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GAS SENSITIVITY OF CuO/ZnO HETERO-CONTACT

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Gas sensitivity of CuO/ZnO hetero-contact was investigated at 160 - 340 °C. The gas sensitivity changed not only with the kind of gases and measuring temperature but with the voltage applied to the hetero-contact. Very high sensitivity and selectivity for CO gas was observed at 260 °C under the applied voltage of 0.1 - 0.9 V.

It is well known that electrical properties of metal oxides are changed when contacted with reducing gases. This phenomenon has already been found in the 1950's by Wagner,[1)] Hauffe,[2)] and other workers. Since the idea of gas sensing utilizing this phenomenon was first proposed by Seiyama et al. in 1962,[3)] many types of gas sensors have been developed and some of them have already been commercially available.

Diode type gas sensors were studied by Maclver,[4)] Tsubomura et al.[5)] and appeared to have high selectivity for reducing gases, especially for H_2. The authors have studied the current-voltage (I-V) characteristics of p-n junction diodes made of two ceramic pellets contacted by mechanically pressing. The diodes such as Li-doped NiO/ZnO,[6)] Li-doped CuO/ZnO,[7)] and CuO/ZnO[8)] have been found to show good humidity-sensing characteristics. In this study, the gas sensing characteristics of the CuO/ZnO diode (The authors call it p-n hetero-contact) were investigated and its high selectivity and sensitivity for a CO gas were found.

Zinc oxide powder (Kanto Kagaku Co., Ltd., Research grade) was pressed into a disc (2-3 mm thick and 10 mm in diameter) under 19.6 MPa and sintered at 1400 °C for 3 h in air. Basic cuprous carbonate ($CuCO_3.Cu(OH)_2.H_2O$) powder (Shuzui-Hikotaro Co., Ltd.) was calcined at 600 °C for 4 h, pressed into a disc (2-3 mm thick and 10 mm in diameter) under 98.0 MPa and sintered at 820 °C for 3 h in air. The relative density was 94% and 89% for ZnO and CuO pellets, respectively. They were polished with a SiC abrasive paper (1500#), washed with acetone and dried at 80 °C. The hetero-contact was made by contacting CuO and ZnO pellets by mechanically pressing using a hand-made sample holder. Ohmic electrodes were silver paste for CuO and indium for ZnO, respectively. The hetero-contact sample was placed in the middle of the tube furnace and a mixture of O_2 and N_2 (1:3) was fed as a carrier gas. The flow rate was fixed at 130 cm^3/min. Reducing gases (CO, C_3H_8, and H_2) were then introduced with a carrier gas, while the forward current was continuously monitored by a controlled potential method.

The concentration of the reducing gases was varied from 890 to 8000 ppm in the carrier gas.

Figure 1 shows the current-time behavior (I-t curve) of the CuO/ZnO hetero-contact at 0.5 V forward bias at 260 °C. When the reducing gases were fed to the hetero-contact, the current across the interface increased in all cases. The line-shapes of I-t curve at different forward bias voltage and temperatures were almost the same, although the magnitude of current change was different and at lower temperatures the response time tended to be a little longer.

The current-voltage characteristics of the CuO/ZnO hetero-contact with and without a CO gas (4000 ppm) under forward bias are shown in Fig. 2. It can be noticed that the relation between the applied voltage and the logarithm of the current is not linear, being quite different from that observed at normal p-n junctions. In addition, the relation between the applied voltage and the logarithm of the increase in the current ΔI, which is defined as $\Delta I = I - I_0$, where I is the saturation current with a reducing gas in the carrier gas and I_0 the current with no reducing gases (carrier gas only), can be divided into two straight lines which cross at the voltage 0.5-0.7 V.

Figure 3 shows the temperature dependence of the gas sensitivity of the CuO/ZnO hetero-contact. In the present paper, the gas sensitivity was defined as I / I_0. The optimum working temperature for the CO gas sensing is judged to be around 260 °C. This temperature for the gas sensing is relatively lower than that reported previously for a ZnO gas sensor whose optimum temperature was about 500 °C.[9,10] The sensitivity for CO gas at 260 °C is twice to three times higher than that for C_3H_8 or H_2.

