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PHYSICO-CHEMICAL PROPERTIES AND MODELS OF SENSORS BASED ON NANOSCALE OXIDE SEMICONDUCTORS

233.01 NANO-MICROELECTRONICS AND OPTOELECTRONICS

Summary of the doctoral thesis in engineering sciences

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RESEARCH CONCEPT GUIDELINES

The actuality of the research. Due to continuous evolution, nanotechnologies have been developed for various application fields and are used from light industry to machinery manufacturing industry for various branches of the world economy, from natural sciences to biomedicine and various applications. Along with the development of technologies, a series of materials and tools were developed and applied, ending up being implemented at the smallest scale, the nanometric scale. Thanks to nanomaterials and structures developed very intensively by the scientific community worldwide, an important area of their application has been reached, which is gas sensor technology. The volume of inventions worldwide for obtaining gas sensors is continuously increasing. In recent years, the budget allocated to studying sensors is increasing from 1.1 billion USD in 2021 to 1.5 billion USD by 2026, because today sensors are used in all areas of world industry. Among the key factors driving the growth of this market include the high demand for gas sensors, we can name the detection of, for example, hydrogen, ethanol and volatile organic compounds (VOCs) which are a class of chemicals that can evaporate at ambient temperature (vapor pressure ≥ 0.01 kPa at 20°C). VOCs, numbering in the thousands, are ubiquitous in the environment and originate from a variety of natural and anthropogenic sources. VOCs mainly include alkanes, alkenes, aromatic hydrocarbons, esters, ethers, ketones, aldehydes, etc. About 30% of VOCs are toxic and odorous compounds according to Chen et al. (2011) [1]. VOCs can irritate the eyes and upper respiratory system, and short-term exposure can cause headaches, nausea, vomiting, and limb weakness; convulsions, coma and memory loss may occur in some cases. Several types of VOCs are synthetic chemicals with high production volume and are used in household and industrial products, including paints, wood preservation, aerosol sprays, disinfectants, moth repellents, construction, materials and furniture, office equipment (e.g. copiers, printers, markers and correction fluids), hobby supplies, craft materials and in the production of synthetic rubber, resin and polymers, pesticides for which different hydrocarbons are used during production. Due to the fact that several types of VOCs are mutagenic, genotoxic, neurotoxic and carcinogenic, studies have shown that exposure to VOCs increases the risk of developing various dangerous diseases [2]. Tobacco smoke and automobile exhaust contain hundreds of VOC types [2–8]. Thermal processing of food and biomass burning can emit a range of VOCs [4]. It is also known that chlorinated solvents can persist underground in soils and shallow aquifers for decades and pollute groundwater. VOCs can enter underground environments through various pathways, such as: surface discharges (leaking pipes and spills), underground releases (underground tanks), leaking sewer lines. The detection of VOCs in subsurface environments is based on a variety of techniques, but all of them require special attention to limit the loss of volatile compounds during the collection process. A current field where gas and VOC sensors are widely used is biomedicine. Although several studies have reported adverse health effects from exposure to VOCs, assessment of internal body burdens has been challenging due to the lack of appropriate analytical methods. Traditional methods of assessing exposure to VOCs include determining these chemicals in air, particularly indoor air, and calculating the inhalation exposure dose. Such methods involve several assumptions related to exposure scenarios and their associated uncertainties. In recent years, internal dose measurement is recognized as an ideal approach to assess human exposure to VOCs. Human specimens such as respiratory components, blood and urine have been used to quantify internal exposure dose, and traces of VOCs have been found in exhaled breath immediately after exposure. However, breath VOC concentrations decline rapidly after exposure, which may underestimate actual exposure doses. Because VOCs can be released into the blood before reaching organs such as the liver, assessment of their blood concentrations can provide reliable information about exposures. However, collecting blood is an invasive procedure. VOCs have very short half-lives in blood (typically on the order of hours) and can evaporate rapidly into the air during sampling. Blood levels of VOCs may decline rapidly after exposure ceases. The detection of small amounts of acetone vapor allows glucose control to monitor diabetes [3].

