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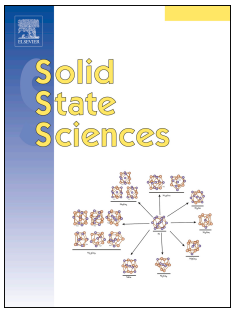

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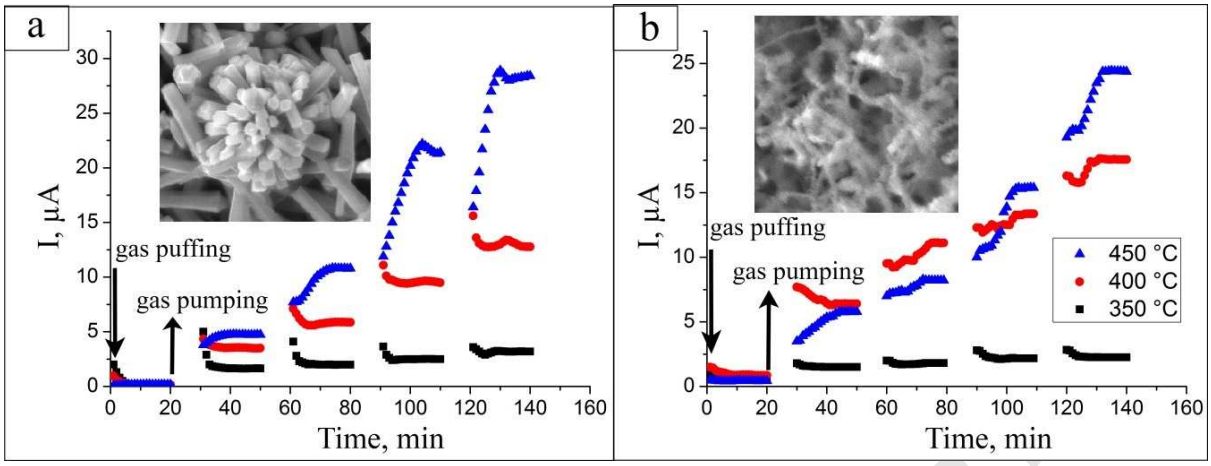

Nanostructured ZnO films for potential use in LPG gas sensors

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The aim of the work was to obtain ZnO nanostructures with heightened surface area and to study relationship between formation method and gas sensor properties towards propane-butane mixture (LPG). In order to synthesize ZnO nanostructures chemical and physical formation methods have been utilized. The first one was chemical bath deposition technology and the second one magnetron sputtering of Zn followed by oxidation. Optimal method and technological parameters corresponding to formation of material with the highest sensor response have been determined experimentally. Dynamical gas sensor response at different temperature values and dependencies of the sensor sensitivity on the temperature at different LPG concentrations in air have been investigated. It has been found, that sensor response depends on the sample morphology and has the highest value for the structure consisting of thin nanowires. The factors that lead to the decrease in the gas sensor operating temperature have been determined.

Keywords: zinc oxide; gas sensors; LPG; chemical bath method; magnetron sputtering.

1. Introduction

Zinc oxide (ZnO) is a promising material for application in optoelectronics [1], UV lasers [2], dye sensitized solar cells [3-5], photocatalysis [6, 7] and etc. Furthermore, it has already found application as a sensitive layer of cheap resistive gas sensors [8, 9]. Among different gases, the possibility to control propane-butane mixture (LPG) content in air is of high importance due to its high explosiveness. This gas is widely used in internal combustion engines, industry and households.

There are only few papers devoted to investigation of sensor properties of ZnO based structures towards LPG [10-21]. To the best of our knowledge, in the majority of publications the sensitive structures were formed by chemical methods, such as spray-pyrolysis [10-13], sol-gel [14], chemical bath deposition [15-20]. For those methods, the gas sensor sensitivity had different values, which can be explained by the different surface area of the samples.

