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Mixed Oxide Capacitor of $CuO-BaSnO_3$ as a Sensor for CO_2 Detection over a Wide Range of Concentration

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The mixed oxide capacitor, $CuO-BaSnO_3$, exhibits high CO_2 sensitivity. A monotonic and approximately logarithmic relationship exists between the sensitivity and the concentration of CO_2 below 50%. The system, $CuO-BaSnO_3$, is promising for sensing CO_2 over a wide range of concentration.

Control of CO_2 concentration is critical in various advanced technologies. Although most reports concerning CO_2 sensors are based on the solid electrolyte-type,[1,2] this type of sensor requires rather a long time to respond and its EMF is strongly affected by humidity. Yamazoe et al. recently reported that the problem of interference due to humidity could be solved by the application of binary carbonates on the electrode of the concentration cell.[3] However, a new type of CO_2 sensor, one highly sensitive to CO_2 and with a simple structure is sought. In our previous study, it was reported that the change in capacitance of PbO on exposure to CO_2 was negligibly small, whereas it was greatly enhanced by combining with $BaTiO_3$.[4] CO_2 sensing characteristics depend strongly on the type of metal oxides mixed with $BaTiO_3$. In particular, the mixed oxide capacitor of $CuO-BaTiO_3$ was highly sensitive and selective to carbon dioxide.[5] However, detectable concentrations of carbon dioxide were limited to 2% on $CuO-BaTiO_3$. In the present study, we investigated the CO_2 sensing characteristics of mixed oxides combined with CuO.

Mixed oxides consisting of Ti, Sn, Zr, or Nb, which are generally used as dielectrics, were prepared by the calcination of a mixture of calculated amounts of component oxides at 1473 K for 12 h. Commercial CuO without further purification was mixed mechanically with the obtained mixed oxide, and then pressed into disks (13 mm in diameter, and 1 mm thick). After calcination at 773 K for 5 h, Ag paste was applied on both faces of the disk to make an electrode. After connecting the Pt lead wire,

Table 1. CO_2 sensing characteristics on CuO-mixed oxide capacitor

Mixed oxide[a]	Relative permittivity[b]	Operating temperature /K[c]	Sensitivity[d] C_{CO2}/C_{air}	Upper limit of detectable CO_2/%[e]
$BaTiO_3$	868	729	2.98	2
$BaSnO_3$	375	838	2.24	50
$CaTiO_3$	1080	548	0.69	30
$SrTiO_3$	128	945	0.17	10
$PbTiO_3$	135	—	1.00	0
$BaZrO_3$	3	—	1.00	0
$PbNb_2O_6$	72	—	1.00	0
$BaNb_2O_6$	25	—	1.00	0
$CaNb_2O_6$	26	—	1.00	0

a) Mixed oxide combined with CuO. b) Relative permittivity at 300 K.
c) Optimum operating temperature for CO_2 detection.
d) Sensitivity to 2%. e) Upper limit of detectable CO_2 concentration.

the sensor elements were dried at 373 K for 12 h. The capacitances of the elements were measured with a two probes method by using a LCR meter (Hioki 3520) in a flow system. Sample gases were obtained by diluting the commercial CO_2 gas with dry air. The sensitivity to CO_2 was defined as the ratio of capacitance of an element in a sample gas to that in air, C_{CO2}/C_{air}.

