ХІМІЧНІ СЕНСОРИ
CHEMICAL SENSORS

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CHARACTERISTICS OF GAS SENSORS BASED ON ZnO OF DIFFERENT DIMENSIONS

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Abstract. Sensor's sensitivity dependence for samples based on ZnO thin film, micro- and nanostructures on their active area was investigated under the influence of ethanol, ammonia and acetone vapors. The impact of the morphology type and the size effects on the main characteristics of the ZnO resistive sensor elements was studied. For the first time the nanostructures of ZnO with a p-type conductivity have been fabricated by electrodeposition in the water solution.
Keywords: ZnO; nanostructures; size-effect

ХАРАКТЕРИСТИКИ ГАЗОВИХ СЕНСОРІВ НА ОСНОВІ ZnO РІЗНОЇ РОЗМІРНОСТІ

Г. О. Лубочкова, О. П. Станько, Б. І. Турко, Б. Я. Кулик, Р. Я. Серкіз, В. Б. Капустяник

Анотація. Вивчено вплив морфології поверхні та розмірних ефектів на характеристики резистивних сенсорів на основі ZnO. Досліджено залежність чутливості на пару етилового спирту, аміаку та ацетону датчиків, створених з тонких плівок, мікро- та наноструктур ZnO, від розміру структурних елементів активного матеріалу. Вперше отримано методом електроосадження з водного розчину наноструктури ZnO з p-типом провідності.
Ключові слова: ZnO; наноструктури; розмірний ефект

ХАРАКТЕРИСТИКИ ГАЗОВЫХ СЕНСОРОВ НА ОСНОВЕ ZnO РАЗЛИЧНОЙ РАЗМЕРНОСТИ

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Аннотация. Изучено влияние морфологии поверхности и размерных эффектов на характеристики резистивных сенсоров на основе ZnO. Исследована зависимость чувствительности на пары этилового спирта, аммиака и ацетона датчиков, созданных из тонких пленок, микро- и наноструктур ZnO, от размера структурных элементов активного материала. Впервые получены методом электроосаждения из водного раствора наноструктуры ZnO с p-типом проводимости.

Ключевые слова: ZnO; наноструктуры; размерный эффект

1. INTRODUCTION

Sensors have become the essential elements both in daily life and industry. Though there is known a large variety of their types, widely used in the different branches of industry, environmental safety, medicine and many other areas, development of the new sensing capabilities is currently proceeding at high rate. One of the most important fields of the sensor technology concerns the thin film gas sensors, since the gas contain would be considered as one of the key measured values in many of the industrial and domestic activities.

Semiconductor metal-oxide based gas sensors are commonly used for environmental monitoring and industrial applications due to their advantages such as small size, affordable and convenient operation. SnO_2, ZnO and In_2O_3 are the most usable metal oxides in the commercial production [1]. Zinc oxide, in particular, is used as a material for gas sensors, owing to its conductivity changes in the environments with the hydrogen or oxygen content. ZnO is one of the earliest-discovered and well-known gas sensing oxides, which has been widely studied for detection of inflammable and toxic gases, such as NO_2, C_2H_5OH, CO and H_2.This material attracts great attention because of high sensitivity, chemical hardness, safety and low price.

Small-scale gas sensors based on ZnO nanostructures possess higher sensitivity and smaller response time comparing to the thin film ones. Some of them can operate even at room temperature. A larger work area is one of the reasons of sensors sensitization based on ZnO nanostructures [2]. Unfortunately, not enough attention was devoted to investigations of ZnO sensors with different microstructure characteristics. In this article we report the data concerning the size effects impact on the resistive ZnO sensor's parameters. The sensor's sensitivity dependence for the samples with the active area based on thin film, micro- and nanostructures was investigated under the influence of the ethanol and acetone vapors.