Another current worldwide problem is the energy problem, which aims to use alternative energy resources or use ecological fuels. As ecological fuels can be the use of hydrogen and ethanol. Lithium-ion batteries (LIBs) are of increasing interest due to their high potential to provide efficient energy storage and sustainability of the operating environment. This type of batteries are used not only in portable devices such as personal computers, mobile phones and others, but are basic components of electric cars, which are gaining popularity day by day. Today the world market is dominated by lithium-ion based batteries which due to their advantages compared to other battery systems, such as high capacity and specific voltage, lack of memory, low self-discharge and wide operating temperature range. An important role for the use of batteries is safety, and to avoid the occurrence of accidents and fires that can lead to serious consequences, such as the continuous generation of heat and gas leaks, which can ultimately cause damage to materials and ignition of combustible materials, therefore it is necessary to increase the level of safety. The safety of the battery is determined by the materials that are used during production. Thus, the explanation of the electrochemical reactions that occur during the operation process of the batteries, the properties of the materials and the secondary reactions that occur in LIBs is fundamental in the assessment of the safety of the electric battery. The most important factors controlling the reactions inside the battery are voltage and temperature. Thus, obtaining micro- and nanometer-scale gas sensors to meet the growing demands of the global market also requires new approaches in production technology, as well as obtaining them with improved or even new parameters, and oxide-based nanostructures and nanowires semiconductors are excellent candidates to face these challenges and provide real solutions.

One of the gases that can be eliminated during the operation of electric batteries following the chemical reactions that take place is hydrogen (H_2), and development strategies for the formation of 100% renewable smart cities are unattainable without smart energy systems in which hydrogen, with zero carbon emissions, play a crucial role in mitigating the variability of long-term electricity storage production. As a colorless, odorless, and tasteless flammable gas, hydrogen cannot be detected by the human senses, and therefore other means are needed to detect its presence and quantify its concentration. Rapid and accurate measurement of the concentration of hydrogen gas is essential to warn of the formation of potentially explosive mixtures with air and to help prevent the risk of explosion. That is why there is a need to develop new solid-state sensors and devices based on nanowires that allow the detection of hydrogen even at the lowest concentrations and at high relative humidity. Likewise, hydrogen is considered to be an environmentally friendly fuel as one of six alternative fuels for vehicles and identified as a development of the energy resource market [4], because it is a gas with zero carbon dioxide (CO_2) emissions, which is gas with greenhouse effect (GHG). Therefore, the production, storage and transportation of hydrogen gas becomes very risky and it becomes essential to monitor the concentration level of hydrogen gas to avoid any dangerous situations. In addition to being considered as one of the alternative fuels, hydrogen has a wide range of uses such as in various manufacturing processes such as oil processing and ammonia production. Also, applications in medicine are developing because it possesses therapeutic characteristics, acting as an antioxidant, according to many previous researches, mainly because it selectively eliminates hydroxyl radicals and increases antioxidant enzymes in the human body or the production of electronic devices, and hydrogen is a vital component that functions either as a reactant, as an O_2 scavenger, or as a carrier gas [5]. Thus, it is necessary to analyze hydrogen because its chemical structure allows the elucidation of its reactivity in many manufacturing processes. The strong single bond in the H_2 molecule is easily replaced by equally strong bonds of other elements. This allows hydrogen to form compounds with a wide range of elements, resulting in H_2O, peroxide, hydride, acid, alkali, organic compounds, and many other compounds. The availability of different charges (H^+, H_0, H) and sizes in various H-containing compounds results from the addition or removal of an electron. In most cases, molecular hydrogen acts as a reducing agent (for example: it reacts with non-metals or participates in the process of producing metals, such as molybdenum, tungsten, platinum group metals, germanium). Large-scale applications of hydrogen in production also require the availability of varieties of hydrogen sensors, as the given sensors have several advantages over conventional hydrogen detection methods mentioned above, including their lower cost, smaller size, and more responsive fast. These advantages make them more suitable for portable hydrogen detection and in a wide range of applications. Such sensors are well established for use in industry, where they can be regularly calibrated and operated by trained personnel. However, the emergence of a hydrogen economy provides the impetus to produce low-cost, low-maintenance, easy-to-install, easy-to-use, and accurate hydrogen sensors suitable for use by untrained individuals in a variety of applications.

