—Communication—

Impedance Studies on the CO₂ Detection Mechanisms of the Mixed Oxide, CuO–BaTiO₃, as a Capacitor Type CO₂ Sensor

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1. INTRODUCTION

Carbon dioxide is highly stable and it is very difficult to be detected selectively by the conventional sensors. However, control of CO₂ concentration is demanded critically in the various advanced technologies such as automatic air conditioner and environmental monitoring. Various types of sensors have been proposed for sensitive CO₂ detection.¹⁻³⁾ Little is known about the chemical sensors based on the capacitance change to date except for a humidity sensor. Recently, we found that the mixture of CuO and BaTiO₃ was usable for the sensitive and selective CO₂ detection based on capacitance change.^{4,5)} Furthermore, sensitivity to CO₂ remarkably increased by the addition of Ag to CuO–BaTiO₃ and consequently, this sensor can detect CO₂ in the range from 10 to 500000 ppm without the interference by H₂O.⁶⁾ In this study, we investigated the mechanisms of the capacitance increase by exposure to CO₂ from the impedance analysis.

2. EXPERIMENTAL

Mixed oxide capacitor as the sensor element was prepared by mixing BaTiO₃ mechanically with commercial CuO, which is used without further purification. The mixture of CuO–BaTiO₃ thus obtained was pressed into disks of 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 electrode and a Pt lead wire was connected to it with Ag paste. The X-ray analysis and the electron probe micro analysis suggest that the mixed oxide of CuO–BaTiO₃ is just a two phase mixture. BET surface area and the average diameter of pores in element are 3 m²/g and 100 nm, respectively. The complex impedance measurements were made with the two probe method in a flow system over the frequency range, 30 MHz–1 Hz using an impedance analyzer (Solartron, type 1260).

3. RESULTS AND DISCUSSION

Figure 1 shows the complex impedance plane plots for the element at X=0, 0.25, 0.35, and 0.5 in

(CuO)_x(BaTiO₃)_{1-x}. The complex impedance plane plots of BaTiO₃ consist of an apparent single arc with large resistance, which is actually a superimposition of two arcs of grain and grain boundary. On the other hand, the arcs appeared in a low frequency region by mixing CuO with BaTiO₃, and the top frequency and the intercept on the real axis of the second arc increase and decrease, respectively, with increasing the content of CuO in element. At X=0.5, three arcs are seemingly observed on the complex impedance plane plot. However, the complex impedance plane plot of (CuO)_{0.5}(BaTiO₃)_{0.5} was divided into four arcs in this study due to the four arcs at X=0.35. It is known that the arcs corresponding to the intragrain region and electrode interface generally appear in the frequency range of a few hundred kHz and below 100 Hz, respectively, and also the arc corresponding to the grain boundary appears between them. On the other hand, the third arc at X=0.5 disappeared when Au was used as an electrode. Since ohmic contact is attained on Au electrode, the impedance between electrode and electrolyte seems to disappear on CuO–BaTiO₃ element with Au electrode. Furthermore, the intercept of second and third arcs on the real axis decreased with increasing the applied dc bias voltage. Since it is known that the interface impedance depends on the dc bias voltage, second and third arcs in impedance plots can be assigned to the interface impedances such as grain junction or the interface between electrode and electrolyte. Considering the above results, the four arcs could be assigned to the arcs corresponding to the intragrain region, grain junction between CuO and BaTiO₃, electrode interface, and electrode itself in the order of the decrease in the top frequency.

Equivalent circuit of the sensor element at X=0.5 was estimated from the ac impedance measurement in Fig. 2. Under the air stream at 830 K, the observed complex impedance plots consist of three arcs with the top point at 250 kHz, 620 Hz, and 80 Hz, except for the arc of the electrode itself. In this paper, we assumed, as the first approximation, that the equivalent circuit of the mixed oxide capacitor can be expressed by the series connection of a simple RC parallel circuit as shown in Fig. 2. The resistances, R, were estimated from the interception of each arcs in the real axis, and the apparent capacitances, C, were determined by the following equations: $C = (2\pi f_T R)^{-1}$, where f_T is the frequency corresponding to the top of the each impedance arc. Since

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Fig. 1 Complex impedance plane plots for the element at $X=0, 0.25, 0.35$, and 0.5 in $(\text{CuO})_X(\text{BaTiO}_3)_{1-X}$. Measurement was performed under an air stream at 729 K.

the resistance of BaTiO_3 is measured to be larger than that of CuO by three orders of magnitude, the geometric morphology of sensor element is closely related to a barrier-layered capacitor. Therefore, one role of CuO mixed with BaTiO_3 is in decreasing the resistance and increasing the capacitance of element. Plus sign in the complex impedance plane plot in Fig. 2 shows the point at 50 kHz, which is the operating frequency of sensor element. Since the point at 50 kHz is on the arc corresponding to the grain interface between CuO and BaTiO_3 , the capacitance of the element at 50 kHz, which is used for CO_2 detection, corresponded to that of the grain junction of CuO and BaTiO_3 .

The observed complex impedance plot after exposure to 2 % CO_2 also consists of three arcs which, as before, correspond to the intragrain region, grain junction, and electrode interface. Comparing with the values of resistor and capacitor in the equivalent circuit of the element (Figs. 2 and 3), exposure of the element to 2 % CO_2 decreased the resistance of each arc, but as for the capacitance, only the capacitance corresponding to the grain junction between CuO and BaTiO_3 increased. It is also noted that the point at operating frequency also exists on the arc corresponding to the interface between CuO and BaTiO_3 . Therefore, the change in the values of capacitor of the equivalent circuit well reflected the CO_2 sensing characteristics of the CuO - BaTiO_3 element, and it becomes evident that the capacitance of the interface between CuO and BaTiO_3 was exclusively changed by the exposure to CO_2 . Although the basic mechanisms on the decreased resistance of each impedance arc upon the exposure to CO_2 are not clear at the present, carbonation or adsorption of CO_2 seems to bring about the requisite increase in the capacitance of the grain interface between CuO and BaTiO_3 . In conclusion, complex impedance studies suggest that the depletion-layer capacitance at the grain junction between p-type semiconductor, CuO and n-type semiconductor, BaTiO_3 , is sensitive to CO_2 . Detailed characterization of the energy band at the p-n junction between CuO and BaTiO_3 is currently studied in relation with the adsorption of CO_2 .

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Fig. 2 Complex impedance plane plots and equivalent circuit for a CuO - BaTiO_3 element under an air stream at 729 K. The plus sign in the complex impedance plot shows the point at operating frequency.

Fig. 3 Complex impedance plane plots and equivalent circuit for CuO - BaTiO_3 element after exposure to 2 % CO_2 for 30 min at 729K.

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