2. EXPERIMENTAL DETAILS

Thin film ZnO samples were deposited by radio-frequency (rf) sputtering from a ZnO target [3] in the argon atmosphere with working gas pressure 10^{-3} Torr, under sputtering power of 100 W without substrate heating. The distance between substrate and target was about 60 mm. The target was made from pressed ZnO powder (99.99 % of purity). According to the ellipsometric measurements data, the thickness of the thin films was about 300 nm.

The microstructures (tightly packed vertical microrods) were obtained by a solid-vapor-phase process in a horizontal tube furnace in air atmosphere [4] using ZnO powder (purity 99.99 %).

ZnO nanostructures were synthesized by a two-step process. First, the seed layer of ZnO nanoparticles was deposited on the substrate by SILAR (Successive Ionic Layer Adsorption and Reaction) method [5]. Then the substrate was immersed for 15-20 sec. into 0.5 M distilled water solution of zinc salt and $Zn(CH_3COO)_2$ and hexamethylenetetramine (HMT) at room temperature, washed in distilled water, and dipped for 15-20 sec. into distilled water at the temperature about 80^0C. This cycle was repeated 40-45 times. The nanowires were synthesized by electrodeposition from an aqueous solution in the electrochemical cell with two electrodes. For nanostructures obtaining we used 20 mM nitrate hexahydrate zinc $Zn(NO_3)_2 \cdot 6H_2O$ and hexamine solution in distilled water. To increase the conductivity of the solution we added a solution of 0.1 M KCl. Hexamine was added to increase the concentration of hydroxyl groups.

As it is known from the literature growth mechanism of ZnO nanowirres by electrochemical deposition can be described by the following reactions:

$$Zn(NO_3)_2 \rightarrow Zn^{2+} + 2NO_3^-,$$
$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-,$$
$$Zn^{2+} + OH^- \rightarrow Zn(OH)_2,$$
$$Zn(OH) \rightarrow ZnO + H_2O.$$

The substrate and graphite sheet were the working and counter electrodes, respectively. The process was carried out potentiostatically. After the synthesis samples were rinsed in water and dried at room temperature.

The fabricated resistive sensors consisted of Ag contact sites deposited by thermal evaporation at a residual presser about 10^{-6} Torr on glassy-ceramic substrate and on top of that sensing element of ZnO structure. Distance between Ag electrodes did not exceed 100 µm [Fig. 1].

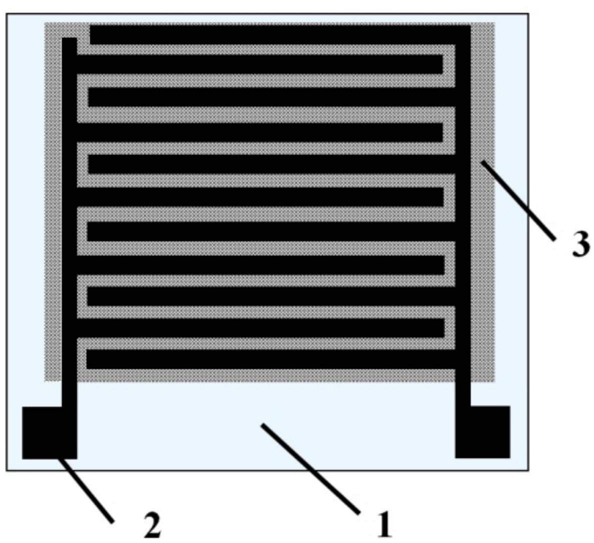

Fig.1. Schematic representation of the resistive sensor, where 1- glassy-ceramic substrate, 2- Ag contact sites, 3 – sensing element

The ellipsometric measurements for estimation of the thin film thickness were performed using the ellipsometer with He-Ne laser (632.8 nm) as a light source.

Morphology of the samples was examined using Atomic Force Microscope Solver P47-PRO at a contact mode with sweep frequency 1 Hz and Scanning Electron Microscope-Analyzer REMMA-102-04.