CO_2 sensing characteristics of the mixed oxide capacitors containing CuO are summarized in Table 1. In this table, sensitivities to 2% CO_2, optimum temperatures for CO_2 detection, upper concentrations of detectable CO_2, and relative permittivities at 300 K are listed. The introduction of 2% CO_2 does not affect the capacitances of mixed oxides containing $PbNb_2O_6$, $PbTiO_3$, $CaNb_2O_6$, $BaZrO_3$, or $BaNb_2O_6$. Since the relative permittivities of these mixed oxides are small, the capacitances of these sensors seem to be unaffected upon exposure to CO_2. On the other hand, capacitances of mixed oxide capacitor containing $BaTiO_3$, $CaTiO_3$, $SrTiO_3$, or $BaSnO_3$ depended strongly on the CO_2 concentrations. Upon exposure to 2% CO_2, capacitances of CuO-$BaTiO_3$ and CuO-$BaSnO_3$ increased, but those of CuO-$CaTiO_3$ and CuO-$SrTiO_3$ decreased. According to our previous study, it seems most likely that the capacitance change results from the changes in the height of energy barriers at the boundaries between $BaTiO_3$ and the metal oxides.[6] $BaTiO_3$ and $BaSnO_3$ are n-type, and $CaTiO_3$ and $SrTiO_3$ are p-type semiconductors under the operational conditions.[7] Direction of the capacitance change upon exposure to CO_2 depends on the semiconducting properties of the oxide combined with a p-type semiconductor, CuO. This is because the Fermi level of oxides combined with CuO determines the energy barriers at the junctions between the semiconductors. Sensitivity to 2% CO_2 on CuO-$SrTiO_3$ is almost the same as that on CuO-$BaTiO_3$. The mixed oxide, CuO-$SrTiO_3$, is useful for the detection of CO_2 in a low concentration range (a few hundreds ppm). On the other hand, the mixed oxide capacitor of CuO-$BaSnO_3$ exhibits high sensitivity to CO_2 and can detect CO_2 over a wide range of concentration among the elements examined in this study. Further study was focused on the CuO-$BaSnO_3$ system.

Figure 1 shows the time dependences of capacitance of CuO-$BaSnO_3$ and CuO-$BaTiO_3$ after exposure to air containing 2% CO_2. On exposure to CO_2, capacitance of CuO-$BaSnO_3$ increased rapidly within 30 s in a manner similar to CuO-$BaTiO_3$. The eighty percent responses in capacitance of CuO-$BaSnO_2$ and CuO-$BaTiO_3$ were 29 s and 25 s, respectively. Upon reexposure to air, the capacitances of these mixed oxide capacitors rapidly returned to their original levels. Compared with response characteristics of CuO-$BaTiO_3$, CuO-$BaSnO_3$ requires a slightly longer time to respond but a much shorter time to recover. Since the response time of this sensor depends on the formation rate of $CuCO_3$,[6] the dissimilarity of response characteristics between CuO-$BaSnO_3$ and CuO-$BaTiO_3$ may result from differences in the micro structures, i.e., porosity or degree of sintering, of sensors.

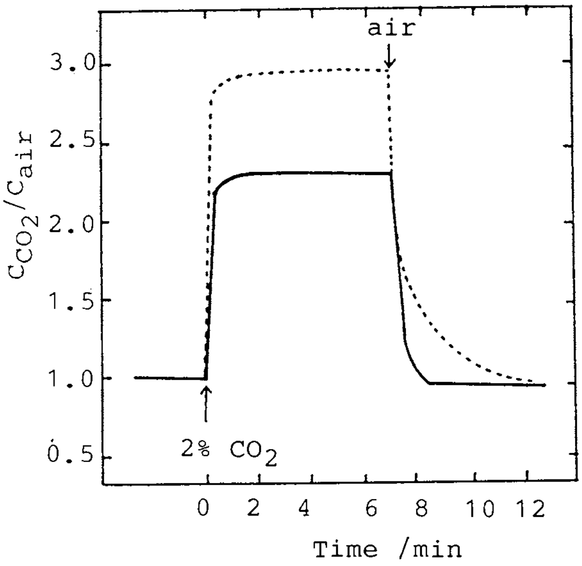

Fig. 1. Time dependences of the capacitance after exposure to 2% CO_2. (CuO-$BaTiO_3$; 729 K, CuO-$BaSnO_3$; 830 K)
——— CuO-$BaSnO_3$ ------ CuO-$BaTiO_3$

