Abstract

Integrated temperature-humidity-sensitive thick-film structures based on spinel-type semiconducting ceramics of different chemical compositions and magnesium aluminate ceramics were prepared and studied. It is shown that temperature-sensitive thick-film structures possess good electrophysical characteristics in the region from 298 to 358 K. The change of electrical resistance in integrated thick-film structures is 1 order, but these elements are stable in time and can be successfully used for sensor applications.

Keywords: Spinel; Ceramics; Thick films; Integrated nanostructure; Simultaneous measurements

Background

Nanostructured functional spinel-type ceramics based on magnesium aluminates and mixed transition metal manganites are known to be widely used for temperature and humidity measurement [1-5]. But their sensing functionality is restricted because of bulk performance allowing no more than one kind of application.

A number of important problems connected with hybrid microelectronic circuits, multilayer ceramic circuits, temperature sensors, thermal stabilizers, etc. require such resolution, when not bulk (e.g., sintered as typical bulk ceramics), but only the thick-film performance of electrical components (possessing the possibility to group-technology route) is needed [5]. 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 [6]. 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 integrated nanostructured thick films based on spinel-type compounds for multifunctional temperature-humidity sensors is a very important task [6-8].

To fabricate the integrated temperature-humidity thick-film sensors, only two principal approaches have been utilized, they being grounded on temperature dependence of electrical resistance for humidity-sensitive thick films and/ or on humidity dependence of electrical resistance for temperature-sensitive thick films. The first approach was typically applied to perovsite-type thick films like BaTiO3 [9]. Within the second approach grounded on spinel-type ceramics of mixed Mn-Co-Ni system with RuO2 additives, it was shown that temperature-sensitive elements in thick-film performance attain additionally good humidity sensitivity [10]. Despite the improved long-term stability and temperature-sensitive properties with character material B constant value at the level of 3,000 K, such thick-film elements possess only small humidity sensitivity. This disadvantage occurred because of relatively poor intrinsic pore topology proper to semiconducting transition metal manganites in contrast to dielectric aluminates with the same spinel-type structure.

The thick-film performance of mixed spinel-type manganites restricted by NiMn2O4-CuMn2O4-MnCo2O4 concentration triangle has a number of essential advantages, non-available for other ceramic composites. Within the above system, one can prepare the fine-grained semiconductor materials possessing p'-type (Cu0.1Ni0.1Mn1.2-Co1.6O4) and p-type of electrical conductivity (Cu0.1Ni0.8Mn1.6Co0.2O4). Prepared thick-film nanostructures involving semiconductor NiMn2O4-CuMn2O4-MnCo2O4 and insulating (i-type) MgAl2O4 spinels can be potentially used as simultaneous thermistors and integrated...
temperature-humidity sensors with extremely rich range of exploitation properties.

The aim of this work is to develop the separate temperature- and humidity-sensitive thick-film nanostructures based on spinel-type ceramics, in which the semiconducting thick films based on NiMn$_2$O$_4$-CuMn$_2$O$_4$-MnCo$_2$O$_4$ ceramics are used not only as temperature-sensitive layers but also as conductive layers for humidity-sensitive thick films based on MgAl$_2$O$_4$ ceramics.

**Methods**

Previously studied and selected samples of 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$_4$, and MgAl$_2$O$_4$ spinel ceramics with optimal structural properties [11-18] were used for the preparation of temperature- and humidity-sensitive thick-film layers.

Temperature-sensitive ceramics were prepared by a conventional ceramic processing route using reagent grade copper carbonate hydroxide and nickel (cobalt) carbonate hydroxide hydrates [11]. The Cu$_{0.1}$Ni$_{0.1}$Co$_{1.6}$Mn$_{1.2}$O$_4$ ceramics were sintered at 1,040°C for 4 h and Cu$_{0.1}$Ni$_{0.8}$Co$_{0.2}$Mn$_{1.9}$O$_4$ ceramics at 920°C for 8 h, 1,200°C for 1 h, and 920°C for 24 h [19-23]. As a result, we obtained single-phase spinel Cu$_{0.1}$Ni$_{0.1}$Co$_{1.6}$Mn$_{1.2}$O$_4$ ceramics (temperature constant $B_{25/85} = 3,540$ K) and Cu$_{0.1}$Ni$_{0.8}$Co$_{0.2}$Mn$_{1.9}$O$_4$ ceramics ($B_{25/85} = 3,378$ K) with additional NiO phase (10%) [12].

