Gas sensing properties of 1-D ZnO obtained by hydrothermal process

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ZnO was obtained by hydrothermal process using $Zn(CH_3COO)_2 \cdot 2H_2O$ like precursor and cationic surfactant tetra-n-buthylammonium bromide-TBAB. The molar ratio surfactant/Zn precursor was 0.6. The gel obtained was stirring for 24 hours and transferred to an autoclave for 3 days at the 100^0C. The obtained powder was calcined at 500^oC for 2 hours and pressed in the disc form with the dimensions $\varnothing 6 \times 1$ mm at 2 tone force/cm^2. For the sensor fabrication, the disc was mounted on the transistor ambasis. TGA of the uncalcined sample under air static and 10^oC/min heating rate, showed the loss of the water below 81.8 ºC and surfactant loss started at 164-186.3 ºC being completely removed at about 450 ºC. X-ray diffraction was effected on the calcined powder where was obtained a cristalline structure type hexagonal wurtzite with lattice constants a=0.324982 nm and c=0.520661 nm, crystal domain size is estimated to be 48.9 nm using Debye-Scherrer. The N_2 adsorption desorption isotherm shows that the powder calcined ZnO is composed by the mesopores and micropores. The specific surface area determinated by BET method was 6 m^2/g. ZnO disc was scanned using white light interferometry technique and the profilograms show the maximum surface peaks are around 27 µm and maximum valleys dimensions are 24 µm. The average roughness that exists on all selected areas was 2 µm. The sensor was tested in dynamic regime in the conditions: the flow of 300 cm^3/min CO_2 at the 25, 50 and 70^oC gas testing chamber temperature and was measured the voltage values in function of the time. The maximum voltage values obtained were 320 mV, 430 mV and 245 mV corresponding for 25, 50 and 70^oC respectively and after 6, 4 and 5 minutes gas exposure.

1. Introduction

In recent years, the quasi-one-dimensional materials were intensive studied because of their unique quantum properties and their potential to be integrated into electronic and optoelectronic devices.

Zinc oxide is one of the earliest discovered oxide for gas sensing semiconductor materials. ZnO is a n type semiconductor oxide of wurtzite structure with a wide bandgap of 3.37 eV and large excitation binding energy of 60 mV at room temperature [1-2]. ZnO is a material with great potential for a variety of practical applications, such as piezoelectric tranduscers, optical waveguides, transparent conductive oxides, chemical sensors [3]. Various methods have been developed for the synthesis of ZnO nanostructures, such as sol-gel [3], hydrothermal [4], chemical vapor deposition CVD [5], electrophoretic deposition [6], vapor-liquid-solid VLS method [7-8] and thermal decomposition [9]. Recently, 1D ZnO nanostructures have attracted attention due to their unique physical properties as well as their applications in optoelectronic nanodevices and functional materials. For example, nanolasers, transistors, field emission display and UV detectors fabricated with 1D-ZnO nanostructures have been raported [10-12]. In addition, 1D ZnO nanostructures have been extensively used for gas sensing applications because their resistances are adjusted by the types of adsorbed gas species onto their surfaces [13]. In this paper we obtained ZnO by hydrothermal process using tetra-n-buthylammonium bromide cationic surfactant for application in gas sensing.

2. Experimental

Materials
Zinc acetate dihydrate 98% Alfa Aesar
Tetra-n buthylammonium bromide 98% Alfa Aesar

Apparatus
X-ray analysis was performed with a X Bruker-AXS type D8 ADVANCE difractometer under CuKα radiation (λ=1.54059 Å), 40kV / 40 mA, filter k_β of Ni. pas: 0.04 ^{o}, measuring time on point: 1 s, measure range $2\theta = 10^o – 100^o$.

Thermal analysis was effected with NETZSCH STA 409 PC/PG derivatograph, in the conditions of air static and heating rate of 10^oC/min in alumina crucible. The mass sample was 12, 330 mg.

N_2 adsorption desorption isotherms were performed with a AUTOSORB-1, Quantachrome Instruments, United Kingtom in the conditions: working gas N_2, measure temperature: -196^oC and the range mesure P/P_o 0.001-0.99.

ZnO probe was scanned using white light interferometry technique with VEECO Interferometry microscope-USA, composed from different parts: a CCD camera with digitized intensity and data acquisition, a

detector array, magnification selector, beam splitter, illuminator, filter, translator, microscope objective and Mirau interferometer.

