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Improvement of response characteristics of TiO_2 humidity sensors by simultaneous addition of Li_2O and V_2O_5

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Abstract

Porous TiO_2 ceramics were prepared by adding various amounts of Li_2O and V_2O_5 and the humidity sensitivity of the resulting ceramics was investigated by means of electrical measurements, scanning electron microscopy and mercury intrusion porosimetry. Simultaneous addition of Li_2O and V_2O_5 to TiO_2 enabled sintering at temperatures as low as 700 °C and also decreased the impedance of the ceramics. Furthermore, in the ceramics including these additives simultaneously, excellent humidity sensitivity as well as good response characteristics were observed. The microstructures of these ceramics depended on the firing temperature and the amount and ratio of Li_2O/V_2O_5, and optimum humidity sensitivity was observed for the sample including both 0.25 mol% Li_2O and 0.75 mol% V_2O_5 fired at 700 °C. These results indicated that the humidity sensitivity and its response characteristics were closely related to the microstructure, and that improving the uniformity of microstructure is important for improving humidity sensitivity and its response characteristics.

Keywords: D. TiO_2; E. Sensors; Hysteresis

1. Introduction

Ceramic humidity sensors are in widespread use for humidity measurement and control in harsh environments such as high-humidity and high-temperature atmospheres and in living spaces. This is because ceramics offer advantageous chemical and physical stability, which is inherent to ceramic materials. However, the humidity-sensing mechanisms of ceramic humidity sensors are wide-ranging, and popular humidity sensors measure humidity by detecting the change in resistance associated with the adsorption and desorption of water [1–3].

Among these ceramic humidity sensors, titanium oxide (TiO_2) has been used for producing commercial ceramic humidity sensors. Nevertheless, when TiO_2 is intended to be used for humidity sensing, higher mechanical strength and lower electric resistance are required. So far, efforts have been made to satisfy these requirements such as improvement of mechanical strength by adding Li_2O and reduction of resistance by adding V_2O_5 or Nb_2O_5 [4,5]. However, existing sensors have not yet fully satisfied these requirements; furthermore, low cost and high performance such as no hysteresis in humidity sensitivity are also required. The modification of humidity sensitivity for TiO_2 ceramics has been studied for many years [6–9]. For example, Katayama et al. found that the humidity sensitivity of TiO_2 ceramics was greatly improved by the addition of vanadium oxide, and that both the addition of phosphor oxide and aging in a humid atmosphere stabilized the humidity sensitivity of TiO_2 ceramics [10]. In the previous paper, we revealed that the simultaneous addition of Li_2O and V_2O_5 decreased the impedance and hysteresis in humidity sensitivity of TiO_2 humidity sensors. However, the reason for the change in sensitivity by adding these chemicals has not been investigated.

In this study, with the goal of developing a humidity sensor with no hysteresis, we studied the dependence of the pore structure in TiO_2 ceramics on the humidity sensitivity.

2. Experimental procedure

As starting materials, TiO_2 (rutile), Li_2CO_3, and V_2O_5 powders with a purity of 99.9% (Wako Pure Chemical

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Industries, Ltd.) were used. The starting materials had been weighed to the chemical composition of $Ti_{0.99}V_{0.01-x}Li_xO_2$ (x = 0–0.01), $Ti_{0.995}V_{0.00375}Li_{0.00125}O_2$, and $Ti_{0.98}V_{0.015}Li_{0.005}O_2$, and then mixed in ethanol. The mixture was dried and calcined at 700 °C for 1 h in the atmosphere. The resulting calcined mixtures were ground in an agate mortar and then shaped into tablets (10 mm diameter, 1–2 mm thick) under a pressure of 50 MPa. The tablets were fired at 700–1000 °C for 1 h in the atmosphere. Specifically, they were heated at a rate of 10 °C/min, kept at a given temperature for a given time period, then left to cool in the furnace. The density of the fired samples was calculated from their volume and mass.

Their microstructures were observed using a SEM and the specific surface area was measured by the BET method. Pore volume and the pore size distribution of the fired samples were measured by mercury intrusion porosimetry.

