Alcohol Sensor by Using a p-n Semiconductor Contact

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p-n 半導体コンタクトを用いたアルコールセンサ

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An easy, convenient and widespread applicable detection of chemical species in a liquid was realized by using a contact of p- and n-type semiconducting ceramics (it was called p-n hetero-contact). This p-n hetero-contact was constructed by mechanically pressing together the polished surfaces of p-type CuO and n-ZnO sintered pellets. When this system was put into an alcohol and a c. bias was applied across its interface, a characteristic current-voltage (I - V) relation with hysteresis and rectifying nature was observed, depending both on the kind and the concentration of the alcohol. It was possible to discriminate the chemical species and to estimate the alcohol concentration in alcohol-water solutions by estimating three parameters reflecting the magnitude of hysteresis, current flow and rectifying nature, respectively, calculated from the observed I - V curve. That is, the former two parameters decreased and the latter one increased, when the number of carbon atoms in an alcohol molecule increased, or when the water content in an alcohol solution decreased. It was recognized that the observed I - V relation is generated not only from the physical properties of the liquid, such as electrical conductivity and dielectric constant, but also from the interface states formed by the chemical interaction between alcohol molecules and semiconductor surfaces.

Key-words : Hetero-contact, Liquid sensor, Alcohol, Zinc oxide, Copper oxide, Surface state

1. Introduction

The detection of chemical molecules in a liquid phase has played very important roles in various modern industrial fields, for example, inspection of drainage quality, inspection of raw materials and control of productivity. It has required the development of stable liquid sensors. For example, it is possible to detect ions in a liquid by using an ion selective elec-

trode. On the other hand, many types of gas sensors have been developed and some of them have been commercially available until today. A semiconductor-type gas sensor among them is widely acceptable as a sensing device utilizing the resistivity change in a semiconducting oxide, depending on the nature of its surrounding atmosphere. Such a phenomenon was already found in 1950's by Wagner,¹⁾ Hauffe et al.²⁾ and other workers. Further, the gas sensor utilizing this kind of phenomenon³⁾⁻⁷⁾ was first proposed in 1962 by Seiyama et al.⁸⁾ However, it is very difficult to develop liquid sensors, because liquid molecules have stability and inactivity during chemical or electrochemical processes. In other words, there cannot be strong chemical nor physical interaction, for instance strong adsorption or chemical reaction, between the surface of the sensor device and liquid molecules. Therefore, liquid sensors are necessary to operate by means of even such a weak interaction. On the other hand, although many complicated analytical precision instruments to detect chemical species in liquids have been developed, they are still expensive and need troublesome pretreatments.

The authors have developed a new type of sensor for combustible gases, such as CO⁹⁾⁻¹¹⁾ and H₂,¹¹⁾ and incombustible gases, such as CO₂,¹²⁾ Cl₂,¹³⁾ NO_x,¹⁴⁾ or humidity¹⁵⁾⁻¹⁹⁾ by means of a p-n hetero-contact made of two different ceramic pellets of p- and n-type semiconductors. Its excellent selectivity depends on the specific interface state at the contact area due to its characteristic structure. Because of surface roughness of contacted sintered specimens permitting penetration of gas molecules into the interface, and of the closeness among two semiconductor (p- and n-type) surfaces and gas molecules, the electrical properties across the interface depend on gas molecular species in the surroundings. Therefore, the changes can be used as detecting signals. In fact, we also reported that the p-n hetero-contact type device was effective to discriminate indistinguishable molecules such as CO and H₂.¹²⁾

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In this study, the p-n hetero-contact composed of CuO and ZnO ceramics was produced and the effectiveness of this system as a sensor to detect the chemical species in liquids was examined, and one model for working mechanism was proposed.

2. Experimental

2.1 Sample preparation

Basic cuprous carbonate ($\text{CuO} \cdot \text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$) powder (94% pure, Shuzui-Hikotaro Co., Ltd.) and zinc oxide (ZnO) powder (99.99% pure, Ko-Jundo Kagaku Co., Ltd.) were employed as the starting materials. The former was calcined at 600°C for 4 h, and CuO powder was obtained. It was pressed into a disk (5 mm thick and 10 mm diameter) in a unidirectional mold, and subsequently pressed isostatically under 40 MPa in a rubber mold and then sintered at 970°C for 8 h in air. On the other hand, the ZnO powder was pressed into a disk and sintered under the same condition. The relative densities of sintered specimens were 80% and 98% for CuO and ZnO, respectively.

