Nanoscale Ceramic Materials for Power-Efficient Semiconductor Gas Sensors for Carbon Dioxide Detection

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INTRODUCTION

One of the most important requirements in the development of gas sensors is their low power consumption, that enables to create autonomous sensory systems. For this purpose, it’s first necessary to develop semiconductor materials with a high selective sensitivity to CO2 at low operating temperature. At present semiconductor oxides with wide band gaps depleted own charge carriers and therefore highly sensitive to any change in the volume charge density are widely used as materials for the sensitive elements of gas sensors. However, these materials have insufficient high sensitivity and selectivity. Alternatively, there are considered semiconductor materials on the basis of the modified BaTiO3. They have unique physical properties that allow to create sensitive elements of sensors with improved performance. In this paper we investigated materials based on $0.9\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-y}\text{R}_y\text{O}_3-0.1\text{LaOCl}$ (where R – Mn, Fe, Co, Ni, Cu) as sensing elements of power-efficient semiconductor CO2 gas sensors.

EXPERIMENTAL PROCEDURE

For the synthesis of ceramic materials were used mixtures of BaCO3, TiO2, LaCl3, and a salt one of the dopant metal. Synthesis was carried out by high-temperature sintering at 1250 °C, followed by fine grinding material and adding a solution of LaOCl. The resulting suspension was dried and calcined. X-ray diffraction and Raman spectroscopy were performed on the heat-treated powders for the synthesized materials in order to characterize their crystalline structure. Crystallite sizes were determined from the Scherrer’s equation. Microstructure of the materials was investigated by SEM observation. Thermodynamic properties were investigated using DSC 404 F3 Pegasus differential calorimeter.

For measurements of electrical properties of materials and sensors characteristics the obtained powders were deposited on the substrates of anodized alumina with platinum electrodes. After sensors were placed in an isolated measuring chamber into which investigated gases were pumped. Gas mixtures on the base of the artificial air with concentration of carbon dioxide of 5000, 10000 and 15,000 ppm, CO – 100 ppm, H2 – 0.5 ppm and CH4 – 100 ppm were chosen for the study.
RESULTS AND DISCUSSION

According to data analysis of X-ray patterns and Raman spectrums, it was found that the major crystalline phases in the synthesized materials are barium-lanthanum titanate of tetragonal and pseudocubic polymorphic modifications and LaOCl. The analysis of the obtained data showed that the introduction of such ions as iron, nickel and copper as dopants leads to the growth $c/a$ parameters. It's indicating increased tetragonality of crystal lattice of barium-lanthanum titanate (BLT). At the same time, manganese and cobalt ions are stabilized pseudocubic polymorphic modification of BLT. According to calculations, the average crystallite size of the synthesized material lies in the range from 95 to 240 nm depending on the dopant kind. The highest degree of dispersion are characterized materials containing iron and manganese ions. For materials containing ions of nickel, cobalt and especially copper increasing the average crystallite size was observed. Thus, iron ions and manganese ions together with lanthanum ions act as inhibitors of crystal growth, while ions of nickel, cobalt and copper promote reduce of dispersion. This factor has an impact on the structure of semiconductor, which in its turn, together with the phase composition determines operational properties of materials and products based thereon.

For semiconductor materials on the basis of ferroelectrics used in thermocatalytic sensors for various purposes, it is important to know the profile of changes in the material's structure, and hence its properties depending on temperature. These features determine the method and conditions of use of materials and products based on them. In gas sensors are most in demand materials in the paraelectric polymorphic modification. Calorimetric analysis is one of the most accurate methods for determining and illustrative temperature ranges and energy of polymorphic transitions. DSC curves of materials on the basis of BTL with Mn and Co ions as dopants in the investigated temperature range is not set explicit thermal effect, typical for the polymorphic phase transition. This suggests that these materials are in non-ferroelectric crystal modification, and hence for these materials should be expected monotonic change in the the electrophysical properties in a wide range of temperatures and frequencies.

DSC curves of materials doped with copper and nickel show the thermal effects caused by the phase transition from ferroelectric to paraelectric polymorphic modifications have gently sloping character. The transition is performed in a large temperature range from 75 to 150 °C. Transition energy close to the energy of undoped BLT.

Materials doped with iron ions have significantly higher temperature range of the ferroelectric phase transition to the paraelectric polymorph. Beginning the effect shifted to 420°C, and the transition energy is more than 2 times higher than energy of the phase transitions of others compositions. The results can be explained by the fact that the iron ions contribute to the stabilization of the tetragonal crystal structure of BLT, and when combined with a high degree of dispersion of the material, wherein the individual grains are mechanically clamped and experiencing high internal tension, uniaxial compression may impede the restructuring of the crystal structure. On the basis of DSC data it can be concluded that the most satisfying requirements for the phase transition temperature materials are doped with manganese, cobalt, nickel and copper.

The study of the electro physical properties of synthesized materials and operational characteristics fabricated sensors showed that BLT, doped with manganese and iron have very low values of sensitivity to carbon dioxide. The highest sensitivity to CO₂ was observed in the material doped with copper. Sensitivity of sensors with materials doped with
nickel and cobalt ions is below for 30 and 50%, respectively. Highest selectivity to carbon dioxide have 0.9Ba1-xLa1-xTi1-yCuyO3–0.1LaOCl and 0.9Ba1-xLa1-xTi1-yNi2–0.1LaOCl. During research found that the sensors on the basis of BLT with copper and nickel ions are characterized by the low values of energy consumption in comparison with other materials. Power consumption of equal fabricated sensors (70-90 mW) allows their use in energy-efficient autonomous alarm systems.

CONCLUSION

In this paper, were synthesized and investigated semiconductor nanomaterials based on doped barium-lanthanum titanate. The phase composition, structure and properties of the materials and operational characteristics of CO2 gas sensors on their base have been studied.

IMPEDANCE OF FUNCTIONALIZED CNT/EPOXY RESIN COMPOSITES

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Conductive polymer composites are used for number of applications such as flexible transparent displays, printing electronic circuits, biosensors, heating elements, electromagnetic shielding etc. [1-3]. Therefore fabrication of polymer composites with desirable physical properties is one of the most important tasks of modern material science. Epoxy resin is a well-known thermosetting polymer applied as a matrix material for composites’ fabrication due to good processability characteristics and excellent mechanical properties [4]. Carbon nanotubes (CNTs) have advantage among different types of fillers because they possess ability to strongly improve electrical, mechanical properties of polymers and their thermal conductivity at low weight content due to their nanoscale diameter and high aspect ratio [5]. Functionalization of CNTs is used in order to enhance interfacial bonding between CNTs and polymer matrix and to provide more homogeneous distribution of CNTs in composites [6, 7]. The aim of this work is to study AC electrical properties of functionalized CNT/epoxy resin composites with different weight content of CNTs fillers.

Commercially available CNTs and epoxy resin were utilized for nanocomposite fabrication. CNTs have the following parameters: 10–20 nm diameter, 5–20 µm length, 95% purification degree. Detailed description of the nanocomposites’ fabrication procedure is presented in [8, 9]. For homogeneous distribution of CNTs in epoxy resin nanotubes were functionalized using NH2. Weight content of CNTs fillers varied within range 0.25–1 wt. %.

Electrical contacts were made by Ag paint.

Impedance measurements in the frequency range from 20 Hz to 1 MHz at the temperatures 4.2, 77 and 300 K were used for the electrical characterization of the CNT/Epoxy resin composites. LCR meter Agilent 4284A was utilized for the measurements of frequency dependences of the real Z’ and imaginary Z’’ components of the samples’ imped-