CHEMISTRY LETTERS, pp. 1793-1796, 1994. © 1994 The Chemical Society of Japan

Quantitative Analysis of Ethanol in Water Solution by a Heterocontact-type Sensor of CuO / ZnO

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Methods of quantitative analysis in the system of ethanol-water were investigated using a heterocontact-type sensor consisted of semiconducting ceramics of copper oxide (CuO) and zinc oxide (ZnO). The current-voltage (I-V) characteristics of the heterocontact in the solutions changed depending on the ethanol concentration when measured at AC 50 Hz at room temperature. It was found that the ethanol concentration can be determined quantitatively by analyzing the shape of I-V hysteresis loop.

Both copper oxide ceramics (CuO) and zinc oxide ceramics (ZnO) are widely utilized for sensing devices. It is well known that, the surface states of metal oxides are affected by water vapor,oxygen, or reducing gases, and electrical properties of metal oxides are changed.1) This phenomenon was found and reported by Wagner,2) Hauffe,3) and many other investigators. Many kinds of gas sensors utilizing this property have been investigated from the first report by Seiyama,4) and some of those already have been commercially available.

Metal/semiconductor diode type ceramic gas sensors have been studied by Tsubomura and his colleagues.5) In the last decade, number of papers concerning on gas sensors have accumulated the understanding of the sensing mechanism. The concept of using a heterocontact of p-type and n-type semiconducting ceramics was firstly proposed by Yanagida in 1979 as a new type of ceramic humidity sensor,6) and thus the current-voltage (I-V) characteristics of the heterocontact type devices have been investigated.7,8) Recently, solvent sensing characteristics were studied at high frequencies of 1kHz and 1MHz, and a solvent sensor9) and an alcohol sensor10) have been proposed by using p-n heterocontacts. Changes in I-V characteristics depending an solvent species were considered to be due to changes in surface states at the contact interface by chemical reactions or chemisorptions of liquid molecules. However, the sensitivity measured at a high frequency was not enoughly large to determine the ethanol concentration quantitatively, and not linear to the ethanol concentration. In addition, the frequency dependence of I-V characteristics has not been examined yet.

In this study, I-V characteristics of a p-CuO/n-ZnO heterocontact in ethanol-water solution system were measured at a low frequency of AC 50Hz at room temperature, and methods of quantitative analysis for ethanol concentration were evaluated.

Figure 1(a) and 1(b) illustrate schematic views of the preparation process of the p-n heterocontact and the system for measuring I-V characteristics, respectively. Powders of CuO and ZnO in reagent grade were used as starting materials. Each powder was pressed into discs as 5 mm in thickness and 10 mm in diameter under 80

MPa. Thus obtained discs of CuO and ZnO were sintered in air for 3 h at 850 ℃ and 900 ℃, respectively. Both pellets were polished with a SiC abrasive paper (#400), cleaned with acetone and then dried. Silver paste for a p-type semiconducting CuO and indium for an n-type semiconducting ZnO were used as ohmic electrodes, respectively. The CuO and ZnO pellets were mechanically pressed to make a p-n heterocontact-type solvent sensor, as shown in Fig.1(a). The constructed heterocontact element was placed in an objective solvent for electrical measurements. An alternating current (AC) bias of 5 V was applied across the heterocontact interface and I-V characteristics were measured using an oscillator at room temperature, as shown in Fig.1(b).

Figure 2 shows I-V characteristics in 50 vol% ethanol solution measured at various frequencies. As the frequency decreased, asymmetric shape of the hysteresis loop became evident. Since the I-V characteristic at 5 Hz was unstable, that at 50 Hz was used for evaluation of sensing properties. Figure 3 shows I-V characteristics of the p-n contact in various ethanol-water solutions measured at 50 Hz at room temperature. The shape of the hysteresis loop was changed by the existence of ethanol and its concentration. Especially, the height of peak, observed during sweeping bias from plus to minus, was changed drastically. The changes of the hysteresis loop by changes in ethanol concentration were reproducible.