The bulk MgAl$_2$O$_4$ ceramics were prepared via conventional sintering route as was described in more details elsewhere [13-18]. The pellets were sintered in a special regime with maximal temperature $T_s = 1,300$°C for 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 (72.8% of sintered bulk ceramics were preliminarily destroyed, wet-milled, and dried) with ecological glass powders (2.9%) without PbO, inorganic binder Bi$_2$O$_3$ (2.9%), and organic vehicle (21.4%). The next content was used for the preparation of humidity-sensitive thick-film pastes: MgAl$_2$O$_4$-based ceramics (58%), Bi$_2$O$_3$ (4%), ecological glass (8%), and organic vehicle (30%).

The pastes were printed on alumina substrates (Rubalit 708S, CeramTec, Plochingen, Germany) using a manual screen printing device equipped with a steel screen. Then, thick films were sintered in PEO-601-084 furnace at 850°C [20,23]. The insulating (i-type) paste in two layers was printed on temperature-sensitive (p-type) thick-film layer previously formed on alumina substrate. In contrast to previous works [21,23], the p$^+$-conductive paste was formed on humidity-sensitive i-type layer as conductive layer. Then, these structures were sintered in the furnace. The topological scheme of integrated p-i-p$^+$ thick-film structure is shown in Figure 1.
240 h was carried out in order to study sample stability in time. The maximal overall uncertainties in the electrical measurements did not exceed approximately ± (0.02 to 0.04) MΩ in electrical resistance. The confidence interval in RH measuring bar restricted by equipment accuracy was no worse than ±1% and in temperature measuring bar ±0.5°C.

**Results and discussion**

Bulk dielectric MgAl₂O₄ ceramics, which are used for the preparation of humidity-sensitive thick-film layers, are characterized by tri-modal pore size distributions (Figure 2). This distribution covers the charge-transferring micro/nanopores (the first peak centered near 4 nm) depending on sintering conditions, water-exchange inside-delivering or communication mesopores (the second peak centered near 65 nm), and water-exchange outside-delivering macropores (the third peak centered near 350 nm) depending on the specific surface area of milled MgO-Al₂O₃ powder [24]. According to Kelvin equation [25], for capillary condensation processes of humidity in ceramics and their thick film at room temperature in the investigated range of RH (20% to 99%), the cylindrical pores with a radius from 1 to 20 nm are required. Meso- and macropores with radius more than 20 nm (the second and third peaks) are not involved in the capillary condensation process, but they ensure the effective transfer of water into ceramic bulk. Thus, the presence of pores in each area provides effective adsorption and desorption humidity processes in material bulk.

As it follows from visual inspection of SEM images shown in Figure 3, the microstructure of humidity-sensitive ceramics is characterized by grains, grain boundaries, and pores. The grains are integrated into agglomerates.
Spherical and cylinder pores are located near the grain boundaries. Average grain size for these ceramics is approximately 300 - 500 nm.

Typical pore size distribution for temperature-sensitive bulk ceramics are shown in Figure 4. It differs significantly from the pore size distribution for humidity-sensitive ceramics. This distribution covers only charge-transferring pores centered near 3.5 and 5.5 nm. But the amount of such pores is higher in comparison with MgAl₂O₄ ceramics.

In respect to the SEM data, the microstructure of temperature-sensitive ceramics is characterized by separate pores with 1 to 3 μm in sizes (Figure 5). White NiO film appears as bright layer of 10-μm thickness on the grain surface of these samples. The grain structure of ceramics attains monolithic shape. Individual pores of relatively large sizes (near 3 to 5 μm) are observed in these ceramics, the NiO appearing as uniform layer on the whole ceramic surface. The observed additional NiO phase is non-uniformly distributed within ceramic bulk, being more clearly pronounced near the grain boundaries [12].

These examined samples of temperature and humidity-sensitive ceramics with best microstructural and electrical properties have been used as base materials for the preparation of thick-film structures.

The SEM micrograph of integrated p-i-p⁺ thick-film structure based on p⁺-type Cu₀.₁Ni₀.₁Mn₁.₂Co₁.₆O₄ and p-type Cu₀.₁Ni₀.₈Mn₁.₉Co₀.₂O₄ ceramics is presented in Figure 6. Micrograph reveals grains of basic ceramics, surrounded (‘covered’) by glass and pores. Thick films show higher density and microstructure homogeneity with uniform distribution of grains, glass additives, and pores. Contacting area of partially removed and peeled...
thick-film layers is evident from this micrograph. During the sintering process of thick-film structures, the diffusion of elements occurs from one layer into the near-surface region of the next layer with other conductivity [23]. Novel in this work is using p'-conductive Cu0.1Ni0.1Mn1.2Co1.8O4 layers to the preparation of contact area for humidity-sensitive i-type layers (see Figure 1). Such approach eliminates diffusion processes in the contact element material to thick films. So, we not only prepared an integrated multilayer p-i-p+ structure but also increased the active adsorption-desorption surface area for humidity-sensitive thick-film layers using the same spinel material not only as a temperature-sensitive layer but also as a conductive layer.

