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Improvement of Sensing Characteristics of the Capacitive Type CO_2 Sensor, CuO–$BaTiO_3$, by Addition of Metal or Metal Oxide

Tatsumi ISHIHARA, Yuichiro NISHI, Kazuhiro KOMETANI,
Yukako MIZUHARA, and Yusaku TAKITA*
Department of Applied Chemistry, Faculty of Engineering, Oita University,
Dannoharu 700, Oita 870–11

Effects of additives on CO_2 sensing characteristics were studied on CuO–$BaTiO_3$ mixed oxide capacitor. Although the operating temperature shifted slightly to a higher temperature and the response time was prolonged, sensitivity to CO_2 was increased by the addition of ZnO, Bi_2O_3, SrO, and Ag. In particular, CuO–$BaTiO_3$ mixed oxide added with Ag was highly sensitive and selective for CO_2 detection.

Carbon dioxide is one of the most familiar gases, but it is too stable chemically to be detected sensitively by conventional gas sensors. However, control or measurement of CO_2 concentration is demanded critically from various advanced technologies, such as air conditioning, agriculture, biological technology, medical services, and environmental monitoring. Therefore, various methods have been studied for development of a CO_2 sensor with small size and low cost.[1-3] In our previous study, it was found that capacitance of the mixed oxide, CuO–$BaTiO_3$, depended strongly on the CO_2 concentration in air.[4-5] However, the sensitivity of CuO–$BaTiO_3$ is not satisfactorily high for practical applications. On the other hand, additions of some noble metals to semiconductor type gas sensors are sometimes effective for enhancing the sensing characteristics.[6] In the present study, we have investigated the effects of some additives on the sensing characteristics to CO_2 of CuO–$BaTiO_3$ mixed oxide for improving the sensitivity.

Equimolar amounts of commercial CuO (99.9% pure) and $BaTiO_3$ prepared by the calcination at 1473 K were stirred in water for mixing physically. Aqueous solutions of additives, mainly nitric aqueous solutions, were added to this mixture and then the slurry was evaporated to dryness. The amount of additives was 1.0 mol% to CuO–$BaTiO_3$ mixed oxide, unless otherwise noted. Oxidation states of additives were determined with X-ray diffraction analysis. Oxide powders thus obtained were pressed into disks (13 mm diameter and 0.6 mm thickness). After calcination at 773 K for 5 h, Ag paste was applied on both faces of the disks to make an electrode (5 mm in diameter). Before measurement of CO_2 sensing characteristics, the elements were calcined at 773 K for 5 h in air stream. The capacitances of elements were measured with a two probe method at the operating frequency, 50 kHz, by using a LCR meter (Hioki, type 3520) in a flow system. Sample gases were obtained by diluting the commercial CO_2 gas with dry air. Sensitivity to CO_2 was defined as a ratio of the capacitance

Table 1. CO_2 sensing characteristics of $CuO-BaTiO_3$ added with metal or metal oxide

Additives	Operating temperature /K	Capacitance /nF		Sensitivity
		Air	2% CO_2	C_{CO2}/C_{air}
None	729	30.0	86.7	2.89
Au	748	140.3	210.5	1.50
CeO_2	842	0.6	1.5	2.50
Pt	795	29.7	81.7	2.75
MgO	889	0.5	1.5	3.00
NiO	797	4.6	14.4	3.13
Pd	846	4.7	20.9	4.45
Co_3O_4	799	7.9	38.5	4.87
SrO	886	1.3	8.7	6.69
La_2O_3	903	1.7	12.4	7.29
Ag	743	5.7	44.1	7.74
ZnO	855	4.1	33.2	8.10
Fe_2O_3	746	1.1	0.8	0.73
Rh	642	88.0	57.2	0.65
Bi_2O_3	948	100.7	9.1	0.09

of the element in a sample gas to that in air, C_{CO2}/C_{air}

Effects of additives on the sensitivity and the optimum operating temperature are summarized in Table 1. Although the optimum operating temperature for CO_2 detection shifted slightly to a higher temperature and a longer response time was recognized, sensitivity to 2% CO_2 was enhanced by addition of metals or metal oxides except for Au, Fe_2O_3, CeO_2, and Rh. Additions of Ag, ZnO, La_2O_3, SrO, Bi_2O_3, and Co_3O_4 were effective for enhancing the sensitivity to CO_2 of $CuO-BaTiO_3$. In particular, the sensitivity to 2% CO_2 on $CuO-BaTiO_3$ added with Ag, ZnO, SrO, and La_2O_3 was about two times larger than that of $CuO-BaTiO_3$ without additives. On the other hand, capacitance of Bi_2O_3-, Fe_2O_3-, and Rh-added elements decreased upon exposure to CO_2, the sensitivity to 2% CO_2 being highest with Bi_2O_3 addition. The elements added with basic oxides such as ZnO, Bi_2O_3, SrO, and La_2O_3, generally exhibit a high sensitivity to CO_2 but operating temperatures become higher than 873 K. An excessively high temperature for operating is not desirable for a practical application and a long term stability. Considering from the operating temperature and sensitivity to CO_2, silver is the most suitable as an additive to $CuO-BaTiO_3$ mixed oxide. In the following paragraphs, effects of Ag addition on CO_2 sensing characteristics are discussed.

