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NO_2 Sensitive Ga-doped ZnO Thin Film

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The resistivity of a Ga-doped ZnO film in a NO_2 atmosphere remarkably increases with decreasing the thickness of the film while that in air remains unchanged. A Ga-doped ZnO film with 75 nm in thickness shows high sensitivity and rapid response to NO_2 at 400 °C.

The NOx concentration in air has been usually measured by equipments utilizing chemical luminescence and infrared absorption. These apparatuses, however, are not only expensive, but also inapplicable to determination of the NOx concentration. In contrast, gas sensors using ceramics surpass them in some of gas-sensing properties (gas sensitivity, response time, and long-term stability), in maintenance and in commercial price. Ceramic gas sensors for detecting NOx have been developed using metal oxides such as SnO_2,[1)] ZnO,[2)] TiO_2,[3)] and WO_3.[4)] In particular, a ZnO film with 100 nm in thickness exhibits fairly high sensitivity to NOx.[2)] Nevertheless, the relationship between the film thickness and the gas sensitivity is not clarified. Moreover, higher electric resistance of the ZnO film is unsuitable for a practical application.

In the present work, we fabricated Ga-doped ZnO films with various thickness, and then investigated the relationship between the film thickness and the resistivity of a Ga-doped ZnO film in air and NO_2 atmospheres.

ZnO thin films were fabricated by rf magnetron sputtering method in an Ar atmosphere. A powder of Ga-doped ZnO was calcined at 1000 °C in air and then used as a sputtering target. A Ga-doped ZnO thin film was deposited on a quartz substrate on which comb-like Pt electrodes were deposited, followed by annealing at 500 °C in dry air for 3 h. The sputtering conditions are listed in Table 1. The thickness of a sputtered film was controlled by changing a sputtering period. The thickness was estimated from the interference effect in absorption spectra and from the measurements using a surface-roughness meter. The crystal structure of these films was

Table 1. Sputtering conditions for preparation of Ga-doped ZnO film

Target	2at% Ga-doped ZnO powder
Vacuum (Pa)	0.67
Atmosphere	$Ar:O_2$ = 1:0
R.F. power (W)	70
Substrate temperature (°C)	200
Deposition rate (nm/h)	500

analyzed by X-ray diffraction measurement. Then, the sensor element was set in a measurement chamber in which either dry air or 44.8 ppm NO_2 diluted with dry air was introduced at a flow rate of 100 cm^3/min.

Figure 1 shows temperature dependence of the resistivity of the Ga-doped ZnO film with 75 nm in thickness in air. The resistivity-temperature profile was measured in air flow (100 cm^3/min) at a heating rate of ca. 10 °C/min. The resistivity of the Ga-doped ZnO film at 300 °C is much lower than that of an undoped ZnO film reported by Chang.[2] Obviously, the resistivity of the ZnO film in air at 300 °C is sufficiently lowered by doping Ga atoms in ZnO. The resistivity of the film primarily decreases with elevating temperature up to 300 °C because of the thermal excitation of carriers. The value of the resistivity is about 0.67 ohm-cm even at 400 °C, although the resistivity gradually increases due to O_2 chemisorption.[5]

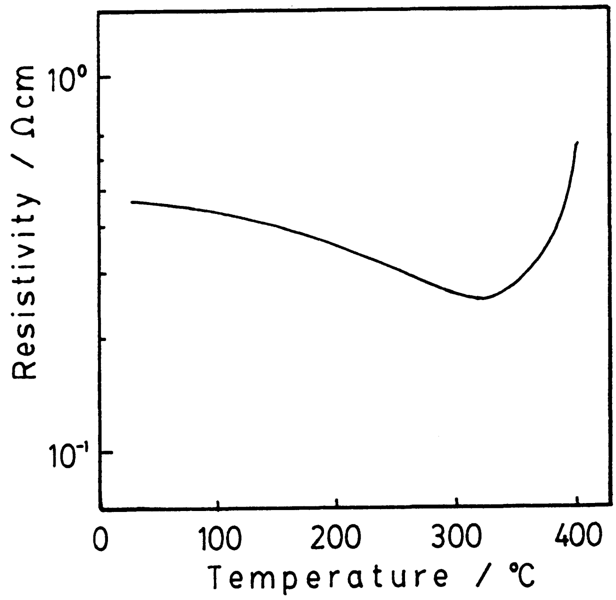

Fig. 1. Temperature dependence of the resistivity of a Ga-doped ZnO film in air.

Figure 2 shows the resistivity of the Ga-doped ZnO film as a function of the film thickness. In general, the resistivity is independent of the film thickness if the surface resistivity is negligible. The resistivity of a film in NO_2, Rg, remarkably increases at the film thickness less than 100 nm, compared with the resistivity of a film in air, Ra. This shows that thinner Ga-doped ZnO film has higher gas sensitivity to NO_2 and that the control of the film thickness is useful to develop a gas sensor showing higher sensitivity to NO_2. The remarkable change in Rg can be explained as follows: NO_2 is adsorbed on the n-type semiconductor surface by capturing electrons of the semiconductor and subsequently the depletion layer is formed near the semiconductor surface. As for the NO adsorption, it was confirmed that NO formed deeper adsorption states than O_2.[1)] As the adsorption behavior of NO is similar to that of NO_2,[6)] deeper NO_2 adsorption states are expected to be located in the forbidden gap of the ZnO surface. Thus, the band bending across the depletion layer of Ga-doped ZnO kept in NO_2 is larger than that of O_2. Accordingly, the resistivity of the ZnO remarkably increases by the adsorption of NO_2.

