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The Reliability to Gamma Radiation of Gas Sensors Based on Nanostructured ZnO:Eu

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***Abstract*—In this work it was investigated the reliability to ionizing radiation of Eu-doped ZnO nanostructured films functionalized with Pd. Morphological, sensorial and electrical properties of sensors were studied initially, after irradiation and after 6 months to observe the influence of irradiation.**

Keywords: gas sensors, ZnO, Eu doping, gamma irradiation, reliability.

I. INTRODUCTION

In present time, electronic devices, sensors and other devices that are used in spatial missions have requirements regarding weight, energy consumption, reliability to different types of radiation, such as ionizing radiation. To obtain reliable devices that are immune to radiations in cosmic space, new nanoscale materials have been studied in this domain. Nanomaterials are a promising source of crystalline structures for the use and research of nanoelectronics.

ZnO is one of the most important binary semiconductors in group II-VI, with a large band gap of 3.37 eV at room temperature, with *n*-type conductivity. This material has high chemical, thermal and mechanical stability, which makes it one of the most promising materials for use in different applications (fig. 1) such as solar cells, photodetectors, LED, laser systems, medicine, sensors, etc. [1-3].

There are a lot of methods to obtain ZnO, with the possibility to change its electro-optical properties by doping, which makes it an attractive and cost-efficient material for use in different domains [4,5].

Gas sensors based on ZnO are useful in the detection of dangerous gases and monitoring of air quality, which can be used in cabin crews of spaceships or for fast and reliable detection of leaks of gases on board, to avoid explosions. Sensors can also be used in the detection and analysis of existing gases in space. Technological possibilities allow the achievement of sensor systems that are selective, light and small. This allows testing instantly, monitoring of space habitats and other space objects from distance, without the need of sending probes to laboratories on Earth. Another advantage of nanosensors is their high sensitivity which allows detection of the presence of individual gas molecules or single photon. The potential self-powering of sensor systems from sources of cosmic radiation allows autonomy in use that is limited by the reliability of the used material.

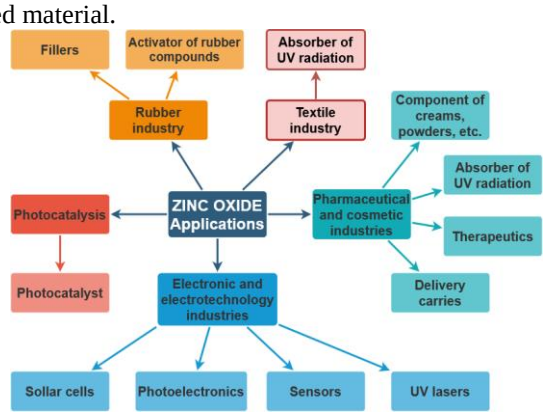

Figure 1. Domains of use of structures based on ZnO.

The main goal of this work is to test the reliability of gas sensors based on Eu-doped ZnO films. These sensors are chemical based, can be used to detect the concentration or presence of a gas [4]. Their sensing mechanism is based on the change of electrical properties of the sensor surface, by adsorption of different molecules. These reactions on the surface of the sensor lead to a change in the number of charge carriers that can move in a crystalline network of the detecting material.

II. METHOD OF OBTAINING

Eu-doped ZnO films were deposited using chemical synthesis from the solution method [4], using $ZnSO_4$ and NaOH as precursors. Different quantities of $EuCl_3$ were added to obtain different doping concentrations in layers. After deposition samples were thermal annealed in air at different temperatures (450, 550, 650 °C) for 2 hours to improve crystallinity and sensor properties. Surface functionalization of ZnO: Eu films with Pd was achieved using $PdCl_2$, to improve selectivity, and gas response and decrease the working temperature, compared to non-functionalized ZnO: Eu [4,5]. Gold contacts were deposited afterward by sputtering.