Besides that, in the above-mentioned publications [10-20] the dependencies of gas sensors sensitivity on the temperature have been measured. The authors have proved that the increase in the temperature up to a certain value leads to enhancement in the sensitivity. However, the further temperature growth results in the decrease in the sensor sensitivity. Thus, there is an optimum temperature value corresponding to the maximum sensitivity of the sample. In various studies, the optimal temperature has value in range from 200 to 400 ° C. It is important to emphasize, that these ZnO based sensors had no impurities, which naturally

eliminates the one of the possible reason for this effect - doping. Clarification of the nature of this effect could be an important step towards the creation of low-temperature ZnO based LPG gas sensors operating even at room temperature.

It is known, that ZnO formation method (chemical or physical) has strong effect on the structural-phase state of the samples and the ensemble of the defects [22-24], which in turn, determine the structure dependent sensor properties of the material. It can be assumed, that these characteristics also affect the gas sensor properties of ZnO. Therefore, it is interesting to compare the sensor properties towards LPG of the samples obtained by physical and by chemical method.

This work is the starting point in our study of gas sensor properties with respect to LPG of various ZnO structures obtained by chemical bath deposition and by magnetron sputtering. The aim of the work is to determine the optimal method and technological parameters corresponding to formation of material with the highest sensor response, as well as to identify the factors that lead to the decrease in the sensor operating temperature.

2. Material and methods

In this study two different methods have been used in order to obtain gas-sensitive layers. The first was chemical bath deposition [25, 26]. The second one was magnetron sputtering of zinc followed by oxidation.

Chemical bath deposition was carried out by immersing the substrate in an aqueous solution containing a zinc nitrate precursor ($Zn(NO_3)_2$) at a concentration

of 0.1 M under continuous magnetic stirring. The solution was heated to 90 ^{o}C and kept at this temperature for a certain time. To maintain the pH of the solution at 10 level, ammonia solution (NH_4OH) was slowly added to the mixture. To investigate the dependence of the surface on the sensor properties the deposition time was varied from 60 min to 120 min and two series of samples were obtained assigned as (Ch60) and (Ch120).

The second method consisted of two stages. At first, zinc layers were formed using magnetron sputtering of zinc target in high-purity argon atmosphere. In this case, the modified magnetron sputtering method was utilized, which consisted in reverse flows of the sputtered substance deposition [27]. Two sets of the samples were obtained at the discharge power values 15 W (Ph15) and 30 W (Ph30). The working gas pressure was 8 Pa and the deposition time 60 min for the both experiments. On the second stage, obtained structures were oxidized in oxygen atmosphere at pressure $5 \cdot 10^4$ Pa and temperature 400 °C. The above oxidation conditions allow to save the initial layers morphology almost unchanged [28].

Structural investigations of the samples were carried out using an X-ray diffractometer (Bruker D8 Advance) with Ni-filtered Kα radiation of copper anode in a range of angles $20^o < 2\theta < 80^o$, where 2θ is the Bragg angle. XRD patterns were normalized to the intensity of the (002) peak of the hexagonal ZnO phase. Phase analysis was performed by comparing interplanar distances and relative intensities of the investigated samples with the standard according to JCPDS 79-0207 [23]. The X-ray beam was focused using the Bragg–Brentano method.

The texture quality of the ZnO films was estimated using Harris method [24, 25]. The pole density was calculated using the equation:

$$P_i = \frac{(I_i / I_{0i})}{\frac{1}{N}\sum_{i=1}^{N}(I_i / I_{0i})}, \quad (1)$$

where I_i and I_{0i} are the integral intensity of the *i*-th diffraction peak for the investigated film and for the standard, respectively; *N* is the number of lines in the diffraction pattern. Then we built the dependences P_i versus $(hkl)_i$ and P_i versus φ. Here φ is the angle between the chosen direction and normal to crystallographic planes corresponding to the reflection in the XRD pattern and $(hkl)_i$ are Miller indices. This angle was calculated for the hexagonal lattice, using the equations given in Ref. 25. The axis of the texture has indices corresponding to the maximal value of P_i. The orientation factor was estimated via equation:

$$f = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(P_i - 1)^2}\ . \quad (2)$$

The interplanar distances of ZnO wurtzite structure were found from the position of $K_{\alpha 1}$ component of all of the most intense lines present in the XRD pattern.

