IOP Conf. Series: Journal of Physics: Conf. Series **872** (2017) 012005 doi:10.1088/1742-6596/872/1/012005

A new type of vacuum sensors with sensitive elements based on multicomponent oxide nanomaterials with fractal structures

A A Karmanov[1], I A Averin[1], I A Pronin[1], N D Yakushova[1], S E Igoshina[1], V A Moshnikov[2] and G V Vishnevskaya[1]

[1] Department of Nano- and Microelectronics, Penza State University, 440026, Penza, Russia
[2] Department of Micro- and Nanoelectronics, Saint Petersburg Electrotechnical University "LETI", 197376, St. Petersburg, Russia

E-mail: nano-micro@mail.ru

Abstract. A new type of vacuum sensors with sensitive elements based on two- and three-component oxide nanomaterials with fractal structures is proposed. It is shown that a sensory response for two-component oxide systems based on SiO_2-SnO_2 is determined by their quantitative composition – mass fraction of tin dioxide. An increase in sensitivity to changes in ambient pressure for three-component oxide nanomaterials has been demonstrated.

At present, to measure low pressures, a variety of devices different inoperational and dimensional characteristics are used, e.g., thermocouple, capacitance, ionization, and other types of vacuum gauges [1]. However, they have a number of drawbacks that limit the scope of their practical applications (e.g., large weight and size, energy consumption, narrow operating pressure range, etc.). Vacuum sensors based on nanomaterials are one of the developing branches of nanoengineering. Today, this subject is represented by few publications in the world highly-rated literature. Most of research in this area is based on the idea of replacing the traditional sensitive element of a gauge with a nanostructured one with dimensional effects. In particular, it is proposed to use the effect of field emission of carbon nanotubes [2], or nanomaterials based on zinc oxide [3], whose sensitivity mechanism to reduce the pressure below the atmospheric one is not fully understood at present. The nanotechnological direction associated with the creation of vacuum sensors based on nano- and microelectromechanical systems is actively developing [4].

Nanomaterials based on wide band gap semiconductor oxides with *n*- and *p*-type electrical conductivity (e.g. SnO_2, ZnO, TiO_2, In_2O_3, etc.), as well as multicomponent oxide systems (e.g. SiO_2-SnO_2, SiO_2-SnO_2-ZnO) are classical for the purposes of gas sensing. To synthesize such nanomaterials, various physical and chemical methods are used, which along with the technological modes of a wide range production, depend on their structure, qualitative and quantitative composition, and a number of other parameters. A promising method for obtaining nanomaterial data is a sol-gel technology that allows the synthesis of hierarchical structures of a fractal type spatial organization [5]. Within the framework of this technology, gas-sensitive nanomaterials based on a two-component silicon dioxide-tin dioxide system with a high sensory response to reducing gases, in particular, ethanol vapors have been developed. Structures with a percolation cluster appearing and disappearing upon the emergence of the analyzed gas, and as a consequence, having ultrahigh sensitivity [6], are also proposed. It should also be noted that multicomponent oxide nanomaterials with fractal structures have an undisclosed potential in the measurement of low pressures. In [7] it was demonstrated that for two-component oxide systems based on tin dioxide-silicon dioxide, a high sensory response to a decrease in pressure below the atmospheric one is characteristic, depending on the structure type of the nanomaterial to be synthesized (quasi-spherical aggregates, labyrinthine, percolation net).

The aim of this work was to study the sensory response of sensitive elements of vacuum sensors based on two- and three-component oxide nanomaterials with fractal structure, depending on their qualitative and quantitative composition. The synthesis was carried out within the framework of the sol-gel technology, using filmforming sols based on the following components: tetraethoxysilane ($Si(OC_2H_5)_4$, TEOS), ethyl alcohol, distilled water, hydrochloric acid as a catalyst, tin (II) chloride dehydrate ($SnCl_2 \cdot 2H_2O$) and zinc chloride ($ZnCl_2$) as alloying components. The mass fraction of dopants was selected on the basis of the following conditions: 1) the formation of an ultrathin silica mesh (matrix) with embedded modifiers (tin and zinc heterototoms) of the "guest-host" type; 2) the formation of a conducting cluster that permeates the entire volume of nanostructures.The sol was coated on the substrates of monocrystalline oxidized silicon of 5×5 mm^2 by centrifugation at the table rotation speed of 4000 rev/min. The annealing was carried out at a temperature of 600 °C for 30 min in the air. Planar silver contact pads were formed by thermal evaporation in the vacuum. The main feature of the synthesized two- and three-component metal oxide nanomaterials is a fractal type of structural organization (figure 1).