III. EXPERIMENTAL AND DISCUSSIONS

Initially, volt-ampere characteristics of ZnO: Eu functionalized with Pd samples were measured using source meter Keithley 2400 controlled through Labview software on a computer [6]. Afterward, samples were tested to a series of gases: acetone, *n*-butanol, methane, ethanol, hydrogen, ammonia and 2-propanol at a different operating temperature range from room temperature, up to 350 °C, using a homemade setup.

Irradiation of sample is done by using a Caesium 137 source. At the same time, the resistance value is measured and recorded in real-time using the Keysight U1252B digital multimeter. The measurement process takes place as follows: for 30 seconds the electrical resistance of the sample is measured without irradiation, and then the sample is irradiated for 60 seconds, after which data are collected for a further 60 seconds to observe the tendency of the sample resistance to change its value.

Eu-doped ZnO film properties have been studied between irradiations with different periods between irradiations of 1, 2, 3, and 6 months.

Variation of irradiation dose was done using attenuators of 1000, 100, and 10, positioned in the way of gamma irradiation (fig. 2). For attenuator of 1000 times, the amount of radiation absorbed is about ≈512 nGy/min, 100 times ≈6430 nGy/min and 10 times attenuator is approximately 63 μGy/min. The measurements took place at a temperature of about 20 ℃.

The same radiation debit was achieved by placing the samples at the same distance for Caesium 137 (Cs-137) source. The debit was determined using the inverse-square law.

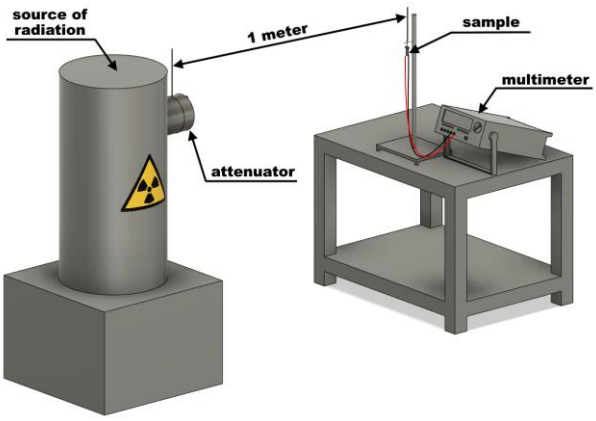

Figure 2. Schematic representation of sample measurements in gamma field

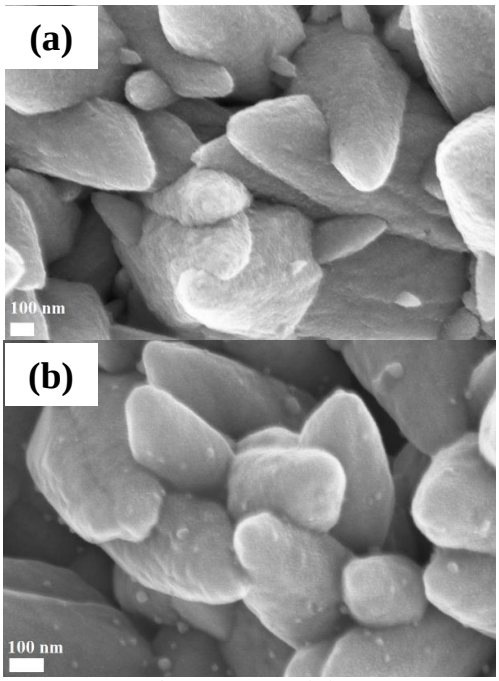

Figure 3. SEM images of thermally annealed at 550 °C Eu-doped ZnO Pd-functionalized films containing 0.2 at% Eu (Eu4 sample set). (a) - before irradiation/initial. (b) - after first irradiation.

Morphology was studied using SEM before and after irradiation.

SEM images of ZnO: Eu films are presented in figure 3, where it was observed that nanostructures are well packed on the glass substrate, and at higher magnification, it was observed that they have columnar form and often interpenetrated.

No difference in morphology or change of form of nanostructures, because of low intensity, but a slight difference in surface roughness of the columnar structures after irradiation and different gas measurements.

