GAS SENSITIVITY OF ZnO:Mn NANOCRYSTALS TO HYDROGEN

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In this work, the effect of hydrogen heat treatment of ZnO:Mn nanocrystal samples obtained by ultrasonic aerosol pyrolysis on their physical and sensory properties is investigated. It is found that hydrogen heat treatment leads to the appearance of an absorption line of abnormal intensity in the EPR spectrum of ZnO:Mn nanocrystals, indicating the presence of a large number of defects. The possibility of improving the gas sensitivity of ZnO:Mn nanocrystals by thermal treatment with hydrogen is demonstrated. This method of modifying the surface of nanocrystals also allows significantly reducing the operating temperature of gas sensors.

Keywords: gas sensors, ZnO nanocrystals, X-ray phase analysis, EPR spectra, hydrogen heat treatment, sensitivity.

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1. Introduction

ZnO-based gas sensors are widely used in practice. It is due to such properties of ZnO as chemical inertness, thermal stability, and resistance to weathering. Therefore, the physical and chemical properties of zinc oxide and its application in gas sensors are the subject of active research [1]. Knowledge of the effect of ZnO dopants and hydrogen heat treatment on sensor sensitivity is essential for the development of efficient gas identification systems.

One of the challenges faced by ZnO-based gas sensors is their lack of sensitivity to gases such as methane, hydrogen, and carbon monoxide. In addition, their efficient operation requires the use of high operating temperatures (T ~ 250–300°C). This limitation is due to the low conductivity of polycrystalline ZnO. To overcome these limitations, developers use nanocrystalline (NC) ZnO and doping it with transition group metals. The NC structure of ZnO provides a larger surface area and an increased number of surface defects, which contributes to increased sensitivity to gases [1]. The work [2] shows a significant effect of oxygen vacancies (V_O) on the gas sensitivity of ZnO sensors. The doping of ZnO with transition group metals, such as manganese ions (Mn^{2+}), also increases the sensitivity of gas sensors. The work [3] shows that Mn^{2+} ions are donor impurities, and their incorporation into the ZnO crystal structure leads to an increase in the concentration of free electrons, and therefore to an increase in conductivity.

Recently, it has become known that modifying the surface of sensors based on NC materials with hydrogen opens prospects for increasing their sensitivity. For example, SO_2 NCs heat-treated in hydrogen at T = 150°C for 5 hours became more sensitive to organic substances such as methanol and ethanol [4]. Also, an increase in sensitivity to acetone and ethanol in gas sensors based on NiO_2 NCs was achieved by heat treatment in hydrogen at T = 200°C [5]. Hydrogen causes an increase in the concentration of surface defects and vacancies V_o, which leads to an increase in the sensor efficiency. The paper [6] also showed a significant increase in the gas sensitivity of sensors based on ZnO nanowires to NO_2 gas at T = 225°C after their heat treatment in hydrogen. It is concluded that this result is due to the presence of vacancies V_O, which become mainly centers of adsorption of target gas molecules. It is known that the mechanism of detection of target gases in metal oxide-based gas sensors is based on the balance of the reaction on the sensor surface between adsorbed oxygen and target gas molecules. Thus, the sensitivity and selectivity of gas sensors depends on the number of oxygen adsorption centers.

An analysis of the literature indicates that today the strategy of increasing the sensitivity of gas sensors by thermal treatment with hydrogen is used for such target gases as

ethanol, methanol, acetone, and others. It is important to establish the possibility of using it for such a gas as hydrogen. In the present work, we investigate the possibility of increasing the gas sensitivity to hydrogen of Mn-doped ZnO NCs obtained through ultrasonic pyrolysis of aerosol (UPA) by thermal treatment in hydrogen.

