FEATURES OF GAS ENVIRONMENT INFLUENCE ON THE ELECTRICAL PROPERTIES OF NANO- AND MICROCRYSTALS ZnO

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Nanocrystalline powder based on ZnO:Mn is used to create sensitive elements of gas sensors. It is shown that the nanocrystalline material has a structure similar, from an energy point of view, to the structure of micro-sized ZnO:Ag ceramics, which contains intercrystalline potential barriers formed by chemisorbed oxygen.

Adsorbed water can have a significant effect on the electrical conductivity of sensors at operating temperatures below T = 100°C. When evacuated, flammable gases such as propane or butane influence electrical conductivity opposite to what is observed in a normal air atmosphere containing oxygen.

Keywords: sensor, zinc oxide, electrical conductivity, nanomaterial, ceramics, chemisorption.

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1. Introduction

Polycrystalline metal oxide semiconductors have long been widely used as high-performance gas sensors with low cost. Such sensors find applications in the chemical industry, in mining, and in air quality monitoring. This area is receiving increasing attention due to environmental degradation in many countries and increasing industrial production.

To control the content of harmful impurities in the air, various control methods are used - spectroscopic, chromatographic, chemical, as well as analysis using catalytic and semiconductor sensors. However, determination of harmful gases concentration requires significant financial expenses both for the equipment itself and for the measurement itself. Recently, the use of autonomous measuring sensors for air monitoring has become widespread. For these sensors it is important to increase sensitivity and reduce power consumption by reducing operating temperatures. The lack of such sensors limits the possibilities of real-time monitoring and significant granularity [1].

Metal oxide semiconductor gas sensors have low cost and high speed, which makes them promising for large air quality monitoring networks. However, the disadvantage of such sensors is low selectivity and high values of operating temperatures T = 300-400°C [2-4].

One of the directions for improving the properties of semiconductor gas sensors is the use of nanomaterials and activation of the surface of nanocrystals, which leads to an increase in sensitivity, as well as to a decrease in operating temperatures [5-6]. This will make it possible to transform semiconductor nanomaterials from an object of laboratory research into a material for industrial production of sensitive elements (SE) of sensors. However, achieving this goal is impossible without a detailed study of the processes occurring in such structures under various conditions of gas environment. Such studies are carried out in this work by measuring the electrical conductivity of SEs in different gas environments.

2. Samples and measurements

ZnO:Mn nanocrystal powders and ZnO:Ag ceramics with micro-sized crystals were used as materials for experimental studies. Nanocrystals in the form of nanopowders were synthesized from solutions of zinc nitrate ($Zn(NO_3)_2 \times 6H_2O$) and manganese nitrate ($Mn(NO_3)_2 \times 6H_2O$) by ultrasonic aerosol pyrolysis according to the technological regimes given in [7]. The Mn content did not exceed 2 at. %. The synthesized powder was subjected to thermal treatment in hydrogen at temperature T = 550°C, in a mixture of argon and hydrogen gases (H_2:Ar = 1:3) for 20 min. The powder was cooled briefly (15 min) in the flow of argon gas. From the obtained material, disks with a diameter of 5 mm and a thickness of 1-

1.5 mm were produced by pressure molding (P = 140 MPa). These disks were used as the SE of the gas sensor.

Micro-sized powders were produced by adding the required amount of $AgNO_3$ solution to the colloidal aqueous solution of ZnO powder. During the reaction, uniform precipitation of silver oxide on ZnO crystals occurred. From the obtained precipitate after drying of the charge by the method of molding under pressure (P = 100 MPa), disks with a diameter of 12 mm and a thickness of 2-3 mm were obtained. Silver doping of ZnO crystals took place during annealing of the obtained disks in air at temperature T = 900°C for 1 hour.

The SE was made on the basis of a ceramic resistor with a resistance of 100 Ohm, power 5 W. A disk was fixed on its side edge using liquid ceramic (Al_2O_3 powder mixed with liquid glass). Electrical contacts on the disk were made with a paste containing silver or formed by burning silver paste at temperature T = 700°C. Heating of the SE was carried out by the current passing through the ceramic resistor when it was connected to the voltage source.

