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EFFECT OF STEPWISE DOPING OF Al_2O_3 AND Li_2O ON MICROSTRUCTURE AND ELECTRICAL RESISTIVITY OF ZnO CERAMICS

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Porous and high-resistive ZnO ceramics were obtained by a stepwise doping method of Al_2O_3 and Li_2O. Lithia increased the resistivity of ZnO doped with Al_2O_3 without a change of porous microstrucrure. The sensitivities of the stepwisely doped specimens to reducing gases at 300°C were improved compared to that of the singly doped specimens.

Zinc oxide is one of the prominent candidates as gas sensing materials. The gas sensing mechanism has been explained as follows;1)2)3)4) potential barriers near the surfaces of grains owing to the adsorbed oxygen are lowered by desorption of the adsorbed oxygen through the reactions with reducing gases. Therefore, the shape of the potential barriers changes with adsorption and desorption of oxygen and the resistivity of ZnO decreases by introduction of reducing gases.

Two models are proposed to explain the flow of electrons through necks and grain boundaries.2)5)6) One is that the number of electrons which can go over the barrier increases exponentially due to the decrease of the barrier height by desorption of oxygen (gate action). The other is that a neck works as the gate described above, when the width of the neck is narrower than twice the Debye length "L_D" or the width of a space charge layer "l". Here, L_D is given by the following equation;5)

$$L_D = \sqrt{\varepsilon kT/e^2N_d} \qquad (1)$$

ε ; dielectric constant k ; Boltzmann's constant
T ; absolute temperature e ; electronic charge N_d ; donor concentration

In either case, a characteristic of ZnO gas sensor is influenced by the number and the distribution state of grain boundaries, the widths of necks, and donor concentration.

Zinc oxide dissociates and generates electrons according to the following quasi-equilibrium reactions;

$$ZnO = Zn_i^* + 1/2\ O_2(g) \qquad (2)$$

$$Zn_i^* = Zn_i^{\cdot} + e' \qquad (3)$$

$$Zn_i^{\cdot} = Zn_i^{\cdot\cdot} + e' \qquad (4)$$

Interstitial zinc ions contribute to sintering of ZnO ceramics.7)8)9)10)11)12)

Alumina and lithia dissolve into ZnO as follows;

$$Al_2O_3 = 2Al_{Zn}^{\bullet} + 2ZnO + 2e' + 1/2\ O_2(g) \qquad (5)$$

$$Li_2O + 2e' + 1/2\ O_2(g) = 2Li_{Zn}' + 2ZnO \qquad (6)$$

where $Al_{Zn}^{\bullet}$ and Li_{Zn}' represent Al^{3+} and Li^{+} at normal Zn^{2+} sites, respectively. Doping Al_2O_3 to ZnO decreases the resistivity[13)] according to the equation (5) and suppreses the sintering of ZnO ceramics[11)14)] due to the shifts of the equilibrium of the equations (2), (3), and (4) to the left; whereas doping Li_2O increases the resistivity[13)15)] and accelerates the sintering.[11)15)16)]

To obtain porous ZnO ceramics with high resistivity which should have high sensitivity as a gas sensor, the microstructure of ZnO ceramic controlled by doping Al_2O_3 and the resistivity increased by doping Li_2O were investigated in the present work. Then the gas sensing characteristics were examined on some kinds of specimens.

An aqueous slurry containing ZnO powder (99.99% pure) and $Al(NO_3)_3$ was dried, ground in an agate mortar, calcined at 600°C for 4 hr in an alumina crucible, and ground again. The resulting powders were pressed into pellets 10 mm in diameter and 2-3 mm thick under the pressure of ∿160 kg/cm^2. The pressed bodies were placed on the powder of the same composition and heated up to 900°C at the rate of 300°C/hr