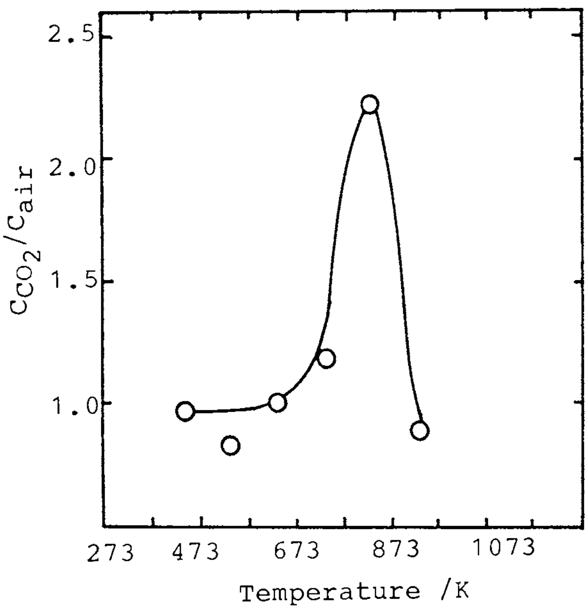

Fig. 2. The sensitivity of the CuO-$BaSnO_3$ capacitor as a function of operating temperature.

The sensitivity of the CuO-$BaSnO_3$ capacitor depends strongly on the operating temperature as shown in Fig.2. The sensitivity to CO_2 increased with increasing operating temperatures and attained a maximum at 830 K.

The sensitivity of CuO-$BaSnO_3$ at 830 K is plotted as a function of CO_2 concentration (Fig. 3). A monotonic and approximately logarithmic relationship exists between the sensitivity and the concentrations of CO_2 below 50%. These characteristics enabled us to evaluate CO_2 concentrations below 50%. The sensitivity of CuO-$BaSnO_3$ to CO_2 concentrations of a few hundreds ppm is almost the same as that of CuO-$BaTiO_3$. However, upper limits of detectable CO_2 concentrations on CuO-$BaSnO_3$ are higher than that of CuO-$BaTiO_3$ by an order of magnitude. As a result, the mixed oxide of CuO-$BaSnO_3$ is suitable for the detection over a wide range of CO_2 concentrations. This study revealed that CO_2 sensing characteristics of mixed oxide capacitors depend strongly on the kind of mixed oxide combined with CuO. Also, the system, CuO-$BaSnO_3$, is able to distinguish CO_2 concentrations from 0 to 50%.

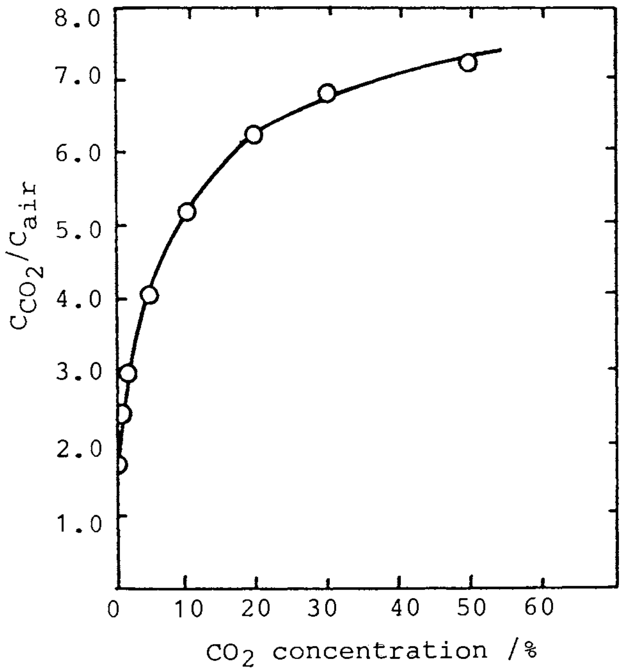

Fig. 3. The sensitivity of CuO-$BaSnO_3$ as a function of CO_2 concentration. (operating temperature; 830 K)

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