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A Remarkable Sensitivity of CaO-loaded In_2O_3 Element to CO_2 Gas in the Presence of Water Vapor

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The In_2O_3 element modified by 5.5 wt% CaO showed the sensitivities (the ratio of resistance of the element in air containing no CO_2 to that in a diluent CO_2 gas) to 2080 ppm CO_2 as high as 12.9, 9.9, and 6.6 in the presence of 0, 1.1, and 1.8 vol% water vapor, respectively.

The demand of the simple detection of ppm-level CO_2 gas has grown up for the controlling of the industrial processes and environmental technologies.[1-10] To date, solid electrolyte,[1-3] mixed oxide capacitor,[4] K_2CO_3-polyethylene glycol solution supported on porous ceramics,[6] hydroxyapatite,[7] and SnO_2-based semiconductor[8-10] have been reported as CO_2 sensing materials. However, several problems remain to be solved; the sensitivity of these sensors to the ppm-level CO_2 gas is still low and the presence of water vapor greatly decreased the sensitivity.[10] Here we wish to report a pronounced sensitivity of CaO-loaded In_2O_3 element to 2080-ppm CO_2 gas both in the absence and in the presence of water vapor.

In_2O_3 was prepared by the hydrolysis of $InCl_3 \cdot 4H_2O$ with aqueous ammonia followed by the calcination at 1123 K for 5 h in air. The formation of cubic In_2O_3 was confirmed by XRD. The sensor element was prepared by the impregnation of In_2O_3 element with aqueous solution of metal nitrate or acetate by coating with a brush as described previously.[9] Sample gas containing 2080 ppm CO_2 in dry air balance was used. Prior to each resistance measurement, each element was exposed to dry air (60 $cm^3 \cdot min^{-1}$) at 773 K for 1 h. The resistance was measured at 573 K. The sensitivity to CO_2 was defined as the ratio of resistance of an element in air containing no CO_2 to that in a sample gas, R_{air}/R_{CO_2}. Transient response usually became the same after the second turning-on and -off cycle.

Figure 1a shows the response transient of the pure In_2O_3 at 573 K. The sensitivity and 90% response time was 7.8 and 64 min, respectively. The sensitivities of In_2O_3 elements were changed by the loading of the metal oxides as summarized in Table 1. The sensitivities of In_2O_3-based elements increased approximately in the following order; rare earth metal oxides < alkali metal oxides ≤ transition metal oxides ≤ alkaline earth metal oxides. The sensitivity of CaO(5.5 wt%)-loaded In_2O_3 element was the greatest. The response transient is shown in Fig. 1b. The sensitivity and 90% response time were 12.9 and 40.0 min, respectively. The sensitivity to ca. 2000-ppm CO_2 was the greatest among those reported so far; for example, 3.0 on Ag/CuO-$BaTiO_3$[4], and 1.8 on La_2O_3-loaded SnO_2.[9]

The effect of the 1.1 vol% water vapor on the sensing characteristics of CaO(5.5 wt%)-loaded In_2O_3 is shown in Fig. 1c. The sensitivity was 9.9 in wet air. The value was further decreased in 1.8 vol% water vapor and was 6.6. However, it is noteworthy that the sensitivity was still high in the presence of water vapor. On the other hand, in 1.1 vol% water vapor the sensitivity of the pure In_2O_3 was more greatly decreased to be about half of that in dry air. In addition, the 90% response time of CaO-loaded In_2O_3 element was greatly shortened from 40.0 to 12.0 min by the presence of water vapor. These facts show that the CaO-loaded In_2O_3 element would have the bright prospect of detecting CO_2 with high sensitivity in the presence of water vapor.

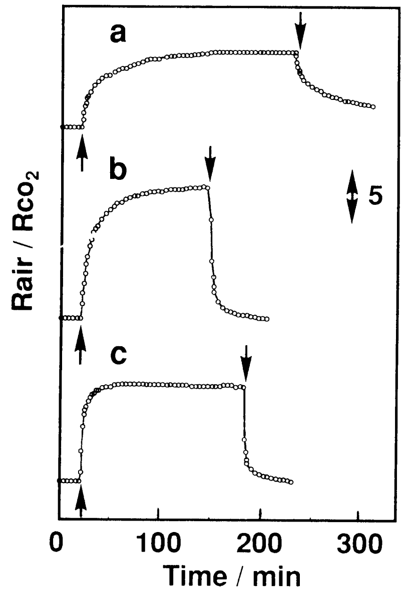

Fig. 1. Response transients (second turning-on and -off cycle) to 2080 ppm CO_2 of In_2O_3 (a) and CaO(5.5 wt%)-In_2O_3 (b, c) elements at 573 K. (a) and (b), in dry air; (c), in wet air (1.1% water). ↑, CO_2 on; ↓, CO_2 off.

Table 1. Sensitivities of metal oxide-loaded In_2O_3 elements to 2080-ppm CO_2 at 573 K

Metal oxide loaded	Sensitivity
None	7.8
Li_2O(6.3)[a]	2.7
Na_2O(1.0)	1.9
K_2O(1.1)	3.9
MgO(1.0)	4.4
CaO(5.5)	12.9
SrO(1.3)	10.2
BaO(1.2)	9.7
V_2O_5(1.1)	3.1
NiO(1.5)	5.0
ZnO(1.2)	2.7
ZrO_2(1.1)	3.8
Pr_2O_3(3.7)	1.1
Nd_2O_3(8.2)	1.3

a)Amount of metal oxide loaded/wt%.

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