The gas testing apparatus

The detection testing of gas CO_2 was performed in the apparatus presented in Fig. 1. The voltage measurements were effected by testing module, in automated process mode. An control panel, provides a lot of measuring value, by rate 1/10 second. The bench of testing for the gas sensor consists in an enclosure where there are set the testing conditions of the sensor as well as in connected equipment. The whole process of testing is automated, being controlled by a programmable automaton. The gas for testing is introduced in a controlled way in the testing enclosure, through a mass debit meter. In the testing enclosure is set a constant temperature, controlled by a temperature regulator.

Fig. 1. The apparatus for the gas sensor testing.

The ZnO synthesis

ZnO was obtained by hydrothermal process using $Zn(CH_3COO)_2x2H_2O$ 98% purity Alfa Aesar like precursor and cationic surfactant tetra-n-buthylammonium bromide-TBAB 98% purity, Alfa Aesar. The molar ratio surfactant/Zn precursor was 0.6. The solution of zinc acetate dihydrate was acidified with HCl 1:1 to pH 2 was added in drops to the surfactant solution and was stirring for 1 hour at the room temperature.The pH was adjusted to 9 using NH_4OH aqueous solution. The gel obtained was stirring for 24 hours and transferred to an autoclave for 3 days at the 100^0C. The obtained materials were filtered, washed and dried at 100^oC calcined at 500^oC for 2 hours and pressed in the disc form with the dimensions $\varnothing 6x1$ mm at 2 tone force/cm^2 .

For the sensor fabrication, the disc obtained by pressing of the ZnO powder was mounted on the transistor ambasis and metallized with Ag ink like electrodes.
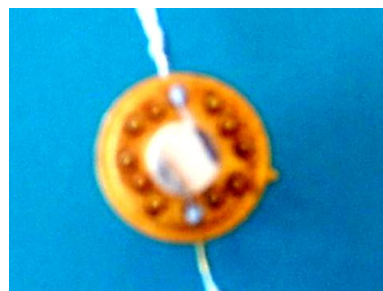

Fig. 2. The sensor image.

3. Results and discussion

The thermal behaviours of dried ZnO gel (ZnO-TBAB) have been investigated by thermogravimetric analysis (TG), differential termogravimetric analysis (DTG) and differential scanning calorimeter (DCG). The TG-DTG-DSC results is shown in Fig. 3.
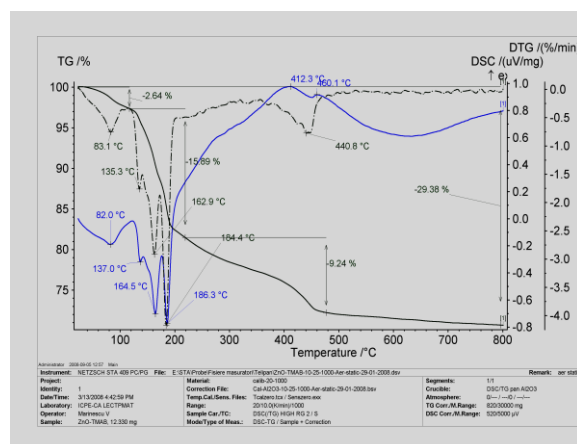

Fig. 3. The thermal analysis of ZnO dried gel.

For the synthesized material we observe the following stages: first, water loss of 2.62% is observed at 81.8^oC in DSC curve and 83.1% in DTG curve, it is followed by a second water loss with mass variation 2.29% evidenced by DSC curve endothermic peak at 136.7^oC. The next process are decomposition of the organic part showed by 2 endothermic peaks in DSC curve at 164.6^oC and 186.3^oC, also evidenced in DTG signals at 162.4^oC and 184.4^oC. Both have a mass loss of 6.74% and 6.99% from initial mass. The last phenomena it is the decomposition of zinc acetate occurred at 450^oC in DSC curve and at 440.8% in DTG curve. This process have a totality mass loss of 9.46%. The analysis of the sample revealed 29.83 % total weight loss on heating to 800 ^oC.

The X-ray diffraction analysis for ZnO powder calcined at 500 ^oC for 1 hour is shown in Fig. 4. XRD diffraction peaks belonging to (100), (002), (101), (102), (110), (103) (201).

The structure obtained is hexagonal wurtzite with lattice parameters a=b=0.324982 nm and c=0.520661 nm,

in agreement with literature values (card number 01-089-1397 a=0.3253 nm, c=0.5213 nm for commercial ZnO) and α=β=90° and γ=120°. For the peaks (100), (101), (102) and (110) were calculates the grain sizes with the Debye-Scherrer formula:

$$D = \frac{0.9\lambda}{B\cos\theta} \qquad (1)$$

where:

D is grain size, λ is the wavelength of this X-ray λ=0.154059 nm, B is the full width at half maximum (FWHM) and θ is the half diffraction angle of crystal orientation peak.

