JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 8, No. 3, June 2006, p. 1001 - 1003

The magnetic oxide semiconducting ceramics as gas sensor

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Magnesium ferrite doped with manganese, a n–type semiconducting oxide with an inverse spinel structure has been used as a gas sensor to sensitivity detection gases. The samples were obtained by selfcombustion method. Scanning electron microscopy (SEM) was used to investigate the morphology and pore structure of the sensing ferrite. Further, the sensing sample were characterized by X-ray diffraction (XRD) to identify the changes in their crystallographyc structures. The relation between structure of the films and gas sensitivity is discussed.

(Received March 15, 2006; accepted May 18, 2006)

Keywords: Ceramics, Magnetic oxide, Gas sensor

1. Introduction

Metal oxide sensors have been utilized for several decades for low-cost detection of combustible and toxic gases. However, issues with sensitivity, selectivity and stability have limited their use, often in favor of more expensive approaches. Recent advences in nanomaterials provide the opportunity to dramatically increase the response of these materials, as their performance is directly related to exposed surface volume. The recent availability of various metal oxide materials in high-surface-area nanopowder form, as well as implementation of newly developed nanofabrications techniques, effer tremendous opportunities for sensor manufactures [1].

Nanostructured materials present new opportunities for enhancing the properties and performances of gas sensors because of the much higher surface-to-bulk ratio in nanomaterials compared to coarse micrograined materials [2-4]. In addition to the enhanced sensitivity demonstrated by the nanostructured sensors, the sensors responded more quickly, a distinct advantage for certain application.

However, it should be noted that the effects of grain size are often complicated by other factors, in particular those related to heat treatement of the sensor during manufacturing. As the result of considerable in-house research, a significant body of knowledge now exists within the company regarding the effects of composition and microstructure on sensor performance [5].

In our previous papers [6,7] we reported on doped Mg based ferrites and nickel ferrites used as humidity and gas sensors, respectively.

In the present study, magnesium ferrite doped with manganese and prepared by self-combustion method was investigated as gas sensor. Grain size and pore structure have a major effect on the properties in polycrystalline materials and their full characterization should be the first step in the study of materials. Also, the microstructure has a major role in the performance of a ceramic sensor. We examined the microstructures of the end products by scaning electron microscopy (SEM) to obtain quasi-three dimensional information on the grain shape, size and pore sizes. It was investigated the variation of the electrical resistance in the presence of five gases: ethyl alcohol (C_2H_5OH), methane (CH_4), liquefied petroleum gas (LPG), formaldehide (CH_2O) and ammonia (NH_4). Detailed results on the microstructure and the gas sensing propertiers are given in the paper.

2. Experimental

The chemical formula of the investigated ferrite composition is $MgMn_{0,2}Fe_{1,8}O_4$. The samples were prepared by self combustion method using metal nitrate and ammonium hydroxide as raw materials. The coprecipitation of the metal hydroxides takes place into a colloidal medium. By a quick combustion takes place the calcination of metal hydroxides and the reaction between metal oxides. The obtained powder was pressed into disk shapes and subjected to thermal treatment at 1000 ^oC for 30 minutes. The microstructure and phase composition were performed by SEM and X-ray powder difraction (XRD). Average grain size was determined by the linear intercept technique from SEM micrograph on fracture surface.

The disk samples were silvered in order to measure the electrical resistance. The schematic of the sensor assembly is shown in Fig. 1. Gas sensing properties were investigated at various operating temperatures from 300 to 500 ^oC. The experiments were performed with five test gases: ethyl alcohol (C_2H_5OH), methane (CH_4), liquefied petroleum gas (LPG), formaldehide (CH_2O) and ammonia (NH_4). The sensitivity, S, is defined as the ratio:

$$S = \frac{\Delta R}{Rg} = \frac{|Ra - Rg|}{Rg} , \qquad (1)$$

where R_a and R_g are the sensor resistances in air and in presence of the test gas, respectively.

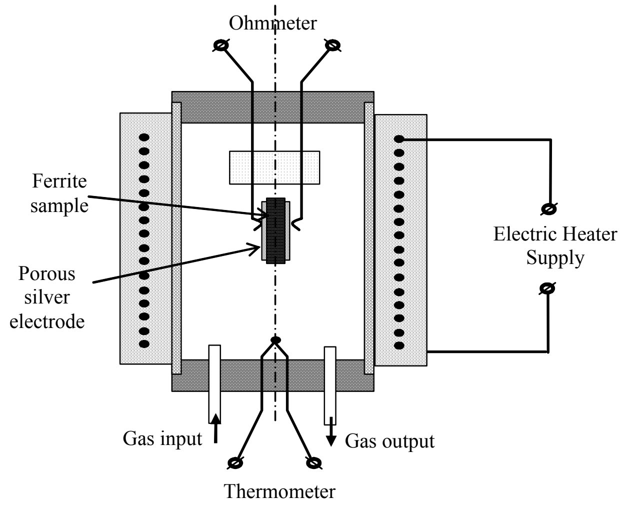

Fig. 1. The assembly for measuring the gas sensitivity of the sample.

