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Ethanol Gas Sensing Properties of $Pd-La_2O_3-In_2O_3$ Thick Film Element

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The doubly doped In_2O_3 thick film element, $Pd-La_2O_3-In_2O_3$, was found to show excellent ethanol gas sensing properties in sensitivity, selectivity and response rate, in addition to having an electric resistance low enough to be compatible with a conventional circuitry. Such properties resulted from the modifications of In_2O_3-based element with the dopants and the thick film structure applied.

Gas sensors using semiconductive oxides such as SnO_2 detect an objective gas in air from a change in electric resistance caused by the adsorption and/or reaction of the gas. There have been many reports showing that the gas sensing properties of a semiconductor sensor are greatly affected by the addition of a noble metal[1-3] or a metal oxide[4,5] to the sensor element, and the treatment[6] or coating[7] of the element surface with foreign materials. Such surface modification techniques can be useful for developing a sensor which has high sensitivity and/or selectivity to a particular gas.

In fact, these techniques were utilized in our recent attempt to develop a highly sensitive alcohol sensor to be applicable for a breath alcohol checker.[8,9] It was found that the addition of a basic metal oxide, typically La_2O_3, to an SnO_2-based sensor element markedly improved the sensitivity to ethanol gas at 300 °C, while the addition of Pd was especially effective to increase the rate of response. Thus the doubly doped element $Pd-La_2O_3-SnO_2$ showed good alcohol sensing properties with respect to sensitivity and response rate. However, the addition of La_2O_3 and Pd also caused the electric resistance of the element to increase to ca. 10^9 Ω in air which is beyond a practical level acceptable in a conventional circuitry. To get out of this difficulty, we examined the use of In_2O_3 in place of SnO_2 in this paper because In_2O_3 has much smaller electric resistivity than SnO_2. The fabricated thick film element $Pd-La_2O_3-In_2O_3$ was found to be acceptable in electric resistance as well as excellent in alcohol sensitivity and selectivity as described below.

In_2O_3 was prepared from $InCl_3$. Five g of $InCl_3$ was dissolved in 100 ml of 0.5 M HCl and then neutralized with an aqueous solution of ammonia (28%). The precipitate obtained, $In(OH)_3$, was washed thoroughly with deionized water. After drying, it was calcined at 850 °C for 5 h in air. La_2O_3 and Pd were loaded by 5 and 0.5 wt%, respectively, by impregnating the In_2O_3 powder with an aqueous solution of $La(CH_3COO)_3$ and a sulfuric acid solution of $PdCl_2$ in turn, followed by evaporation to dryness and calcination at 850 °C for 5 h in air. The Pd-loaded sample was reduced under H_2 flow (30% in air) at 300 °C for 4 h before the calcination. To prepare a thick film sensor element shown in Fig. 1, the powder sample was mixed with an aqueous solution of polyvinyl alcohol and the resulting paste was screen-printed on an porous alumina substrate attached with comb type Au electrodes (electrode separation: 0.3 mm), followed by calcination at 700 °C for 4 h in air. The film was about 50 μm thick after calcination as observed with SEM. The gas sensing properties were evaluated by measuring changes in electric resistance (R) of the element when the surrounding atmosphere was switched between an air flow and a sample gas flow. The gas sensitivity S was defined by $S = R_{air}/R_s$ where R_{air} and R_s are the R values of element in air and the sample gas, respectively.

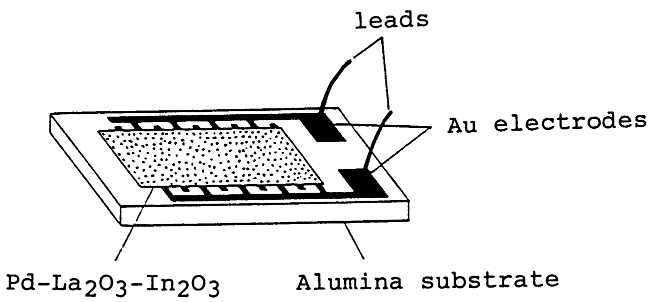

Fig. 1. $Pd-La_2O_3-In_2O_3$ thick film element with comb type Au electrodes.

Figure 2 shows the response curve of $Pd-La_2O_3-In_2O_3$ thick film element to 1000 ppm ethanol gas in air at 300 °C. The resistance of the element decreased sharply on exposure to the ethanol gas with the 90% response time of about 35 seconds, and returned back to the original level rather quickly when the air flow was resumed. The sensitivity to 1000 ppm ethanol gas was as high as S=1429 at 300 °C, which appears to be the highest value reported so far. Moreover, R_{air} of this element was at the order of 10^6 Ω, being sufficiently low to be compatible with a conventional circuitry.