The response curve of the sensor is characterized by the following five parameters (sensitivity, response time, recovery time, selectivity, and long-term stability) [8].

A high value of *S* for a particular gas indicates that the material is a very good sensor. Gas response (*S*) was determined using the ratio of electrical current measured in air and current at gas exposure as follows:

$$S = \frac{I_{gas}}{I_{air}} \quad (1)$$

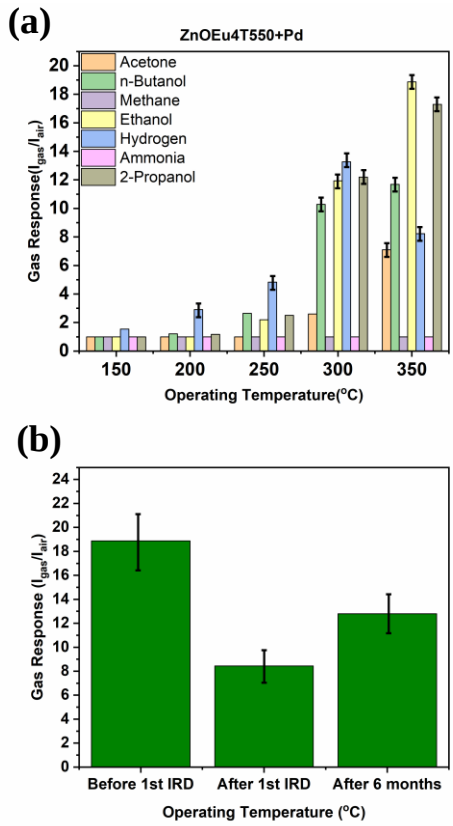

Figure 4. (a) Gas response of thermally annealed at 550 °C Eu-doped ZnO films (with 0.2 at% Eu (Eu4)) and Pd-functionalized measured to 100 ppm of different gases at different operating temperatures before irradiation; (b) Comparison of response to 100 ppm ethanol gas before first irradiation, after first irradiation and after 6 months at 350 °C operating temperature.

In figure 4 is represented the gas response before and after irradiation from a Cs-137 source of same samples, where it was observed a maximum gas response of ~19 (figure 4a), which was achieved at the operating temperature of 350 °C for 100 ppm ethanol vapor.

To study the stability of gas sensors between repeated measurements and irradiations, in Figure 4b is presented a response to 100 ppm ethanol vapor at 350 °C operating temperatures before first irradiation, after first irradiation, and after 6 months. Response value decreased after the initial gas test and after irradiation, but recovered after 6 months, with the tendency towards the initial values, with a maximum response value of ~13 at 350 °C for 100 ppm of ethanol gas. No improvement in selectivity was observed. In figure 5 is compared the dynamic gas response to 100 ppm of ethanol gas at 350 °C, where we determined gas response value (*S*), response (t_{resp}) and recovery times (t_{rec}), summarized in table 1.

