Gas sensors based on optical fiber coated with nanocrystalline TiO_2 and nanofibrous ZnO

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***Abstract* – The paper is divided into two main sections: first, we report on magnetron sputtering of zinc oxide and titanium dioxide; second, the results of the investigation of the morphology and sensing characteristics of the optical fiber sensors are presented and discussed. We describe the fabrication route of the liquid petroleum gas (LPG) optical sensors, based on optical fiber coated with ZnO and TiO_2 nanacrystalline films. The obtained sensors attain 2.77% sensitivity for ZnO and 24.4% for TiO_2.**

***Index Terms* —optical fiber, magnetron sputtering, nanocrystalline film, nanofibrous, SEM, TiO_2, ZnO.**

I. INTRODUCTION

In this paper, we report on fabrication of opto-chemical sensors which sensing performance is related to an enhancement effect of the optical near-field induced by nanostructures of zinc oxide, titanium dioxide, tin oxide or indium-tin oxide. The listed oxides are commonly used for resistive gas sensors for human security, environmental and industrial applications. The operation of such sensors is based on adsorption of gas molecules on semiconductor surface changing electrical resistivity and also optical refractive index. These two parameters can be measured for electrical and optical gas sensors. The adsorbed gases modify the intrinsic electronic defect formation in the wide-band-gap semiconductors. The gas sensitivity of such materials is determined by chemisorption of molecules, formation of space charged areas, and variation of the concentration of the charge carriers in the subsurface layer [4]. Zinc oxide attracts increasing attention in comparison with other oxides because of its numerous applications (sensors, solar cells, antimicrobial and anticorrosive surfaces, piezoelectric devices, luminescent devices) [1, 2]. As to titanium dioxide, it represents a multifunctional material with outstanding sensing, optical properties and biocompatibility, and it is a widely utilized redox photocatalyst. As an active element of gas sensor, ZnO and TiO_2 may be utilized for detection of reductive gases (CO, H_2, NH_3) or humidity. Recently, smart sensors based on semiconductor films for detection of toxic gases and food quality were elaborated. There are diverse methods to obtain ZnO films and nanostructures like spray coating, metal-organic chemical deposition (MOCVD), pyrolysis, magnetron sputtering, various chemical approaches. It is well known that gas detection depends on crystal quality and surface to volume ratio inherent to nanocrystalline films [3-5, 7].

Gas sensors based on semiconductor oxides attracted a huge interest of industrial companies and research groups dealing with environmental monitoring and health. Liquid petroleum gases (LPG), like propane-butane, are used in household and cars and thus people contact with them very often [5-6, 9]. LPG vapors are dangerous because of their autoignition at 2.1-9.5% of propane in mixture with air and 1.5-8.5% of butane, but 1 liter of LPG at evaporation turns into 250 liters of gas. LPG gases are dense and accumulate near to the place of leakage and have no natural smell, while in combination with its toxicity, these parameters make LPG rather dangerous. The rate of propane and butane in technical LPG is approximately 60/40% or 40/60% depending on the season, also propylene, butylene, ethylene and methane are constituents of LPG in small proportions. In such conditions, the fabrication of highly sensitive LPG sensors represents an imperative task. In this work, we present results of morphological study and gas detection experiments of ZnO and TiO_2 optic fiber gas sensors prepared by the magnetron sputtering techniques.

Our efforts fit with the goal of researchers to improve many aspects of the quality of life, to make it safer, to make medical diagnostics cheaper and faster, to provide reliable monitoring of the environmental parameters.

II. EXPERIMENTAL PART

For the oxide film deposition, we utilized RF magnetron sputtering equipment. The technical parameters of the RF deposition consist of specific magnetron power, gas pressure in the chamber, substrate heating and gas flow rate. The main advantages of this technological approach are related to high rate of film deposition and high reproducibility of chemical composition of the material. RF deposition rate is in direct dependence on the magnetron power, gas pressure inside the chamber and the substrate heating. This method is described in previous articles [8].

ZnO and TiO_2 films were grown by magnetron sputtering in Ar atmosphere. As targets we used ZnO 99.99% and TiO_2 99.9%. Optical fiber was cut with manual cleaver under 90° to obtain smooth straight surface. Care was taken to prevent signal lose at sensor measurements. The prepared fibers were washed in acid mixture (7 g K2Cr2O7, 10 ml H2O, 100 ml H2SO4) at room temperature as well as in distilled water, to remove accidental residues for better adhesion of the oxide films.

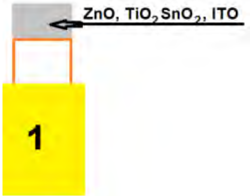

Fig.1. Scheme of oxide deposition on top of the optical fiber.