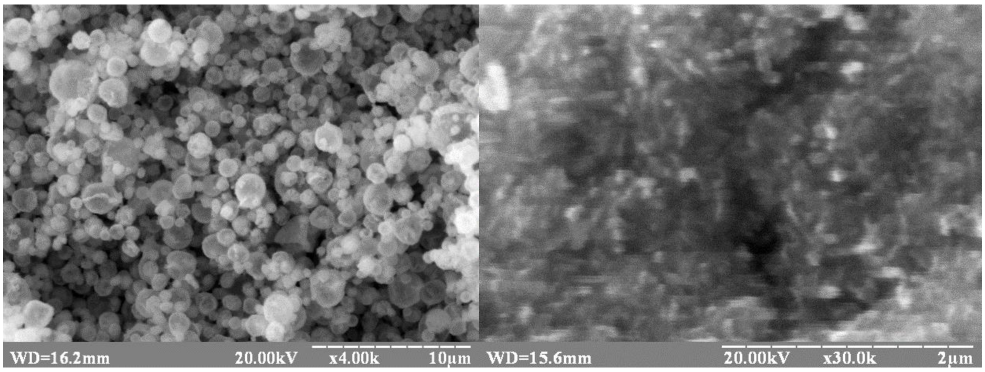
The electrical conductivity of the SE samples was measured in a sealed chamber under creation of the necessary gas medium or vacuum. Vacuum was formed with the help of VUP-5 unit. The pressure in the vacuum chamber was measured by a calibrated manometer transducer PMT-2. The samples were heated to the working temperature and were kept in vacuum for 1 hour. After that, the necessary atmosphere was formed in the chamber and changes in the electrical conductivity of the SE were made with time. The resistance of the SE was measured with the help of the circuit diagram given in [8] using a voltmeter B7-27.

The surface microstructure of the PE samples was investigated by scanning electron microscopy using REMMA-102-02 and Nova NanoSEM 200 electron microscopes.

3. Experimental results and discussion

From the electron microscopy data (Fig. 1a), it can be seen that the initial nanoscale powder consists of spherical granules with a diameter of 2-3 μm. The X-ray diffraction data showed that the granules consist of agglomerates of nanoparticles of about 30 nm in size [7]. As a result of pressing, under the action of mechanical stress, these granules were fractured and a mixture of 0.5-1.5 μm sized fragments was created (Fig. 1b).

Analysis of the microstructure of ceramic samples of ZnO:Ag system showed that the material of all samples had a polycrystalline structure (Fig. 2). The average size of crystallites was 0.2-0.5 μm. Silver clusters ranging in size from 1.5 to 0.2 μm were detected only after removal of the surface layers of ceramics by grinding. Thus, Ag inclusions are more characteristic of the bulk regions of the ceramics than of the surfaces. The probable reason for this structure may be more intensive evaporation of silver from the surface during the firing process.



a b

Fig. 1. Microphotographs of nanocrystalline powder ZnO:Mn (2 at.%) after synthesis (a) and after pressing (b).

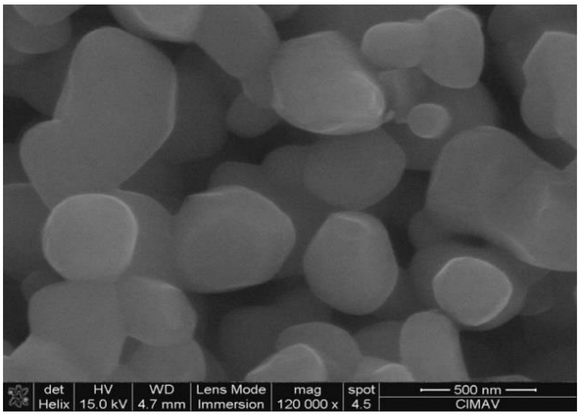


Fig. 2. Microphotograph of the surface of ZnO:Ag ceramics.

