Effect of Water Vapor on Electrical Resistance of Acid-Base Hetero-Contact

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Surface electrical resistance along the interface of acid-base hetero-contact using TiO2 or NiO substrate was measured at 20°C under controlled humidity. Humidity-sensitivity of acid TiO2 was suppressed by the contact with basic oxides and that of basic NiO was enhanced by the contact with an acid oxide. A model in which protons transfer from acid to basic surface by acid-base interaction was proposed.

[Received July 15, 1988; Accepted August 17, 1988]

Key-words: Titanium oxide, Nickel oxide, Hetero-contact, Humidity-sensor, Acid-base, Proton

1. Introduction

There are many reports on humidity-sensitive porous compound oxides which use surface ionic conduction at room temperature, such as MgCr2O4-TiO2. Their surface electrical conductivity are enhanced with water vapor adsorbed, and the protons dissociated from water were reported to be the dominant charge carrier. Mostly, the humidity-sensitive compounds comprise acid and basic oxides, but it is not clear why those compound systems are highly sensitive to humidity. In this study, in order to make elucidate the sensing mechanism, effects of acid-base interaction on humidity-sensing property were investigated by use of acid-base hetero-contact. Titanium oxide and NiO were chosen as typical acid and basic substrate materials, respectively. The surface electrical resistance of these substrates in contact with various oxides were measured, and compared with them without using contacted oxides.

2. Experimental

TiO2 powder (99.99 pure, Rare Metallic, Co., Ltd.) was pressed into rectangular bars (5×1×2 mm) under 20 MPa and sintered at 1300°C for 5 h in Ar gas. For obtaining porous TiO2 ceramics, TiO2 powder was mixed with Nb2O5 at a Nb concentration of 0.5 mol %, ground in an agate mill for 30 min with ethanol, calcined at 900°C for 3 h, and ground again. The resultant powder was pressed under 20 MPa and sintered at 1000°C for 1 h in air. Relative density of the former was 80 % and that of the latter was about 50 % of theoretical. MgCr2O4 powder was prepared by the co-precipitation method reported by Anderson. NiO ceramics were prepared by pressing NiO powder (99.99 pure, Rare Metallic, Co., Ltd.) under 100 MPa and sintering at 1000°C for 1 h in air. Relative density was 70 % of theoretical.

As shown in Fig. 1, sintered pellet of specimen B was contacted or powder of specimen B was adhered on polished surface of A. For pellet specimens, a polished surface of the pellet was contacted by mechanically pressing under about 0.1 MPa. For powder specimens, a slurry containing the powder and ethanol was painted on the surface of A and dried at 150°C. The thickness of powder layer was about 1 mm. Those hetero-contacts are denoted as B/A, hereafter. Surface electrical resistance of the substrate material (TiO2 or NiO) was measured at 20°C under controlled humidity with a LCR meter (Kokuyo KC-535 B) at 100 Hz. As ohmic electrodes, indium-gallium alloy was smeared to TiO2 (n-type semiconductor) and gold metal was vacuum deposited to NiO (p-type semiconductor).

Fig. 1. Schematic view of hetero-contact specimen.
Relative humidity was controlled by changing the flow ratio of dry and wet air bubbled through water at 20°C, and monitored with an adjusted humidity detector (Vaisara Inc., Humicap HM 132).

3. Results and discussion

Figure 2 shows surface electrical resistance of TiO₂ substrates under various relative humidities at 20°C. Humidity sensing characteristics of TiO₂ depended on the species of oxide in contact with TiO₂, but not on the shape of the oxides, i.e., sintered pellet or powder. It is generally accepted that the decreased surface resistance of TiO₂ under high humidity is due to ionic conduction and protons are the dominant charge carrier of the conduction.¹,² In the present system, the ionic conduction was confirmed by polarization under d.c. bias. When some materials are kept in contact with the surface of the TiO₂ substrate, the surface resistance of TiO₂ is expected to be further decreased with increasing relative humidity by the capillary condensation of water vapor at the interface. Actually, when TiO₂ ceramics or powder was contacted with the TiO₂ substrate, the humidity sensitivity was enhanced slightly. However, when the basic MgCr₂O₄ was contacted the humidity sensitivity was suppressed.

To examine generally, the effects of contact on the humidity-sensitivity of TiO₂ the humidity sensing characteristics of porous TiO₂ substrates
in contact with various metal oxide powders were measured. As a result the contacting oxides were, on the whole, classified into two groups. As shown in Fig. 3 one group of the oxides did not influence the logarithmic slope of surface electrical resistance of TiO$_2$ against humidity, such as Al$_2$O$_3$, and another group of the oxides suppressed humidity-sensitivity of TiO$_2$, such as Cu$_2$O.

The results are summarized in Fig. 4, where the ratio of humidity sensitivity (logarithmic slope of the surface resistance between 30 and 70% relative humidities that is reliable range for the humidity detector) of porous TiO$_2$ substrates with (S) and without (S$_0$) the contacting oxide were plotted against the electro-negativity of metal ions of contacting oxides. The electro-negativity is generally used as a criterion indicating acidity of an oxide. Figure 4 shows that the basic oxides with a low electro-negativity suppress the humidity-sensitivity of TiO$_2$, but neutral (or amphoteric) and acid oxides with a high electro-negativity do not affect it. From those results, it is assumed that the protons, dissociated from physisorbed water, transfer from the surface of an acid oxide to that of a basic oxide. Accordingly, a decrease in resistance of acid TiO$_2$ at high humidities would be prevented by the contact of basic oxides, as shown in Fig. 3. Figure 5 shows humidity-sensitivities of basic NiO in contact with TiO$_2$ and NiO. NiO itself and NiO/NiO was almost insensitive to humidity. However, when TiO$_2$ powder was contacted, surface resistance of NiO decreased at high humidities. It would be due to increased ionic conduction by protons transferred from acid TiO$_2$ to basic NiO surface.

From the present results, it is demonstrated that humidity sensing characteristics is suppressed for acid oxides and is enhanced for basic oxides at the interface of the acid-base heterocontacts. This would suggests the proton transfer from acid to basic surface by acid-base interaction.

References