2. Experimental part

The mechanism of hydrogen interaction with the surface of a ZnO-based sensor is its adsorption and subsequent formation of donor complexes OH^+, which increase the conductivity of the near-surface layer (Fig. 1) [4]. In normal conditions, intrinsic defects (V_O, zinc-Zn_i internodes, zinc-V_{Zn} vacancies) and Mn^{2+} ions, as well as broken covalent bonds on the surface of ZnO NCs are the sites of adsorption of atmospheric oxygen. Under the influence of covalent forces, the oxygen molecule dissociates and decomposes into two ions O^{2-} and O^-, which act as acceptors. They reduce the concentration of free electrons in the near-surface zone, decreasing its conductivity. Therefore, the electrical conductivity will be determined as a result of the balance of adsorption and desorption processes of O_2 molecules on the surface of the sensing element.

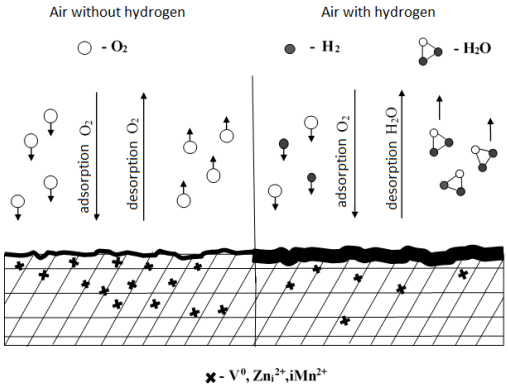


Fig. 1. The mechanism of gas sensitivity of the ZnO-based sensor to hydrogen [4].

In the presence of hydrogen molecules H_2 in the air, its adsorption process takes place according to formula (1). Also, hydrogen molecules will react with adsorbed oxygen ions to form H_2O molecules according to formula (2), which are desorbed from the surface of the sensing element:

$$H_2 \rightarrow 2H_{ads} \rightarrow 2H^+ + 2e^- \quad (1)$$

$$H_2 + O^-_{ads} \rightarrow H_2O + e^- \quad (2)$$

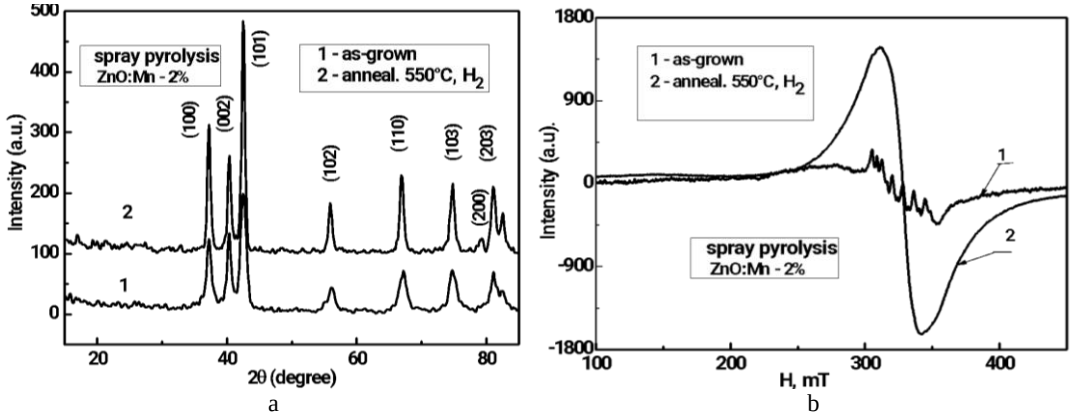
In this case, hydrogen, acting as a donor, increases the conductivity of the near-surface zone. This conductivity will be determined by the balance of opposite processes – adsorption of oxygen molecules O_2 and desorption of water molecules H_2O.

To investigate the effect of hydrogen heat treatment of ZnO:Mn NCs on their physical and sensory properties, ZnO:Mn NCs with a manganese concentration of 2 at.% were synthesized by the UPA method according to the technological modes reported in [7]. For this purpose, a solution of the starting components zinc nitrate ($Zn(NO_3)_2 \times 6H_2O$) and manganese nitrate ($Mn(NO_3)_2 \times 6H_2O$) was prepared. A part of the synthesized ZnO: Mn NC was subjected to hydrogen heat treatment at temperature T = 550°C in a mixture of argon and hydrogen gases (Ar 70% + H_2 30%) for 20 min. The NCs were cooled for a short time (15

min) in a stream of argon gas. The obtained NCs were pressed into pills with diameter d = 5 mm and thickness 1 mm, which were further used as sensor elements.

