This paper investigates the dependence of operating parameters of a gas sensor based on zinc oxide obtained by the method of direct current magnetron sputtering. The production of gas sensor films was carried out using a VUP-5M vacuum unit with an original material-saving magnetron. The study of the dependence of the working parameters of the gas sensor was carried out under standard conditions. It was found that with increasing humidity, the electrical resistance of the gas sensor decreases and, accordingly, the sensitivity to the target gas decreases. A significant reaction of the gas sensor to an increase in humidity was observed in the range of 65–80% relative humidity. The mechanism of influence of relative humidity on the sensitivity of a gas sensor based on ZnO was investigated. The change in resistance of the gas sensor is caused by trapped electrons on adsorbed oxygen molecules on the surface of the sensitive layer. The capture of electrons from the conduction zone leads to bending of the conduction zone and an increase in the space charge zone, respectively, to a change in the resistance of the sensitive layer of the gas sensor. In the atmosphere, when O₂ molecules are adsorbed on the ZnO surface, they remove an electron from the conduction band. The reaction of oxygen adsorbed on the ZnO surface with reducing gases and the replacement of adsorbed oxygen with other molecules changes the bending of the conduction band and reduces the area of space charge. Adsorption of water on the surface of zinc oxide occurs according to the dissociation mechanism, which consists in the adsorption of steam molecules or hydroxyl groups with the subsequent displacement of previously adsorbed oxygen and free electrons and, accordingly, leads to a decrease in the sensitivity of the gas sensor. In addition, the adsorption of water vapor (H₂O) molecules leads to less chemisorption of oxygen species on the ZnO surface due to the reduction of the surface area, which is responsible for the sensor response. Approaches to reduce the influence of relative humidity on the sensitivity of a gas sensor based on zinc oxide have been proposed.

Keywords: gas sensor, zinc oxide, magnetron sputtering, relative humidity, standard conditions

1. Introduction

Metal oxides are increasingly attracting the attention of scientists from the point of view of designing gas sensors based on them. This is due to the low cost of building such instrument structures, their large receiving surface, and ease of use. In addition, to design gas sensors based on metal oxides, there is a wide variety of ways to obtain their...
sensitive surface [1]. Gas sensors based on metal oxides are sensitive to many toxic, chemically hazardous, and explosive gases [2]. This expands the possible fields of their application and, accordingly, predetermines the search for approaches to design resistive type gas sensors with high performance characteristics [3]. The following metal oxides can be singled out as the most suitable for detecting combustible, reducing, or oxidizing gases $\text{In}_2\text{O}_3$, $\text{WO}_3$, $\text{TiO}_2$, $\text{V}_2\text{O}_5$, $\text{Fe}_2\text{O}_3$, $\text{NiO}$, $\text{Cr}_{2}\text{O}_3$, $\text{GeO}_2$, $\text{Nb}_2\text{O}_5$, $\text{MoO}_3$, $\text{Ta}_2\text{O}_5$, $\text{La}_2\text{O}_3$, $\text{CeO}_2$, $\text{Mn}_2\text{O}_3$, $\text{Nd}_2\text{O}_3$, $\text{ZnO}$, $\text{SnO}_2$, etc. [1]. It is accepted to divide these metal oxides into two groups for designing gas sensors based on them. The first group includes oxides of transition metals, namely $\text{Fe}_2\text{O}_3$, $\text{NiO}$, $\text{Cr}_{2}\text{O}_3$, and others. The second group includes oxides of non-transition metals, which include previous oxides of transition metals, such as $\text{Al}_2\text{O}_3$ and oxides of subsequent transition metals ($\text{ZnO}$, $\text{SnO}_2$, etc.). Inorganic metal oxide such as $\text{ZnO}$ is the most interesting due to its high biocompatibility, high ability to transfer electrons, chemical stability, and high mechanical strength and non-toxicity [2]. In addition, there are many methods for obtaining a $\text{ZnO}$ layer, both chemical and vacuum. Depending on the method of obtaining the zinc oxide layer, its morphology would vary between one-dimensional and three-dimensional structures. Examples of one-dimensional structures based on $\text{ZnO}$ are nanoneedles, nanorods, nanospirals, nanowires, etc. $\text{ZnO}$-based two-dimensional structures include layers and nanosheets. Examples of three-dimensional structures of zinc oxide are nanoflowers, snowflakes, etc. $\text{ZnO}$ provides one of the largest assortments of various particle structures among all known metal oxides [4]. The working parameters of the gas sensor are determined by the material of the sensitive layer – chemical composition and crystal structure, and also depend on the properties of all the constituent elements of the sensor – the material of the substrate, measuring electrodes, and the design of the sensor.