These characteristic data of the present thick film sensor based on $Pd-La_2O_3-In_2O_3$ are compared with those of the previous sintered element based on $Pd-La_2O_3-SnO_2$ in Table 1.

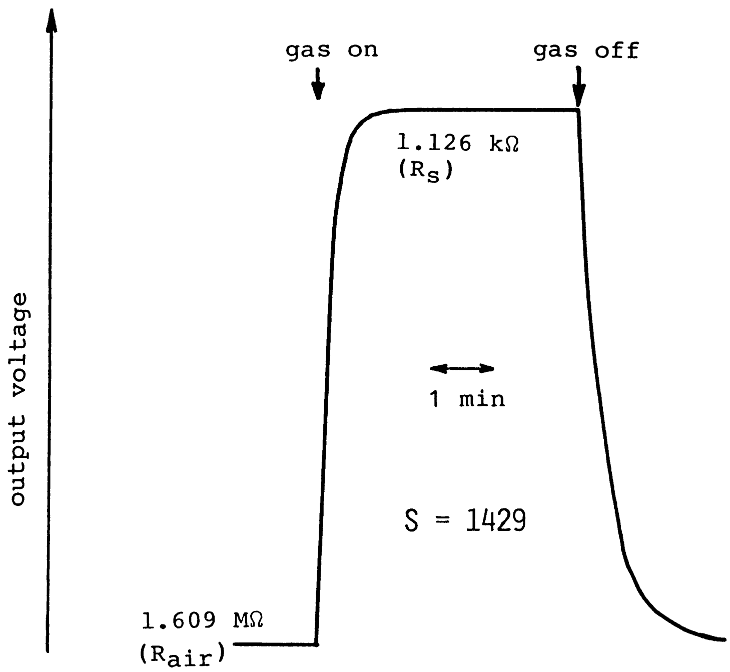

Fig. 2. Response transient of $Pd-La_2O_3-In_2O_3$ thick film element to 1000 ppm C_2H_5OH in air (300 °C).

Table 1. Ethanol gas sensing properties of In_2O_3 and SnO_2 based elements (300 °C)

Sensor[a)] material	Type[b)]	Electric resistance / Ω In air	Electric resistance / Ω In C_2H_5OH[c)]	Sensitivity	90% response time / min
In_2O_3	SB	6.5×10^2	2.3×10^1	28	0.3
La_2O_3-In_2O_3	SB	4.9×10^5	1.5×10^3	335	3.1
La_2O_3-In_2O_3	TF	2.6×10^4	1.4×10^2	186	1.7
Pd-La_2O_3-In_2O_3	TF	1.6×10^6	1.1×10^3	1429	0.6
Pd-La_2O_3-SnO_2	SB	9.2×10^8	7.6×10^5	1210	3.1

a) Loading of the dopants: La_2O_3 5 wt%, Pd 0.5 wt%.
b) SB: sintered block type with distance between electrodes of 3 mm, TF: thick film type with distance between electrodes of 0.3 mm.
c) 1000 ppm C_2H_5OH diluted with air.

It is obvious that the present sensor is superior over the previous one in all respects of sensitivity, response rate and compatibility to the circuitry. It is considered that the improvement of the compatibility, which was the main aim of this study, was achieved with the replacement of SnO_2 with In_2O_3, while the improvements in other respects, especially the response rate, were contributed by the difference in element structure. Table 1 also shows how the ethanol sensing properties of In_2O_3 based elements were modified with the addition of La_2O_3 and Pd, and the change in element structure. A thick film element using pure In_2O_3 showed too low resistance in air so that a conventional sintered block elements[7)] having two Pt coil electrodes 3 mm apart were fabricated by using pure In_2O_3 and La_2O_3-doped In_2O_3. As expected by analogy with the previous case of SnO_2 based elements, it was found that the sensitivity to 1000 ppm ethanol gas was improved from 28 to 335 by the addition of La_2O_3 although the response time also increased. The change in element structure from the sintered block type to the thick film type almost halved the response time because the latter allowed easier access of ethanol gas to the gas sensitive part of the element. Further addition of Pd to the thick film element not only shortened the response time from 1.7 to 0.6 minutes, but also increased the sensitivity drastically.