In spite of the same chemical type (spinel-like) of each thick-film layers, such effects correspond to the changes in their sensitivity, in particular, decreasing of sensitivity on i-type thick-film layer, due to diminishing of pores connected with capillary condensation processes [15] and additional phases near the grain boundaries [14].

All obtained p- and p'-conductive temperature-sensitive thick-film elements based on spinel-type NiMn2O4-Cu Mn2O4-MnCo2O4 ceramics have good electrophysical characteristics. These thick-film elements show linear temperature dependences of resistances (Figure 7). The values of B25/85° constant were 3,589 and 3,630 K for p-type Cu0.1Ni0.8Mn1.5Co2.2O4 and p'-type Cu0.1Ni0.1 Mn1.2Co1.6O4 thick films, respectively. Both thick films possess good temperature sensitivity in the region from 298 to 358 K.

The studied thick-film elements based on i-type MgAl2O4 ceramics possess linear dependence of electrical resistance on RH in semilogarithmic scale with some hysteresis in the range of RH ~ 60% to 99% (see Figure 8). But after degradation transformation at 40°C for 240 h, the hysteresis is minimized (Figure 9). This effect corresponds to saturation of some nanopores of water, which provide effective adsorption-desorption processes in elements.

Since all components are of the same chemical type (spinel-like) and possess high temperature/humidity sensitivities, they will be positively distinguished not only by wider functionality (simultaneous temperature-humidity sensing) but also by unique functional reliability and stability. In the case under consideration, the main advantages proper to bulk transition-metal manganite ceramics (wide range of electrical resistance with high temperature sensitivity) and humidity-sensitive MgAl2O4 ceramics will be transformed into thick-film multilayers, resulting in a principally new and more stretched functionality.

Conclusion

Integrated temperature-humidity sensitive thick-film p-i-p+ structures with optimal grain-pore structures, where p'-conductive layers was used as a conductive layer, were obtained and studied. Temperature-sensitive thick-film structures possess good temperature sensitivity in the region from 298 to 358 K. The humidity-sensitive elements possess linear dependence of electrical resistance on relative humidity in semilogarithmic scale with some hysteresis in the range of RH ~ 60% to 99%. After degradation transformation, the hysteresis is minimized due to saturation of some nanopores by water, which provide effective adsorption-desorption processes in elements.

Competing interests

The authors declare that they have no competing interests.

Authors’ contributions

HK performed the experiments to study the temperature and humidity effects in thick-film structures and drafted, wrote, and arranged the article. IH proposed an idea of the development of integrated thick-film structures and performed the experiments to obtain bulk spinel ceramics and thick films. OS is a supervisor of the whole work, the results of which are presented in this article. MB supervised the experiments performed by IH. All authors read and approved the final manuscript.

Acknowledgements

The authors acknowledge the support from the Fakultät für Informations-, Medien- und Elektrotechnik, Fachhochschule Köln/University of Applied Sciences Cologne (Köln, Deutschland).

Authors details

1Lviv Polytechnic National University, 12 Bandera str, Lviv 79013, Ukraine.
2Drohobych State Pedagogical University, 24 Ivan Franko str, Drohobych 82100, Ukraine.
3Lviv Institute of Materials of Scientific Research Company ‘Carat’, 202 Stryjska str, Lviv 79031, Ukraine.
4Institute of Physics of Jan Dlugosz University, 13/15, al. Armii Krajowej, Czestochowa 42201, Poland.
5Fachhochschule Köln/University of Applied Sciences, 2 Betzdorfer Strasse, Köln 50679, Germany.