2.2 Construction of a hetero-contact

The obtained pellets were roughened on contacting sides using SiC polishing powder (#400). They were also cleaned ultrasonically in an acetone bath, and were dried. Sputtered Pt-Pd alloy and indium-gallium alloy electrodes were applied to the opposite sides of CuO and ZnO pellets, respectively. Silver wires were attached to the electrodes and epoxy resin was used to isolate the electrodes from liquids. The contacting faces of both pellets were pressed together mechanically at a pressure ranging from 1.0×10^5 to 8.0×10^5 Pa.

2.3 Measurements

To reproduce an initial condition, the p-n contact

device in a measuring system illustrated in Fig. 1 was washed with acetone and dried in vacuum before each measurement. After filling this system with alcohols or alcohol solutions, the current-voltage (I - V) relation across the contacting interface was measured with an oscilloscope (Iwatsu DS-6411) at 1 kHz. The resulting I - V curves were transmitted to a personal computer (NEC 9801) through a GP-IB cable, then the data were analyzed numerically. The applied voltage and measuring temperature were from 2 to 20 V (peak-to-peak) and 298 K, respectively.

3. Results and discussion

3.1 Evaluation of I - V relation

Typical I - V relations of the device soaked in normal monohydric alcohol series ($\text{C}_n\text{H}_{2n+1}\text{OH}$) are shown in Fig. 2. Each I - V curve has hysteresis and rectifying nature. It is obvious that the kind of liquid affects the shape of I - V curve. In order to evaluate the obtained I - V relations objectively, the following analytical method was adopted. First, the area of a hysteresis loop is calculated and defined as S . Second, the current under the same voltage is averaged as shown in Fig. 3, and the averaged I - V curve is ap-

Fig. 2. Current-voltage characteristics of CuO/ZnO hetero-contact in various alcohols. All measurements were carried out at 1 kHz at 298 K, applied voltage was 16 V (peak-to-peak), and mechanical pressure was 8.0×10^5 Pa.

Fig. 1. Experimental setup for measuring I - V characteristics of CuO/ZnO hetero-contact in a liquid.

Fig. 3. Analytical method for I - V characteristic of CuO/ZnO hetero-contact.

proximated to Eq. (1), using the least squares fitting,

$$I = I_0 \{ \exp(qV) - 1 \} \quad (1)$$

where I is the current under the applied voltage, V . Equation (1) was derived from Eq. (2) based on the diode theory,

$$I = I_0 \{ \exp(eV/kT) - 1 \} \quad (2)$$

where e , k and T are an electron charge, Boltzmann's constant and absolute temperature, respectively. Equation (1) gives two parameters I_0 and q . In this way, the I - V relation for one liquid is characterized by the above three parameters S , I_0 and q . The values of S , I_0 and q indicate the magnitude of hysteresis, the degree of electrical conduction and the magnitude of rectifying nature, respectively. For a diode with the ideal junction, the parameter q is expressed as e/kT , as shown in Eq. (2), which is equal to 38.9 V^{-1} at 298 K. However, in this CuO/ZnO system, the calculated q was as low as 0.1 to 0.5 V^{-1} . It is because this system is not a junction but a contact where the gap is filled with a liquid. This will be discussed later in this paper.

3.2 Discrimination of normal monohydric alcohol series

Figure 4 shows the calculated parameters S , I_0 and q for normal monohydric alcohol series in the CuO/ZnO system. The measurement was carried out at 298 K at 1 kHz, and the applied voltage was 16 V (peak-to-peak). The reason why this condition was adopted is discussed later in this paper. Both S , I_0 decreased and q increased with increasing number of carbon atoms in an alcohol molecule, n . This result suggests the possibility for discrimination of kinds of pure alcohols by this method.

Figure 5 shows the three parameters for the CuO/alcohol/ZnO system. The surfaces of CuO and ZnO were at a distance of about $100 \mu\text{m}$ by putting an alumina plate between them. The measurements were carried out in the same condition with that of Fig. 4. This result shows the existence of electrical conduction through the liquid. Furthermore, it was appar-

Fig. 4. The values of S , I_0 and q for normal monohydric alcohol series in CuO/ZnO system. The measuring condition was the same with that in Fig. 2.