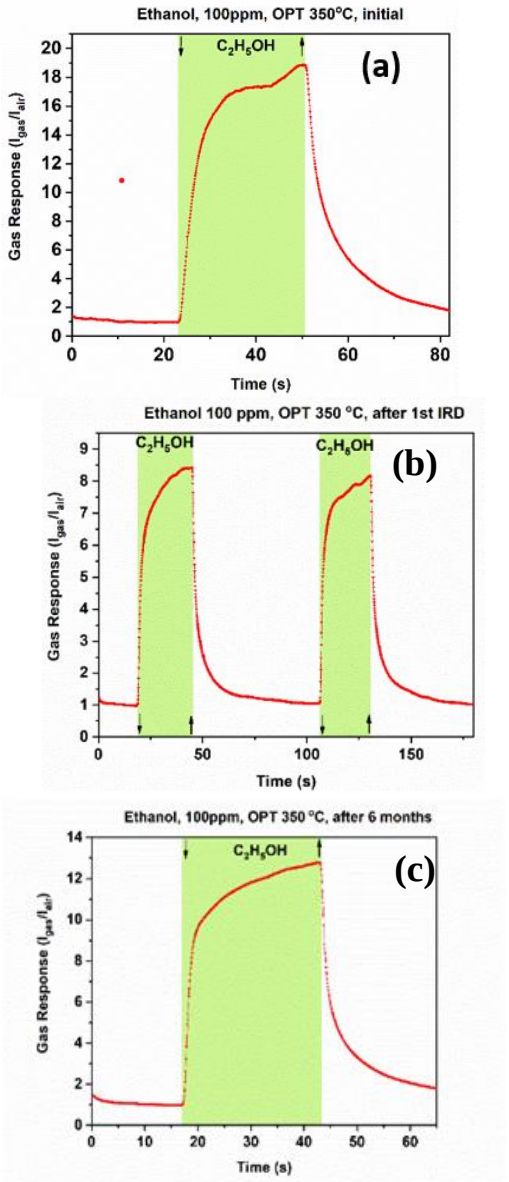

Figure 5. Dynamic response of thermally annealed at 550 °C Eu-doped ZnO films (with 0.2 at% Eu (Eu4 sample set)) and Pd-functionalized measured to 100 ppm of ethanol gas at 350°C operating temperature: (a) initial; (b) after first irradiation; (c) 6 months after first irradiation

Response time represents the time it takes for the response value to increase from 10% to 90% of the maximum response value, while the recovery time represents the time it takes for the response value to decrease from 90% to 10%, with an error rate of about ~0.5 s [7].

It was observed that the response value decreases after initial measurement for this VOC from about 18.9 down to 8.4 after first irradiation, with a slight recovery to ~12.8 after 6 months. It can be seen that sample properties are almost recovered after irradiation and this period. No correlation was found for response and recovery times between measurements, with the fastest response and recovery times of ~10 s and ~9.2 s, respectively, for the measurement after the first irradiation.

Table 1. Response value, response and recovery times for 100 ppm ethanol vapor at 350 °C

	Response value (*S*)	Response time (t_{resp})	Recovery time (t_{rec})
Initial	18.9	22.5 s	30 s
After first irradiation	8.4	10 s	9.2 s
After 6 months	12.8	11 s	15.8 s

To test the repeatability of the ZnO: Eu sensor, we applied 100 ppm ethanol gas a second time, as shown in figure 4b, where it was observed a similar response value of ~8, compared to the initial time.

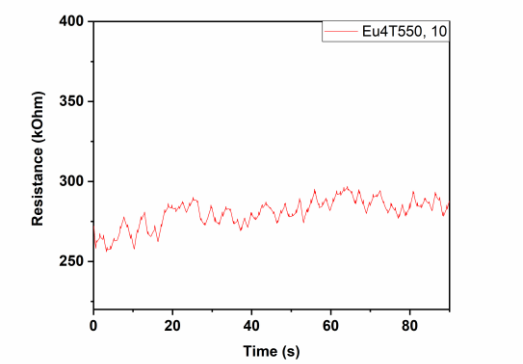

Figure 6. Variation of electrical resistance during first irradiation of thermally annealed at 550 °C Eu-doped ZnO films (with 0.2 at% Eu (Eu4 sample set)).

Measurements of electrical resistance of the samples took place during and after irradiations (figure 6) with a Cesium-137 source. A slight rise in resistance was observed for all experiments. Resistance values recover after a longer period between measurements, which can be an indication that sample properties can be recovered in time. This effect needs further theoretical and experimental investigations.

CONCLUSIONS

Morphological, electrical, and sensor properties of gas sensors based on Eu-doped ZnO columnar layers have been studied, observing the influence of irradiation under 60 seconds in gamma radiation fields. Minor changes in the surface morphology of sensors were observed between measurements. Sensors showed no selectivity to any test gas, with a maximum response of ~19 for 100 ppm ethanol vapor at 350 °C operating temperature. After the first irradiation response value to 100 ppm ethanol vapor decreased to ~8.4 at 350 °C. After repeated measurements, the sensor time response value and resistance value tend to be the initial values.

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