In order to investigate the gas sensor properties, the samples were placed inside a quartz reactor, which was equipped with resistive heater outside. Before the sensor test, the samples were heated to the desired temperature value. The temperature was regulated by chromel-alumel thermocouple with an accuracy of 1 °C. The samples were contacted by molybdenum gold-plated contacts and the voltage 5 V was applied. After that, the value of the current passing through the

sample was measured at different concentrations of propane-butane in air inside the quartz reactor.

3. Results and discussion

The morphologies of ZnO samples produced using two different methods are presented in the Fig.1. Zinc oxide layers obtained through the decomposition of zinc nitrate precursor in the presence of complex agent via chemical bath deposition consist of hexagonal rods that have different inclination angles to the substrate surface. At the same time, the increase in the reaction time from 60 min (Fig 1a) to 120 min (Fig 1b) leads to the increase in the thickness (from 0.2-0.8 μm to 1.0 - 1.9 μm) and in the rods length. Besides that, the merging of the gaps between rods by thin lamellar crystallites is observed, which leads to the formation of a very porous layer. The samples prepared by magnetron sputtering followed by oxidation, also have a developed surface. At the discharge power 15 W, a porous structure consisting of interconnected particles (Fig. 1c) was formed. With an increase in the discharge power up to 30 W, a structure consisting of nanowires with a diameter of 100 - 300 nm start to grow (Fig 1d).

The phase analysis of the samples produced by chemical bath deposition and magnetron sputtering has shown that the layers have hexagonal structure of ZnO. The maximum intensity has the reflections from the crystallographic plane (001) which indicated the presence of growth texture [002] coinciding with the crystal lattice axis. In addition, we have registered fairly intense lines at angles 31.65º,

36.13º, and 47.52º in the diffraction patterns. They were identified as the reflections from (100), (101), (102) ZnO wurtzite planes, respectively [JCPDS 79-0207].

