HUMIDITY-SENSITIVE CHARACTERISTICS OF Cu-P-Y-O COMPOUNDS: ACCESS OF WATER VAPOR TO THE SURFACES OF HUMIDITY SENSORS

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Abstract A Cu-P-Y-O composite oxide compact with a specified composition (denoted as CPY) is an excellent material for humidity sensor. As for how water vapor accesses to the surfaces of a disk-shaped CPY were studied, and it was found that water vapor accessed to the surfaces of CPY mainly through the electrode layer. Also, the relation of pasty electrode material with the humidity characteristic was investigated, and it follows that the type of paste affected strongly not only the humidity characteristic but also the adhesive strength between the electrodes and the surfaces of a CPY disk.

INTRODUCTION

Much work has been performed on humidity-sensitive materials. Most of metal phosphates also show good humidity-sensing characteristics. Of inorganic phosphorous compounds, a Cu-P-Y-O composite compact (denoted as CPY) which was prepared by sintering a compact consisting of Cu3(PO4)2·3H2O and Y2O3 at 950 ºC has been reported to be an excellent material for humidity sensor elements. In general, CPY involves four crystalline phases YPO4, Y2O3, CuO, and Cu2Y2O5, and a key material for humidity-sensing is believed to be YPO4. In CPY, coexisting CuO (and/or Cu2O) also seems to play a role for lowering the resistance in the lower relative humidity range. The reaction pathway for producing crystalline substances mentioned above and the effect of sintering temperature of a CPY on the humidity-sensitive characteristics were also examined.

However, the way in which water vapor accesses to the surfaces of a disk-shaped CPY has not been revealed. In CPY sensors, electrodes are often made by screen-printing using appropriate pastes. The effect arising from the choice of pastes has not been investigated in
terms of humidity-sensitive characteristic and adhesiveness between the electrodes and the surfaces of a sensor element. In the present work, therefore, we mainly deal with those subjects.

EXPERIMENTAL

The preparative method of CPY samples and the CPY sensor elements as well as the device for measuring its electric resistance were the same as in the literature. As pasty electrode precursors, six different silver pastes (NOF, Nihon Oil and Fat; H-4161, H-4563, H-4939, H-5698, Shoei Chem.; Ohmic Ag, Demetron) and a ruthenium paste (Electro Science Lab.) were obtained commercially. Unless otherwise mentioned, silver paste H-5698 was used.

Scanning electron microscope (SEM) micrographs, and energy dispersive X-ray spectroscopy (EDX) images were obtained using a JEOL JSM-T200 and JED-2001 system.

RESULTS AND DISCUSSION

There are two possible ways for water vapor to access to the surfaces of a disk-shaped CPY humidity-sensing element: one is an immediate way in which water vapor adsorbs on the bare side plane of the element and the other is a series of ways in which water vapor primarily approaches onto the electrode planes and then diffuses through the electrode layer to the surfaces of a CPY disk. Figure 1 shows the humidity sensitivity of CPY-10-950 element, which was prepared by heating an equimolar mixture of Cu3(PO4)2·3H2O and Y2O3 at 950 °C, and that of CPY-10-950 element of which side plane was covered by epoxy resin to prevent access...
of water vapor. Clearly, no significant difference in humidity dependence of resistivity is observed between the resin-covered sensor element and uncovered one. However, difference is observed in response time: the time for covered sensor was longer than that for uncovered one (not shown).

When the electrode planes were covered by epoxy-resin (Fig.2), the resistivity became higher compared to uncovered one. When all the surfaces of the sensor element were covered, the resistivity did not change in spite that the humidity environment changed (not shown). These findings clearly indicate that water vapor accesses to the surfaces of a sensor element mainly through the electrode planes.

Figure 3a shows the scanning electron micrograph of the top surface of silver electrode of CPY-10-950 sensor. The surface is composed of interconnected hills (bright areas) and basins (dark areas). Figs. 3b and 3c show the composition images of the electrode surface.
by EDX. The EDX analysis of the electrode surface confirms that Ag exists on the hills (Fig. 3b) and Cu in the basins (Fig. 3c). Considering that the elements (Cu, Y, P) presented in the basins were the same as those of the CPY disk beneath the silver electrode layer, the basins are thought to be entrances which can lead water vapor to the surfaces of the disk. This finding is consistent with the fact that when the electrodes of CPY-10-950 were covered with resin, high resistivity and very long response time were observed.

Three CPY-10-950 sensor elements were prepared by changing the thickness of the electrode layers, and their humidity characteristics were compared. It was found that the humidity dependence of resistivity of the CPY sensor elements was similar regardless of the thickness of the electrode layers, but as for response time, that of the sensor with thicker electrode layers was longer than that with thinner electrode layers (not shown). When the electrode layer was too thin, the resistivity shifted to high side in the whole humidity range and consequently, the humidity dependence of the resistivity became different from that described above. Figure 4 depicts the scanning electron micrographs of the top surface of the electrodes with different thickness. Clearly, on the thin electrode layer, several hills are disconnected and the area of basins is large (Fig. 4a), while on the thick electrode layer, all the hills are well interconnected, but the area of basins or holes is very small (Fig. 4c). In other words, the degree of interconnection of hills and the number of holes depend on the thickness of the electrodes. In this sense, the surface shown in Fig. 4b seems to be optimum. These results
account well the difference in response time described above.

As seen in Fig. 5, the humidity-sensing characteristics of CPY-10-950 sensor elements made from different pastes H-4563, H-4939, H-5698, and NOF were similar, but those made from H-4161, ohmic Ag, and Ru paste were inferior to the former pastes in many respects. Figure 6 shows selected SEM micrographs of the top surfaces of the electrodes made from different pastes. On the electrode made from H-5698 are interconnected silver hills and basins (Fig. 6a). On the other hand, in the case of Ohmic Ag paste, the size of Ag particles in the electrodes was very small, and interconnected hills were not observed (Fig. 6b). Similar situation was also seen for the electrode made of Ru paste (Fig. 6c). A comparison of Fig. 5 and Fig. 6 indicates that the size of silver interconnected particles and the optimum number of holes seem to be crucial factors for
low resistivity and good humidity sensitivity of CPY-10-950 sensor element. In this sense, H-5698 paste seems most favorable electrode material. However, the SEM observation on silver electrode surface made of e.g. H-5698 is one of the physical features. There may be other predominant factors. For example, some binding agents are contained in the pastes, and so there may be effects due to insulating layers formed by reactions of such agents and the constituents of a CPY.

CPY sensor elements, which were made from different pastes H-4563, H-4939, H-5698, and NOF were used repeatedly in the whole humidity range. In CPY-10-950 sensor made from H-5698, and the humidity dependence of resistivity was well duplicated, and besides good jointing between the electrodes and the surfaces of the CPY disk was also confirmed. Regarding to the adhesion, in CPY sensors made from other pastes, the resistivity tended to increase when they were subjected to cycle exposures to the whole humidity range.

REFERENCES