Combined Thick-film Structures Based on Modified Nanoceramics for Sensor Electronics

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***Abstract* – Combined temperature and humidity sensitive thick-film structures based on technological modified nanostructured ceramics ($Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$ with p^+-type of electrical conductivity, $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ with p-type of electrical conductivity and magnesium aluminate i-type $MgO-Al_2O_3$), as well as temperature-sensitive p-p^+ and p-p^+-p structures were prepared and studied. It is shown that increasing of the quantity of thick-film layers results in the improvement of the temperature sensitivity of thick-film structures. Humidity-sensitive thick films with temperature-sensitive films as conductive layers posses linear dependence of electrical resistance on relative humidity with hysteresis in the range of 30-95 %.**

Key words – sensor, thick film, structures, nanoceramics, temperature, relative humidity.

I. Introduction

It is known that the problem of combined temperature and relative humidity control consists in principally different sensitivities of monitored solid-state system to thermally- and water-activated environmentally-induced processes [1]. The basis functioning principle of temperature-measuring systems are grounded, as a rule, on some changes in their physical properties, such as electrical conductivity, resistance, 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 relative-humidity 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 relative humidity-measuring solid systems can be achieved.

Thick-film performance of mixed manganite ceramics 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. The multilayer thick-film structures involving semiconductor $NiMn_2O_4$-$CuMn_2O_4$-$MnCo_2O_4$ and insulating (i-type) $MgO-Al_2O_4$ ceramics can be used as combined temperature and humidity sensors. The aim of this work is investigation of exploitation properties of combined thick-film structures prepared from technologically modified nanostructured $MgO-Al_2O_4$ and $(Cu,Ni,Co,Mn)_3O_4$ ceramics.

II. Experimental

Bulk temperature-sensitive ceramics were prepared by a conventional ceramic processing route by using the reagent grade copper carbonate hydroxide and nickel (cobalt, manganese) carbonate hydroxide hydrates as described in [2]. The $Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$ ceramics were sintered at 1040 °C for 4 h, $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ ceramics were sintered at 920 °C for 8 h, then 1 hour at 1200 °C and 920 °C for 24 h. Bulk $MgO-Al_2O_3$ ceramics were prepared via conventional sintering route [3]. The pellets were sintered in a special regime with maximal sintering temperature of 1300 °C for 5 h.

Temperature- and humidity-sensitive pastes were prepared by mixing powders of basic ceramics with ecological glass powder, Bi_2O_3 (inorganic binder) and an organic components [4,5]. Thus, two temperature-sensitive pastes and one dielectric paste based on spinel-type ceramics were obtained.

The prepared pastes were printed on alumina substrates (Rubalit 708S) with Ag-Pt 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 temperature-sensitive (p-type) thick-film layer previous formed on alumina substrate. The p^+-conductive paste was formed on humidity-sensitive i-type layer. Then these structures were sintered in the furnace. For investigation we used p-p^+, p-p^+-p thick-film structures and integrated p-i-p^+ thick-film structure (Fig. 1).

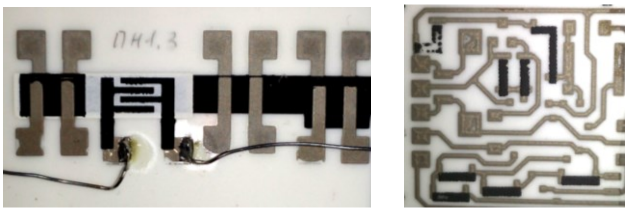

Fig. 1. View of combined p-i-p^+ thick-film structures and temperature-sensitive thick films.

The electrical resistances of thick-film structures were measured using temperature chambers MINI SABZERO and HPS 222. Electrical resistance of the humidity-sensitive structures was measured in PR-3E "TABAI" chamber at temperatures 50 °C and relative humidity from 30 to 98 %. The necessary temperature and humidity were set by using two temperature sensors placed on the front panel of this chamber. The value of relative humidity for studied elements was determined on the basis of the wet thermometer measurements using psychometric tables. As a result, the values of electrical resistance R as function of relative humidity at temperatures 50 °C and frequencies of 500 Hz were obtained as in [4].