The surfaces of the samples were polished with #2000 abrasive paper, and on one of the flat surfaces of each tablet sample two 6 mm × 2 mm Au electrodes with an inter-electrode distance of 0.4 mm were formed by vapor deposition. The impedance of the elements was measured by applying a 1-kHz alternating current while changing the humidity of the atmosphere (20–90% RH) using various saturated salt solutions or a commercially available constant temperature and humidity chamber. In addition, response characteristics of humidity sensitivity were measured in a commercial constant temperature and humidity chamber according to the following procedure. (1) After humidity had been kept at 60% for 10 min, the impedance of the samples was measured. (2) Humidity was sequentially increased to 70%, 80%, and 90% at a rate of 10% RH/30 min and the impedance was measured after 10 min of humidity stabilization. (3) Humidity was decreased from 90% to 60% in the same way as above and the impedance was also measured likewise.

3. Results and discussion

Fig. 1 shows the relative density of the samples including various molar ratios of Li_2O/V_2O_5 although the total amount of additives was kept constant at 1.0 mol%. In the figure, TiO_2, Li_2O, and V_2O_5 are expressed as T, L, and V, respectively. The densities of these samples are similar, irrespective of the molar ratio of Li_2O/V_2O_5, and increase with increasing firing temperature. The samples fired at 650 °C or below were fragile, and could not be used for further study. Of the samples, those fired at 700 °C had the lowest density, and were expected to have high porosity.

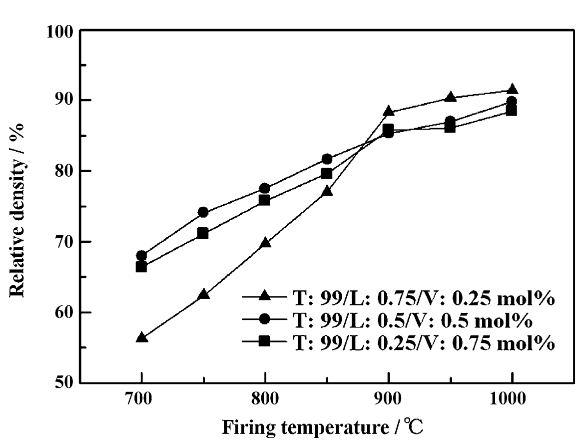

Fig. 1. Effect of firing temperature on relative densities of various samples.

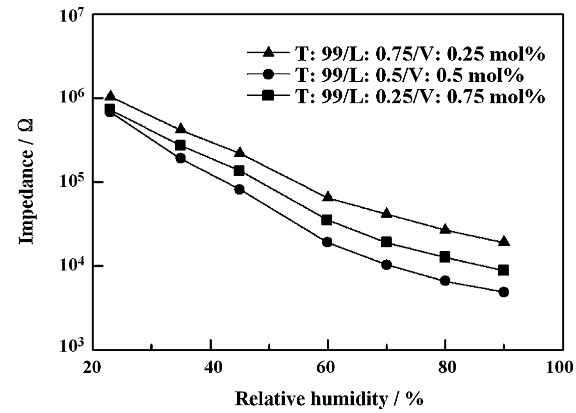

Fig. 2. Humidity sensitivity of various samples fired at 700 °C.

Fig. 2 shows the humidity sensitivity at 25 °C of samples that contained the different compositions as shown in Fig. 1 and that were fired at 700 °C. The impedance varies according to the

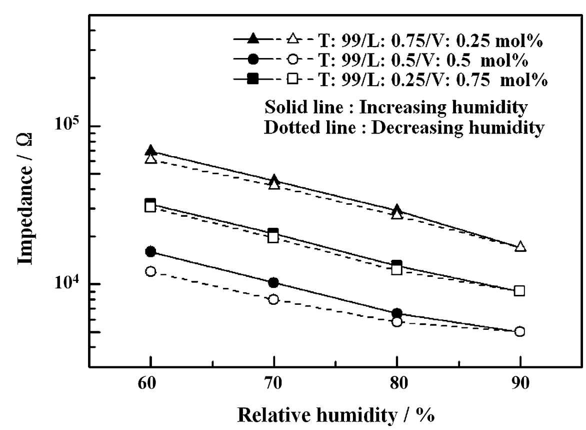

Fig. 3. Response characteristics of humidity sensitivity of various samples.