In the sensitive layer of a resistive semiconductor sensor under the action of a gas impurity, a set of interdependent processes takes place: electronic processes, surface and volume diffusion of adsorbed particles, transfer of charge carriers between the grains of polycrystalline samples. Accordingly, the description of the response of a semiconductor gas sensor is carried out on the basis of theories that establish the relationship between molecular and electronic processes on the surface of a semiconductor, mainly according to the electronic theory of chemisorption [5]. Models describing the signal of a gas sensor operating in an air environment take into account the presence of adsorbed oxygen on the surface of the sensor [6, 7]. The process of charge transfer between crystallite grains is calculated within the framework of percolation theory, the model of surface traps and barrier conductivity [8]. Approaches developed in heterogeneous catalysis are used to describe diffusion in the sensitive layer. Diffusion of adsorbed particles and charge transfer between crystallites are considered in connection with the crystal structure and morphology of the sensitive layer of the gas sensor. Despite intensive research, currently the development of sensors with given operating parameters, in general, is not possible, only certain issues regarding the connection between the conditions of formation of the instrument structure and its characteristics have been resolved. The task to design sensors necessitates modeling the sensor signal depending on the parameters of the sensitive layer and external environmental factors such as temperature and relative humidity.

Therefore, it is a relevant task to carry out studies on establishing regularities related to the effect of relative humidity on the operating parameters of a gas sensor based on zinc oxide.

2. Literature review and problem statement

$\text{ZnO}$ is an II-VI n-type semiconductor with a wide band gap (3.37 eV), high excitation binding energy (60 meV), and high electron mobility ($\sim 400 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) [9]. The properties of the $\text{ZnO}$-based gas sensor depend on the shape of the synthesized nanostructures, their size, morphology, and crystallinity [10–12]. In [10], the results of studying the effect of temperature on the resistance of a gas sensor based on $\text{ZnO}$ under the influence of ethanol are reported. It was found that the temperature of the substrate should be 400 °C; lowering or increasing the temperature of the substrate leads to a decrease in the sensitivity of the sensor to the target gas. However, there are no data on changes in the sensitivity of such a sensor to ethanol when the humidity of the surrounding air changes. The authors of work [11] investigated the sensitivity of gas sensors based on $\text{ZnO}$ obtained by hydrothermal synthesis in the form of a flower and a nanorod under the influence of $\text{NO}_2$. In the work, the temperature and concentration of the target gas were changed but the authors did not mention taking into account the influence of the change in relative humidity on the sensitivity of the resulting structures. An overview of the use of two-dimensional structures of metal oxides, including those based on $\text{ZnO}$, for the identification of toxic gases and radiation is given in [12]. The authors raise the question of the influence of changes in relative humidity on the sensitivity of such sensors, but the results of the study are not given. It is also stated in [12] that the method for obtaining the structure of the gas sensor affects its morphology and, accordingly, the operating characteristics. The authors of work [13] obtained $\text{ZnO}$ samples with a porous mesh structure with oxygen vacancies using the electrospinning method. The resulting structures demonstrated high sensitivity and reaction speed, as well as selectivity to acetone vapors. $\text{ZnO}$ samples modified with polyvinylpyrrolidone (PVP) demonstrated similar operating characteristics to acetone vapors. The reaction and recovery time of the gas sensor is 10 s and 150 s, respectively [14]. In [15], the authors studied $\text{ZnO}$ samples obtained by the sol-gel method. The obtained samples demonstrated high sensitivity to ethanol gas. The response time of the studied structures ranges from 10 s to 40 s, depending on the concentration of the studied gas. The authors of [16] synthesized $\text{ZnO}$ doped with $\text{Ag}$ using a light hydrothermal method for use as an ethanol gas sensor. The optimal operating temperature of the instrument structure was set at 320 °C. The samples studied in [17] demonstrated a response to the target gas at the level of 33 relative units at an ethanol concentration of 200 ppm, excellent reaction time and recovery, selectivity, stability, and repeatability [18]. In work [19], the deposition parameters were as follows: the working pressure of the argon-air mixture during the sputtering process was $(2.1–2.6)\times10^{-2} \text{ mm Hg}$, the temperature of the substrate was set at 300 °C. The research carried out by the authors showed that the change in the resistance of the obtained instrument structure is directly proportional to the change in the concentration of the gas that needed to be detected. The change in
the resistance of the device structure occurred until the surface of the metal oxide became saturated with adsorbed molecules. A further increase in the concentration of the target gas did not affect the change in the resistance of the instrument structure.

Under actual conditions, emergencies with the leakage of dangerous gases, which are detected with the help of gas sensors, are usually accompanied by fires. Localization of an emergency occurs with the use of water-based fire extinguishing agents, which leads to an increase in the relative humidity of the environment. In this case, the working parameters of the gas sensor may differ significantly from the standard conditions, which could lead to unreliable measurement results in the atmosphere of the target gas. All this gives reason to assert that it is expedient to conduct a study on establishing the relationship between the change in relative humidity and the operating parameters of the gas sensor.