The sensing properties of different samples in respect to their resistive changes were determined by means of the special experimental setup (Fig.2). The test probes were placed in indoor heated volume into which the capillary introduced alcohol, ammonia or acetone. The temperature of the sensor was measured using a chromel/alumel thermocouple, which was attached to the sensor on the opposite side of the net glassy-ceramic substrate. Registration of temperature was carried by multimeter BM 859CFa (BRYMEN, Taiwan). The working temperatures for the three types of sensors based on ZnO were chosen experimentally. They correspond to the highest sensitivity of the sensors to the tested.

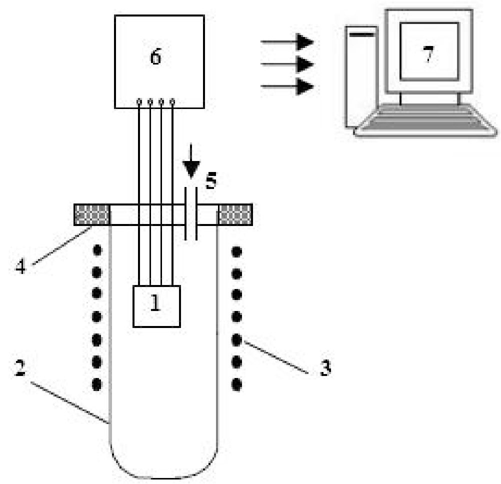

Fig.2. Experimental setup for testing of sensor's sensitivity to ethanol, ammonium and acetone vapor for different samples: 1 – sensor; 2 – quartz tube; 3 – heater; 4 – sealant; 5 – capillary for matter vapors delivery; 6 – multimeter BM 859CFa (BRYMEN, Taiwan), 7 – computer

The working area for the different types of ZnO sensitive elements was estimated using the "Gwiddion" computer program for AFM-images processing.

3. RESULTS AND DISCUSSION

Figure 3 shows AFM and SEM images of the different types ZnO samples. Table 1 presents the structural parameters of the sensing elements (average grain size of the film, average diameter of the structure elements, roughness), and the ratio of surface area to projection area, obtained by AFM and SEM data. The relations of surface area to projection area increase from 1.07 till 1.45 at transition from the films to the microstructures, and further to the nanostructures. In our case the physical meaning of the surface area ratio to the projection area is the same as the ratio of the sample's surface to its volume. These numerical values of the ratio of surface micro- and nanostructures to their projections obtained through the program, the core of which is the statistical processing of the entire surface of the resulting image. Visually, it may seem that this ratio should be higher. However, it's not, given that three-dimensional image for a better visual representation of surface topology on Z-axis scale is different from that of the axes X and Y. Therefore, the calculated value for the reduced image is genuine. Real values of the surface area of micro- and nanostructures is somewhat reduced, this is due to the fact that the surface of the resulting image contains artifacts (errors) due to the geometry of the scanning probe [5]. Despite the fact that there are artifacts, tendency to increase the ratio of surface to the projection of the transition from film to micro- and nanostructures takes place.

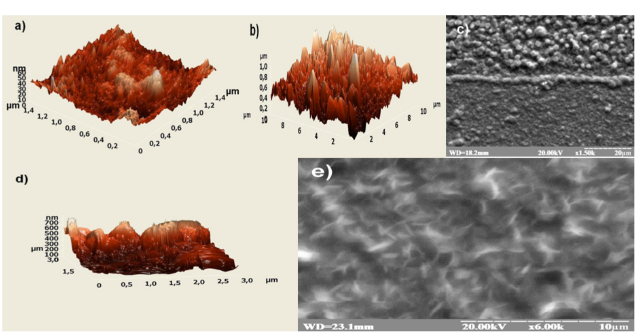

Fig. 3. AFM (a, b, d) and SEM (c, e) images of the ZnO samples: a) film; b),c) microstructure; d), e) nanostructure

Table 1. Structural characteristics of the sensing elements

	AFM-data			SEM-data
ZnO structure type	RMS (Root mean square) (nm)	Aver. grain size or the structure element diameter (nm)	Ratio of the surface area to the projection area	Structural parameters
film	6	28	1.07	-
micro-structure	73	2000	1.36	Hexagonal vertical tightly packed rods of 2 μm average diameter
nano-structure	102	216	1.45	Nanowires with the length of about 1.5 μm, and diameter of about 100 nm