The crystal structure and phase composition of the samples were studied by X-ray phase analysis (XRD) on the DRON-2 diffractometer using Co K_α (λ = 1.7902 Å). Samples were studied by EPR method on RADIOPAN SE/X 2543 radiospectrometer.

By X-ray phase analysis, it was found that the obtained homogeneous phase of ZnO:Mn (2 at.%) has a wurtzite crystal structure, and there are no impurity phases. It was shown that hydrogen heat treatment does not affect the structural parameters of the samples (Fig. 2a). The average size of NCs increases after heat treatment from 49nm to 67nm.



a b

Fig. 2. X-ray diffraction patterns (a) and EPR spectra (b) of ZnO:Mn NC samples (2at.%): 1 - synthesized sample, 2 - sample after hydrogen heat treatment.

It has been found that the EPR spectra of ZnO:Mn NCs after hydrogen heat treatment change significantly (Fig. 2b). Before the treatment, a weak intensity group of lines of the ultrafine structure of Mn^{2+} ions (line 1) is recorded in the EPR spectra, and after the treatment, a broad absorption line of high intensity (line 2) is recorded. The appearance of this line is due to the action of hydrogen, which forms many intrinsic defects, vacancies (V_O), hydroxyl groups, and complexes ($V_O + H^{2+}$) in NC [8]. All these defects have electrons with uncompensated spins and therefore make an additional contribution to the absorption line (line 2).

The sensing element (SE) of the sensor was made on the basis of a ceramic resistor with a resistance R = 100Ω and a power W = 5 W. The manufactured pill was attached to its side edge using liquid ceramics (Al_2O_3 + liquid glass) (Fig. 3a). Electrical contacts for the pill were made using a paste containing silver. The SE was heated by a current that passed through a ceramic resistor.

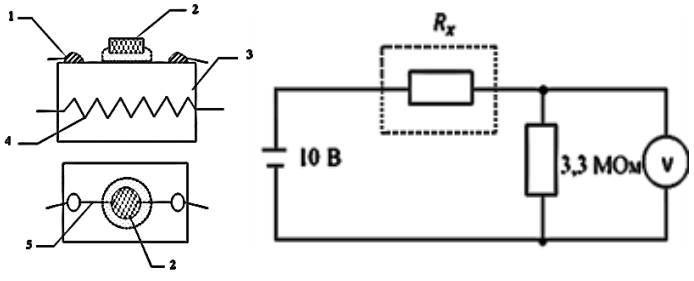


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Fig. 3. Schematic representationof SE: 1 - ohmic contacts, 2 - ZnO:Mn NC pill, 3 - ceramic resistor body, 4 - heater, 5 - contact track (a); electrical circuit for measuring the resistance R_x (b).

To study the characteristics of the SE, an experimental setup was made that allowed measuring the resistance of 3 SEs simultaneously during their purging with target gases. At the same time, it was possible to maintain the required temperature of the SE. Also, in order to exclude the influence of other external factors, it was possible to study the physical characteristics of the SE in vacuum at residual pressure P = 1000 Pa. The electrical circuit used to calculate the resistance of the SE is shown in Fig. 3b. According to this scheme, the values of the SE resistance were obtained in accordance with the formula: $R_x = R\,(E/U - 1)$, where E is the supply voltage (E = 10 V), U is the voltage across the resistor R = 3.3 MΩ.

The effect of hydrogen heat treatment on the sensory properties of ZnO:Mn (2 at.%) NCs was studied on the following SE samples:

- sample №1 – SE tablet made of NC at specific pressure P = 140 MPa without hydrogen heat treatment;
- sample №2 – SE tablet made of NC at specific pressure P = 280 MPa and heat treated with hydrogen;
- sample №3 – NCs were first heat-treated with hydrogen, and then the tablet was made from them at specific pressure P = 140 MPa.