Received: 10 December 2013 Accepted: 18 March 2014 Published: 26 March 2014

References

1. Sheftel IT: Thermoresistors. Moscow: Naucha; 1973:415.
2. Zaharov VI, Olesk AO: Materials and technology for NTC thick-film thermistors manufacturing. Elektronnaja Tekhnika, Ser. Radiodetali i Komponenty 1989, 63:30–34.
3. Zaharov VI, Olesk AO: Film thermistors. Zarubeznaja Elektronnaja Tekhnika 1983, 543–74.
4. Zhong J, Bau HH: Thick-film thermistors printed on LTCC tapes. J Am Ceram Soc Bull 2001, 80:39–42.
5. Feingold AH, Wahlers RL, Amstutz P, Huang C, Stein SJ, Mazzochette J: New microwave applications for thick-film thermistors. Microe J 2000, 1:90–98.
6. Ou W: Development of multi-functional sensors in thick-film and thin-film technology. Meas Sci Technol 2000, 11:1111–1115.
7. White NW, Turner JD: Thick-film sensors: past, present and future. Meas Sci Technol 1997, 8:1–4.
8. Dzierzic A: Thick-film resistive temperature sensors. Meas Sci Technol 1997, 8:78–81.
9. Holc J: Temperature characteristics of electrical properties of (BaSn)TiO3 thick-film, humidity sensors. Sensor Actuat A 1995, B 26/27:99–102.
10. Huang J: Preparation and characteristic of the thermistor materials in the thick-film integrated temperature-humidity sensor. Mat Sci Eng 2003, B 99:523–526.
11. Vakiv M, Shpotyuk O, Mroz O, Hadzaman I: Controlled thermistor effect in the system Cu0.1Ni0.8Co1.2Mn0.2O4. J Europ Ceram Soc 2001, 21:1783–1785.
12. Shpotyuk O, Balitska V, Hadzaman I, Klym H: Sintering-modified mixed Ni-Co-Cu oxymanganospinels for NTC electroceramics. J Alloys and Compounds 2011, 509:447–450.

13. Shpotyuk O, Ingram A, Klym H: PAL spectroscopy in application to humidity-sensitive MgAl2O4 ceramics. J Europ Ceram Soc 2005, 25:2981–2984.

14. Bondarchuk A, Shpotyuk O, Glat A, Klym H: Current saturation in In2O3-SrO ceramics: a role of oxidizing atmosphere. Rev Mex Fis 2012, 58:313–316.

15. Klym H, Ingram A, Shpotyuk O, Filipecki J, Hadzaman I: Extended positron-trapping defects in insulating MgAl2O4 spinel-type ceramics. Phys Status Solidi C 2007, 4:715–718.

16. Klym H, Ingram A: Unified model of multichannel positron annihilation in nanoporous magnesium aluminate ceramics. J Phys Conf Ser 2007, 79:012014–1–6.

17. Filipecki J, Ingram A, Klym H, Shpotyuk O, Vakiv M: Water-sensitive positron-trapping modes in nanoporous magnesium aluminate ceramics. J Phys Conf Ser 2007, 79:012015–1–4.

18. Klym H, Hadzaman I, Shpotyuk O: Influence of sintering temperature on pore structure and electrical properties of technologically modified MgO-Al2O3 ceramics. Mater Sci 2014, in press.

19. Klym H, Ingram A, Shpotyuk O, Filipecki J, Hadzaman I: Structural studies of spinel manganite ceramics with positron annihilation lifetime spectroscopy. J Phys Conf Ser 2011, 289:012010–1–5.

20. Hadzaman I, Klym H, Shpotyuk O, Brunner M: Temperature sensitive spinel-type ceramics in thick-film multilayer performance for environment sensors. Acta Phys Pol A 2010, 117:233–236.

21. Vakiv M, Hadzaman I, Klym H, Shpotyuk O, Brunner M: Multifunctional thick-film structures based on spinel ceramics for environment sensors. J Phys Conf Ser 2011, 289:012011–1–5.

22. Klym H, Ingram A, Hadzaman I, Shpotyuk O, Popov A, Kostiv Y: Characterization of microstructural features of technologically modified MgO-Al2O3 ceramics. J Phys Conf Ser 2014, in press.

23. Klym H, Hadzaman I, Shpotyuk O, Fu Q, Luo W, Deng J: Integrated thick-film p+p+ structures based on spinel ceramics. Solid State Phenom 2013, 200:156–161.

24. Klym H, Ingram A, Hadzaman I, Shpotyuk O: Evolution of porous structure and free-volume entities in magnesium aluminate spinel ceramics. Ceram Int 2014, in press.

25. Traversa E: Ceramic sensors for humidity detection: the state-of-the-art and future developments. Sensor Actuator B 1995, 23:135–156.

doi:10.1186/1556-276X-9-149
Cite this article as: Klym et al: Integrated thick-film nanostructures based on spinel ceramics. Nanoscale Research Letters 2014 9:149.