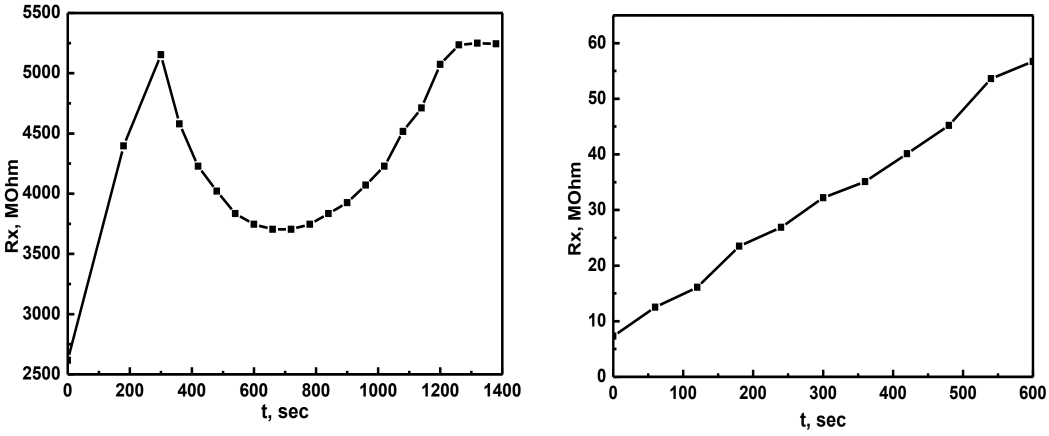
Thus, in spite of different technological conditions of manufacturing and different composition, the following common points in the structure of nanocrystalline powder ZnO:Mn and ceramics ZnO:Ag can be observed:

1) in both materials the sizes of elementary blocks, fragments of granules in ZnO:Mn and grains in ZnO:Ag, are of values from tenths of microns to units of microns;

2) in both cases, a cellular structure is created in which gases penetrate well.

For both materials, weakly nonlinear volt-ampere characteristics were observed [8-9], which indicates the existence of intergranular potential barriers, the main role in the formation of which on the surface of ZnO is carried by chemisorbed oxygen [10]. To establish the role of oxygen in the formation of gas-sensitive properties of zinc oxide-based materials, experiments on the effect of vacuum and various gas media on their electrical conductivity were carried out.

The dependence of the resistance of SE made of nanocrystalline ZnO:Mn on the time of air pumping from the vacuum chamber at temperature T = 90°C and pressure change from 1 atm. to 100 Pa. was investigated. It was found that the change in the resistance of the SE during air pumping is not regular (Fig. 3). This character of resistance change with temperature can be explained by the process of desorption of water molecules, as well as oxygen and carbon dioxide from the volume and surface of the nanomaterial. The mechanism of gas sensitivity of oxide semiconductors is based on this process. Moreover, the removal of water leads to an increase in the resistance of the material, while the desorption of carbon dioxide and oxygen leads to its decrease [11]. Therefore, it can be assumed that at the beginning of pressure reduction in the vacuum chamber (Fig. 3) for a time interval from 0 to 300 s the desorption of water molecules with the increase of the SE resistance takes place, and then at t >300 s the desorption of oxygen molecules occurs. The increase in the SE resistance at t > 700 s can be explained by the diffusion of adsorbed oxygen from the volume of the SE material to its surface. Initially, this diffusion prevails over the oxygen desorption, so its concentration on the surface of the SE increases, which increases the resistance. Subsequently, these processes are balanced, so after the pumping time interval t > 1250 s the value of resistance does not change and becomes equal to Rx = 5250 MOhm.



a b

Fig. 3. Change of resistance of the SE made of nanocrystalline ZnO:Mn during pumping of air (a) and argon (b) from the vacuum chamber.