Figure 4 shows the relation between the gas sensitivity and the forward applied voltage, where the sensitivity also varies with the applied voltage and has the optimum value for gas sensing. The optimum value (≈0.5 V)

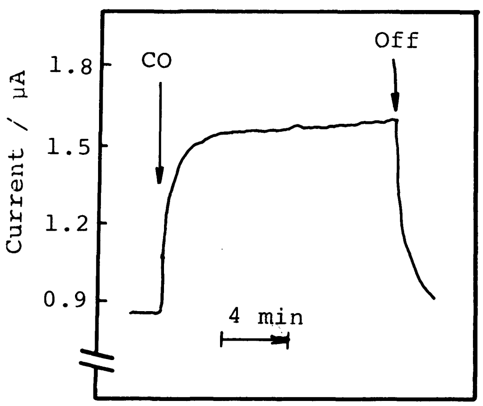

Fig. 1. The current-time behavior of CuO/ZnO hetero-contact at 0.5 V forward bias at 260 °C upon contact with a CO gas pulse (4000 ppm).

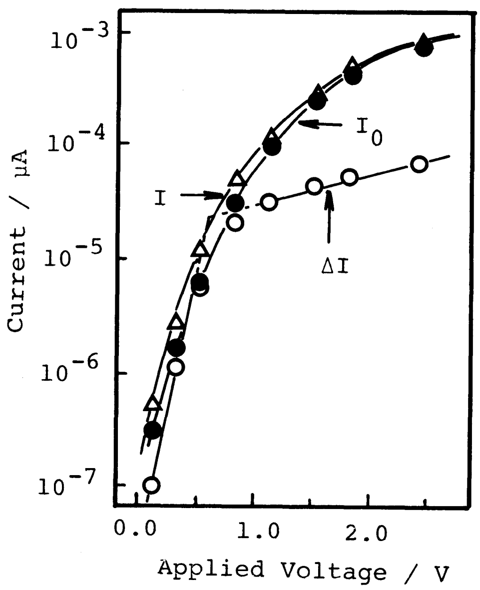

Fig. 2. The current-voltage (I-V) characteristics of CuO/ZnO hetero-contact.
I : The current in the presence of CO.
I_0: The current in the absence of CO.
ΔI : The current due to CO ($\Delta I = I - I_0$).
CO gas concentration: 4000 ppm.
Measuring temperature: 260 °C.

corresponds to the crossing point of two straight lines of ΔI in Fig. 2. When the large forward bias is applied to this contact, both sensitivity and selectivity for CO gas markedly decrease. The relation between the CO gas sensitivity and gas concentration is shown in Fig. 5. The sensitivity increased with increasing CO gas concentration and the relation between the sensitivity and the logarithm of gas concentration was linear.

From the present results, it can be concluded that the CuO/ZnO hetero-contact possesses very high selectivity and sensitivity for a CO gas. The reason of the current change by the introduction of a CO gas or other reducing gases is not well understood presently. In the present study, the p-n junction was made by placing CuO and ZnO pellets in contact. But this hetero-contact is quite different from normal hetero-junction in that this has a large amount of non-contacting area which is exposed to the surrounding atmosphere. It was already reported by the present authors that the mechanically contacted CuO/ZnO hetero-junction shows better humidity-sensing characteristics than a CuO/ZnO hetero-junction having a large contacting area made by the CVD method.[8] This fact firmly suggests that in cases of the presence of a large non-contacting area the electrical characteristics of the junction can be changed by the interaction with the gas phase either by 1) the adsorption of gases to the interface of the junction or by 2) the desorption of adsorbed oxygen on the CuO or ZnO surface. The generally accepted gas sensing mechanithm of ZnO gas sensors is relied on the decrease in adsorbed oxygen concentration due to oxidation of reducing gases, which result in a decrease in resistivity.[11] If the gas sensing mechanism of the CuO/ZnO hetero-contact is supposed to be similar, the high selectivity for CO gas cannot be