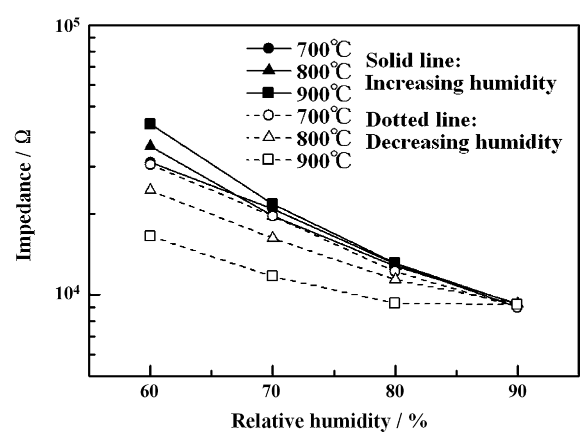

Fig. 4. Response characteristics of humidity sensitivity of T: 99/L: 0.25/V: 0.75 mol% samples fired at 700–900 °C.

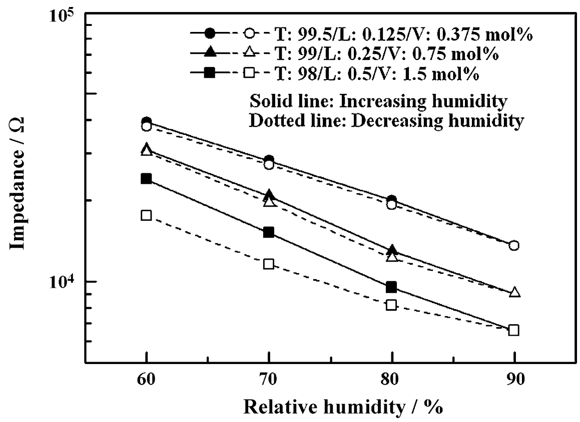

Fig. 5. Response characteristics of humidity sensitivity of the samples with various total amounts of additives.

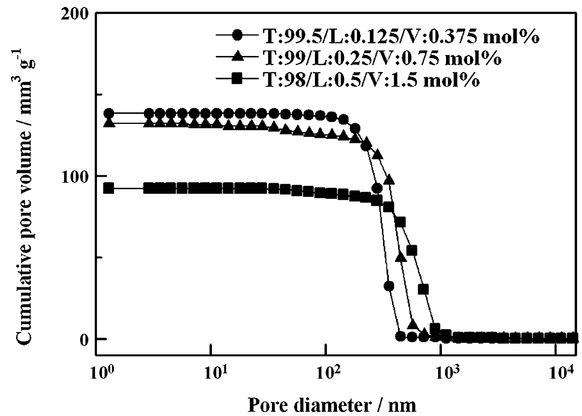

Fig. 7. Pore size distribution of the samples as shown in Fig. 5.

molar fraction of Li_2O/V_2O_5 and decreases with increasing relative humidity. Fig. 3 shows the response characteristics in humidity sensitivity of the samples shown in Fig. 2. Almost no hysteresis in response was observed only in the sample with 0.25 mol% Li_2O and 0.75 mol% V_2O_5, while the other two samples exhibited small hysteresis. The previous study revealed that no hysteresis was observed in the sample with only V_2O_5 added although its impedance was a little higher. From these results, the addition of V_2O_5 seemed to favorably affect the response characteristics.

Fig. 4 shows the effect of firing temperature on the response characteristics of samples with a constant ratio of Li_2O/V_2O_5 of 1:3. Larger hysteresis was observed for samples fired at higher temperatures: that is, lower firing temperature resulted in good response characteristics. The specific surface area of the samples decreased with increasing firing temperature, and the actual values were 2.64, 2.39 and 1.23 $m^2\,g^{-1}$ for the samples prepared by firing at 700, 800 and 900 °C, respectively. Needless to say, adsorption sites for water molecules are considered to increase with surface area, and therefore, these results indicated that firing at 700 °C would be the best for preparing humidity sensors in this study. Fig. 5 shows the effect of amounts of additive on the response characteristics of the samples fired at 700 °C while the concentration of additive was kept constant at a Li_2O to V_2O_5 ratio of 1:3. The impedance of the samples slightly decreased with increasing amounts of additive, and the sample including 2.0 mol% additive shows larger hysteresis in humidity sensitivity, while the other two samples exhibit little hysteresis.