The development of sensor models will allow to simulate the sensory properties using modern software. Thus, following the obtained results, it will be possible to anticipate the responses to gases in laboratory conditions and to integrate it more easily in detection systems.

The importance of addressed issue. Nanomaterials and individual oxide structures, such as ZnO, Al_2O_3, CuO/Cu_2O, TiO_2 and ZnO nanowires, have certain disadvantages among which we can mention: low selectivity towards a gas or several compounds, degradation over time is also a disadvantage because there is destruction of the materials used in the production of nanostructures and/or the influence of relative humidity on the sensitivity value [6,7]. The disadvantages listed above have increased efforts to combine all methods of sensor production using today's latest generation technologies. It is known that the sensitivity and selectivity of sensors based on semiconductor oxides are based on such approaches as: control of their morphology, crystallinity, porosity, diameter and effective surface area. The use of the ALD atomic deposition method allowed the possibility of obtaining different types of heterostructures, namely p-n, n-n and n-p [8]. As a result, different sensors can be obtained that can detect different types of gases, from hydrogen to volatile organic compounds (2-propanol, n-butanol, acetone) [8–10]. Different oxides can be deposited by the ALD method, e.g. NiO or different type (p-n) CuO-TiO_2, CuO-ZnO [11,12], thus obtaining structures and heterojunctions with improved or even new sensory properties. Another method that allows to obtain new structures that can detect many gases is to dope during production with various impurities, such as Al, Fe and other metals [11,13] or sputtering with noble metals so the formation of new multilayer structures. Thus, by spraying with different noble metals, depending on the sprayed material, sensors can be obtained that can detect hydrogen, as well as volatile organic compounds [14,15]. The use of polymers also becomes an effective method for improving the sensor properties of ZnO-based structures [13], and combining the synthesis methods from chemical solutions, the ALD method and the use of a polymer layer allows to obtain sensors that can detect volatile organic compounds [16]. The development of ZnO nanowires for rapid hydrogen detection may lead to the design of nanodevices in the near future that can be integrated into electric cars to increase safety and avoid accidents caused by fuel leaks. It is known that a car can burn for only a few minutes, and the availability to prevent such accidents is essential [17].

The purpose and objectives of the research. The doctoral thesis aims: obtaining $Au/Al_2O_3/ZnO$, $Au/TiO_2/CuO/Cu_2O$, $Au/CuO/Cu_2O/ZnO$:Fe structures and ZnO nanowires through cost-effective methods and technologies; identification of nanowires with sensitivity and selectivity to gases: (H_2) and volatile organic compounds (VOCs) (2-propanol and ethanol); obtaining stable sensor structures at relative humidity; detection of the compounds in the composition of electric batteries with the help of elaborated structures; proposing sensor models.

Proposed research objectives

1. Research of the sensory properties of the obtained oxide nanomaterials:

(I) $Au/Al_2O_3/ZnO$ with different aluminum oxide thicknesses;

(II) $Au/TiO_2/CuO/Cu_2O$ with different copper oxide thicknesses;

(III) $PV/CuO/Cu_2O/ZnO:Fe$ by PV polymer deposition;

(IV) ZnO nanowires grown at different post-deposition treatments.

2. Determination of the physical-chemical properties of these oxide structures.

3. Research of sensory properties over time and at high relative humidity.

4. Explanation of gas detection mechanisms and proposal of elaborated sensor models.

Research hypothesis: maintaining the stability of the physico-chemical characteristics over a long period, tuning the sensitivity and selective selectivity, as well as increasing the response to volatile organic compounds (VOCs), H_2 and compounds in the composition of electric batteries of $Au/Al_2O_3/ZnO$, $Au/CuO/Cu_2O/ZnO:Fe$, $PV/CuO/Cu_2O/ZnO:Fe$, $Au/TiO_2/CuO/Cu_2O$, of hydrothermally treated ZnO nanowires and the development of sensor models from oxide nanomaterials.

Synthesis of research methodology and justification of chosen research methods. The $Au/Al_2O_3/ZnO$ structures with different thicknesses of the aluminum oxide layer (5-18 nm) were obtained by the SCS and ALD methods. Using the metallic copper sputtering method and ALD, $Au/CuO/Cu_2O$ and $Au/TiO_2/CuO/Cu_2O$ structures were obtained. The combination of the SCS method and the sputtering of metallic copper and the deposition of a polymer layer allowed to obtain new structures, $Au/CuO/Cu_2O/ZnO:Fe$ and $PV/CuO/Cu_2O/ZnO:Fe$, and the use of different post-deposition treatments allowed to obtain different ZnO nanosensors.