The dislocation density δ, which represents the amount of defects in the film oxide is determined with formula:

$$\delta = 1/D^2 \qquad (2)$$

where:

δ is the dislocation density and D is the grain size.
The larger values for D indicate a better crystallization of the film. The structural parameters obtained at the X-ray diffraction for ZnO were presented in Table 1.
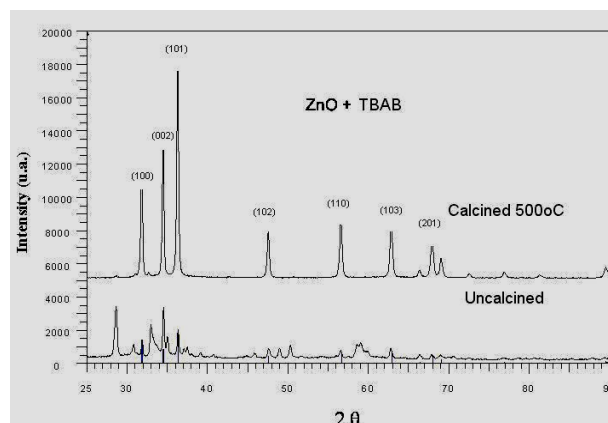

Fig. 4. The X-Ray diffraction for ZnO gel.

The Zn-O bond length L, is given by equation

$$L = \sqrt{\frac{a^2}{3} + \left(\frac{1}{2} - u\right)^2 c^2} \qquad (3)$$

Where u has the semnification:

$$u = \frac{a^2}{3c^2} + 0.25 \qquad (4)$$

Table 1. The structural parameters of the ZnO.

Sample	2θ	hkl	a (Å)	c (Å)	D (nm)	δx10⁻⁴ (nm⁻²)	L(Å)
ZnO-TBAB	31.769	100	3,253	5,209	67.2	2.21442	1.97940
	36.252	101			53.6	3.48073	
	47.538	102			55.7	3.22321	
	56.602	110			35.1	3.54658	

The N$_2$ adsorption desorption isotherm shows that the powder calcined ZnO is composed by the mesopores and micropores. The specific surface area determinated by BET method- Fig. 5 was 6 m^2/g. The total volume of the pores was $8,74\times10^{-2}$ cm^3/g.
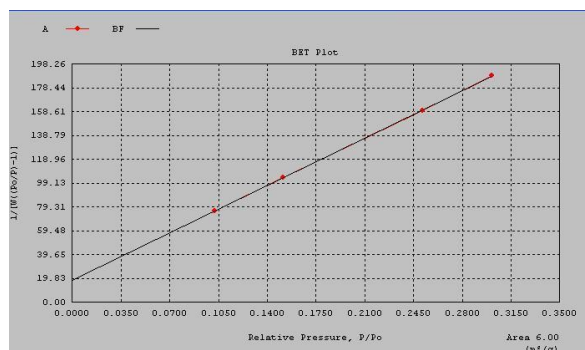

Fig. 5. Then plot of BET specific surface area ZnO powder calcined at 500°C.

ZnO probe surface was analyzed by using the white light interferometry technique in three different zones, covering an area of 255 μm length (X axis) and 191 μm width (Y axis) for each focusing. Each profile can give us a complete information about roughness and height variation for X axis and Y axis. As we can observe in profilogram - Fig. 6, the maximum surface peaks are around 27 μm and maximum valleys dimensions are also 24 μm. The average roughness that exists on all selected areas is 2 μm