Fig. 6 shows SEM micrographs of the same samples as shown in Fig. 5. The grain size of these samples became larger as the amount of additive increases. In the samples including 0.5 and 1.0 mol% additives, homogeneous microstructures composed of uniform grains and pores are observed, while in the sample including 2.0 mol% additive, heterogeneous microstructures with anisotropic grains and some aggregation were observed. The specific surface areas of these samples were 4.37, 2.64 and 2.18 $m^2\,g^{-1}$ for the samples including 0.5, 1.0 and 2.0 mol% additives, respectively. Although the specific surface area decreased with increasing amount of additive, larger voids were observed in the sample including 2.0 mol% additive. This may due to the anisotropic shape of the grains, but the detailed reason is unclear.

Fig. 7 shows the pore sizes and cumulative pore volumes in the same samples as shown in Fig. 5. Pore size increases and the volume decreases with increasing amounts of additives. The average pore diameters of the samples including 0.5, 1.0 and 2.0 mol% additives are 143, 206 and 270 nm, which were calculated from porosimetry. Furthermore, no pores with diameter 10 nm are detected in all samples, while only in the

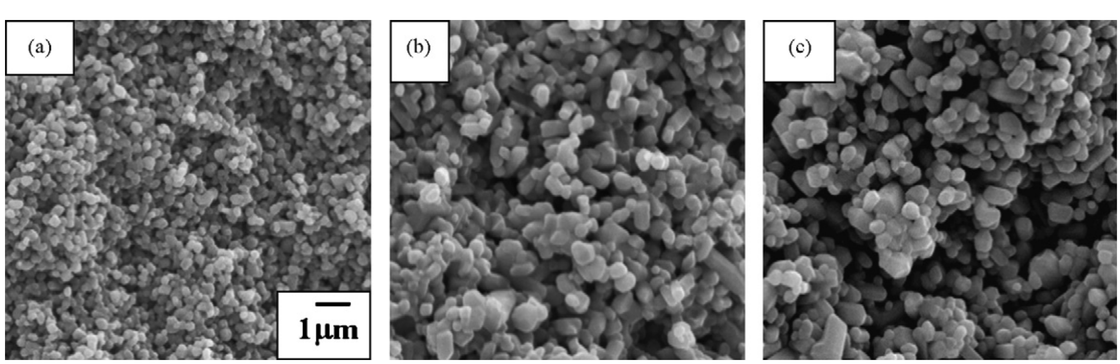

Fig. 6. SEM micrographs of various samples fired at 700 °C. (a) T: 99.5/L: 0.125/V: 0.375 mol%, (b) T: 99/L: 0.25/V: 0.75 mol% and (c) T: 98/L: 0.5/V: 1.5 mol%.

sample including 2.0 mol% additive, small amounts of pores with diameter more than 1000 nm are detected. As shown in Figs. 3–5, the sample including 2.0 mol% additive, which shows larger hysteresis in humidity sensitivity, possesses relatively large pores than those of the other two samples, which exhibit little hysteresis. These results indicated that response characteristics in humidity sensitivity are affected by pore structure, but further study will also be required. We intend to continue investigating the relationship between response characteristics and microstructures including pore structure.

4. Conclusions

Humidity sensitivity of porous TiO_2 ceramics containing both Li_2O and V_2O_5 was investigated to achieve a humidity sensor exhibiting no hysteresis in response characteristics. Simultaneous addition of Li_2O and V_2O_5, and firing at lower temperatures such as 700 °C, largely changed the microstructure of the ceramics with uniform grain size, and also resulted in higher mechanical strength than that achieved by separate addition of each additive. The impedance of TiO_2 ceramics including both Li_2O and V_2O_5 was measured for various levels of atmospheric humidity, and the results indicated that simultaneous addition decreased impedance to suitable orders of magnitude and largely improved response characteristics. Especially, for the sample including both 0.25 mol% Li_2O and 0.75 mol% V_2O_5 fired at 700 °C, almost no hysteresis in humidity sensitivity cycle was observed.

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