The optical fiber was mounted inside the magnetron chamber on a support with heating element. The distance between the substrate and target was kept at 8 cm. The chamber was purged to $1.2 \cdot 10^{-6}$ Torr and filled with Ar to obtain a constant pressure of $4.5 \cdot 10^{-3}$ Torr. The gas flow of 99.99% pure Ar in chamber was kept at 60 ml/min. The film thickness is controlled in the process of deposition by microbalance MTM-10/10A. ZnO and TiO_2 nanostructures were grown in 10 - 30 min under magnetron power of 200 W and substrate temperature of 20° C.

The sample morphology was studied with Hitachi SU 8230 and Vega Tescan 5130MM Scanning Electron Microscopes equipped with EDX detector. The sensor response was investigated using a fiber optic refractometer set-up, which monitors the reflectivity as a function of time in the presence of different butane concentrations. A schematic view of the basic sensor design is reported in Fig. 2. It is a chamber with three gas inlets with possibility to control flow rates. In the initial state, when the sample is loaded, the chamber is filled with nitrogen and sensor's base line is measured. Subsequently, the LPG is purged inside the chamber and the sensor response is collected. The equipment permits to pump the gas mixture in different proportions. One of the inlets introduces nitrogen, two others - LPG with resulting flow rate of 50 sccm or 500 sccm of LPG in mixture. The light source represented a superluminescent diode (40 nm bandwidth) operating at 1310 nm.

Reflectance itself depends on the refractive index of the optical fiber, n_f, of the sensible film, n and of the external medium, n_{ext}, so as assuming the film thickness d and the wavelength of the probe light λ:

$$I = \alpha R = \alpha \frac{(r_{12}+r_{23})^2 4 r_{12} r_{23} \sin^2\delta}{(1+r_{12}r_{23})^2 - 4 r_{12} r_{23} \sin^2\delta} \quad (1)$$

$$r_{12} = \frac{n_f - n}{n_f + n};\ r_{12} = \frac{n - n_{ext}}{n_{ext} + n};\ \delta = \frac{2\pi n d}{\lambda}. \quad (2)$$

where r_{12} and r_{23} are the reflectivity coefficients at the fiber–layer and layer–external medium interfaces, respectively, while δ is the phase shift that the light wavelength λ undergoes when it passes through the sensible layer of thickness d, and α is an optical coupling factor. The setup, described above, allows to perform an on-line monitoring of sensor signal [9].

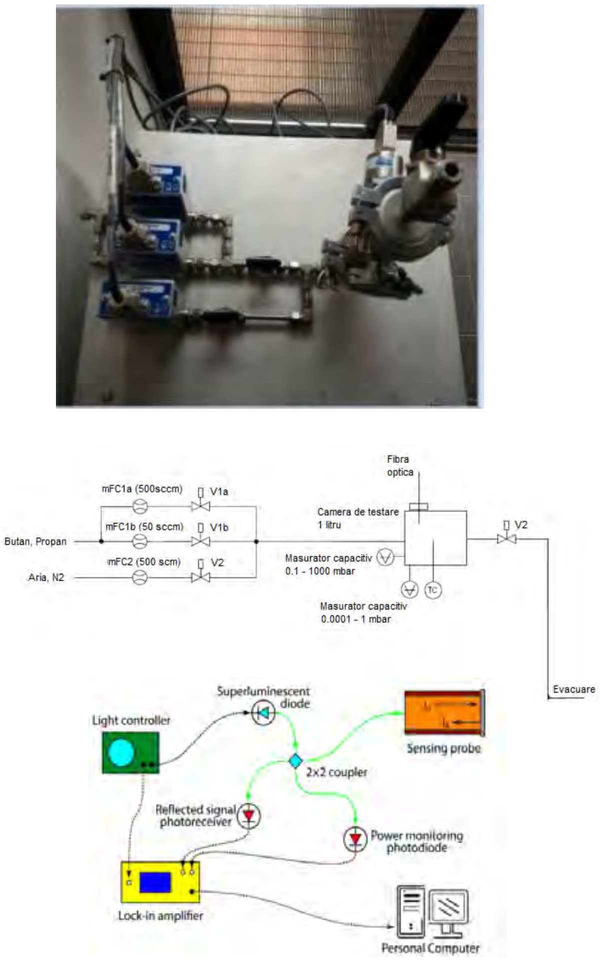

Fig. 2 Gas testing equipment: image of the chamber with gas inlets (top), scheme of gas flow controlling system (middle), and schematics of the optical measurement system (bottom).