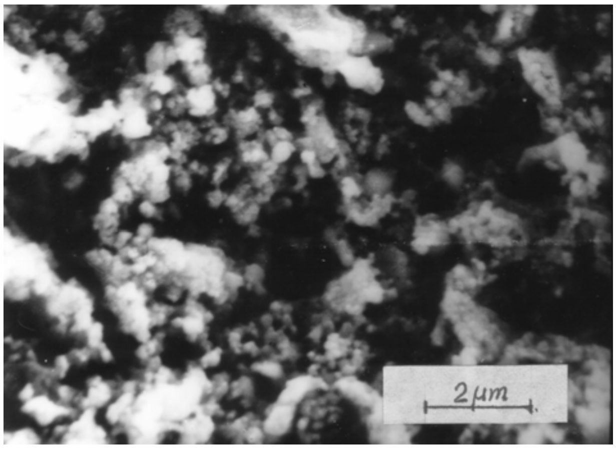

Fig. 3. SEM micrograph for the ferrite $MgMn_{0,2}Fe_{1,8}O_4$ treated at 1000 ^0C for 30 minutes.

3. Results and discussion

Fig. 2 shows the powder X-ray diffractogram for the sample treated at 1000 °C in air for 30 minutes. All the peaks belong to the spinel ferrite. No other separate phase oxides could be identified by X-ray diffraction. The lattice constant was found to be 8.366 Å.

Scanning electron micrographs for the sample is presented in Fig. 3. This figure shows that sample consists primarily of irregularly shaped of 1 to 6 μm aggregates of fine (0.1 μm) particles. It can be seen that the crystallite size of the sample is extremely fine, on the order 100 to 500 nm. The material is characterized by high intergranular porosity (about 40%). The bulk density was evaluated to be 2.05 g/cm^3. Many large and small pores are present in all material.

The gas sensitivity depends largely on the microstructure, such as grain size, surface area and pore size.

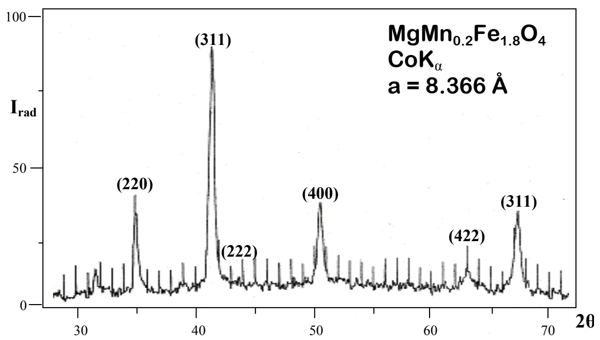

Fig. 2. X-ray diffractogram for the studied sample.

It was investigated the temperature variation of the electrical resistance (Fig. 4). The investigation was limited to the temperature interval of 300 to 500 °C. The log R_a vs. 1000/T (K^{-1}) graph shows a linear decrease of the log R_a with increasing the temperature. In the investigated temperature interval, R_a decreases by two orders of magnitude. The increase in the conductivity with temperature must mainly regarded as due to the thermally activated mobility of the carriers (electrons or holes) rather than to a thermally activated generation of these. The value of the activation energy (0.5 eV) is in agreement with those reported for other ferrites [6].

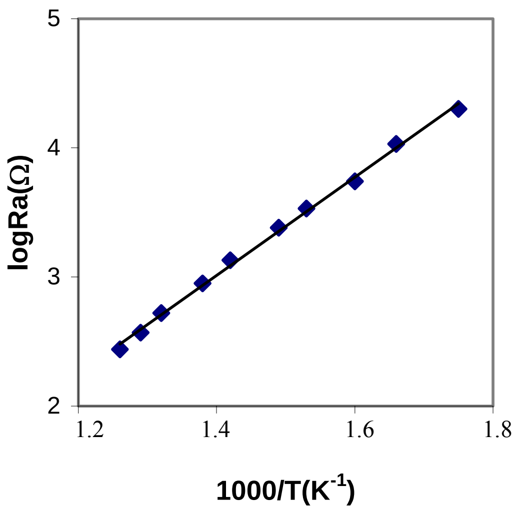

Fig. 4. Log R_a vs.1/T for studied sample.

Fig. 5 shows the gas sensing measurements for ethyl alcohol (C_2H_5OH), methane (CH_4), liquefied petroleum gas (LPG), formaldehide (CH_2O) and ammonia (NH_4) at various temperatures between 300 and 500 °C. It is clear from the graph that the sensitivity of the ferrite to LPG is the best, whereas the ferrite is almost insensitive to ammonia. As expected the sensitivity increases with increasing the operating temperature and reaches a maximum value around 450 °C and decreases further with temperature. The maximum sensitivity to ethanol, formaldehide and methane is much lower, around 400 °C. Usually, the gas sensing mechanism depends on the work temperature, because this mechanism is thermally activated [4].

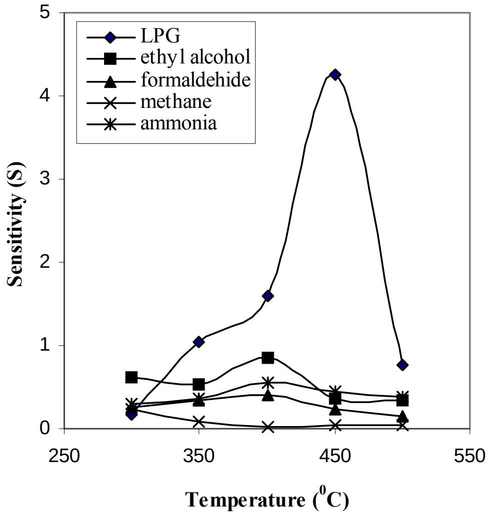

Fig. 5. Gas sensing of the ferrite.

4. Conclusion

Sensitivity studies on $MgMn_{0,2}Fe_{1,8}O_4$ ferrite for LPG, ethyl alcohol, formaldehide, methane and ammonia have shown that the electrical resistivity of this ferrite, prepared by selfcombustion, is more sensitive to LPG and its sensitivity depends on the temperature.

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