3. The aim and objectives of the study

The purpose of our work is to determine the effect of relative humidity of atmospheric air on the sensitivity of a resistive gas sensor based on ZnO. This will make it possible to design a gas sensor for a wide range of uses.

To achieve the goal, the following tasks must be solved:

– to investigate the change in the sensitivity of the gas sensor based on zinc oxide when the relative humidity of the atmospheric air changes;

– to investigate the degradation resistance of a gas sensor based on zinc oxide when the relative humidity of the atmospheric air changes.

4. Research materials and methods

4. 1. Obtaining the tested samples of the ZnO-based gas sensor

Obtaining the investigated samples of the gas sensor based on ZnO was carried out by the method of direct current magnetron sputtering. A VUP-5M vacuum unit was used to obtain the films [20].

The target for obtaining ZnO on the surface of the substrate was a zinc target (99.99 % pure). The length of the discharge gap, which is the distance between the magnetron and the substrate, was 70 mm. The power of the magnetron was 0.2 W/cm². High-purity argon was used as an inert gas, and oxygen as an active gas. The outlet pressure in the vacuum chamber was 3×10⁻⁵ mm Hg, the working pressure of the argon-air mixture during the spraying process was (2.1–2.6)×10⁻² mm Hg. The substrate temperature was 300 °C. The deposition rate was 12 Å/s [21]. A helium-neon laser with a wavelength of 633 nm was used to determine the thickness of the films. The obtained films had a thickness of 2–2.5 μm.

For the manufacture of a gas sensor, contacts were applied to the obtained samples, which were created by vacuum deposition of Al films with a thickness of 300 nm at a residual gas pressure of 10⁻⁴ Pa through a special mask. The connection of aluminum contacts with the wires of the outer circuit was carried out by using conductive glue based on silver “Kontaktol Silver” (Poland). Fig. 1 shows the obtained gas sensor on a glass substrate.

Fig. 1. ZnO-based gas sensor under study on glass substrate [10]

The distance between two adjacent aluminum strips is 3 mm, the contact length L is 15 mm.

4. 2. Studying the effect of relative humidity on the operating parameters of a gas sensor based on ZnO

To study the influence of the relative humidity of the atmospheric air on the working parameters of the gas sensor, the laboratory setup shown in Fig. 2 was used.

Fig. 2. Laboratory setup for studying the effect of relative humidity of the atmospheric air on the working parameters of the gas sensor

The change in humidity in the studied box was measured using a digital thermohygrometer with a remote sensor and an LCD-50 liquid crystal display. The humidity in the test box was changed by supplying water at a temperature of 95 °C through a capillary tube with a diameter of 0.3 mm.

The studied sample of the ZnO-based gas sensor was placed in a box with a volume of 5.5×10⁻⁴ m³. All sensitivity characteristics were studied at room temperature. The resistance was continuously monitored when the relative humidity changed.

The measurement was carried out in real time with the help of an electronic recorder with the possibility of storing all intermediate parameters and accompanied by video recording of the indication of the measuring devices. The variance of experimental errors does not exceed 5 %.

5. Results of investigating the effect of relative humidity on the operating parameters of a ZnO-based gas sensor

5. 1. Results of investigating the effect of relative humidity on the resistance of a ZnO-based gas sensor

The results of investigating the effect of relative humidity on the resistance of the gas sensor are shown in Fig. 3. Fig. 4 depicts the plot of response of the gas sensor depending on relative humidity.
Adsorption of water on the surface of zinc oxide occurs by the mechanism of dissociation. Such a mechanism involves the interaction of water vapor (H\(_2\)O) with adsorbed oxygen (O\(^{\alpha}\)) or (O), as represented in reactions (1) to (3):

\[
\begin{align*}
\text{H}_2\text{O} + 2\text{Zn} + \text{O}^{\alpha} &\rightarrow 2(\text{ZnOH}) + 2e^-, \\
\text{H}_2\text{O} + (\text{O} - \text{Zn} - \text{O}) &\rightarrow (\text{O} - \text{ZnOH} - \text{OH}), \\
\text{H}_2\text{O} + 2\text{Zn} + \text{O} &\rightarrow 2(\text{ZnOH}) + \text{V}_{\text{O}}^{2+} + 2e^-.
\end{align*}
\]

The response of the gas sensor to changes in relative humidity is inversely proportional to the sensitivity of the gas sensor.

As the level of relative humidity rises above 45%, the sensitivity of the gas sensor, which is its main operating parameter, begins to decrease. At a relative humidity of 87%, the gas sensor does not respond to the presence of the target gas.