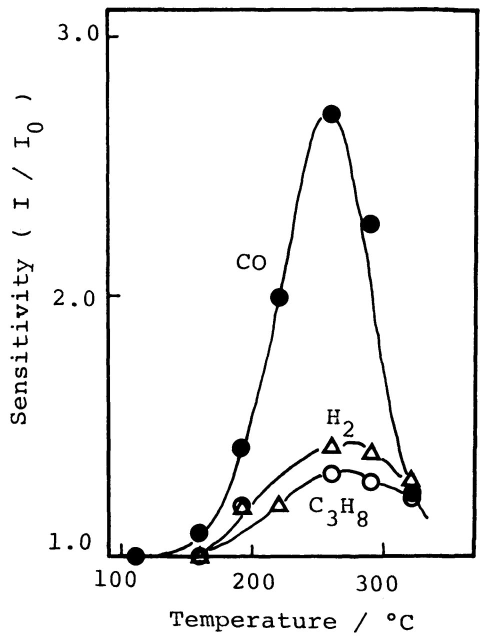

Fig. 3. The temperature dependence of the gas sensitivity of CuO/ZnO hetero-contact.
-●-●- : with CO, -○-○- : with C_3H_8
-△-△- : with H_2.
The concentration of each gas was 8000 ppm.
Applied voltage was 0.5 V.

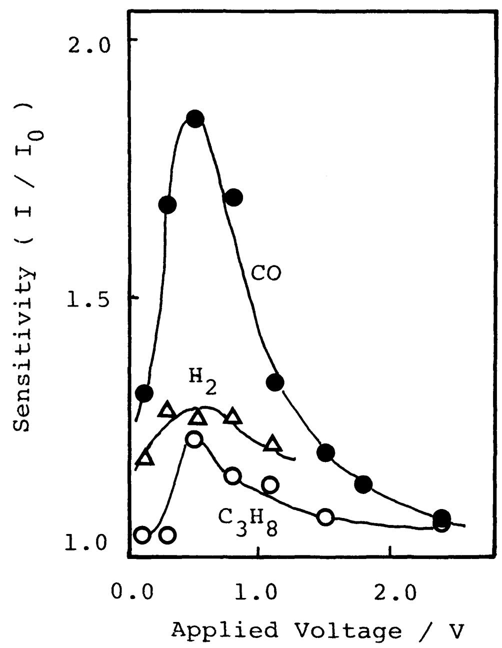

Fig. 4. The relation between the gas sensitivity and the forward applied voltage.
-●-●- : with CO, -○-○- : with C_3H_8
-△-△- : with H_2.
The concentration of each gas was 8000 ppm.
Measuring temperature was 260 °C.

explained, because the sensitivity of ZnO for H_2 is higher than that for CO.[9,10]

The CuO-ZnO system is also applied to the catalyst for the following CO shift reaction,

$$CO + H_2O \rightarrow CO_2 + H_2$$

and adsorbed species of CO at 200 °C were detected by IR spectroscopy.[12]

Electrical conductivity of p-type CuO ceramics is lowered when contacted with CO or H_2 at 190-245 °C[13] due to the chemisorption of these gases. The temperature region where the conductivity change was observed in previous studies is in accord with the working temperature of the present CuO/ZnO hetero-contact.

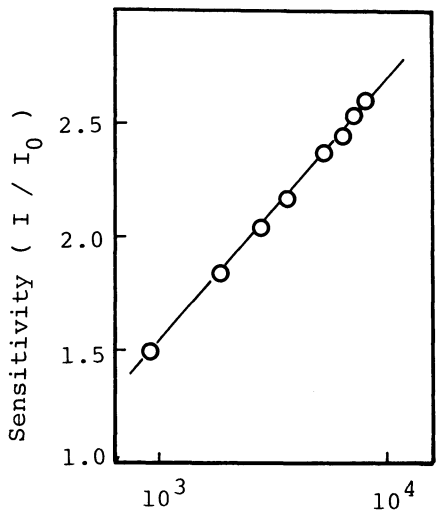

Fig. 5. The relation between CO gas sensitivity and gas concentration. Applied voltage : 0.5 V. Measuring temperature : 260 °C.

It is suggested from above discussion that the adsorbed molecules of reducing gases form interface states and they may alter the potential barrier height of the junction, resulting in the change in the current across the junction. Such gas sensing mechanism was already proposed by Tsubomura et al. for the Pd-TiO_2 diode which showed high selectivity for H_2 gas.[5] In that case, hydrogen adsorption caused a decrease in the work function of Pd and hence a decrease in the Shottky barrier height.

In conclusion, the CuO/ZnO hetero-contact was found to have high selectivity for CO gas with working mechanism different from that previously reported for ZnO and other semiconducting sensors. Further study is now being undertaken to fully understand the whole phenomenon.

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