Effect of Li$^+$ doping on ZrO$_2$–TiO$_2$ humidity sensor

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Received 26 April 1998; received in revised form 28 September 1998; accepted 29 September 1998

Abstract

Humidity sensors are widely used in domestic and industrial environments. The authors have investigated 0.5ZrO$_2$–0.5TiO$_2$ ceramic for its humidity sensing electrical properties at room temperature. The bulk humidity sensors were prepared by the conventional ceramic method. Salt doping with Li$^+$ ions is found to increase the sensitivity by an order of two, and also improves the linearity. X-ray and scanning electron microscopy (SEM) investigations have established that ZrTiO$_x$ phase grows at a sintering temperature of 1200°C. The abnormal behaviour in humidity sensing characteristics for samples sintered at 1150°C may be due to micropores in between the grains.

Keywords: Humidity sensor; Zirconium titanate; Salt doping

1. Introduction

In recent years, sensors have become an integral part of all technological advances. Humidity sensors are greatly in demand for monitoring and controlling various domestic and industrial surroundings [1,2]. Water vapour is present in various concentrations in most surroundings. Because of its unique properties, water vapour greatly influences all living organisms and materials [3]. Thus monitoring and controlling humidity becomes necessary for high product quality and human comfort. Different solid state humidity sensors are available on the market, but research is still going on in order to obtain highly sensitive, selective, reliable sensors which are cheap, compact and microprocessor compatible. The sensors based on resistance and capacitance change are most widely investigated because of their small size and compatibility with electronic circuitry. It is almost impossible for a single humidity sensor to satisfy the requirements for widespread applications, therefore most of the sensor research work is carried out for a particular application.

Ceramic humidity sensors are known for superior sensing properties compared to other materials because of their high mechanical strength, chemical resistance and because they are thermally more stable. Some ceramic humidity sensors show ageing behaviour [4], but this can be overcome by repeated heat cleaning. The authors have investigated ZrO$_2$–TiO$_2$ ceramic for its humidity sensing properties at room temperature, because it has been reported that this is a good catalyst and humidity sensitive material [5,6]. It has also shown excellent stability with time, and hence does not require a heat cleaning cycle. Salt doping in ceramics enhances the humidity sensitivity, therefore, Li$^+$ doping has been used to improve sensing properties.

2. Experimental

2.1. Sample preparation

The device was made using the conventional ceramic preparation method. The basic compositions were prepared using 50% mol ZrO$_2$ (Aldrich, 99.9%) and 50% mol TiO$_2$ (Aldrich, 99.9%) analytical grade chemicals. Lithium was doped in the base material by adding 2 and 5% mol LiOH.H$_2$O reagent grade chemical. Polyvinyl alcohol (PVA) was added in 2% weight as an organic binder. The chemicals were weighed in appropriate molar ratios and mixed and ground using an electric agate pestle mortar for 24 h, with ethanol as a
medium. The mixed powder was dried and pressed in circular disc form (diameter 5 mm and thickness 0.5 mm) using hydraulic pressure at a pressure of 4 tons em⁻². These pellets were then sintered on a high purity alumina plate support at temperatures ranging from 1000°C to 1300°C, in 50°C steps. The heating rate was 10°C min⁻¹ up to 600°C. The pellets were kept at 600°C for 30 min in order to remove the binder. The heating rate from 600°C to final sintering was 8°C min⁻¹. After sintering at the final temperature, the samples were furnace cooled for 2 h. Thin gold electrodes in the capacitive geometry were fabricated on both sides of the pellets using the thermal evaporation method.

2.2. Characterisation

The crystal phases in the pellets were investigated by the X-ray powder diffraction method, using the model Rotaflex RU-200B, Rigaku, Japan. The surface morphology was studied using a scanning electron microscope (SEM), using the Philips SEM-525M model. Different saturated salt solutions were used to obtain different relative humidity (RH) atmospheres (5–95% RH) in a closed chamber. Since the d.c. resistance measurement shows charging of the electrode because of the H⁺ ion accumulation, only a.c. measurements at 100 Hz were carried out on the sample. The impedance was measured with the help of a lock-in amplifier, model 124A, EG&G, USA (see Fig. 1). The sensor impedance is very high at low humidities, making the signal very low, therefore the signal to noise ratio is very poor. To improve the signal to noise ratio, a lock-in amplifier was used.

3. Results and discussion

3.1. Electrical

The relative humidity–impedance characteristics at 25°C of pure ZrO₂–TiO₂ pellets sintered at different temperatures are shown in Fig. 2. It has been found that the samples sintered at 1050°C and 1150°C show high sensitivity (R₉₀%/R₀₉₅% > 10²) and samples sintered...
at other temperatures show significant sensitivity only in the range 60–95% RH. Although samples sintered at 1050°C show the highest sensitivity, still they can not be used for sensor purposes, since their characteristics are not linear in the whole working range, i.e. 20–95% RH. The samples sintered at 1150°C show low sensitivity, but because of their better linearity in the working range, can be used for sensor purposes.