Fig. 5. The values of S , I_0 and q for normal monohydric alcohol series in CuO/alcohol/ZnO system. The measuring condition was the same with that in Fig. 2.

ent from the I - V curve that the electrical conduction through the liquid has rectifying nature, in the CuO/alcohol/ZnO system. Differences in the values of three parameters in Fig. 4 are greater than those in Fig. 5. These results show the efficiency of a p-n direct contact device as a liquid sensor. However, the result of Fig. 4 contains the influence of the physical properties of each alcohol. For example, electrical conductivity, dielectric constant and water solubility of normal monohydric alcohols all decrease with increasing number of carbon atoms, n . It is reasonable that liquids with different physical properties give different curves. Therefore, the following experiments were carried out to examine the effect of chemical properties of alcohols on the I - V relation, excluding physical properties.

3.3 Discrimination of liquids with the same electrical conductivity

To examine the effect of chemical properties of alcohols on the I - V relation, the liquids with the same electrical conductivity with CH_3OH were prepared by adding H_2O into $\text{C}_2\text{H}_5\text{OH}$ and $\text{C}_3\text{H}_7\text{OH}$, and the I - V relations in those liquids were measured. Electrical properties of liquids were measured by using an impedance analyzer (Yokogawa-Hewlett Packard, Model 4192 A) with electrodes for liquids (Ando, LE-22) at 1 kHz at 298 K. The electrical conductivity was calculated from the measured conductance (see Table 1). As shown in Fig. 6, the values of S , q

Table 1. The electrical conductivity and effective dielectric constants for alcohol-water system. The electrical conductivity of each liquid was the same at 1 kHz at 298 K.

liquids	Electrical conductivity ($\text{nS}\cdot\text{cm}^{-1}$)	Dielectric constant (-)
100% Methanol	7.49	177
56.2% Ethanol	7.49	67.9
94.1% Propanol	7.49	39.1

Fig. 6. The values of S , I_0 and q for alcohol-water system with the same electrical conductivity in CuO/ZnO system. The measuring condition was the same with that in Fig. 2.

and even I_0 , which reflected the degree of electrical conduction, were different in spite of the same electrical conductivity.

3.4 Measurement of liquids with the same effective dielectric constant

Figure 7 shows the values of S , I_0 and q for the liquids with the same effective dielectric constant. Dielectric constant was controlled by adding H_2O into C_2H_5OH and C_3H_7OH so as to be equal to that of pure CH_3OH as shown in Table 2. Although the die-

Fig. 7. The values of S , I_0 and q for alcohol-water system with the same dielectric constant in CuO/ZnO system. The measuring condition was the same with that in Fig. 2.

Table 2. The electrical conductivity and effective dielectric constants for alcohol-water system. The effective dielectric constant of each liquid was the same at 1 kHz at 298 K.

liquids	Electrical conductivity (nS·cm ⁻¹)	Dielectric constant (-)
100% Methanol	7.49	177
30.7% Ethanol	26.9	177
53.0% Propanol	22.6	177

lectric constant was the same in all liquids, the obtained three values, even S , which indicates the magnitude of hysteresis, showed differences in each liquid. Figures 6 and 7 show that the observed I - V relations in this system are governed not only by the physical properties of the liquid penetrated into the gap of the contact but also by some chemical interaction between alcohol molecules and CuO or ZnO surfaces accompanied by a charge transfer process.

3.5 P-n hetero-contact as a concentration sensor

Figure 8 shows the concentration dependence of the values of S , I_0 and q for methanol- and ethanol-water system. Both S and I_0 decreased and q increased with an increase in alcohol content. This result shows that this device has an ability not only to discriminate the kind of alcohol molecules but also to detect the concentration of specific alcohol.