Using the thermoprobe method it was determined that the films and the microstructures are characterized by the n-type conductivity, meanwhile the sensor, obtained on the basis of the chemically synthesized nanostructure manifests the p-type one. The p-type conductivity of the nanostructured sensitive element was also confirmed by the response of the sensor's signal upon the presence of vapor under testing. Ethanol and ammonium caused decrease of the film and microstructured sensors resistance, whereas the opposite effect was found to be in the case of the nanostructured sensors (fig.4). Thus, the sensor sensitivity was calculated using the formulas:

$$S = \frac{R_0}{R} \text{ – for the n-type samples,} \quad (1)$$

$$S = \frac{R}{R_0} \text{ - for p-type samples,} \quad (2)$$

where R_0 – resistance of ZnO sensor element without the vapor;

R – its resistance within the target gases.

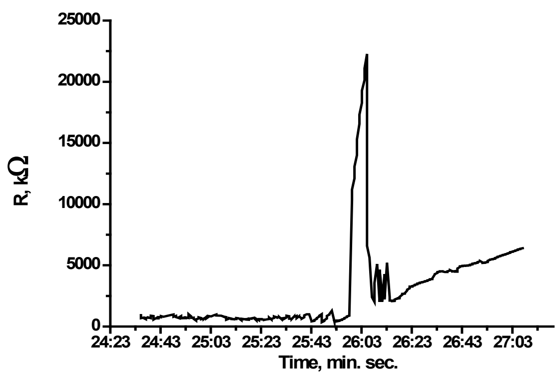

Fig. 4. The response curve of the sensor created on the basis of ZnO nanowires under an ethanol vapor at concentration of 100 ppm at 350^{0}C

Most semiconducting oxide gas sensors are based on the conductivity changes caused by the adsorption and desorption of the gas molecules on the surface of the sensing structure [6]. In ambient air, oxygen molecules can be adsorbed onto the surface of a ZnO sample with n-type conductivity and form O_2^-, O^-, and O^{2-} ions by capturing electrons from the conduction band; the deletion region is formed on the surface of ZnO, resulting in a decrease in carrier concentration and electron mobility [7]. When the sensor is exposed to a reducing gas, such as acetone or ethanol, the reducing gas reacts with the oxygen species adsorbed onto the surface and releases the trapped electrons back to the conduction band, thereby decreasing the depletion and resulting in the increased carrier concentration and electron mobility of the ZnO [8]. As acetone is introduced at moderate temperature, the acetone gas is oxidized by the oxygen species on the surface to form formaldehyde and cause increased conductance, as in Eqs. (3-5) [9].

$$CH_3COCH_3+O^- \rightarrow CH_3C^+O+ CH_3O^-+e^- \quad (3)$$
$$CH_3C^+O \rightarrow CH_3^{\ +}+CO \quad (4)$$
$$CO+O^- \rightarrow CO_2+ e^- \quad (5)$$

According to the paper [10], when *n*-ZnO gas sensor is exposed to air, an oxygen ion molecular is absorbed onto the surface of ZnO sensor to form O_2^- ion by attracting an electron from conduction band of the ZnO as shown in equation $O_2+2e \rightarrow O_2^{2-}$ or $2O_2+1e \rightarrow 2O_2^-$. So the high resistance of ZnO is present in air. For active ethanol gas at moderate temperature, the ethanol gas reacts with oxygen ion molecular on the surface and gives up electron as can be described by:

$$2C_2H_5OH+O_2^{2-} \rightarrow 2CH_3CHO+2H_2O+2e$$
$$2C_2H_5OH+ O_2^- \rightarrow 2CH_3CHO+2H_2O+1e.$$

Thus, the electrons released from the surface reaction transfer back into the conduction band which increase the conductivity and lower resistance of ZnO. In the case of a semiconductor material with p-type conductivity (nanostructure ZnO) situation will be different. Redundant due to reactions, electrons recombine with holes, reducing the density of free carriers leading to an increase in resistance patterns.