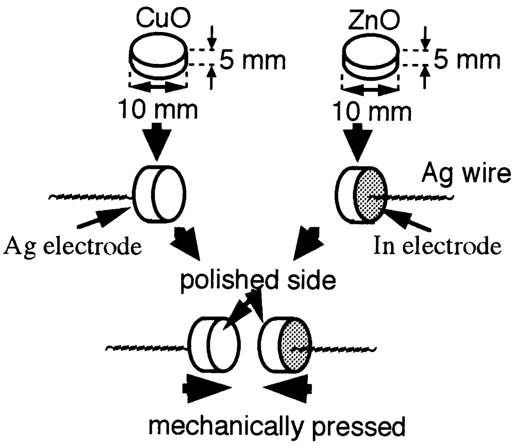

Fig.1(a). The schematic view of the preparation process of the p-n heterocontact.

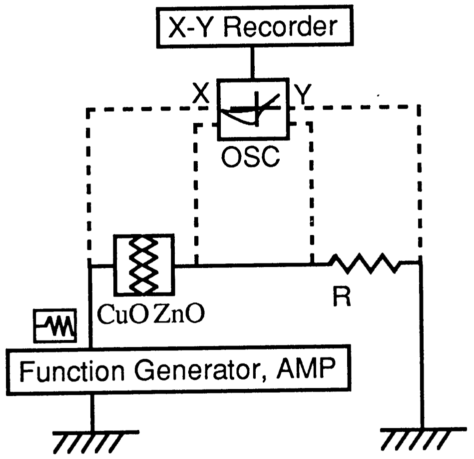

Fig.1(b). The schematic drawing of the system for measuring I-V characteristics.

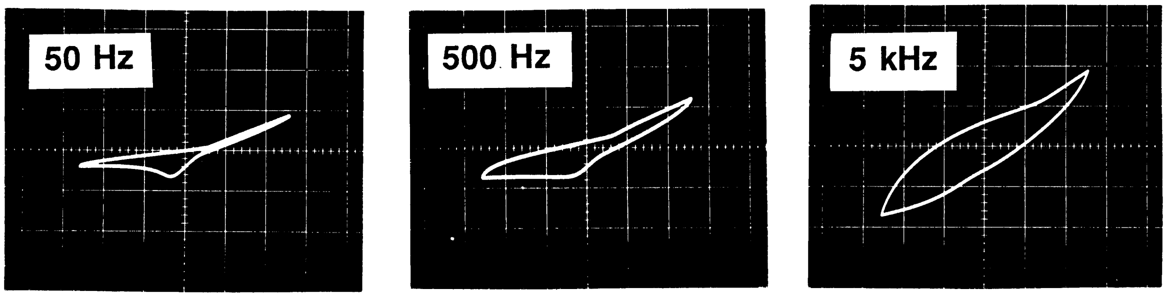

Fig.2. Photographs of I-V characteristics for the p-CuO / n-ZnO heterocontact measured in 50 vol% ethanol solution at various frequencies with AC bias applied at room temperature (2 V/div., 0.5 mA/div.).

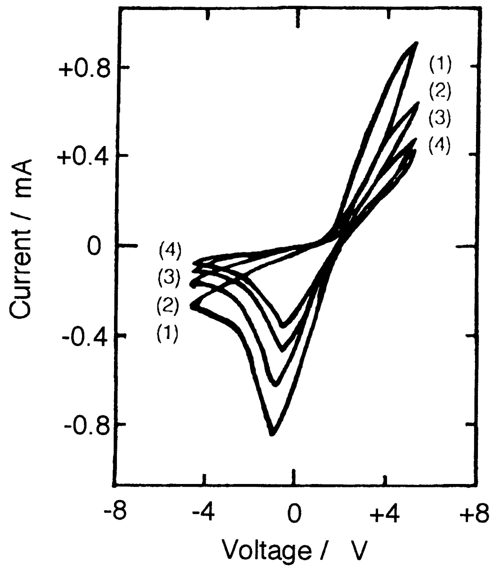

Fig.3. I-V characteristics measured in various ethanol concentrations at AC 50 Hz at room temperature, ethanol concentration; (1) water, (2) 40 vol% ethanol, (3) 60 vol% ethanol, (4) 99.5 vol% ethanol.