Before conducting the studies, the electrical contacts of the SE samples were tested for ohmicity. For this purpose, their current-voltage characteristics were obtained (Fig. 4a) at room temperature. It turned out that they are linear in nature. This, in turn, confirms the ohmicity of the contacts and the possibility of obtaining reliable results.

An important characteristic of SE is the dependence of its resistance on temperature. This dependence was studied in the temperature range T = 50÷95°C in vacuum at a pressure P = 1000 Pa (Fig. 4 b).

The obtained results indicate that at such temperatures, the dependence of the SE resistance has a shape characteristic of a semiconductor material. It is known that ZnO is a semiconductor with n-type conductivity. Sample №1 was not subjected to hydrogen heat treatment, so its resistance was much higher compared to the other samples. This is due to the presence of a low concentration of vacancies V_O and free electrons in the SE material [6].

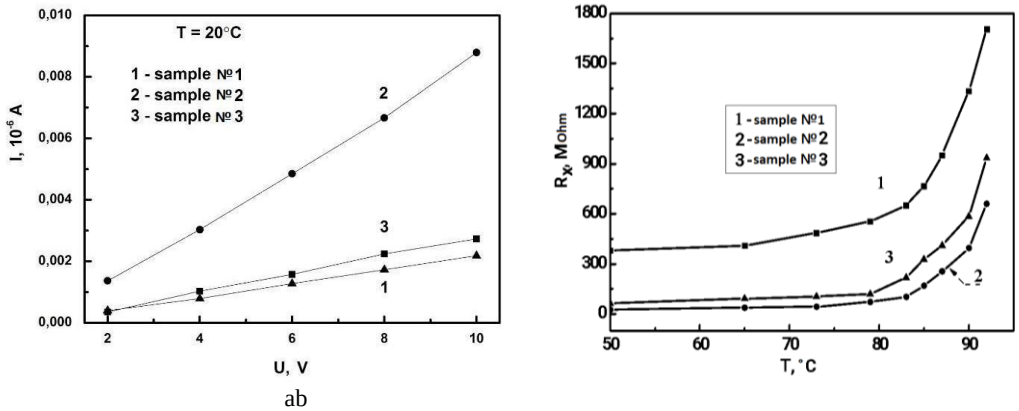

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Fig. 4. Current-voltagecharacteristics of the SE contacts (a) and the dependence of the SE resistance on temperature (b) for samples №1, №2, №3.

It is known that resistive sensors are characterized by the response time. The response is the period of time that elapses from the beginning of the target gas action on the sensor until 90% of the stable final value of its resistance is established. The shorter the response time, the better the sensing properties of the sensor. The sensitivity (S) is determined as the ratio of the

difference in the sensor resistance in the air (R_a) and the sensor resistance under the target gas (R_g) to the sensor resistance in air (R_a), i.e. $S = (R_a - R_g)/R_a$.

The gas sensitivity was investigated for all samples of SE to hydrogen by purging them first with a gas mixture of argon and hydrogen (Ar90% + H_2 10%) and then with air (Fig. 5a). The studies were carried out at temperature T = 95°C. Prior to the measurements, the samples were prepared by heating them at T = 95°C in a vacuum for 1 h.