III. RESULTS AND DISCUSSIONS

Was studied the morphology of ZnO layers before and after annealing at 400°C in air atmosphere. Initially formed ZnO nanocrystalline film consists of particles of different sizes, albeit after thermal annealing it becomes more homogeneous. To observe evolution of ZnO crystal dimensions in report to thermal annealing conditions, the sensor surface was studied in details by using atomic force microscope (AFM).

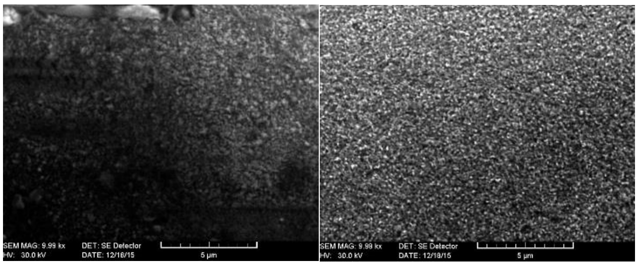

Fig.3 SEM images of ZnO film deposited on the optical fiber: before annealing (left), after annealing (right).

In Fig. 4 one can observe that initial crystallites have diameters below 1 μm, while during annealing in air or oxygen atmosphere they grow to 4 μm and more. In the process of thermal annealing the crystallites oxidize more and accrete into bigger ones.

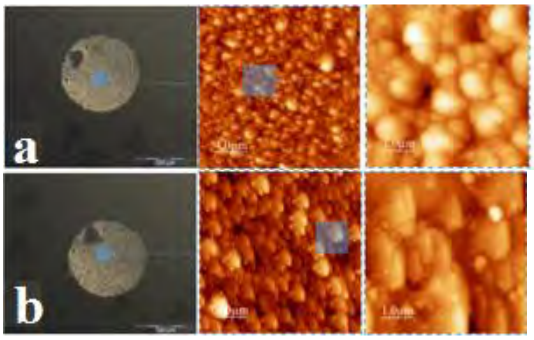

Fig.4. AFM images of ZnO film on optical fiber: not annealed (top), after overnight annealing at 150°C in air (bottom).

A comparative SEM study of ZnO and TiO_2 is presented in Fig. 5. Annealed TiO_2 films consist of close packed micro and nanocrystals, while annealed ZnO films consist of particles and fibers.

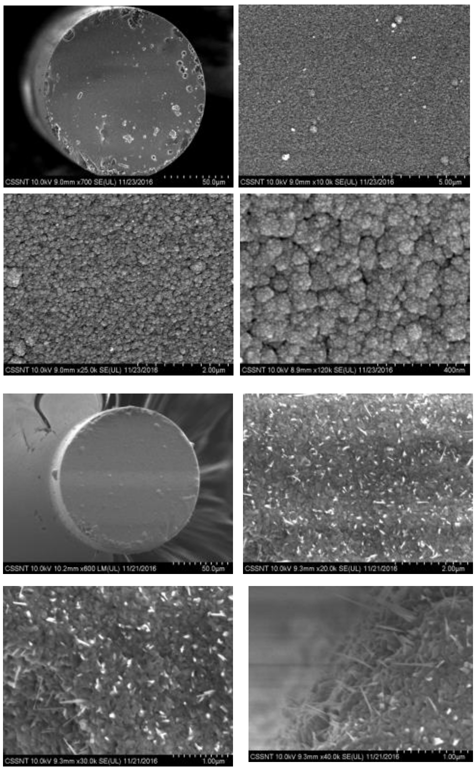

Fig.5 SEM images of TiO_2 (top 4 images) and ZnO (bottom 4 images).

Sensibility tests were performed under exposure to butane in different concentrations during approximately three hours. Fig. 6 illustrates sensor reflectance as a function of butane injections in time. The plot in Fig.6 (top) corresponds to as prepared optical fiber/ZnO sensor with 200 nm thick oxide layer. At higher gas concentrations reflectance level rises, after 10 minutes the baseline stabilizes and measurement is continued for lower butane concentration. These results show the possibility of sensor to recover after the ventilation of chamber and to keep the sensibility to even lower concentrations, that means it may be exploited under real-life conditions. The baseline shift to higher values is attributed to the formation of liquid species on the surface, which normally change the optical parameters of the sensor. The as-prepared sample shows 0.49 % sensibility at high gas concentrations, while after 150°C overnight annealing in the same conditions this sample exhibit a sensibility as high as 0.87%. The finding under consideration highlights the importance of thermal treatment for ZnO samples.