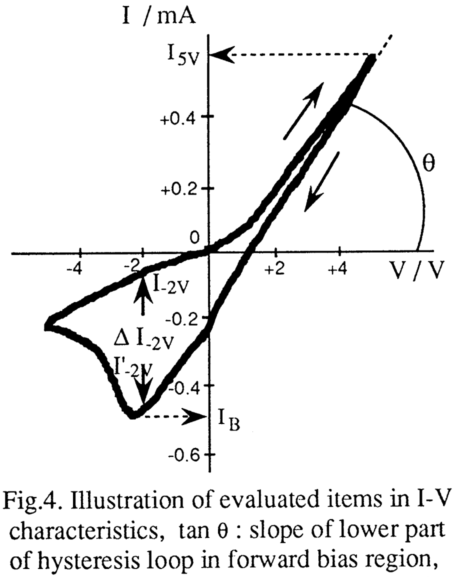

Fig.4. Illustration of evaluated items in I-V characteristics, tan θ : slope of lower part of hysteresis loop in forward bias region, I_{5V}: current at V=5 V, I_B : current at the bottom of hysteresis loop, ΔI_{-2V} : current difference at -2V(=I_{-2V}-I'_{-2V}).

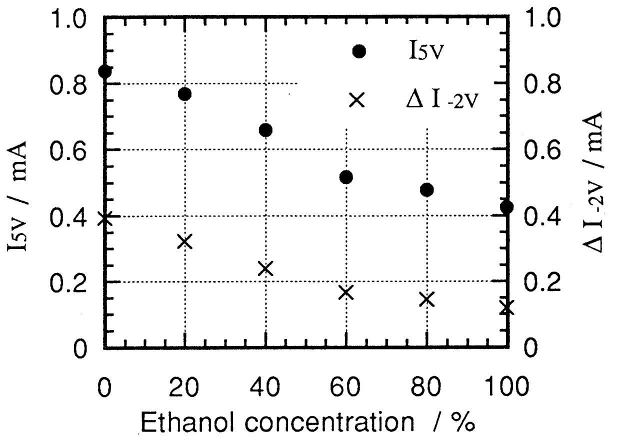

Fig.5. The I_{5V} and the ΔI_{-2V} as a function of ethanol concentration with 50 Hz AC 5 V applied at room temperature.

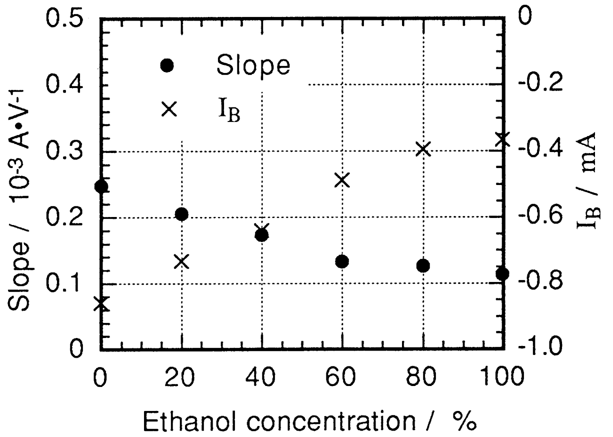

Fig.6. The slope and the I_B as a function of ethanol concentration.

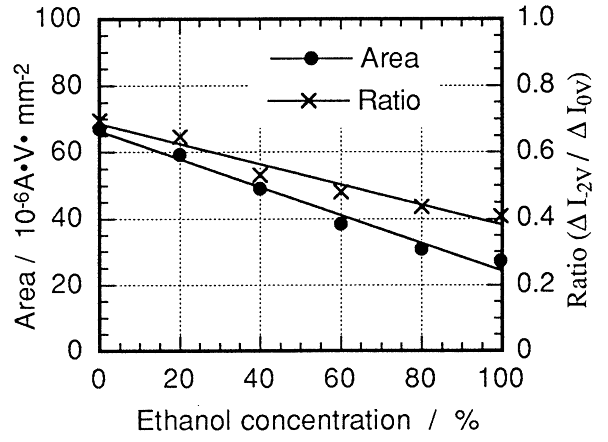

Fig.7. The area and the ratio as a function of ethanol concentration.