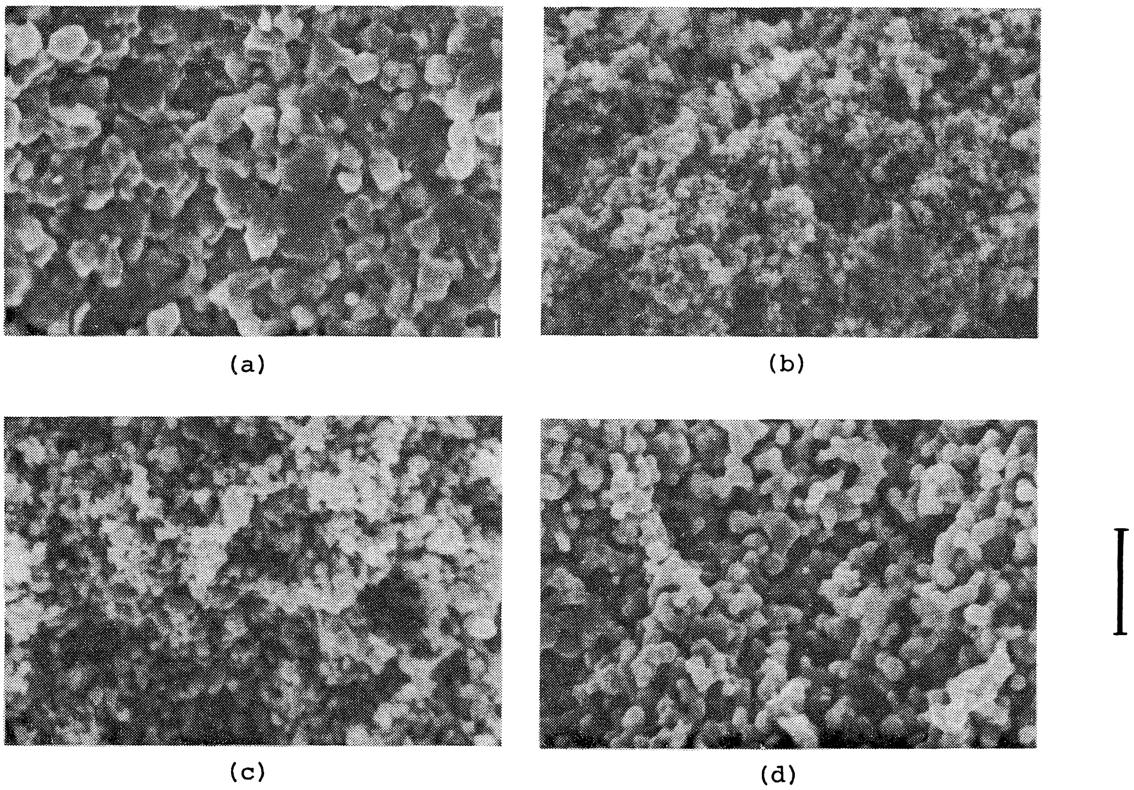

Fig. 1. Scanning electron micrographs of the fracture surfaces of the specimens. (bar : 5μm)

(a) pure ZnO sintered at 900°C for 5 hr (b) Z-1

(c) Z-4·500 (d) Z-4·600

and kept for 5 hr in air, and furnace-cooled. The concentrations of Al_2O_3 were 2 mol% (Z-1) and 10 mol% (Z-2). Lithia was evaporated in vacuum on the surfaces of some Z-1 (Z-3), and other Z-1 were soaked in $LiNO_3$ aqueous solution and dried (Z-4). Z-3 and Z-4 were heated at 400°, 500°, and 600°C; heating time was 7 hr for Z-3 and 5 hr for Z-4. A symbol "Z-3·400" represents the specimen Z-3 heated at 400°C, after this.

Fracture surfaces of the specimens were observed with a scanning electron microscope (Fig. 1). Sintering of ZnO ceramics was suppressed by doping Al_2O_3 (b). Grain growth after doping Li_2O could hardly be observed (c), except for Z-4·600 (d). For Z-3·400, Z-3·500, and Z-4·400 unreacted lithium salt on the surface was detected.

Electrical resistivities of the specimens were measured on cooling from ∿500°C in air with an AC-LCR bridge at a frequency of 10 kHz. Indium metal was used for ohmic electrodes.[14)] Resistivity-temperature characteristics are shown in Fig. 2. The resistivities for Z-3 and Z-4 were higher than that for Z-1 and the resistivity increased with the temperature of heat treatment, which suggests that the dissolving of Li_2O into ZnO proceeded more easily at higher temperature. It is assumed that the differences in resistivities between Z-3 and Z-4 are attributed to the difference of Li_2O concentration, and that the decrease of resistivity for Z-4·600 is caused by the change of microstructure.[14)]

Gas sensing characteristics were measured at 300°C for Z-1, Z-2, Z-3·600, and Z-4·500. The amount of doped Li_2O was controlled not to be excess in order to be used as a gas sensor. Resistivities were measured by DC four-probe method in pure air (ρ_o) and in air containing reducing gas of ∿800 ppm (ρ_g). The ratio ρ_o/ρ_g was defined as a gas sensitivity and plotted against ρ_o in fig. 3. The reducing gases examined were carbon monoxide (CO), propane (C_3H_8), and normal butane ($n\text{-}C_4H_{10}$). Z-3 and Z-4 were found sensitive, especially to $n\text{-}C_4H_{10}$. It is assumed that the decrease of N_d by doping Li_2O brought about the increase of the width and the height of potential barriers, according to the equation (1), with no or rare grain grouth.

