Sensitization of SnO_2-based thick film sensor for ethylene oxide gas

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Ethylene oxide (EO, C_2H_4O) is an important industrial chemical. Besides the same gas is an excellent disinfectant used popularly in hospital and food industry for disinfection of heat-sensitive materials and equipments. As recently recognized, the gas is hazardous to human beings [1,2], and its safety standard at working places has been regulated to be 1ppm in Japan and US. Thus a compact inexpensive EO gas sensor which can cover this standard is in great demand. This situation prompted us to try the possibility to develop such an EO gas sensor based on semiconducting oxides. Although SnO_2 turned out to be one of the most promising oxides for EO sensing, thick film devices using neat SnO_2 remained far from meeting the sensitivity required[3]. It was found further that loading SnO_2 with La_2O_3 was effective in promoting the sensitivity, and that the deterioration of response and recovery rate induced could be restored fairly effectively by additional loading with Pd or Pt. The doubly promoted device thus prepared, Pt(0.5wt.%)-La_2O_3(0.5wt.%)-SnO_2 showed sensor response (R_{air}/R_{gas}) exceeding 10 to 1 ppm EO as well as acceptable rates of response under dry condition at 300°C as shown in Figure 1. Because of the double promotion , however, electrical resistance of the device in air went up almost to reach the upper limit of reliable measurement ($10^8\Omega$) at this temperature(300 ^oC). This suggests it necessary to lower the electrical resistance for further explanation. In this study, we tried to dope SnO_2 with Sb for this purpose.

To prepare Sb-doped SnO_2, a solution mixed of $SnCl_4$ and $SbCl_5$ was added to an aqueous solution of NH_4HCO_3 for hydrolysis. The resulting precipitate, after through washing, was collected by filtration, dried at 120 ^oC, and calcined at 700 ^oC in air. The powder was loaded with additives by an impregnation method. To fabricate sensor devices, the powders were screenprinted on an alumina substrate attached with gold electrodes 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.

Figure 2 shows the electrical resistances of the devices using neat and Sb-doped SnO_2 in air (Ra) and in 20 ppm EO containing air (Rg) as a function of operating temperature. The Sb doping resulted in drastic decreases in resistances, as seen from the comparision among the promoter-unloaded devices. In view of sensor devices, an optimum amount of Sb doping appears to be about 0.05at.%. As stated before, the resistances increased on loading these base oxides with La_2O_3(0.5wt.%). However, the resistance of the La_2O_3-loaded device using Sb(0.05at.%) doped SnO_2 is seen to be about $10^6\Omega$ yet at 250°C, although the resistance after further loading with Pt is to be measured.

Figure 3 shows sensor response to various concentrations of EO for the La_2O_3-loaded devices using neat and Sb(0.05at.%)-doped SnO_2 at 250°C. The both devices could respond to 1-15ppm C_2H_4O fairly well. This confirms that the sensor response is not affected so much by the Sb doping. Further studies on Pt-La_2O_3-doubly loaded devices using Sb-doped SnO_2 are in progress.

References

[1] J. Angerer, M. Bader and A. Kramer, *Int Arch Occup Environ Health*, **71**, 14-18 (1998)

[2] J. S. Evans, L. R. Rhomberg, P. L. Williams, A. M. Wilson and S. J. S. Baird, *Risk Analysis*, **21**, 697-717(2001)

[3] M. Kugishima, G. Sakai, K. Shimanoe and N. Yamazoe, *Proc. of the 36th Chemical Sensor Symposium*, **19**, 239-141 (2003)

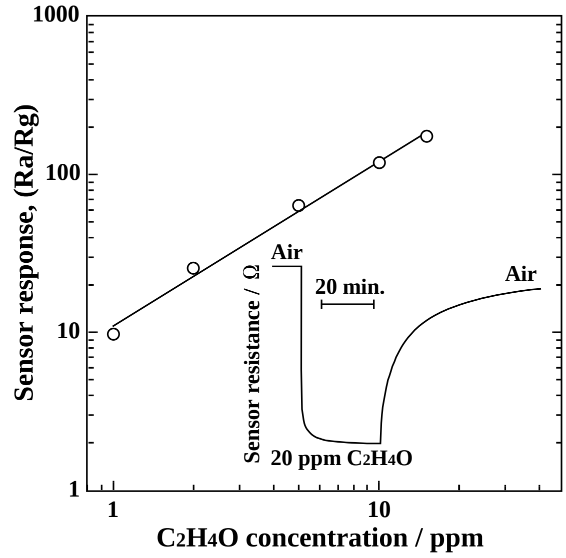

Fig.1 Sensor response to various concentrations of C_2H_4O and typical response transient for Pt(0.5wt.%)-La_2O_3(0.5wt.%)-doubly loaded-SnO_2 device at 300°C.

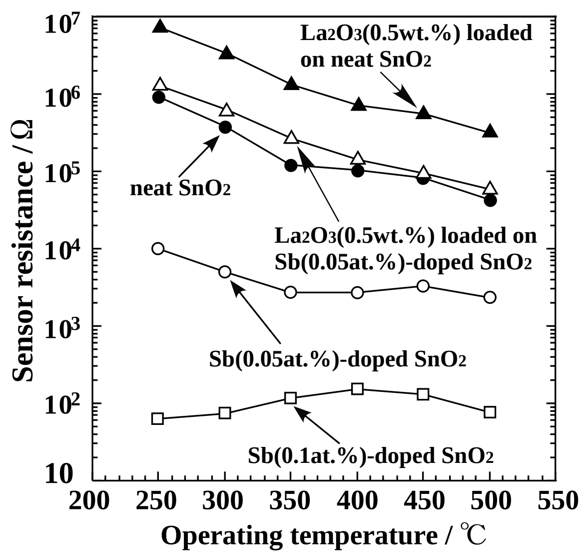

Fig.2 Electrical resistances vs. operating temperature for La_2O_3-loaded or unloaded devices using neat or Sb-doped SnO_2.

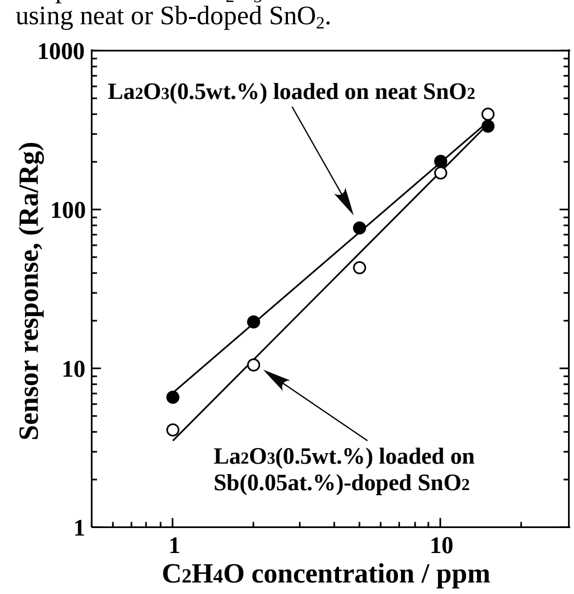

Fig.3 Sensor response to various concentrations of C_2H_4O for La_2O_3(0.5wt.%)-loaded devices using neat and Sb-doped SnO_2 at 250°C.