Statistic variation and raw data image processing tells us that the surface has many irregularities like valleys and peaks, but these aren't exceeding the specified maximum values. The image shows that the deposition of ZnO solution is not covering many surface parts equally creating this gaps.
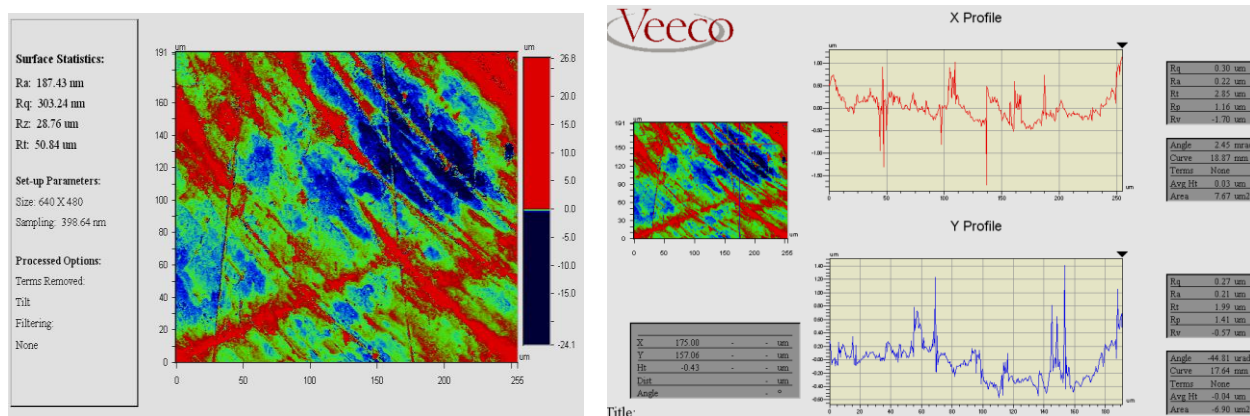
Fig. 6. The prophilograme of the ZnO disc.

The gas testing

The sensor was tested in dynamic regime in the testing apparatus presented in Fig. 1, in the conditions: the flow of 300 cm^3/min CO_2 at the 25, 50 and 70°C gas testing chamber temperature and was measured the voltage values function of the time. Fig. 7 shows the histogram where were obtained the maximum voltage values of 320 mV, 430 mV and 245 mV corresponding for 25, 50 and 70°C respectively and after 6, 4 and 5 minutes gas exposure. It can be see that the ZnO is very sensitive in CO_2 atmosphere, obtaining the great values of voltage for testing temperature of 25 and 50°C and a voltage decrease at the 70°C temperature testing.
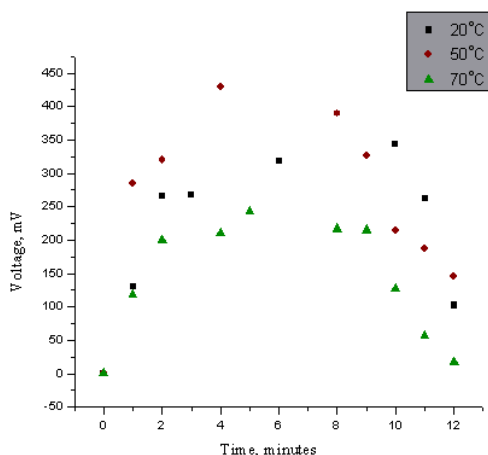

Fig. 7. The response of the sensor voltage-time for CO_2.

4. Conclusions

ZnO was obtained by hydrothermal process using $Zn(CH_3COO)_2x2H_2O$ like precursor and cationic surfactant tetra-n-buthylammonium bromide. The molar ratio surfactant/Zn precursor was 0.6. The uncalcined and calcined sample at 500°C for 2 hours was characterized by

X-ray diffraction, thermal analysis, N_2 adsorption desorption isotherm and white light interferometric microscopy. X-ray diffraction pattern for the powder calcined showed a crystalline structure type hexagonal wurtzite with lattice constants a=0.324982 nm and c=0.520661 nm in accord with commercial ZnO. TGA of the uncalcined sample under air static and 10°C/min heating rate, showed the loss of the water below 81.8 ºC and surfactant loss started at 164-186.3 ºC being completely removed at about 450 ºC. The N_2 adsorption desorption isotherms show that the powder calcined ZnO is composed by the mesopores and micropores. The specific surface area determinated by BET method was 6 m^2/g. The total volume of the pores was 8,74x10^{-2} cm^3/g. The surface characteristics were determined by white light interferometric microscopy on the ZnO sample pressed in disc with the dimensions: $\varnothing$6x1 mm and the specific rugosity was analyzed focusing on three different points, the covered area for each point was about 191 microns x 255 microns. The elevations or valleys give us the maximum height which is around 25 microns. The sensor was tested in dynamic regime at the flow of 300 cm^3/min CO_2 at the 25, 50 and 70°C gas testing chamber temperature. The maximum voltage values obtained were 320 mV, 430 mV and 245 mV corresponding for 25, 50 and 70°C respectively for 6, 5 and 5 minutes exposure. ZnO is very sensitive in CO_2 atmosphere, obtaining the great values of voltage for testing temperature of 25 and 50°C and a voltage decrease at the 70°C temperature testing.

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