NANOSTRUCTURED THICK FILMS BASED ON SPINEL CERAMICS FOR MULTIFUNCTIONAL SENSOR DEVICES

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ABSTRACT

Nanostructured temperature and humidity-sensitive thick-film structures based on spinel-type semiconducting and dielectric ceramics of different chemical composition $Cu_{0,1}Ni_{0,1}Co_{1,6}Mn_{1,2}O_4$ (with p^+-types of electrical conductivity), $Cu_{0,1}Ni_{0,8}Co_{0,2}Mn_{1,9}O_4$ (with p-types of electrical conductivity) and insulating (i-type) $MgAl_2O_4$ ceramics were fabricated and studied. It is shown that temperature-sensitive thick films possess sensitivity in the region from 298 to 358 K and humidity-sensitive thick films are sensitive from 40 to 98 %. Obtained thick-film structures can be successfully applied for integrated temperature-humidity sensors of environmental monitoring and control.

Key words: nanostructure, multilayers, sensor, spinel, thick films

INTRODUCTION

The simultaneous temperature (T) and relative humidity (RH) control consists in principally different sensitivities of monitored solid-state system to thermally- and moisture-activated environmentally-induced processes [1]. The basis functioning principle of T-measuring systems are grounded, as a rule, on some changes in their physical properties, such as electrical conductivity, resistance, capacity, optical absorption, magnetic susceptibility etc. stimulated by ambient temperature variations. Despite time delaying in system response on these variations caused by relative durability of temperature-influenced effects, the controlled parameter can be determined finally with a high accuracy. In contrast, the RH measurements are based on changes in physical properties of solid bulk or surface produced by absorbed water. The greater amount of absorbed water molecules, the better exploitation sensitivity of RH-measuring solid systems can be achieved.

To join both T- and RH-measuring working cycles, the combined resolution built on independent temperature determination for conventional RH-sensitive functional element and, vice versa, – humidity determination for conventional temperature-sensitive element, – was proposed. The first approach

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was typically applied to perovsite-type thick films like to $BaTiO_3$ [2]. Only one work represented the second approach and performed in Engineering Research Centre for Functional Ceramics of Huazhang University of Science and Technology (China) [3] should be mentioned as the most essential scientific achievements in the field of integrated temperature and humidity-sensitive sensors.

The use of spinel-based $NiMn_2O_4$-$CuMn_2O_4$-$MnCo_2O_4$ manganites with negative temperature coefficient (NTC) resistance for fabrication of disc-type NTC thermistors and humidity-sensitive $MgAl_2O_4$ by means of conventional ceramic technology was shown by us earlier [4-6]. However, applications in modern microelectronics (temperature and humidity sensors, fire detectors, power-sensing terminations, temperature-compensating attenuators, etc. [7]) require obtaining these materials in thick-film performance.

The well-known advantages of screen-printing technology revealed in high reproducibility, flexibility, attainment of high reliability by glass coating as well as excellent accuracy, yield and interchangeability by functional trimming are expected to be very attractive now, for new-generation sensing electronics [7]. No less important is the factor of miniaturization for developed thick-film elements and systems, realized in a variety of their possible geometrical configurations. Thus, the development of high-reliable nanostructured thick films and their multilayers based on spinel-type compounds for environmental sensors operating as integrated T-RH sensors are very important task [8-10].

Thick-film performance of mixed spinel-type manganites restricted by $NiMn_2O_4$-$CuMn_2O_4$-$MnCo_2O_4$ concentration triangle has a number of essential advantages, non-available for other ceramic composites. Within the above system, the fine-grained semiconductor materials possessing p^+-type $Cu_{0.1}Ni_{0.1}Mn_{1.2}Co_{1.6}O_4$ and p-type $Cu_{0.1}Ni_{0.8}Mn_{1.9}Co_{0.2}O_4$ conductivity can be easily prepared. So, a real possibility to prepare integrated multilayer thick-film spinel-type structures for principally new device application. In addition, the prepared multilayer thick-film structures involving semiconductor $NiMn_2O_4$-$CuMn_2O_4$-$MnCo_2O_4$ and insulating i-type $MgAl_2O_4$ spinels can be used as integrated T/RH environmental sensors with rich range of exploitation properties.

The aim of this work is development of T/RH-sensitive thick-film structures for ecological environment control and monitoring.

EXPERIMANTAL

Bulk thermistor ceramics were prepared by a conventional ceramic processing route using reagent grade copper carbonate hydroxide and nickel (cobalt, manganese) carbonate hydroxide hydrates. [11]. $Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$ ceramics were sintered at temperature 1040 °C during 4 hours,

$Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ ceramics were sintered at 920 °C during 8 hours, then 1 hour at 1200 °C and 920 °C during 24 hours.