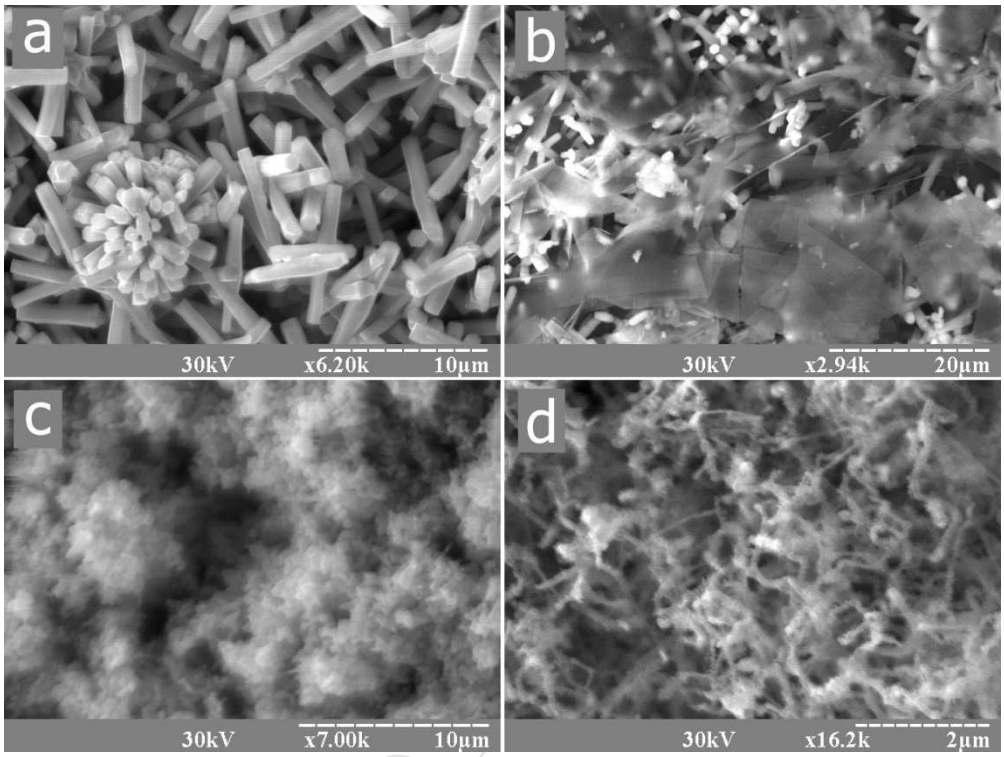

Figure 1. SEM images of ZnO films produced by chemical bath deposition at different reaction time: 60 min (a), 120 min (b); and by magnetron sputtering at different discharge power: 15 W (c) and 30 W (d).

Furthermore, in the XRD patterns of ZnO produced by chemical bath deposition, the presence of another phase was found. It was identified as reflections from (311), (020), (021) planes of $H_{12}N_2O_{16}Zn_5$ compound. [JCPDS 024-1460, 30]. This fact can be explained by residual sediment incorporation into the crystalline lattice of the film during the chemical reaction.

The pole density and the orientation factor calculations of the hexagonal phase of ZnO films (Fig. 2b) confirmed the presence of [002] axial growth texture for the samples obtained by both methods. This growth texture is typical for ZnO films. Furthermore, the orientation factor values have shown that the crystallinity of the films produced by chemical bath deposition is improved by increase in the deposition time from 60 (f = 0.45) min to 120 min (f = 1.1) and in the layer thickness correspondingly. The same dependence was observed for the ZnO samples obtained by magnetron sputtering (Ph15: f = 0.61, Ph30: f = 0.76).

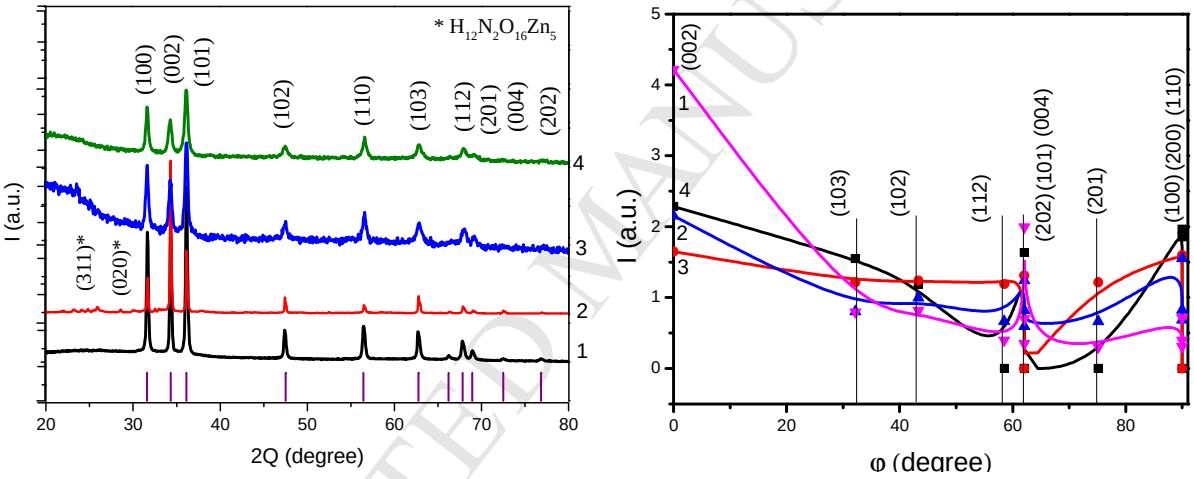

Figure 2. XRD patterns (a) and the dependencies of the pole density on the angle φ between the texture axis and the normal to the reflection plane for ZnO films obtained by chemical bath deposition (60 min (1) and 120 min (2)) and magnetron sputtering 15 W (3) и 30 W (4).