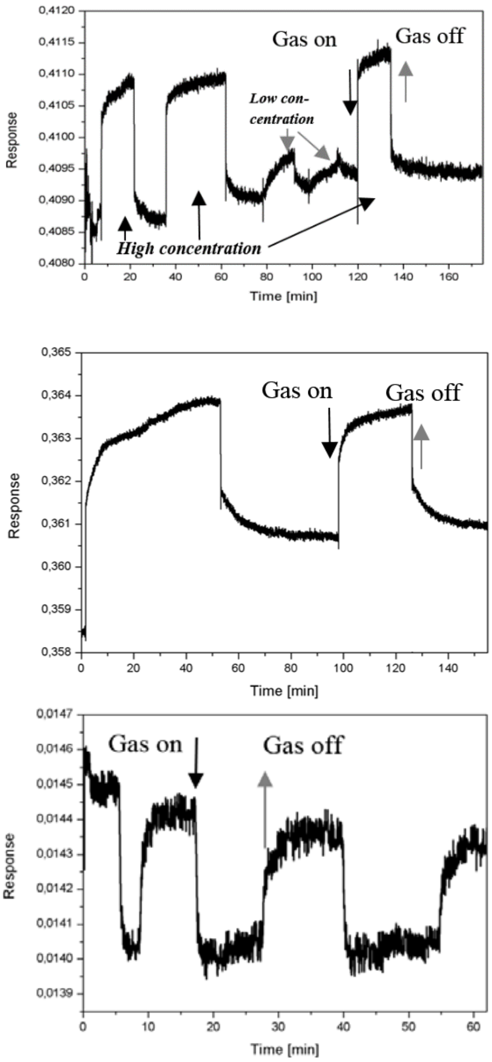

Fig. 6. Reflectance plot for optical fiber with a magnetron sputtered ZnO film of 200 nm thickness: as prepared (top), after 150°C overnight annealing (middle), after 380°C annealing for 1min (bottom).

It is to be noted that the optical fiber is covered with a plastic cladding for mechanical and optical protection. Taking into account that standard annealing at temperatures as high as 400°C for 1 h may destroy the samples, we tried to anneal them at high temperatures in oxygen atmosphere for short time. In our case, the most successful option was annealing at 380°C for 1 min (Fig. 6 bottom) with the sensitivity of 2.77 %.

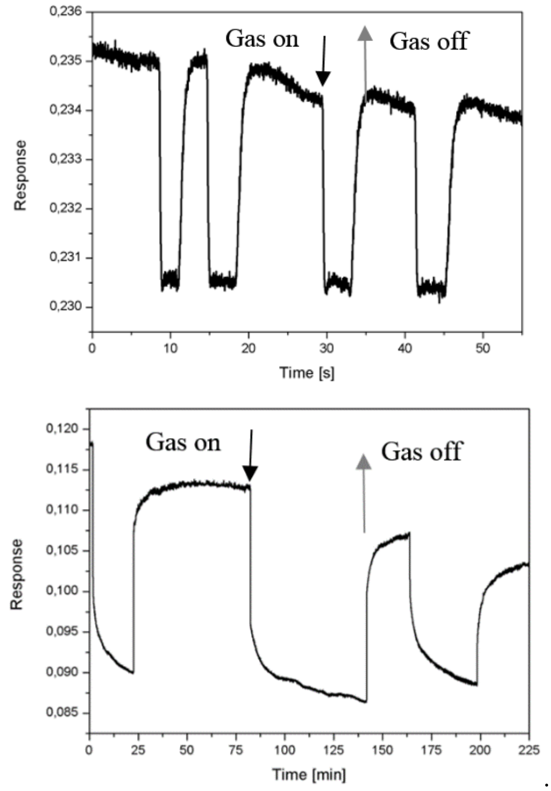

Fig. 7. Reflectance plot for optical fiber with magnetron sputtered TiO$_2$ film of 100 nm thickness (top), and 250 nm thickness (bottom).

Titanium dioxide sensors attain the sensibility values of 14.6 % for 100 nm thick sample and 20.4 % for 250 nm thick sample. Thermal annealing for TiO$_2$ did not lead to significant improvements and may be considered not critical for sensor fabrication. Was observed that the quality of fiber cut, its roughness and angle are crucial for sensor performance.

IV. CONCLUSIONS

We found that both ZnO și TiO$_2$ are prominent candidates for the fabrication of real-life optical LPG sensors. Although TiO$_2$ has higher value of sensitivity, both materials exhibit similar signal variation that may be even more characteristic for such type of sensors, in contrast to electrical metal oxide sensors. Important observations consist in the necessity of attentive fiber preparation and thermal treatment of the working oxide films.

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