These results would indicate the effectiveness of the stepwise doping method, adopted in the present work, in

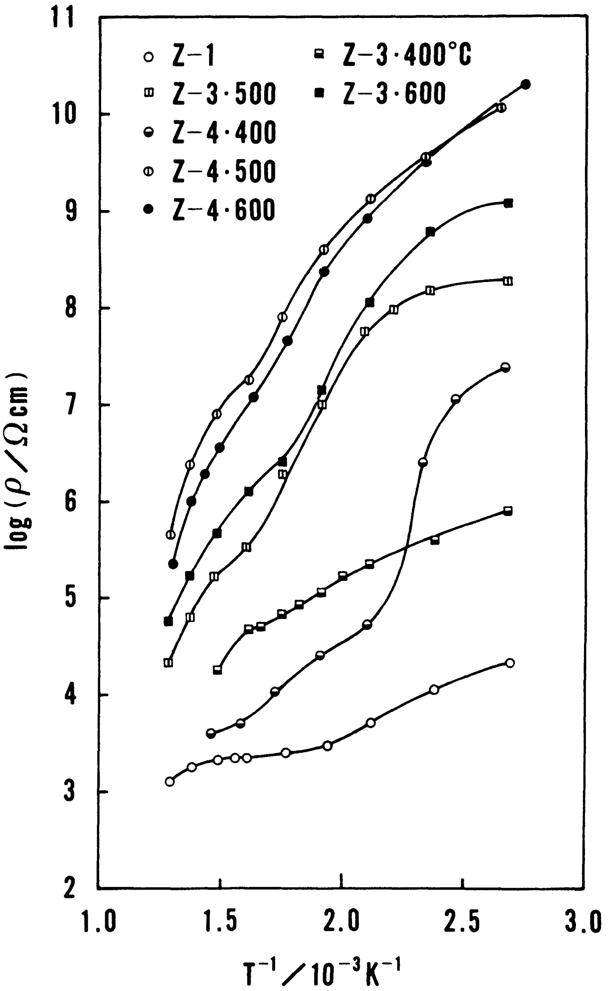

Fig. 2. Resistivity-temperature characteristics of $ZnO\text{-}Al_2O_3\cdot 2mol\%$ doped with Li_2O.

controlling the microstructure and the resistivity of ZnO ceramic to be used as a gas sensor.

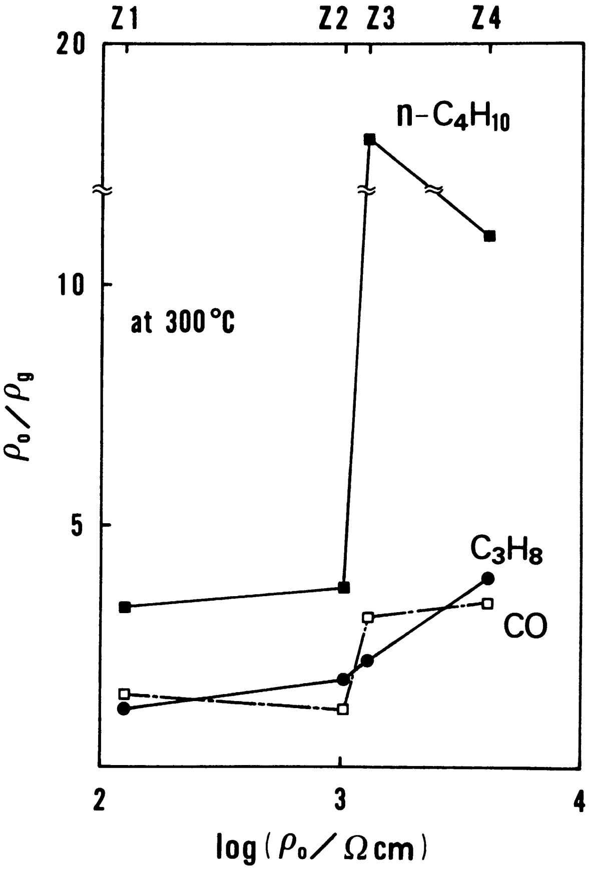

Fig. 3. Dependence of sensitivities of ZnO gas sensors on resistivities in air.

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