It has been established, that measurement of the gas sensor properties was hard to implement for freshly prepared samples by chemical bath methods. In this case, even at constant environment conditions the value of the current through the sample changes significantly. From our point of view, it is caused by presence of

residual impurities, which contaminate the samples. The presence of other than ZnO phases was also confirmed by X-ray diffraction measurements. However, after one hour annealing in air atmosphere at 500 °C, the impurity phases disappear from the X-ray diffraction pattern and the current stabilizes at a constant level.

The gas sensor sensitivity was defined as the ration of the current through the sample in air containing propane-butane mixture at desired concentration to the current value in pure air atmosphere (I_{LPG}/I_{air}). The measurements were performed in the temperature range from 300 °C to 450 °C with 50 °C step. The gas sensor tests have shown, that an increase in propane-butane concentration leads to an increase in the current value (Fig. 3). After the gas mixture introduction, the current dependencies have very similar character for all of the samples. It is necessary to point out, that the current value stabilizes after about 10 min.

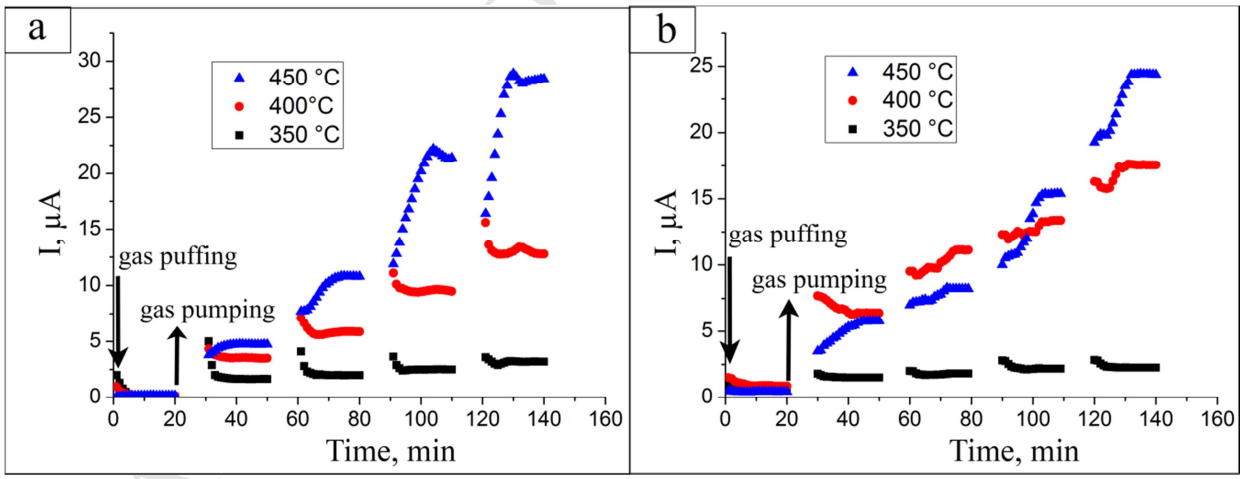

Figure 3. Dynamical response at different temperature values of the samples Ph30 (a) and Ch60 (b) during puffing and pumping of air containing different LPG concentrations (0%, 0.2%, 0.5%, 0.7%).