With the help of modern equipment, the researches were carried out: SEM, XRD, Raman, TEM, HRTEM, SAED, EDX and XPS to determine the quality and different characteristics of the elaborated structures and nanowires. Density functional theory (DFT) calculations of the structures, by simulating the interaction of gas/VOC molecules with the surface of the structures and nanowires, were performed to model the proposed sensing mechanisms and to know the effects and phenomena occurring at the surface and interface of the obtained structures.

It was demonstrated that sensors for VOC detection can be obtained based on $Au/Al_2O_3/ZnO$ structures. In the case of $Au/Al_2O_3/ZnO$ structures with a thickness of 15 nm of Al_2O_3, a selective sensor was developed for 2-propanol vapors, and in the case of a thinner film with a thickness of 10 nm of Al_2O_3, a selective sensor was obtained for the compounds in the composition electric batteries. Thanks to the film of Al_2O_3, which has stabilizing properties, time-stable sensors were obtained for 2-propanol with a constant response for more than 2 years, and in the case of testing the compound $C_3H_6O_2$ for more than 120 days. In the case of $Au/CuO/Cu_2O$ and $Au/TiO_2/CuO/Cu_2O$ structures, it has been shown that they are selective for different compounds in the composition of electric batteries. $Au/CuO/Cu_2O/ZnO:Fe$ and $PV/CuO/Cu_2O/ZnO:Fe$ polymer structures are selective to ethanol vapor and H_2. These types of structures allow the detection of ethanol vapor and H_2 even at high relative humidities, and in the case of $PV/CuO/Cu_2O/ZnO:Fe$ structures, the response to H_2 at high relative humidities does not change. The studied zinc oxide nanowires that were obtained proved to be selective to hydrogen vapor even at the lowest concentrations and with the lowest response and recovery times.

The scientific problem of solved research, consists in obtaining sensitive structures and nanowires and selectivity to gases: (H_2), volatile organic compounds (VOC: 2-propanol, and ethanol) and compounds from the composition of electric batteries ($C_3H_6O_2$, $C_4H_{10}O_2$ and $LiPF_6$) stable over time and at high relative humidity.

The theoretical significance consists to develop the physico-chemical mechanisms for the detection of gases, VOCs and compounds from the composition of electrical batteries by the structures obtained based on $Au/Al_2O_3/ZnO$, $Au/CuO/Cu_2O/ZnO:Fe$, $Au/TiO_2/CuO/Cu_2O$ and based on treated ZnO nanowires, as well as exemplifying applications for sensing gases and various VOC vapors (2-propanol and ethanol) that are stable over time and responsive to high humidities. The proposed detection mechanisms were supported by functional theory calculations and DFT simulations, which allow to simulate the interaction processes of VOC gases or vapors on the surface of the structures.

Implementation of scientific results. The obtained scientific results were partially used in the educational process, in the elaboration of bachelor's and master's theses at the MIB department, within the UTM. Then, based on the scientific results obtained, a certificate of involvement of the results and an invention patent on the topic of the thesis were obtained.

The applicative value of the thesis consists in the following:

1. Obtaining $Au/Al_2O_3/ZnO$ structures with different thicknesses of the aluminum oxide allows sensitive and selective detection of 2-propanol and $C_3H_6O_2$ with time stability controlled by different thicknesses of the Al_2O_3 film;
2. The deposition of the TiO_2 nanolayer over the CuO/Cu_2O structures with different thicknesses of the copper oxide allows changing the selectivity from the $LiPF_6$ compound to $C_4H_{10}O_2$ in the composition of electric batteries and increasing the response to $C_4H_{10}O_2$.
3. Obtaining the $Au/CuO/Cu_2O/ZnO:Fe$ structures sensitive to the lowest concentrations of ethanol and $C_3H_6O_2$, and the deposition of the $PV/CuO/Cu_2O/ZnO:Fe$ polymer layer allows changing the selectivity to H_2 with minimal influence of high relative humidity on their sensory properties;
4. Vapor treatment of ZnO nanowires allows increasing the response and selectivity towards H_2 gas;
5. The development of sensor models will allow the simulation of results that can be obtained in laboratory conditions and facilitate its integration.