Figure 3 shows a variation of the conductivity of the Ga-doped ZnO film heated at 400 °C in air or NO_2 atmosphere. The conductivity of the film decreases with 90% response time of about 12 s when an atmosphere is changed from dry air to NO_2. Although a recovery time of the conductivity after changing from NO_2 to air is not so short as the

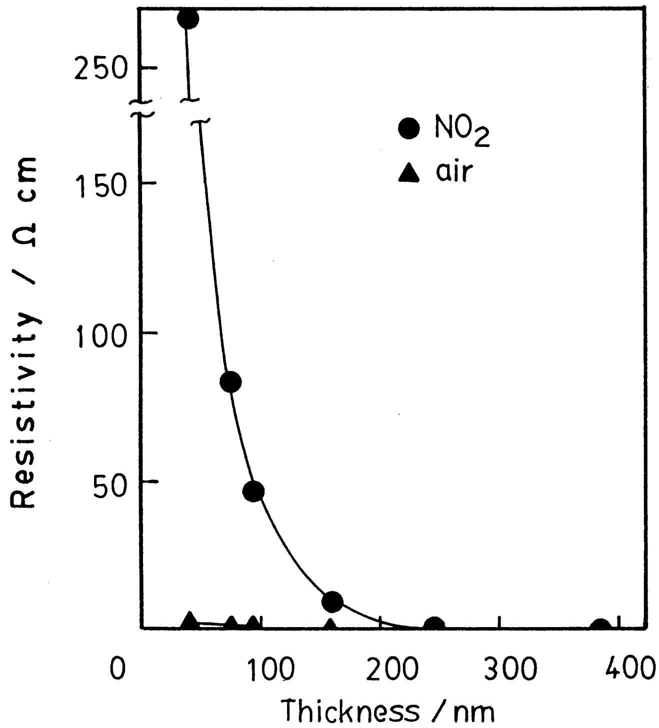

Fig. 2. Influence of the film thickness on the resistivity in air and NO_2 at 400 °C.

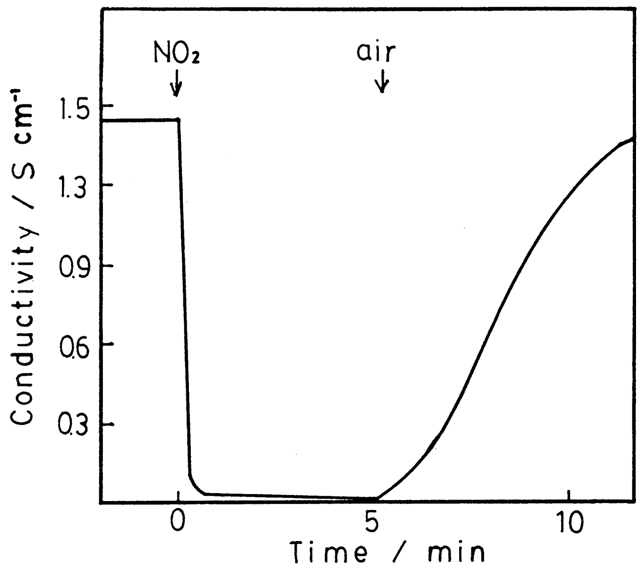

Fig. 3. Conductivity change of a film caused by ambient gas change.
Film thickness : 75 nm ; operating temperature : 400 °C.

response time, the conductivity completely returns to the original level within 15-20 min. The NO_2-gas sensitivity, defined as Rg/Ra, of 110 is obtained at 400 °C. This value appears to be the highest NO_2 sensitivity among those reported so far.[4,7]

Figure 4 depicts the gas sensitivity of the Ga-doped ZnO film with 75 nm in thickness as a function of temperature. No distinct gas sensitivity is found at a temperature lower than 250 °C, and the highest sensitivity is attained at 400 °C. These results indicate that the Ga-doped ZnO thin film heated at 400 °C is an excellent NO_2 sensor with higher sensitivity and faster response.

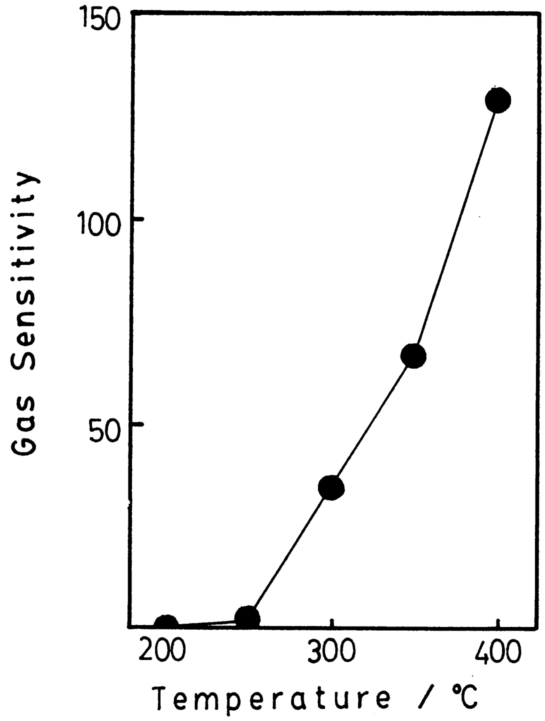

Fig. 4. Temperature dependence of the gas sensitivity of a Ga-doped ZnO film.

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