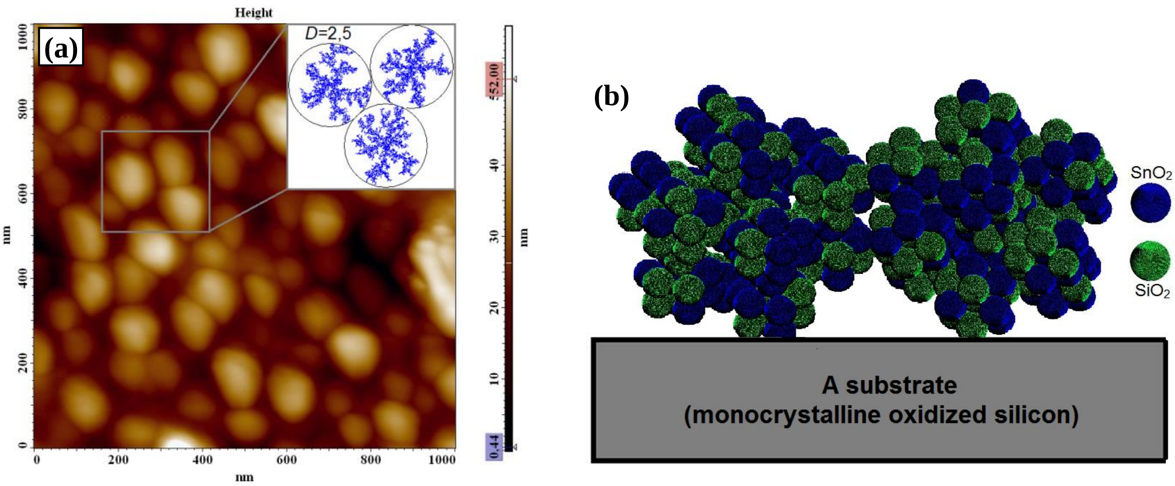

Figure 1. An AFM image of two-component metal oxide nanomaterials of SiO_2-SnO_2 composition with fractal structures **(a)** and the model of sensitive elements of vacuum sensors on their base **(b)**.

Figure 1 shows that the synthesized nanomaterials have a developed surface, formed by clusters of a quasi-spherical form, to describe which it is appropriate to apply either the model of Witten–Sander fractal (box in figure 1(a)), or a three-dimensional Julien fractal (figure 1(b)). However, regardless of the used model, it is well established and confirmed by the experimental data that the multicomponent metal oxide nanomaterials with fractal structures have a high porosity due to a high concentration of macro, micro and mesopores [8]. In turn, the high porosity leads to active gases' interaction with the surface and the volume of the investigated nanomaterials, and their desorption at pressure decrease, lower than the atmospheric one, forms the basis of the offered vacuum sensors operation.The greatest contribution to the sensory response of such sensitive elements at temperatures close to room temperature is made by the adsorption/desorption of oxygen in the form of O_2^-.

Figure 2 shows the relative change in resistance (R/R_0) of sensitive elements of vacuum sensors based on the two-component oxide nanomaterials SiO_2-SnO_2 as a function of pressure.

