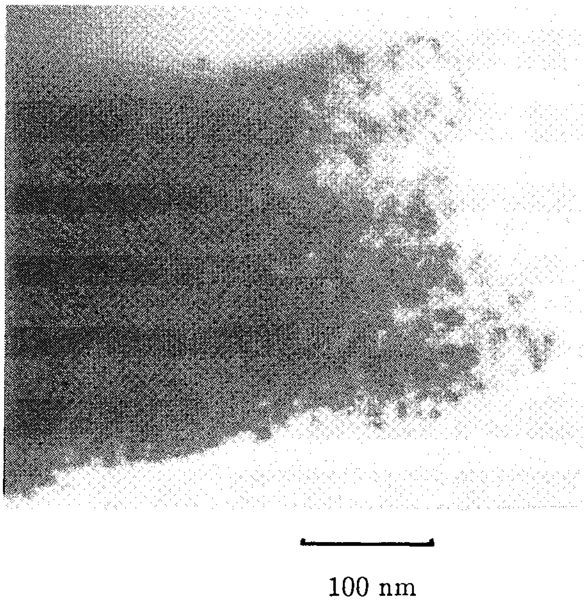

Fig. 2. TEM image of cross section of a SnO_2 film fired at 600 °C.

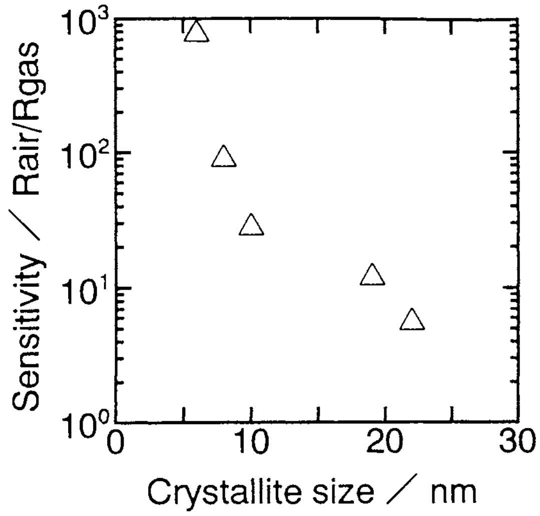

Fig. 3. Variation of gas sensitivity of SnO_2 thin films with crystallite size.

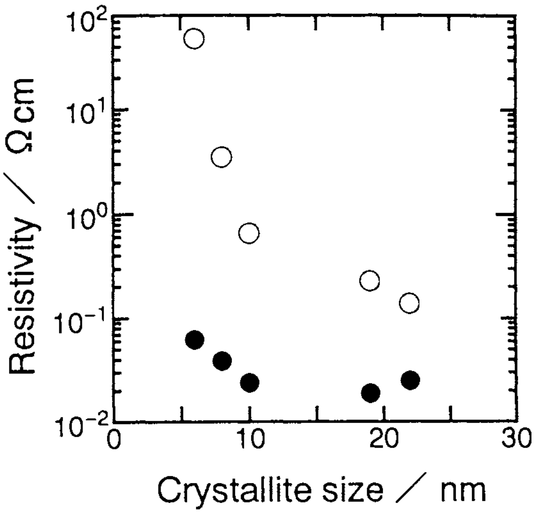

Fig. 4. Resistivity variations of SnO_2 thin films with crystallite size. Open and solid symbols denote the data in air and in test gas, respectively.

Table 2. Effect of firing temperature on carrier concentrations, Hall mobilities and resistivities of SnO_2 films in air and test gas

Firing Temperature/°C	400	500	600	700	800
(in air)					
Resistivity/ohm·cm	3.6	3.2×10^{-1}	1.3×10^{-1}	5.4×10^{-2}	4.3×10^{-2}
Carrier concentration/cm^{-3}	1.5×10^{17}	5.3×10^{17}	1.5×10^{18}	2.6×10^{19}	3.7×10^{19}
Mobility/$cm^2 \cdot V^{-1} \cdot sec^{-1}$	17	42	32	6.6	12
(in test gas)					
Resistivity/ohm·cm	2.2×10^{-1}	4.3×10^{-2}	1.7×10^{-2}	2.8×10^{-2}	3.0×10^{-2}
Carrier concentration/cm^{-3}	1.7×10^{19}	4.8×10^{19}	1.6×10^{19}	1.8×10^{19}	2.6×10^{19}
Mobility/$cm^2 \cdot V^{-1} \cdot sec^{-1}$	3.3	3.3	13	14	9.1
Sensitivity (R_{air}/R_{gas})	16	7.4	7.6	1.9	1.4

and the contact (gold film), especially for the films with lower carrier concentration developed by oxygen adsorption on very small crystallites. In the case of four probe method this barrier has no substantial effect on the resistivity measurement. Therefore, it can be concluded that very high sensitivity of the film fabricated at as low as 400 °C was caused by the dominant effect of crystallite size and additional effects of the Schottky barrier.

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