Approval of scientific results. The basic results of the doctoral thesis were presented and discussed at the meetings and seminars of the Center for Nanotechnologies and Nanosensors, of the Department of Microelectronics and Biomedical Engineering, Technical University of Moldova (2017 – 2022); reported, discussed, positively evaluated and presented at 10 international and national scientific conferences, including: International Conference on Nanomaterials: Application & Properties (NAP), 2018 (Zatoka), 2019 (Odesa), Ukraine; International Conference on Nanotechnologies and Biomedical Engineering (ICNBME), 2019, International Conference on Electronics, Communications and Computing (ECCO) 2019, 2021 Chisinau, Moldova. The investigations in the thesis are part of the priority research-development directions of the Republic of Moldova: the "Institutional 45inst-15.817.02.29A" Project - 1 (2015-2019); The "Young Researchers 17-TC-19.80012.50.04A" project - 1 (2019); The "NATO Science for Peace and Security Program (SPS) G5634" project - 1 (2019-2022), State Program Project 2020-2023 20.80009.5007.09,, Development and launch of the series of nanosatellites with research missions from the International Space Station, their monitoring, post-operation and the promotion of space technologies".

Publications related to thesis subject. The main results of the thesis were published in 18 scientific works, namely an invention patent of the Republic of Moldova; 6 peer-reviewed articles in ISI and SCOPUS rated journals of international circulation, including with an impact factor greater than 19 and one as first author; 1 article in JES magazine from the National Register of professional magazines; as well as 10 papers presented and published at National and International Conferences. Total of 35 publications, SCI Hirsch index= 8. Number of international citations > 160 (according to SCOPUS).

The volume and structure of the thesis. The thesis consists of an introduction, four chapters, general conclusions and recommendations, a bibliography of 421 titles and 5 appendices. Contains 118 pages of basic text, 57 figures and 4 tables.

Keywords: zinc oxide, aluminum oxide, copper oxide, nanotechnologies, structures, electrolytes, gas sensors, batteries, semiconductors.

THESIS CONTENT

The **introduction** describing the actuality and importance of the research topic presents a current level analysis of the importance of the research being carried out for the detection of volatile organic compounds (VOCs), the need to develop alternative energy sources and the description of compounds that can be used as alternative energy resources and sensors for them. The purpose and objectives of the thesis are presented, the main theses submitted for support.

In the **first Chapter**, different methods and techniques for obtaining structures and nanowires based on semiconductor oxides are presented, which are the materials used and the steps. A synthesis of the fields of application of different structures and nanowires as sensors, which can detect volatile organic compounds and those in the composition of electric batteries, is performed. It presents the materials that can be used in the production of cathodes and anodes in electric batteries, as well as the compounds that are used in electric batteries and necessitz in sensors for safety. Some calculations and software for developing sensor models are presented.

In **Chapter 2**, the methods for obtaining oxides and the equipment used to characterize the properties of structures and nanowires based on semiconductor oxides are described; growth of TiO_2 and Al_2O_3 films by the atomic layer deposition method, as well as CuO/Cu_2O by sputtering and oxidation; deposition of ZnO nanostructured films using the chemical synthesis method from SCS solutions by doping with various impurities such as Fe and others; obtaining nanowires through different solution and various regimes of post-growth treatments.

In **Chapter 3**, the results obtained from studying the properties for sensory applications of the $Au/Al_2O_3/ZnO$ and $Au/TiO_2/CuO/Cu_2O$ structures are presented, where they were studied against volatile organic compounds (VOCs) and those from the composition of electric batteries where the achievements of different types of sensors are demonstrated.