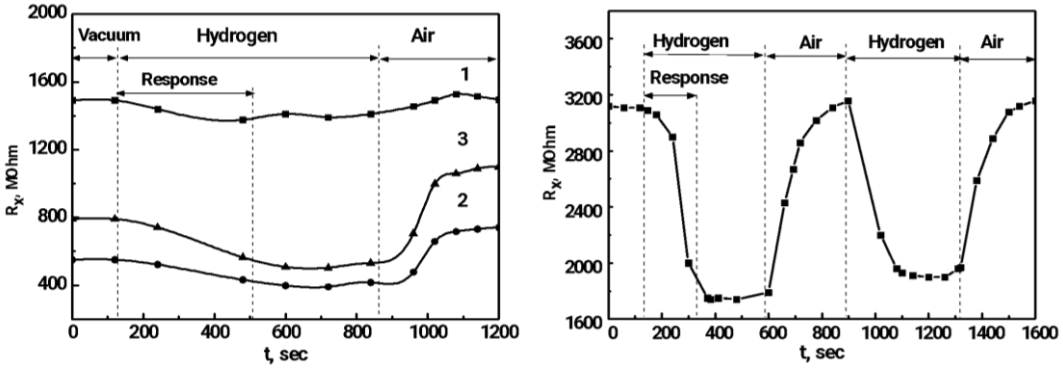

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Fig. 5. Resistance changes of samples № 1, № 2, № 3 in a hydrogen atmosphere and in air (a); resistance change of sample №3 after additional heating in air at T = 95 °C for 1 h in a hydrogen atmosphere and in air (b).

The analysis of the results shown in Fig. 5a shows that the samples have different sensitivities to hydrogen: S_1 = 0.06; S_2 = 0.28; S_3 = 0.36. The response of the samples is approximately the same – about 400 seconds. Thus, sample №3 has the highest sensitivity to hydrogen. Comparing the sensitivity of samples №3 and №2, we can conclude that hydrogen modification before manufacturing the tablet improves the sensory properties of SE. The low sensitivity to hydrogen of sample №1 is explained by the absence of adsorption centers for target gas molecules on its surface in the form of oxygen vacancies. This sample was not subjected to thermal treatment with hydrogen, its total resistance was quite high (1500 MΩ), due to the low concentration of free electrons in the synthesized ZnO:Mn NCs. The conductivity of samples №2 and №3 increases after their thermal treatment with hydrogen due to an increase in the number of defects that cause a high concentration of free electrons. At the same time, due to an increase in the concentration of adsorbed oxygen, the resistance of these samples after air purging increased significantly compared to the initial values after exposure to vacuum from 500 and 800 MΩ to 700 and 1100 MΩ, respectively.

The sensitivity of sample №3 to hydrogen was investigated with the possibility of its use in real conditions. In this case, the sample SE was prepared by heating it in air at T = 95°C for 1 hour. The gas sensitivity of the sample was investigated by recording the resistance R_x during the sequential purging of the SE with hydrogen (Ar 90% + H_2 10%) and air (Fig. 5b). The results obtained indicate that the initial resistance of sample №3, compared to the SE sample that was not preheated (Fig. 5a), increased from 800 MΩ to 3100 MΩ. This is due to an increase in the concentration of adsorbed oxygen on the surface of the SE during heating, which reduces the concentration of free electrons in the near-surface zone. At the same time, the response of sample №3 decreased to 200s, and its sensitivity at T = 95 °C increased from S = 0.36 to S = 0.44.

Thus, using ZnO:Mn NCs (2at.%) heat-treated in hydrogen, a hydrogen gas sensor with attractive characteristics for practical application was fabricated. This conclusion can be made by comparing the results obtained with those reported in [9], where it is shown that the

SE made of ZnO nanorods has a sensitivity S = 0.18 to hydrogen in a mixture of nitrogen and hydrogen gases (N_2 90% + H_2 10%) at T = 112°C.

3. Conclusions

It has been shown that hydrogen modification affects the physical properties of ZnO:Mn NCs obtained by the UPA method. The EPR spectra of such NCs have an adsorption line of high intensity, which confirms the presence of a large number of defects – oxygen vacancies.

It was found that hydrogen modification of ZnO:Mn NCs increases the gas sensitivity of the sensor. To obtain a gas-sensitive material for the sensor, it is necessary to heat treat the ZnO:Mn NCs (2 at.%) in hydrogen, and then to make a pill from the obtained NCs at pressing pressure of P = 140 MPa.

The results obtained can contribute to the development of efficient hydrogen gas sensors for various industrial and scientific applications.

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