To investigate the mechanism of the gas environment influence on the electrical conductivity of the sensor based on ZnO:Mn, the thermal treatment of the sensing element in an inert gas environment in argon was performed. For this purpose, after pumping out the air, the vacuum chamber of the VUP-5 unit was filled with argon gas up to atmospheric pressure and the resistance of the sensitive element was measured when heated up to the temperature $T = 90°C$. The resistance decreased from 5250 MOhm to 9 MOhm. After such thermal treatment the dependence of the sample resistance from of argon pumping time from the vacuum chamber has a linear character - the resistance gradually increased (Fig. 3b). The significant decrease in the SE resistance indicates that oxygen plays a crucial role in the formation of intercrystalline potential barriers that increase the resistance of the material.

Fig. 4 shows the kinetics of the electrical conductivity of ZnO:AgSE. With the beginning of the process of air pumping from the chamber, the conductivity of the material increases, which is explained by the desorption of oxygen from the surface of the SE and, consequently, by a decrease in the value of the surface potential barrier. After induction of a mixture of propane and butane, the conductivity of the SE sharply decreases. It is assumed that the molecules of propane and butane adsorbed on the surface of ZnO, interact with free electrons and dissociate. The formed radicals: methyl and methylene have low electron affinity energy. Therefore, they actively chemisorb on the surface, capture electrons from the surface, thereby increasing the value of the surface potential barrier. This leads to a decrease in the conductivity of the SE material. At the last stage the gas mixture of propane and butane is pumped out and the conductivity grows even more than after the first stage of pumping out. This is because the gas mixture has reacted with the residual oxygen and removed it from the surface of the oxide. When the gas mixture is pumped out, almost all propane and butane molecules leave the surface of the SE. Thus, it is shown that propane and butane under vacuumization act on the electrical conductivity of the SE in a manner opposite to that observed in a normal air atmosphere containing oxygen. Adsorption of radicals, which were formed at dissociation of propane and butane, is reversible after heating the material in oxidizing medium at temperature $T = 250$- 300°C and above.

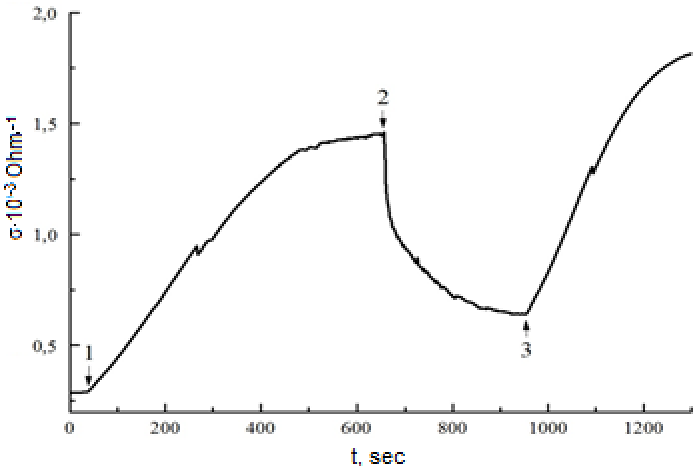


Fig. 4. Dependence of ZnO:AgSE electrical conductivity on time at temperature T = 250°C and changes in the composition of the atmosphere in the measuring chamber: 1 - pumping of air; 2 - injection of propane-butane mixture; 3 - pumping of the mixture.

Thus, the mechanism of influence of different gas media on the electrical conductivity of the SE material has been established, which allows to use it in the creation of gas sensors.

4. Conclusions

The possibility of using nanocrystalline powder ZnO:Mn and ceramics ZnO:Ag as a material for gas sensors has been established. It is shown that the mechanism of interaction of gases with ZnO surface is common both in nanoscale and microscale materials. The degree of dispersibility of the SE material does not affect the character of interaction of the ZnO crystal surface with atmospheric air.Oxygen plays a crucial role in the formation of electrical conductivity and gas-sensitive properties of materials based on zinc oxide.

The removal of oxygen from the surrounding atmosphere as a result of vacuumization and, accordingly, its desorption from the surface of semiconductors based on metal oxides, allows us to establish the mechanisms of the effect of a particular gas on the electrical conductivity of the sensor material.

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