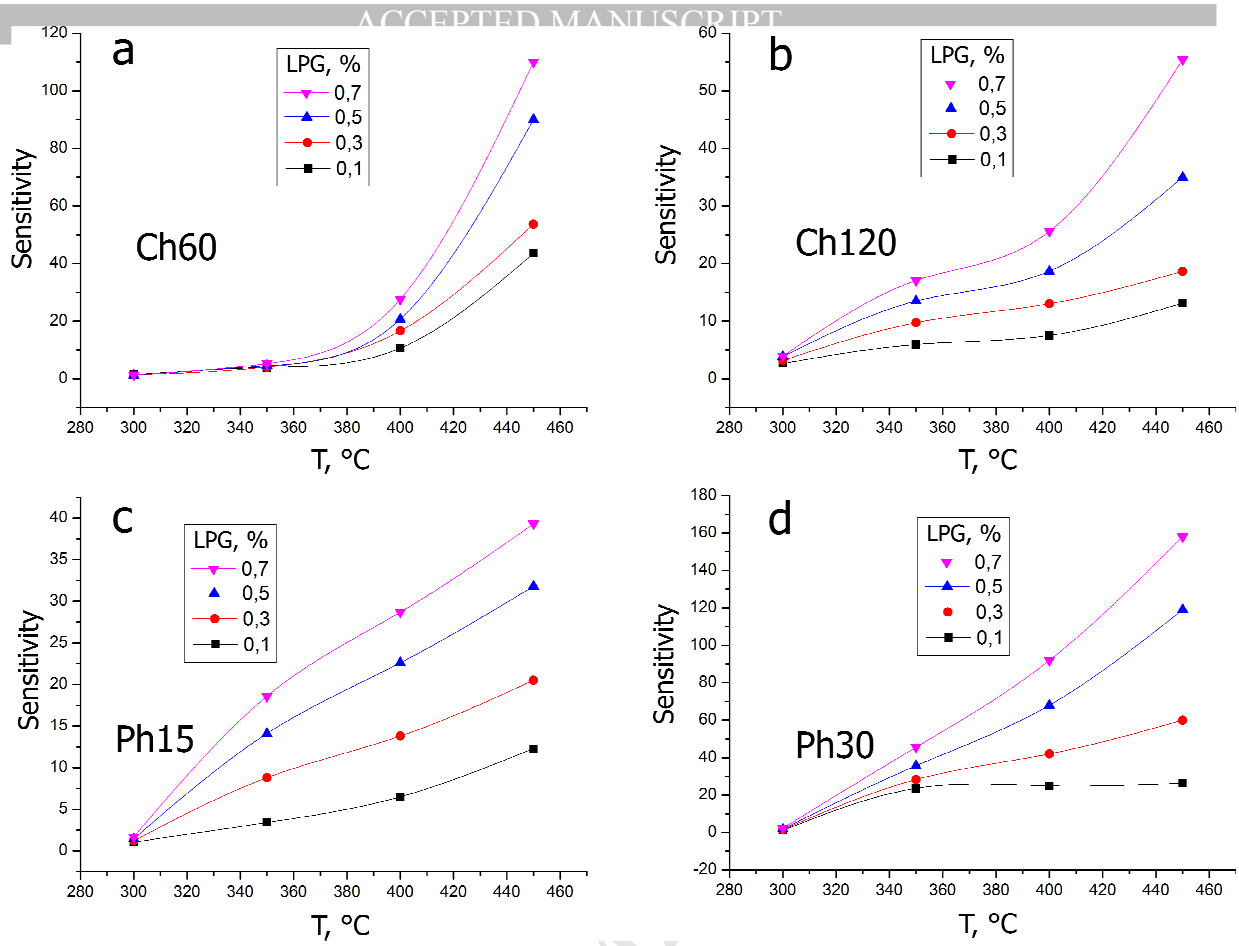

Figure 4. Dependencies of the sensor sensitivity on the temperature for the samples Ch60 (a), Ch120 (b), Ph15 (c), Ph30 (d) at different LPG concentrations in air.