The ALD-deposited and heat-treated Al_2O_3/ZnO structures were examined with TEM to determine the layer thickness for the amorphous Al_2O_3 coatings ranging from 5 to 18 nm. The samples with the thickness of 5, 7, 10, 12, 15, 18 nm were obtained by the ALD method after 50, 70, 100, 120, 150, and 180 deposition cycles, respectively (Figure 1), and then they were subjected to thermal treatment at 620 °C for 40 minutes. The ZnO nanostructures show high crystallinity, which allows the distinct identification of the interface between the amorphous and crystalline components of Al_2O_3 and ZnO, but also precise measurements of the thickness of the amorphous Al_2O_3 shell. High-resolution TEM and HRTEM micrographs are shown for representative Al_2O_3/ZnO structures with 7 and 18 nm of Al_2O_3 in Figure 1a,b before and after heat treatment at 620 °C for 40 min, highlighting the (0001) lattice planes of ZnO coated with the ultrathin layer of Al_2O_3.

Chemical analysis by an EDXS line scan recorded on an Al_2O_3/ZnO structure is shown in Figure 1c. In the given figure, the homogeneity of the aluminum oxide coating around the nanostructure is confirmed. HRTEM analysis as well as extensive selected area electron diffraction experiments (Figure 3.1d) indicate the resistance to crystallization of the amorphous oxide at temperatures up to 620 °C, given the absence of reflections from a second nanocrystalline phase. However, no significant changes were observed in the thickness or homogeneity of the layers after heat treatment. To determine the reliability of the ALD process aiming to deposit 5-18 nm Al_2O_3 layers, the measured film thicknesses are statistically evaluated and compared to the diameter of the ZnO nanostructure (Figure 3.1e) and the targeted thickness in Figure 3.1f. As expected, the scatterplots demonstrate little variation in the Al_2O_3 film thicknesses compared to the ZnO diameter.

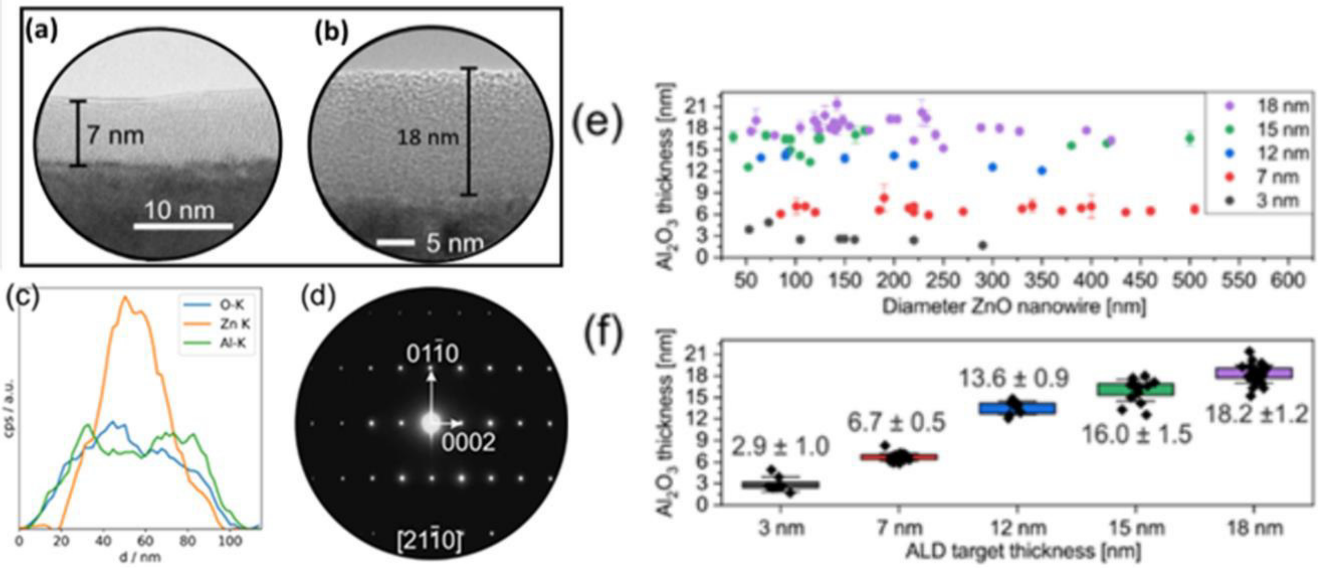

Fig. 1. TEM images of Al_2O_3/ZnO structures coated with 7 and 18 nm of aluminum oxide. HRTEM micrographs show Al_2O_3/ZnO structures before (a) and after (b) heat treatment at 620 °C. (c) Chemical analysis by scanning EDXS lines on a heterostructure. (d) Electron diffraction pattern of Al_2O_3/ZnO structure showing only reflections attributed to ZnO. (e) Scatterplot of measured Al_2O_3 coating thickness versus ZnO diameter for different ALD processes and (f) box plots summarizing the average values of Al_2O_3 thickness versus target thickness.