3.6 The optimum applied voltage and mechanical pressure for sensing

In order to confirm the effects of measuring conditions on the sensing properties and to obtain the optimum condition for sensing, the dependence of applied voltage, measuring frequency and mechanical pressure on the three parameters were examined. Figure 9 shows the applied voltage dependence of three parameters for various alcohols. This measurement was carried out at 1 kHz at 298 K. This result shows that the optimum applied voltage is about 16 V, because three parameters all monotonously change with the number of carbon atoms and the differences among those are largest under this voltage. Figure 10 shows the pressure dependence of the three parameters. This measurement was also carried out at 1 kHz at 298 K. All values of S , I_0 and q monotonously increase with the increasing pressure. However, this result shows that the selectivity little depends on the mechanical pressure. Therefore, the pressure was fixed to be 8.0×10^5 Pa in the

Fig. 8. The values of S , I_0 and q vs. alcohol content of methanol- and ethanol-solution in CuO/ZnO system. The measuring condition was the same with that in Fig. 2.

Fig. 9. Relationship between applied voltage and the values of S , I_0 and q in CuO/ZnO system. All measurements were carried out at 1 kHz at 298 K, and mechanical pressure was 8.0×10^5 Pa.

Fig. 10. Pressure dependence of the values of S , I_0 and q for pure alcohols in CuO/ZnO system. All measurements were carried out at 1 kHz at 298 K, and the applied voltage was 16 V.

former measurements.

3.7 The sensing mechanism

The sensing mechanism of this system is discussed. There are two parallel conduction paths in this system. One is through the contact points directly, and the other is through the liquid. In CuO/liquid/ZnO system, dependences of S , I_0 and q on the kind of alcohol are smaller than those in CuO/ZnO hetero-contact, as shown in Figs. 4 and 5. Therefore, it is supposed that the sensing characteristics are dominated by the conduction through the contact points. For the conduction through the contact points, interface states at the contact points seem to dominate the conduction behavior. Two processes can be assumed for changing the interface states. One is the formation of the new interface state by chemisorption of the liquid molecule, and the other is the change in the original surface state on the semi-

Fig. 11. The proposed model of liquid sensing mechanism for CuO/ZnO ceramic semiconductor hetero-contact.

E_c : the lowest level of conduction band,
 E_F : Fermi level,
 E_v : the highest level of valence band.

conductor based on the exchange reaction of alcohol molecules for the chemical species beforehand combined with semiconductor surfaces. The proposed model on the conduction through the contact points is shown in Fig. 11. There are trap states of electron at the interface, and the state is supposed to go shallow with the increasing carbon number in alcohol molecules. Since the current through a lower potential barrier is larger than that through a higher barrier, the values of I_0 in 56.2% ethanol and 94.1% propanol become larger than that in pure methanol, even though pure methanol, ethanol- and propanol-solution have the same electrical conductivity, as shown in Fig. 6.

According to the diode theory, the I - V relation across a hetero-junction is expressed as Eq. (2), while two theories proposed by Mott and Schottky, respectively. In all theories, the slope of log current vs. voltage, which was defined as q in the present paper, is expressed as e/kT , which is equal to 38.9 V^{-1} at 298 K for a larger voltage. However, the typical observed slope of a contact of CuO/ZnO is much smaller than that of the junction. Because the conduction through either liquid or interface states doesn't obey the diode theory.

The surface state modified by chemical reaction or chemisorption may depend on the kind of liquid molecules or of semiconductors. Therefore, it may be possible to develop a more sensitive sensor or a sensor capable of detecting other kinds of molecules by choosing different combinations of semiconductors for a p-n hetero-contact.

4. Conclusions

A p-n hetero-contact type device was prepared by mechanically pressing together the p-type CuO and n-type ZnO semiconducting ceramics pellets, and the I - V characteristics across the contacting interface in alcohols or alcohol solutions was investigated, and the possibility of this type of device for an alcohol sensor was examined. The following conclusions were obtained from the present study:

(1) The I - V characteristic was strongly influenced by the alcohol molecules, it was possible to discriminate the kind of alcohols by analyzing three parameters, reflecting the magnitude of hysteresis, current flow and rectifying nature, respectively, calculated from the obtained I - V curve. The former two parameters decreased and the latter one increased with increasing carbon number in an alcohol molecule. The optimum applied voltage for sensing was at 16 V (peak-to-peak).

(2) This device also had an ability to estimate the alcohol concentration in a solution. The above three parameters of an alcohol solution changed monotonously between those of pure alcohol and those of water.

(3) The I - V characteristic of a hetero-contact in a liquid depended not only on the physical properties of the liquid but also on the chemical properties. This device was supposed to behave as a chemical sensor accompanied by a chemical interaction between the alcohol molecule and the semiconductor surface.

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