It has been determined experimentally, that regardless of the deposition method the gas sensor sensitivity has negligibly small values below 300 °C (Fig.4). The increase in the temperature up to 350°C greatly intensifies the samples sensitivity, which continues to grow even at higher temperature values up to 450°C. Thus, the distinctive feature of our samples, in comparison to ZnO based LPG sensors reviewed in the literature [10-20], is the absence of the characteristic maximum on the sensitivity versus temperature dependencies. For conventional sensors such maximum is observed in range of temperatures from 200 to 400 °C.

The above described tendency toward monotonic increase in the gas sensor sensitivity is observed for all of the samples. Thus, at the first sight it seems that the sensor properties are not affected by the deposition method. However, it is necessary to point out, that all of the samples were subjected to annealing. The samples Ch60, Ch120 were annealed at 500 °C in order to exclude impurities and Ph15, Ph30 were kept at 400 °C with purpose to transform Zn into ZnO. It is well known, that annealing can greatly influence structure-phase state, the surface morphology, and the defect structure of ZnO films [31-34]. That is why, the monotonic character of the sensor sensitivity towards LPG can be explained by their annealing and corresponding assembling of the defect in the samples. But, this assumption requires additional prove. If to order the samples according to their gas sensor sensitivity, we obtain: Ph15 → Ch120 → Ch60 → Ph30 (Fig. 5).

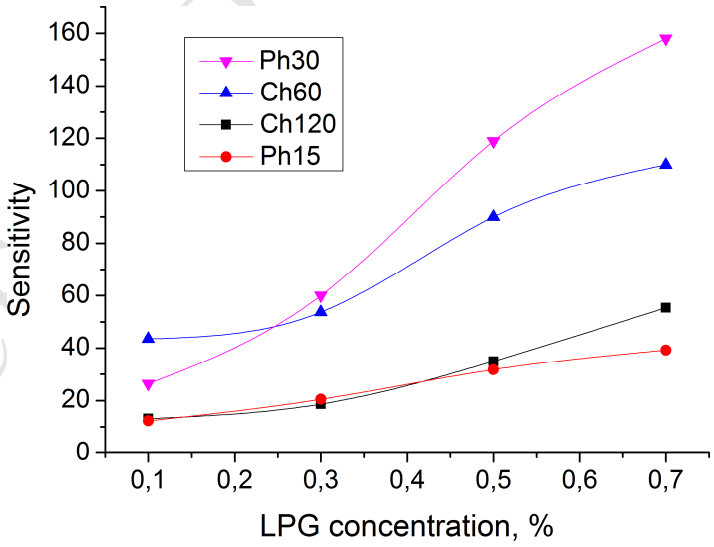

Figure 5. Dependencies of the sensor sensitivity to different LPG concentrations at 450 °C.

The result is quite predictable from their morphology. The highest response has the sample Ph30 that consists of thin ZnO nanowires and has the largest value of the surface area to the volume ration. The sample Ch60 has structural elements of bigger size, and as a result has lower gas sensitivity value.

4. Conclusions

The sensor properties of ZnO films with developed surface obtained by two different methods have been investigated. The first one was chemical bath method and the second magnetron sputtering followed by the samples oxidation. It has been established, that the presence of propane-butane mixture in air atmosphere causes decrease in the samples resistance. The films formed by chemical bath method need annealing before the sensor tests in order to eliminate residual impurity phases and in such a way to stabilize the current value. It has been shown, that the gas sensor sensitivity differs significantly for various samples. This fact is caused by different values of the surface area to the volume ratio. Besides, the time required for the resistance and the temperature to reach stable values at which the sensor properties start to observe is the same for all of the samples. It has been found, that the increase in the temperature in the range from 300 °C to 450 °C causes corresponding increase in the gas sensor sensitivity. The absence of maximum on the sensitivity versus temperature dependencies for the samples obtained by the both methods can be explained by their annealing at 400°C and 500 °C.

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Highlights

- ZnO porous nanostructures have been synthesized by chemical and physical methods;
- influence of deposition method on sensor properties to LPG has been studied;
- it is shown that LPG sensor response depends on the porous layer morphology.

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