5.2. Results of investigating the degradation resistance of the ZnO-based gas sensor

Fig. 5 shows the results of investigating the stability of the gas sensor over 10 days. The resistance of the sensitive layer of the gas sensor, after the cessation of exposure to high humidity (more than 40%) for up to 10 minutes, without additional measures to reduce humidity in the test box, returns to its initial value.

6. Discussion of results of investigating the ZnO-based gas sensor

Analysis of the plot shown in Fig. 3 demonstrates that an increase in relative humidity leads to a change in the resistance of the gas sensor based on ZnO, namely to its decrease. From Fig. 4, it can be seen that in the range of changes in the relative humidity of atmospheric air from 65 to 87%, there is a sharp increase in the response of the instrument structure. Currently, there is no fundamental justification for the sensitivity mechanism of the gas sensor. However, our studies make it possible to state that the change in resistance of the gas sensor is caused by trapped electrons on adsorbed molecules. If we consider the band structure of the semiconductor, the electrons captured by the adsorbed molecules lead to the bending of the conduction band and, accordingly, to the change in the resistance of the sensitive layer. In the atmosphere, when O\(_2\) molecules are adsorbed on the ZnO surface, they remove an electron from the conduction band. This leads to a distortion of the conduction band and an electron-depleted space charge region. The reaction of oxygen adsorbed on the ZnO surface with reducing gases or competitive adsorption and replacement of adsorbed oxygen by other molecules changes the bending of the conduction band and reduces the area of space charge. This leads to an increase in conductivity and, accordingly, to a decrease in the resistance of the sensitive layer. When gas sensors are exposed to oxidizing gas, electrons are released, and the thickness of the space charge layer decreases. In this case, the Schottky barrier between two grains decreases, and electrons will easily pass through different grains and, accordingly, the resistance will decrease.

As a result of the interaction of water vapor (H\(_2\)O) with the sensitive surface of the gas sensor, the basic resistance of the gas sensor decreases (Fig. 3) and, accordingly, this leads to a decrease in the sensitivity of the instrument structure. In addition, the adsorption of water vapor (H\(_2\)O) molecules leads to less chemisorption of oxygen species on the ZnO surface due to...
the reduction of the surface area, which is responsible for the sensor response. That is, when a gas sensor based on ZnO enters the environment with a higher concentration of H₂O vapors, they are adsorbed on its surface in molecular form or in the form of hydroxyl groups. This leads to the release of charge carriers and promotes the displacement of previously adsorbed oxygen and free electrons. Thus, in addition to reducing the sensitivity of the gas sensor, the response time of the gas sensor increases. The results shown in Fig. 5 confirm the degradation resistance and stability of the gas sensor under repeated exposure to humidity. Degradation resistance is an important operating parameter during long-term use of the gas sensor. The sensitive layer of the gas sensor after the termination of the action of the target gas must be restored to the initial state, which is determined by measuring the resistance in the atmosphere of clean air. If this does not happen during each repeated exposure to a target gas of a fixed concentration, the gas sensor will not signal its presence in the atmosphere. In this case, the sensitive layer of the gas sensor has only one use.

In contrast to study [22], in which the differences between the sensitivity of the gas sensor in dry and moist air for the p-type sensor were established, our study examines the dependence of sensitivity on the relative humidity of the n-type sensors. To reduce the effect of humidity on the sensitivity of a gas sensor based on ZnO, it is necessary to apply a thin layer of an absorber of hydroxyl groups on its surface.

The results proposed in the work could be used for gas sensors based on ZnO, which are applied to detect oxidizing gases. Under the action of reducing gases, the phenomenon of cross-influence is possible, which will lead to the influence of relative humidity on the working parameters of the gas sensor not being reduced. Further development of the research may focus on establishing the influence of relative humidity on the performance characteristics of the n-type gas sensor in the atmosphere of the target reducing gas.

## 7. Conclusions

1. The effect of relative humidity on the sensitivity of a gas sensor based on ZnO was studied. It was found that with increasing humidity, the electrical resistance of the gas sensor decreases and, accordingly, the sensitivity to the target gas decreases. When the humidity changes from 65 to 80 %, the response of the gas sensor increases from 10 to 70 % in an atmosphere of clean air without the influence of the target gas.

2. It was established that the ZnO-based gas sensor exhibits degradation resistance upon repeated exposure to moist atmospheric air for 10 days. The resistance of the sensitive layer of the gas sensor returns to its initial value within up to 10 minutes after the cessation of exposure to high humidity.

## Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study and the results reported in this paper.

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## Data availability

The data will be provided upon reasonable request.

## Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

## References


Technology organic and inorganic substances