The sensitivity to 2% CO_2 increased with elevating the calcination temperature before measurement and attained a maximum when the element was calcined at 973 K. This elevation in the sensitivity may be attributed to a higher dispersion of Ag due to the improved decomposition of $AgNO_3$ by elevating calcination temperatures. However, a high temperature lowers the surface area of an element due to sintering, resulting in aggregation of Ag. As a result, the maximum sensitivity was obtained when the element was precalcined at 973 K. Sensitivity to 2% CO_2 of Ag- added CuO-

$BaTiO_3$ precalcined at 973 K was shown in Fig. 1 as a function of the operating temperature. The sensitivity to CO_2 increased extremely with elevating operating temperature and attained a maximum at 743 K. The optimum operating temperature of CuO–$BaTiO_3$ without additives is 729 K. Therefore, addition of Ag slightly elevated the operating temperature. On the other hand, the sensitivity to 2% CO_2 at 743 K is 91, which is 30 times higher than that of CuO–$BaTiO_3$ without additives at 729 K.

Figure 2 shows typical sensor responses to 2% of CO_2, CO, CH_4, H_2, and 2.5% H_2O in air at 692 K. Upon exposure to CO_2 the capacitance of Ag-added CuO–$BaTiO_3$ increased, and upon reexposure to air it returned to the original levels as shown in Fig. 2. The 80% response and recovery were attained within 7 min and 4 min, respectively. Since the 80% response and recovery on CuO–$BaTiO_3$ without Ag addition were attained within 25 s and 3 min, respectively, addition of Ag prolonged the response and recover time extremely, albeit a slightly lower operating temperature. A conventional volumetric adsorption measurement suggested that the addition of Ag promotes CO_2 adsorption. Since the capacitance change of CuO–$BaTiO_3$ seems to be caused by the carbonation of CuO in element, it is expected that added Ag catalyzes the carbonation of CuO and that carbonation reaction proceeds to the bulk of CuO on expo-

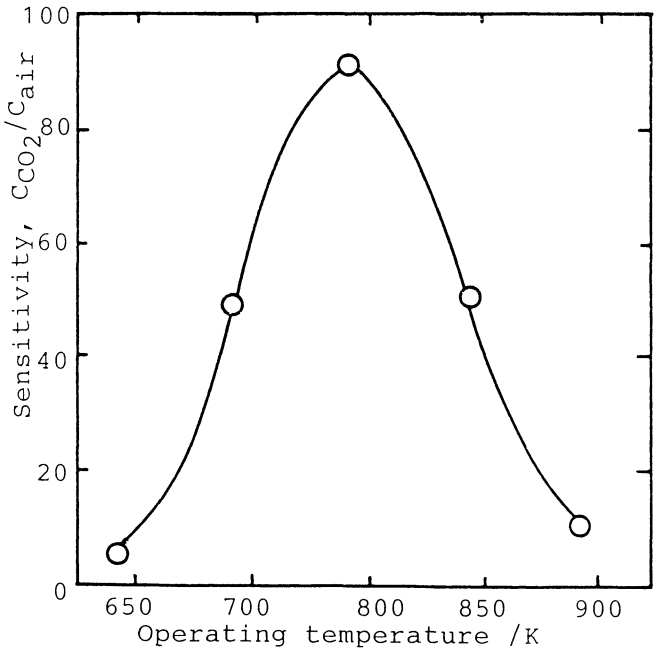

Fig. 1. Temperature dependence of sensitivity to 2 % CO_2 of Ag-added CuO–$BaTiO_3$.
(operating frequency: 50 kHz)