Following parameters were used to express the shape of hysteresis loop: (1) The area surrounded by hysteresis loop. The value of the area was normalized by the area of heterocontact. (2) The slope of lower part of hysteresis loop in forward bias region (tan θ). (3) The currents at 5 V (I_{5V}), and at the bottom of hysteresis loop (I_B). (4) The current difference between upper and lower part of hysteresis loop at -2 V (ΔI_{-2V}). (5) The ratio of current differences between upper and lower part of hysteresis loop at 0 V and -2 V ($\Delta I_{-2V}/\Delta I_{0V}$). The evaluated items in hysteresis loop are indicated in Fig.4.

Figure 5 shows current at 5 V (I_{5V}) and the current difference between upper and lower part of hysteresis loop at -2 V (ΔI_{-2V}) as a function of ethanol concentration. Figure 6 shows the slope in forward bias region (tan θ) and current at the bottom of hysteresis loop (I_B) as a function of ethanol concentration. I_{5V} , ΔI_{-2V} , the slope, and I_B had linear relations to the ethanol concentration only in the region of ethanol concentration of about 0 - 60% ethanol. Figure 7 shows the surrounded area and the current ratio (ΔI_{-2V} / ΔI_{0V}) as a function of ethanol concentration. Both the surrounded area and the current ratio decreased almost linearly with an increase in ethanol concentration in the whole concentration range. Accordingly, determination of ethanol concentration (0-99.5%) in water-ethanol system was found to be practicable by using one of the parameters of the surrounded area and the current ratio. The slope in the forward bias is assumed to correspond to the conductance across the interface of heterocontact. The peak in the reverse bias was maximum in water. However, the voltage giving a peak in the reverse bias was dependent on the ethanol concentration. Accordingly, this peak is assumed to be resulted from not only the redox reaction of water molecules but from some electrochemical reaction of the product generated during the forward bias. The value of surrounded area would include the total changes of those phenomena. An asymmetric shape of I-V characteristics seems to be formed by the differences in conductance and electrochemical reaction between forward and reverse biases. The value of the current ratio would be a parameter which reflects the asymmetric shape of I-V characteristics. The maximum values of above six parameters were observed in water. This result would suggest that the charge transfer and subsequent chemical reaction at the CuO/ZnO interface are more difficult to occur in ethanol than in water.

In conclusions, the area, the current ratio at 0 and -2 V in the I-V hysteresis loop had linear relations to the ethanol concentration. Accordingly, quantitative analysis of ethanol in water solution was found to be practicable by measuring I-V characteristics of CuO/ZnO heterocontact in the solution.

References

1) M.Takata and H.Yanagida, *Yogyo Kyokai-shi*, **87**, 13 (1979).
2) C.Wagner, *J. Chem. Phys.*, **18**, 69 (1950).
3) K.Hauffe and H.Engell, *Z.Electrochem.*, **56**, 36 (1952).
4) T.Seiyama, A.Kato, K.Fujiishi, and M.Nagatani, *Anal. Chem.*, **34**, 1502 (1962).
5) N.Yamamoto, S.Tonomura, T.Matsuoka, and H.Tsubomura, *Surf. Sci.*, **92**, 400 (1980).
6) K.Kawakami and H.Yanagida, *Yogyo Kyokai-shi*, **87**, 113 (1979).
7) Y.Toyoshima, M.Miyayama, H.Yanagida, and K.Koumoto, *Jpn. J. Appl. Phys.*, **22**, 1933 (1983).
8) Y.Nakamura, M.Ikejiri, M.Miyayama, K.Koumoto, and H.Yanagida, *Nippon Kagaku Kaishi*, **1985**, 1154 (1985).
9) H.Ito, S.Fujitsu, M.Miyayama, K.Koumoto, and H.Yanagida, *J. Ceram. Soc. Jpn.*, **100**, 350 (1992).
10)H.Ito, S.Fujitsu, M.Miyayama, K.Koumoto, and H.Yanagida, *J. Ceram. Soc. Jpn.*, **100**, 888 (1992).

(Received June 27, 1994)