Bulk $MgAl_2O_4$ ceramics were prepared via conventional sintering route as was described in more details elsewhere [6, 12]. The pellets were sintered in a special regime with maximal sintering temperature of 1300 °C during 5 h.

Temperature sensitive $Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$/ $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$-based pastes were prepared by mixing powders of basic ceramics (sintered bulk ceramic discs were preliminary crushed, wet-milled in isopropyl alcohol medium and dried) with ecological glass powder, Bi_2O_3 (inorganic binder) and an organic vehicle (contained organic binder and organic solvent). Thus, the two thermistor pastes and one dielectric paste on the basis of the spinel-type ceramics were obtained (*Table 1*).

Table 1 – Composition of T/RH sensitive pastes

Based paste	Paste constituents, % mass			
	Basic ceramics	Bi_2O_3	Ecological glass	Organic vehicle
$Cu_{0,1}Ni_{0,1}Co_{1,6}Mn_{1,2}O_4$/ $Cu_{0,1}Ni_{0,8}Co_{0,2}Mn_{1,9}O_4$	72.8	2.9	2.9	21.4
$MgAl_2O_4$	58	4	8	30

The prepared pastes were printed on alumina substrates (Rubalit 708S) with Ag electrodes using a manual screen-printing device equipped with a steel screen. Then thick films were fired in furnace PEO-601-084 at 850 °C (the temperature-time firing schedule was similar to that, applied for the metallization of dick-type thermistors).

The insulating (i-type) paste was printed on alumina substrates with Ag electrodes and previous formed temperature-sensitive (p-type) thick-film layer. From above of thick film, the p^+-conductive paste electrodes were formed for study of electrophysical properties of humidity-sensitive thick-film elements. Then these structures were fired in furnace.

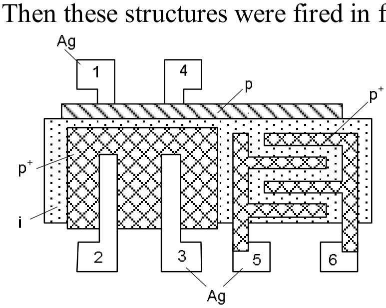

Fig. 1. Topological scheme of T/RH-sensitive thick-film structures

For investigation we used one-layered p-conductive $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$, p^+-conductive $Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$ thick films, double-layered p-p^+ thick-film structure, i-type $MgAl_2O_4$ thick-film formed on substrate with Ag-electrical contacts and integrated T/RH-sensitive thick-film sensor structure (last see in the topological scheme on *Fig. 1*).

The topology of the obtained thick films was investigated using 3D-profilograph Rodenstock RM600. The electrical resistances of T-sensitive thick films were measured with precise digital multimeters using temperature chambers MINI SABZERO, model MC-71 and HPS 222. The temperature constant B for these thick films was calculated according to the equation:

$$B = 2.3026 \cdot \log\left(\frac{R_1}{R_2}\right) \cdot \frac{T_1 \cdot T_2}{T_2 - T_1}, \qquad (1)$$

where R_1 and R_2 were corresponding resistance at T_1 = 25 °C and T_2 =85 °C. accordingly.

The RH-sensitivity thick films based on $MgAl_2O_4$ ceramics is determined by dependence of electrical resistance R on RH of environment.

The electrical resistance of the studied samples was measured in the heat and moisture chamber PR-3E "TABAI" at temperatures 20 and 50 °C on the region of RH = 25-99 %. The values of necessary temperature and humidity were set by two temperature sensors placed on the front panel of this chamber. Transition in the mode of humidity was carried out by the special switch (placed on the forehand of panel). After that, the refrigerator was included for providing of stability. Regulation and stabilization of humidity in the chamber was carried out by the values of humidity. Additionally, the two digital thermometers of TO-ЦО24 (area of measuring of temperatures: –80÷250 °C) were assembled in a chamber for large exactness of experimental results.

The studied thick-film samples were fastened on the special clamps and placed on a chamber. The electrodes were given on the connecting cables of M-ohmmeter of alternating current of МОЦ-0104 at the fixed frequency of current of 500 Hz. The areas of measuring of electric resistance were 0.001-1.999 MOhm; 2.00-19.99 MOhm; 20.0-199.9 MOhm and 200-1000 MOhm. The testing was carried out tested by cycles in direction of increase of RH and in reverse direction.

The value of RH for studied thick-film samples was determined on the result of the wet thermometer using psychrometric tables. As results, the values of electrical resistance R as function of RH at temperatures 20 °C and frequencies of signal 500 Hz were obtained.