Figure 3 shows the ethanol gas sensitivity as a function of ethanol gas concentration in air at 300 °C. Data were collected with another Pd-La_2O_3-In_2O_3 element. For the wide concentration range 0 - 1000 ppm, the sensitivity was not a simple function of ethanol gas concentration, resulting in a S-shaped correlation as shown. Although the reason for this somewhat unusual correlation is not clear at present, this may suggest that there is room for further optimization of the sensor element in composition and structure. Nevertheless it is quite notable that the sensitivity is still very high even at ethanol concentrations below 400 ppm. A breath alcohol checker is said to be designed to give warning for a drunk driver when the ethanol concentration of his breath exceeds 70 ppm. The sensitivity of present sensor at 70 ppm ethanol gas was as high as ca. 70, being sensitive enough to be a breath alcohol checker.

Selectivity is also important for a gas sensor. Table 2 lists the sensitivity of Pd-La_2O_3-In_2O_3 thick film element to various gases at 300 °C. It is seen that only ethanol gas sensitivity is exceptionally high while the sensitivity to CO, H_2, CH_4, or i-C_4H_{10} remains to be modest. It is thus concluded that the modification of In_2O_3-based element with La_2O_3 and Pd is particularly effective to improve the sensitivity and therefore also the selectivity to ethanol gas.

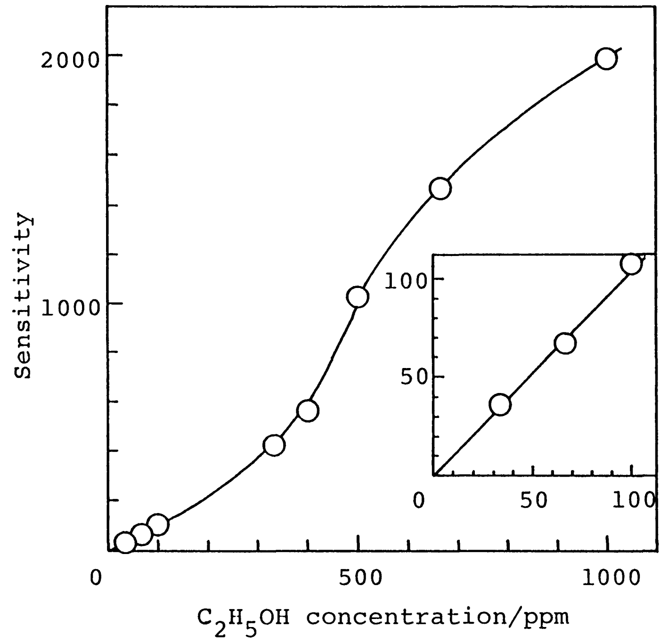

Fig. 3. Relationship between sensitivity and ethanol concentration for Pd-La_2O_3-In_2O_3 thick film element (300 °C).

In conclusion, Pd-La_2O_3-In_2O_3 thick film element developed in this study shows excellent ethanol gas sensing properties at 300 °C with respect to sensitivity, selectivity and response rate as well as a sufficiently low electric resistance in air. With these features, the element seems to be promising for practical applications as an alcohol sensor.

Table 2. The sensitivity of Pd-La_2O_3-In_2O_3 thick film element to various gases (300 °C, 1000 ppm in air)

Gas	C_2H_5OH	CO	H_2	CH_4	i-C_4H_{10}
Sensitivity	1994	34	32	6	22

References

1) N. Yamazoe, Y. Kurokawa, and T. Seiyama, Sens. Actuators, 4, 283(1983).
2) Y. Shimizu, T. Takao, and M. Egashira, J. Electrochem. Soc., 135, 2539(1988).
3) S. Matsushima, Y. Teraoka, N. Miura, and N. Yamazoe, Jpn. J. Appl. Phys., 27, 1798(1988).
4) K. Fukui and K. Komatsu, Proc. Symp. Chem. Sensors, 1987, 187.
5) T. Nakahara, K. Takahata, and S. Matsuura, Proc. Symp. Chem. Sensors, 1987, 55.
6) Y. Okayama, T. Nomura, H. Yajima, and T. Ishii, Denki Kagaku, 54, 777 (1986).
7) N. Yamazoe, Y. Muto, and T. Seiyama, Hyoumen Kagaku, 5, 55 (1984).
8) S. Matsushima, T. Maekawa, J. Tamaki, N. Miura, and N. Yamazoe, Chem. Lett., 1989, 845.
9) J. Tamaki, S. Matsushima, T. Maekawa, N. Miura, and N. Yamazoe, Proc. 40th ISE Meeting, 1989, 566.

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