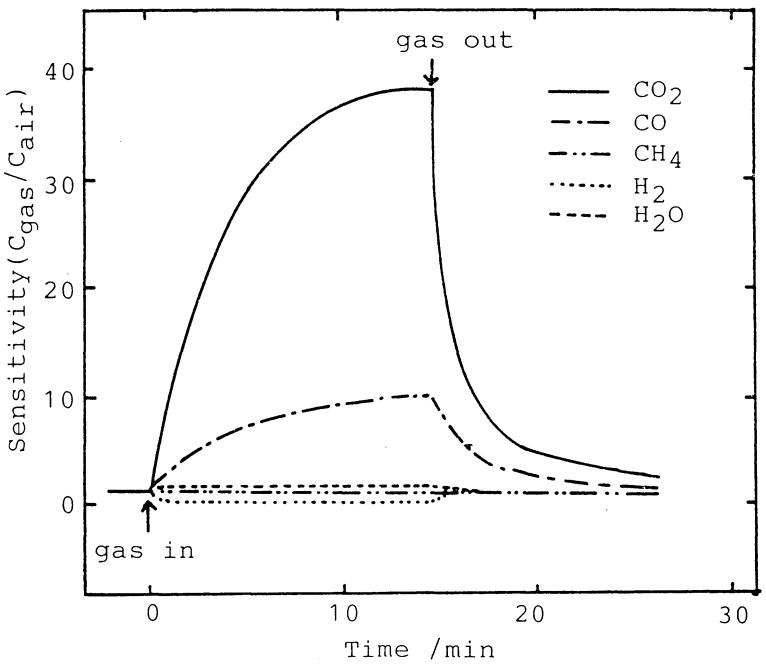

Fig. 2. Responses of Ag-added CuO–$BaTiO_3$ to 2% CO_2, CO, H_2, CH_4, and 2.5% H_2O. (operating temperature: 692 K, operating frequency: 50 kHz)

sure to CO_2. This is because the adsorption amount of CO_2 is far larger than that required for the carbonation of surface first layer of CuO. As a result, addition of Ag enlarged the changes in capacitance upon exposure to CO_2 but prolonged the response time due to the gradual carbonation of the bulk of CuO. The capacitance of the mixed oxide of $CuO-BaTiO_3$ is inherently selective for CO_2 detection. Furthermore, increases in sensitivity with Ag addition can be recognized for only CO_2 and CO. From the effluent gas analysis, capacitance changes on exposure to CO may be brought about not by CO itself but by CO_2 which is formed by the oxidation of CO on the element. In addition, it would be impossible in practical applications that the concentration of CO attained high levels such as in Fig. 2. As a result, $CuO-BaTiO_3$ element added with Ag exhibits an extremely high selectivity for CO_2 detection in spite of a chemical stability of CO_2.

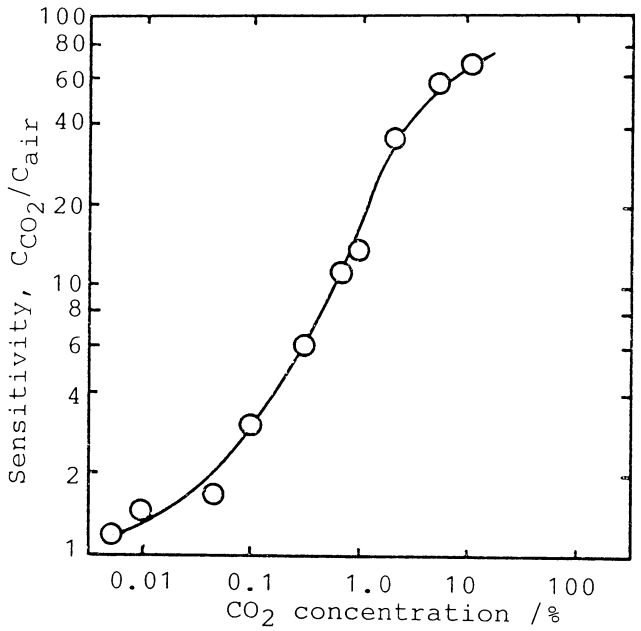

Fig. 3. Sensitivity of Ag-added $CuO-BaTiO_3$ as a function of CO_2 concentration (operating temp 687 K).

Figure 3 shows a plot of the natural logarithm of sensitivity versus that of CO_2 concentration at 687 K. The lower limit of CO_2 detection with $CuO-BaTiO_3$ is 100 ppm. However, it decreases to 50 ppm upon the addition of Ag. Furthermore, capacitance of the element was increased with increasing CO_2 concentrations in the range from 50 ppm to 10% measured. In particular, a linear relationship between capacitance and CO_2 concentration exists in the range of CO_2 concentration from 100 ppm to 1%. Therefore, this element is effective for monitoring CO_2 concentrations in the atmosphere. This study revealed that addition of Ag to $CuO-BaTiO_3$ mixed oxide enables the selective detection of CO_2 without interferences from other gases.

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