Exploration of semiconductor gas sensor for ethylene oxide

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Ethylene oxide (C_2H_4O) is an important industrial chemical to derive glycols, glycol ethers and ethanolamines. On the other hand, the same gas is also known as an excellent disinfectant, which is penetrative and effective at room temperature, and has been used popularly for disinfection of heat-sensitive materials and equipments in hospital and food industry. As recently recognized, ethylene oxide is hazardous to human beings, causing reproductive disorder, genetic disorder, cancer, and so on[1,2], and its safety standard at working places has been to be regulated 1ppm in Japan and US. Thus a compact inexpensive gas sensor, which can detect ethylene oxide in air at low concentration levels covering the standard, is in great demand. This situation prompted us to explore the possibility to develop such an ethylene oxide gas sensor based on semiconducting oxides. This paper aims at reporting the results of the exploration.

The sensor devices were fabricated in a sintered block type or thin film type, and calcined at 600°C for 3h. Gas sensing properties were measured in a conventional gas flow apparatus in the temperature range of 250 - 500°C. The sample gases of ethylene oxide in air balance were prepared by diluting a parent gas of ethylene oxide (105 ppm in N_2 balance) with O_2 and N_2. The gas flow (fixed rate: 100 ml/min) over the sensor devices was switched between the sample gases and synthetic dry air while the electric resistance of each device was continuously recorded. Sensor response was defined as the ratio of the resistance in air (Ra) to that in sample gas (Rg).

Since there was no relevant information available, the exploration was started with a screening test of metal oxides as a base sensing material for C_2H_4O. This test was carried out by fabricating a sintered block type device with each oxide selected. It was found that fairly high sensor response to C_2H_4O could be achieved with several oxides as listed in Table 1. Judging from the magnitude of sensor response, however, SnO_2 and In_2O_3 appeared to be the most promising among the oxides tested. When the two oxides are compared, SnO_2 is superior over In_2O_3 in chemicall stability and thermal stability. Thus we picked up SnO_2 for further studies. The ethylene oxide sensor is requested to be capable of detecting 0.1ppm ethylene oxide in air. The sensitivity in Table 1 is very far from this goal. Generally speaking, the sensitivity is known to be dependent on several morphological factors. A thin film device using SnO_2 was thus fabricated from a colloidal dispersion of SnO_2 by a spin coating method. As a result, the thin film device was found to show higher sensor response to C_2H_4O, as shown Fig. 1. The device has capability to detect C_2H_4O at a few ppm levels with fairly fast response transients. However, even this device still cannot meet the required lower detection limit of C_2H_4O. Further improvements in sensor response by means of sensitizers and/or acid-base modifiers are under investigation.

References

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Table 1 Sensor response of various oxides to 30 ppm C_2H_4O. (sintered block type device)

Oxide	Sensor response (Ra/Rg)	Temperature / °C
In_2O_3	40	350
SnO_2	37	300
WO_3	10	450
ZnO	24	450
TiO_2	12	450

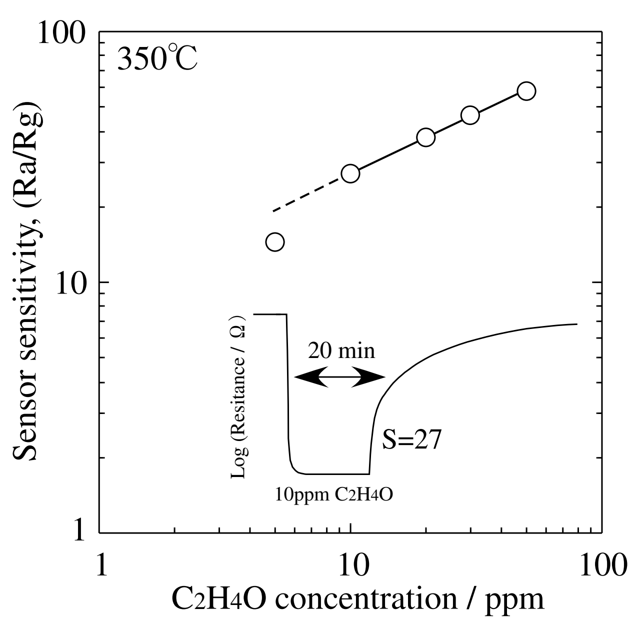

Fig. 1 Sensor responses to various concentrations of C_2H_4O and typical response transients. (SnO_2 thin film device, 350°C)