III. Results and Discussion

It I shown that the temperature-sensitive p-p^+ and triple-layered p-p^+-p structures posses good linear electrophysical characteristics in the region from 298 to 358 K in semi-logarithmic scale (Fig. 2). But the values of temperature constant B (show temperature sensitivity of elements [5]) increase from to 3615 K to 3700 K in double- p-p^+ and triple-layered p-p^+-p thick-film structures, respectively.

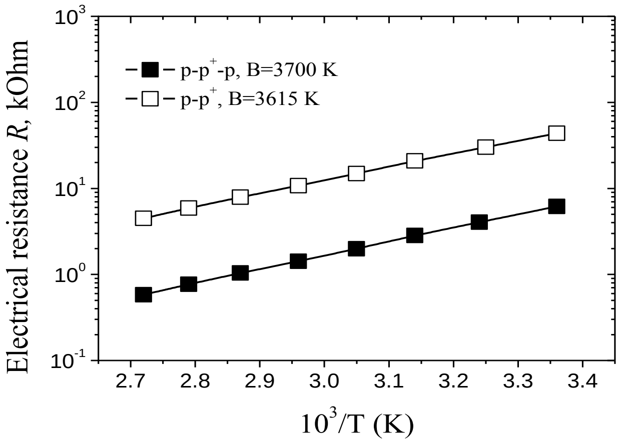

Fig. 2. R/T characteristics for temperature-sensitive p-p^+ and p-p^+-p structures

The insulating i-type humidity-sensitive thick film based on modified MgO-Al_2O_3 ceramics posses linear dependence of electrical resistance from relative humidity with hysteresis in the range of relative-humidity of 30–95 % and can be used for humidity sensors in one order of changes of electrical resistance (Fig. 3).

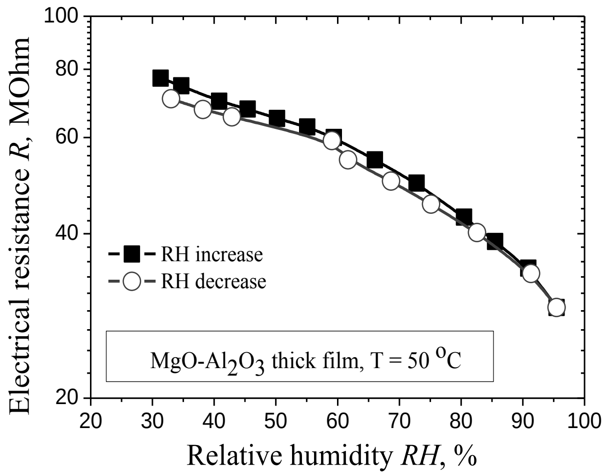

Fig. 3. Relative-humidity characteristic for i-type thick films based on modified MgO-Al_2O_4 nanoceramics

Since all components (p-, p^+- and i-type thick films) are of the same chemical type and possess temperature and (or) humidity sensitivities, they will be positively distinguished not only by wider functionality (combined sensing), but also functional stability.

By using ceramics of mixed Mn-Co-Ni system with RuO_2 additives, the temperature-sensitive elements prepared in thick-film performance attain additionally a better relative-humidity sensitivity. Despite improved good temperature-sensitive properties with character material B constant value, such thick-film elements possess only small relative-humidity sensitivity. This disadvantage occurred, because of relatively poor intrinsic pore topology proper to semiconducting mixed transition-metal manganites in contrast to insulating aluminates with the same spinel structure.

Conclusion

Multilayered temperature/humidity sensitive thick-film p-i-p^+ structures as well as p-p^+ and p-p^+-p structures were obtained and studied. It is shown, that temperature-sensitive thick-film structures possess linear dependences of electrical resistance on the reciprocal temperature. Humidity-sensitive thick films possess dependence of electrical resistance on relative humidity with some hysteresis in the range of 30-95 %. So, the temperature-sensitive thick films with p^+ and p-type of electrical conductivity and insulating i-type MgO-Al_2O_4 were prepared as integrated multilayered p-i-p^+ structures possessing high functional sensitivity.

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