It is well known that salt doping in humidity sensitive ceramic materials enhances the sensitivity [7]. Since pure ZrO₂–TiO₂ samples show less sensitivity, this material has been doped with lithium salt to enhance the sensitivity. The relative humidity–impedance characteristics at 25°C of ZrO₂–TiO₂ (2% mol Li⁺ doping) ceramic pellets with different sintering temperature are shown in Fig. 3. It has been observed that the samples sintered at 1000°C and 1150°C show very high sensitivity (R₂%₅₀/R₃₅₉% > 10⁵), whereas all other samples are insensitive to humidity over a large range, i.e. 5–80% RH. Lithium doping of 2% mol in ZrO₂–TiO₂ ceramic has enhanced the sensitivity by two orders of magnitude. The increase in sensitivity with Li⁺ doping may be due to high charge density of Li⁺ ions, which highly polarise/dissociate the adsorbed water molecules. This in turn will provide more free H⁺ or H₂O⁺ ions for conduction, thus decreasing impedance. The highest sensitivity and the best linear behaviour has been achieved in samples sintered at 1000°C. Thus, in this case the best sensing characteristics are obtained in the samples sintered at a temperature 150°C lower than that of undoped samples. Further increase in doping up to 5% mol caused very little enhancement in the sensitivity, although improvement in linearity has been observed in impedance variation for samples sintered at 1000°C (Fig. 4). An abnormally high sensitivity is observed for samples sintered at 1150°C.
3.2. Structural

The scanning electron micrographs of the surface of ZrO$_2$–TiO$_2$ ceramic pellets, doped with Li$^+$ (2% mol) and sintered at different temperatures ranging from 1000 to 1300°C, are shown in Fig. 5. The X-ray powder diffraction of the same samples is shown in Fig. 6. There are only ZrO$_2$ (monoclinic) and TiO$_2$ (rutile) phases detected for samples sintered at 1000°C. The SEM micrograph (Fig. 5(a)) of these samples shows a highly porous structure with grain size of less than 2 μm. This porous structure is essential for rapid diffusion of water vapour into or out of the materials. As the sintering temperature is increased up to 1100°C, the grain size increases, while the open porosity decreases (Fig. 5(a)–(c)). It has also been observed that the number of pores with smaller diameters reduces, whereas the number of pores with bigger diameters increases with increase in temperature. It becomes easier for water vapour to diffuse into or out of relatively bigger pores, but it is difficult for water molecule to condense in bigger dimension pores [8]. Thus the amount of water vapour condensed is more in the case of samples sintered at 1000°C. Therefore, sensitivity should be highest for these samples, something which was also observed in Fig. 3. Samples sintered at 1150°C show large grain size, i.e. about 2–4 μm (Fig. 5(d)), but here no new phase formation is detected in X-ray diffraction. Hummel and Tien [9] have indicated the possibility of forming a liquid phase in a lithium–titania mixture at 1200°C. They also say that there is little doubt about eutectic reactions above 1230°C, at which temperature 1% mol Li$_2$O would lead to the formation of an appreciable quantity of low viscosity liquid, which would promote crystal growth and inhibit sintering. In the present experiment the authors have also observed large grains of TiO$_2$ in the presence of lithium. Since the growth of rutile crystals is vigorously promoted by the addition of lithium oxide, the regular geometry of the crystallites is lost, and the authors have observed the grains of TiO$_2$ to have an irregular shape, this leaves micropores between the grains (Fig. 5(d)).
Since it has been reported that pores with smaller diameters, between 1 to 30 nm are necessary for good sensitivity at low humidity [8,10,11], therefore micropores for samples sintered at 1150°C enhance their sensitivity. Samples sintered at 1200°C show a highly dense structure with very large grains (~ 2–6 μm) of ZrTiO₄ orthorhombic phase (Fig. 5(e)). Because of the low porosity and higher pore diameters, it is insensitive in the large humidity range (5–80% RH). Further increase in the sintering temperature, up to 1300°C does not show any significant change in microstructure of the ceramic (Fig. 5(f)), therefore, no variation in the sensitivity was observed.

4. Conclusions

It has been observed that Li⁺ doping in ZrO₂–TiO₂ enhances the humidity sensitivity (R₂%/R₉5%) by two orders of magnitude, and also improves the linearity of the characteristics. It also reduces the sintering temperature from 1150°C to 1000°C. The highest sensitivity, greater than 10⁶, was observed for 5% Li⁺ doped samples sintered at 1000°C for 2 h. The higher sensitivity for samples sintered at 1000°C is due to high open porosity. The abnormally high sensitivity of samples sintered at 1150°C is because of the presence of micropores, which were created by the growth of TiO₂ crystallites, with irregular shape and without sharp facets. This growth was due to Li₂O doping. The ZrTiO₄ phase, which was detected above 1200°C sintering temperature, reduces the sensitivity because of absence of the micropores.

Acknowledgements

One of the authors is thankful to The Council of Scientific and Industrial Research for financial assistance.

References

Biographies

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