RESULTS AND DISCUSSION

According to obtained 3D-profilogramph data, the thickness of temperature sensitive p^+-conductive thick films based on $Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$ ceramics and p-conductive thick films based on $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ ceramics were near 47-49 μm and 54-63 μm, accordingly. The thickness of multilayered p^+-d thick-film structures was near 135.94 μm.

The T-sensitive p^+- and p-conductive thick films and their p^+-p structures based on spinel-type $NiMn_2O_4$-$CuMn_2O_4$-$MnCo_2O_4$ ceramics posses good linear electrophysical characteristics in the region from 298 to 358 K in semi-logarithmic scale (*Fig. 2*). The values of B constants were 3589, 3630 and 3615 K for p-, p^+-conductive thick films and p^+-p structure, respectively.

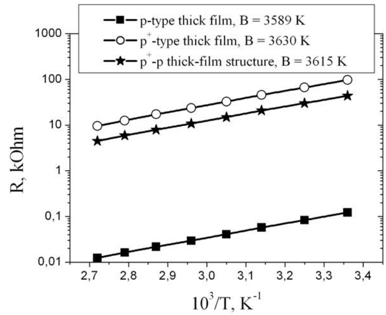

Fig. 1 – Topological scheme of T/RH-sensitive thick-film structures

Fig 2 – R/T characteristics for p- and p^+-conductivity thick films

Firstly, in i-type RH-sensitive thick-film elements we used the Ru-contained paste electrodes from above thick film for study their electrophysical properties. After initial electrophysical investigation these humidity-sensitive thick-film elements based on $MgAl_2O_4$ ceramics posses good linear dependence of electrical resistance from relative humidity without hysteresis in the range of relative-humidity of 40-99 %. But after natural physical storage during 2-3 months, the elements lose of RH-sensitivity (see *Fig. 3*).

It is established [13], that this effect caused by degradation processes in Ag-Ru contacts area. Sensitivity of i-type thick film succeeds to be picked up thread after the repeated update of contact. But this sensitivity can be again lost after some time. So, with the aim of avoid of this problem, the p+-conductive paste was used as the new contact area formed on i-type $MgAl_2O_4$ thick film layer. Since all components (p-, p^+- and d-type thick films) are of the same chemical type (spinel-like) and possess high T/RH sensitivities, they will be positively distinguished not only by wider functionality (simultaneous T/RH sensing), but also unique functional stability. In addition, we obtained integration T/RH sensor structures in the new geometrical design and with the large RH-sensitive active area (see Fig. 1, right part, 5 and 6 electrodes).

The dependences of electrical resistance R from RH for integrated p-i-p^+ structures in new design was shown in *Fig. 4*. In the results of electrophysical measurements, it was established that such thick-film structures posses humidity-sensitivity within one-order change of electrical resistance.

These changes can be connected with diffusion processes of the elements from p- and p^+-conductive T-sensitive thick-film layers on i-type RH-sensitive thick-film. In the results, some active pores will not take part in adsorption-desorption processes. So, this effect needs a future investigation.

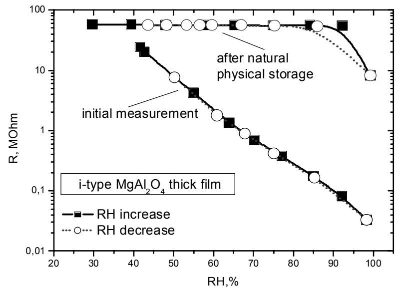

Fig. 3 – RH characteristics for initial i-type thick film and after natural physical storage

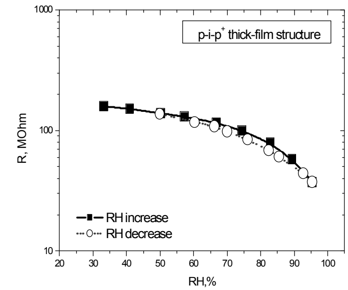

Fig. 4 – RH characteristics for integrated p-i-p$^+$ structure

CONCLUSIONS

In the results of electrophysical measurements, it was shown that just prepared RH-sensitive thick films posses good linear dependence of electrical resistance from RH without hysteresis in the range of RH of 40-99 %. After reiterated electrophysical measurements of theses thick-film sensor elements saved at the normal physical condition was lose of their sensitivity. This effect connected with degradation on contact area. The new integrated spinel-type T/RH sensitive p-i-p$^+$ thick-film structures shown RH-sensitivity within one-order change of electrical resistance.

So, separate T- and RH-sensitive thick-film elements based on spinel-type $NiMn_2O_4$-$CuMn_2O_4$-$MnCo_2O_4$ manganites, their p$^+$-p structures and i-type $MgAl_2O_4$ can be used to produce multilayered T/RH-sensitive thick-film sensor structures for ecological environment monitoring and control.

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