Detection of Dilute Chlorine Gas Using Indium Oxide Thin Film Sensors

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The detection or monitoring of Cl_2 gas in exhaust is needed in relation to air pollution due to Cl-containing compounds. There have been a few papers on the detection of Cl_2 using semiconductor type sensors [1-3]. However, these sensors could detect Cl_2 gas of only sub-ppm level. In this paper, In_2O_3 thin film sensors were prepared by means of an electron beam evaporation as well as a suspension dropping. The In_2O_3 thin film prepared by dropping method showed extremely high sensitivity to dilute Cl_2 gas less than ppm-level.

The substrate used here was a Si substrate equipped with Au comb-type electrodes patterned by micromachining. In evaporation, In_2O_3 thin film was deposited on the substrate by EB evaporation, then the film was calcined at 500 °C for 3 h in air. On the other hand, the suspension was prepared by mixing In_2O_3 powder calcined at 850 °C with deionized water in dropping method. A given amount of suspension was dropped on the substrate. After dryness, the film was calcined at 500 °C for 3 h in air. The resistance of In_2O_3 thin film sensor was measured in air (R_a) and Cl_2 containing air (R_g) at 200-500 °C. The sensitivity was defined as R_g/R_a.

Figure 1 depicts the sensitivities to 5 ppm Cl_2 of In_2O_3 thin film sensors as a function of operating temperature. For both sensors, the sensitivity had a maximum at 250 °C. At this temperature, the In_2O_3 thin film sensor prepared by the dropping method showed extremely high sensitivity to 5 ppm Cl_2, which was higher in two orders than the sensitivity of evaporated In_2O_3 sensor. Further, the response characteristics also improved for the In_2O_3 sensor prepared by dropping method. As shown in Fig. 2, the over-shooting behavior was observed for the evaporated sensor, while it almost disappeared for the sensor prepared by dropping method. It is considered that the resistance increase results from the negative adsorption of Cl_2 to form Cl_{ad}^-, and that the resistance decrease after over-shooting is due to the substitution of Cl^- for lattice oxygen. For the In_2O_3 sensor prepared by dropping method, the lattice oxygen is stabilized because In_2O_3 powder is calcined at high temperature, the substitution being suppressed. Figure 3 shows the correlation between the sensitivity and Cl_2 concentration for the In_2O_3 sensor prepared by dropping method. The sensitivity was as high as 2500 to 5 ppm Cl_2, and decreased with decreasing Cl_2 concentration. The sensor exhibited the sensitivity of ca. 7 to 0.02 ppm Cl_2. However, the sensitivity was less than unity to 0.01 ppm Cl_2, indicating the response in opposite direction. This suggests the lower detection limit of 0.02 ppm for the In_2O_3 sensor prepared by dropping method.

References
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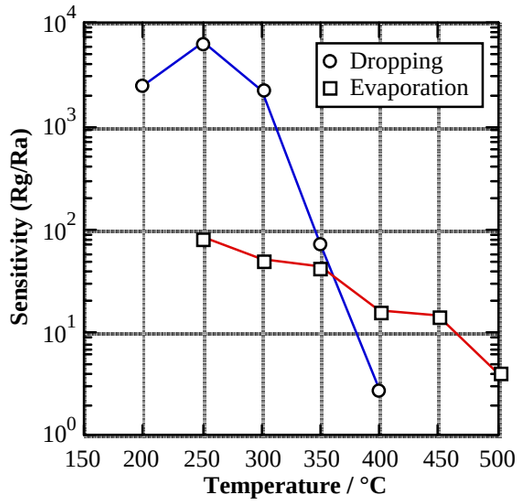

Fig. 1 Sensitivities to 5 ppm Cl_2 of In_2O_3 thin film sensors prepared by evaporation and suspension dropping as a function of operating temperature.

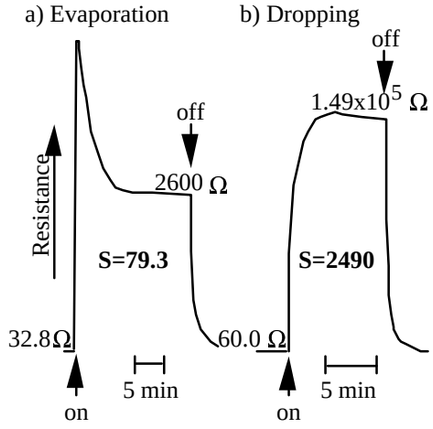

Fig. 2 Response transients to 5 ppm Cl_2 of In_2O_3 thin film sensors at 250 °C.

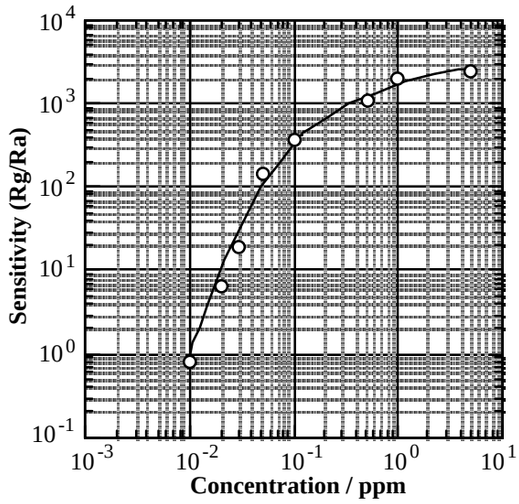

Fig. 3 Sensitivities of In_2O_3 thin film sensors prepared by suspension dropping as a function of Cl_2 concentration.