Table 2 presents the experimental and calculated characteristics of the sensors with ZnO elements of different dimensionality. Fig.5 shows the diagram displaying their dependence on the sensor type.

Table 2. Characteristics of the sensors with ZnO elements of different dimensionality

ZnO sensor's type	Sensitivity, (R_0/R)	Response time, (sec.)	Concentration, (ppm.)	Working temperature, (^{0}C)	Matter under testing
film	4	100	100	400	Ethanol
micro-rods	15	5	100	225	
	13.4	4	100	350	
nano-wires	55	10	100	350	
film	3.7	70	1000	400	Acetone
micro-rods	3	60	1000	225	
	5	20	1000	350	
nano-wires	38	5	1000	350	

It is clearly seen that transition to the nanostructured sensitive elements gives the largest gain in the sensitivity. At the same time, the ratio of the surface area to the projection area in the case of the micro- and nanostructured samples are very close - 1.36 and 1.45, respectively. Taking this into account, one can conclude that some other effect is responsible both for the drastic change of the sensitivity and the change of conductivity type. Such a variation would be connected with doping following the process of the nanostructures growth. Such a conclusion appeared to be very important since we deal with the first evidence concerning the possibility of obtaining of p-ZnO nanostructures by electrodeposition method. As it was shown by theoretical calculations from first principles [11], acceptor impurities in ZnO may be elements I (H, Li, Na, Ag and K) and V group (N, P, As). Besides the p-type conductivity in ZnO may be connected with deviations from stoichiometry. The acceptor levels in the bandgap form own defects of crystal lattice, namely, vacancies of zinc V_{Zn} and oxygen atoms in the interstices O_i [12]. By process of elimination we established that p-type conductivity in our case is not connected with impurities of Ag or K.. In case when we do not use potassium chloride and replacing the silver pads for aluminum ones, there was no change in the conductivity type of ZnO grown nanostructures from hole to electron. We used silver as a material for of contact pads of sensors depressurization to minimize the process of their oxidation.

We suggest that the zinc vacancies V_{Zn} are responsible for the p-type conductivity, as it was evidenced by the results of research [12], where the very close technology was used for receiving of ZnO nanowires with p-type conductivity. To confirm this hypothesis we plan research of thermostimulated luminescence of zinc oxide nanostructures grown by electrodeposition from an aqueous solution in the electrochemical cell with two electrodes.

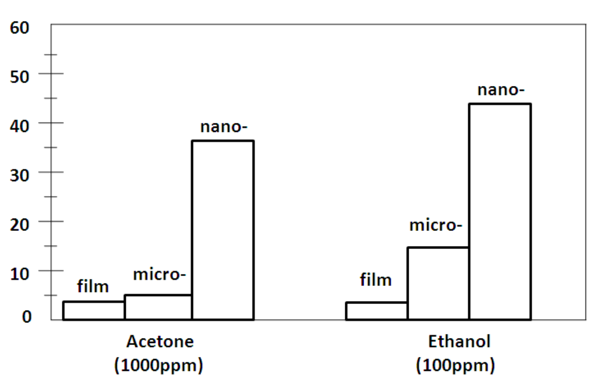

Fig. 5. Diagram displaying the sensitivity dependence to the ethanol and acetone vapor of the sensors with ZnO elements of different dimensionality at the temperature about 400°C

4. CONCLUSIONS

Therefore, impact of the morphology type and size effects on the main characteristics of the resistive sensor elements based on ZnO was investigated. The sensitive elements for the gas sensors have been obtained on the basis of the ZnO micro- and nanostructures by simple and inexpensive methods that can be attractive for a large-scale production. They were found to possess significantly better characteristics comparing to the thin film sensors. For a practical applications it is very important that ZnO nanostructures of p-type have been fabricated for the first time by electrodeposition in water solution.

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