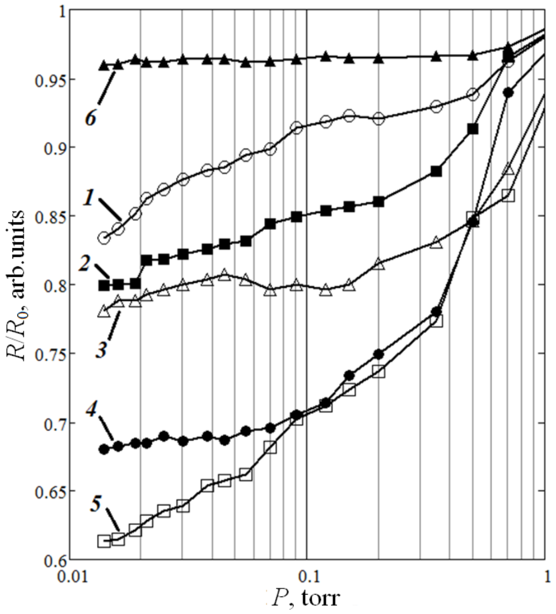

Figure 2. Relative change in resistance of sensitive elements of vacuum sensors based on the two-component oxide nanomaterials SiO_2-SnO_2 at different mass fraction of tin dioxide: *1* – 50 wt. %; *2* – 60 wt. %; *3* – 70 wt. %; *4* – 80 wt. %; *5* – 85 wt. %; *6* – 90 wt. %.

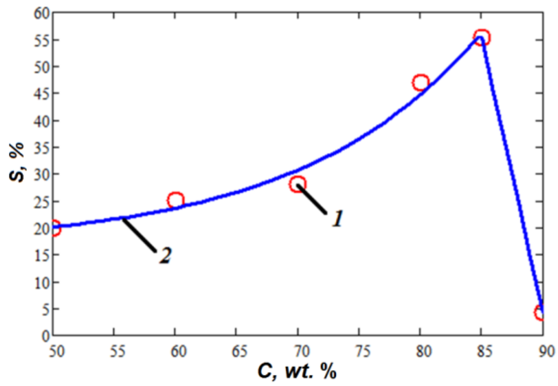

Figure 3. Dependence of sensory response of sensitive elements of vacuum sensors based on the two-component oxide nanomaterials SiO_2-SnO_2 on the mass fraction of tin dioxide: *1* – experimental data; *2* – approximation.

The analysis of experimental data shows that the resistance of the sensitive elements of the developed vacuum sensors decreases monotonically with the pressure decrease. The mass fraction of tin dioxide does not affect shown dependencies (curves 1–6 in figure 2), but it determines the value of the sensor response, which can be calculated using the following formula

$$S = \left|\frac{R_0 - R}{R}\right| \cdot 100\,\%,$$

where R_0 is the initial resistance at the pressure chosen for the reference point; R is the resistance of the sample at a given value of the measured pressure.

Figure 3 shows the sensor response dependence of the sensor vacuum sensing elementson the basis of two-component oxide nanomaterials on the mass fraction of tin dioxide (the measured pressure is taken equal to 0.014 mm Hg). An increase of the alloying component content in the nanomaterial leads to an increase of sensitivity until it reaches its maximum of 55.3 % at 85 wt. % of SnO_2. A further increase of the tin dioxide mass fraction has the opposite effect, which, apparently, is due to the inability of formation of ultrathin silica matrix at low silica dioxide content. It has been proved that when the mass fraction of tin dioxide increases, an increase of the total porosity occurs, since the presence of a modifying inorganic additive in the ash promotesthe pore formation and loosening of the inorganic polymer structure [9].

The use of three-component oxide systems based on SiO_2-SnO_2-Me_xO_y (where Me is the metal *d*-atoms, e.g. Zn) with fractal structures opens great possibilities for controlling the vacuum gauges' characteristics. Figure 4 shows the relative change in resistance of sensitive elements of vacuum sensorsbased on SiO_2-SnO_2-ZnO, and based on SiO_2-SnO_2, for comparison.

It can be seen from figure 4(a) that the resistance of the sensing elements of the proposed vacuum sensors decreases monotonically with the pressure decrease, and the qualitative composition of the multicomponent oxide nanomaterials has practically no effect on the form of the presented dependencies. However, the sensory response for the three-component oxide nanomaterials (SnO_2 and

ZnO mass fractions are 50 and 10 wt. %, respectively) is significantly higher than for the two-component oxide system (tin dioxide mass fraction is 50 wt. %).

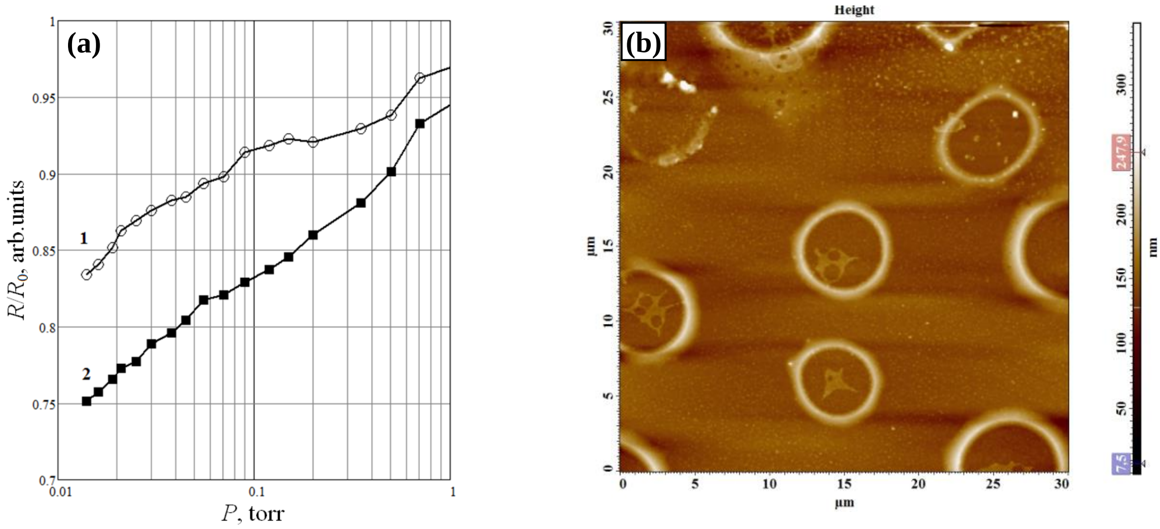

Figure 4. Relative change in resistance of sensitive elements of vacuum sensorsbased on the multicomponent oxide nanomaterials with various fractal structures: *1* – SiO_2-SnO_2; *2* – SiO_2-SnO_2-ZnO **(a)** and an AFM image of the surface morphology of nanomaterials based on SiO_2-SnO_2-ZnO **(b)**.

The analysis of the AFM images presented in figure 4(b) shows that a three-dimensional porous structure with a high concentration of macro and micropores is characteristic for nanomaterials based on SiO_2-SnO_2-ZnO. Apparently, zinc oxide acts as a loosening structure of an inorganic polymer. An increase in the sensory response of the three-component oxide systems can be explained by their high porosity, which determines the concentration of the adsorption/desorption centers, and as a consequence, the sensitivity.

Acknowledgments
The work is financially supported by the Ministry of Education and Science of the Russian Federation within the framework of the project part of the state assignment for Penza State University No. 16.897.2017/4.6, and the Foundation for Assistance to Small Innovative Enterprises in Science and Technology (“UMNIK” program, contract No. 6700 GU2015).

References

[1] Deulin E A and Gatsenko A A 2012 *Vacuum Technique and Technology* **22**(**1**) 3–12
[2] Kim S J 2005 *Technical Physics Letters* **31**(**7**) 597–9
[3] Zheng X J, Cao X C, Sun J, Yuan B, Li Q H, Zhu Z and Zhang Y 2011 *Nanotechnology* **22**(**43**) 435501
[4] Randjelovic D V, Frantlovic M P, Miljkovic B L, Popovic B M and Jaksis Z S 2014 *Vacuum* **101** 118–24
[5] Pronin I A and Goryacheva M V 2013 *Surface and Coatings Technology* **235** 835–40
[6] Karpova S S, Moshnikov V A, Maksimov A I, Mjakin S V and Kazantseva N E 2013 *Semiconductors* **47**(**8**) 1026–30
[7] Averin I A, Igoshina S E, Moshnikov V A, Karmanov A A, Pronin I A and Terukov E I 2015 *Technical Physics. The Russian Journal of Applied Physics* **60**(**6**) 928–32
[8] Moshnikov V A, Gracheva I E, Kuznezov V V, Maximov A I, Karpova S S and Ponomareva A A 2010 *Journal of Non-Crystalline Solids* **356** 2020–5
[9] Kanunnikova O M, Mikhailova S S and Muravyev A E 2006 *Glass Physics and Chemistry* **32**(**2**) 228–33