Figure 2 shows the SEM images of the Al_2O_3/ZnO heterostructures coated using aluminum oxide with a thickness of 15 nm and subsequently thermal annealing at 620 °C for 40 min in ambient air. Figure 2a shows films formed by interconnected columns that are merged over the entire surface, where they form favorable pathways for the flow of electrical current through such samples. From Figures 2b and 2c, we measured the average diameter (D) of the crystallites, which is about 300 nm. Standard deviation of the grain diameter distribution was reported in our previous works [18,19]. Our current SEM measurements display the columnar shape of the nanostructures, see Figure 2, which compares well with the cross-section micrographs of the columnar films reported previously [19]. Due to the highly tilted columns, which form a very rough surface structure, the non-polar side facets are exposed to a large extent, acting as adsorption centers/sites for the VOC molecules during the sensor investigations. One of those active facets is the non-polar $(10\bar{1}0)$ surface, which has been extensively studied for gas sensing applications [20,21].

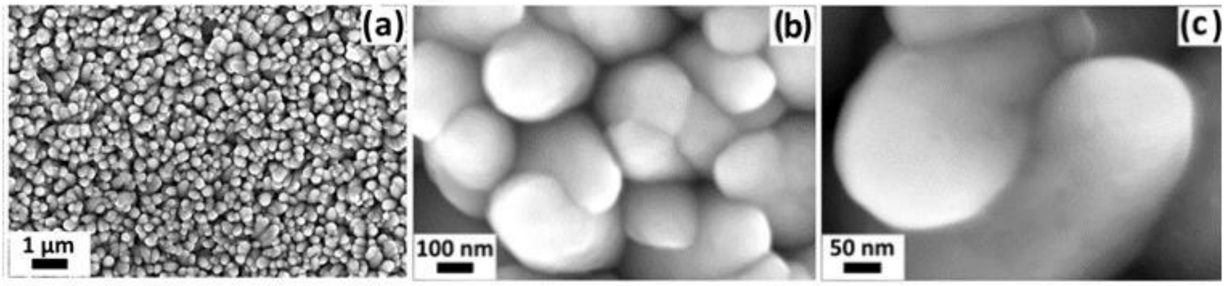

Fig. 2. SEM images at: (a) low magnifications; and (b,c) high-magnification SEM images of Al_2O_3/ZnO thin films containing a 15-nm-thick Al_2O_3 nano-layer subjected to post-deposition heat treatment at 620 °C for 40 min.

X-ray diffraction (XRD) analysis was performed to investigate the crystalline film texture of the columnar Al_2O_3/ZnO heterostructures grown by combining the SCS and ALD approaches. The XRD patterns in the 2θ angular range between 20 and 80° for the ZnO based on PDF #36-1451, ZnO film and Al_2O_3/ZnO heterostructure sample with a coating thickness of 15 nm after thermal annealing at 620 °C for 40 min are presented in Figure 3. Significant hkil reflections correspond to the $(10\bar{1}0)$, (0002), $(10\bar{1}1)$, $(10\bar{1}2)$, $(11\bar{2}0)$, $(10\bar{1}3)$, $(11\bar{2}2)$ and $(20\bar{2}1)$ lattice planes of ZnO (pdf #36-1452, Zincite syn) at the 2θ values of 31.7°, 34.3°, 36.2°, 47.5°, 56.6°, 62.65°, 67.9° and 69.1°, respectively. No reflections associated with crystalline Al_2O_3 phases were detected in our experiments. By comparing the intensity distribution of the ZnO reflections in our samples with reference to XRD powder patterns of ZnO, we found that the increased intensity of the 0002 reflections indicates certain crystalline texture in the film, suggesting that a high fraction of columnar ZnO grows along the *c*-axis direction parallel to the film surface.

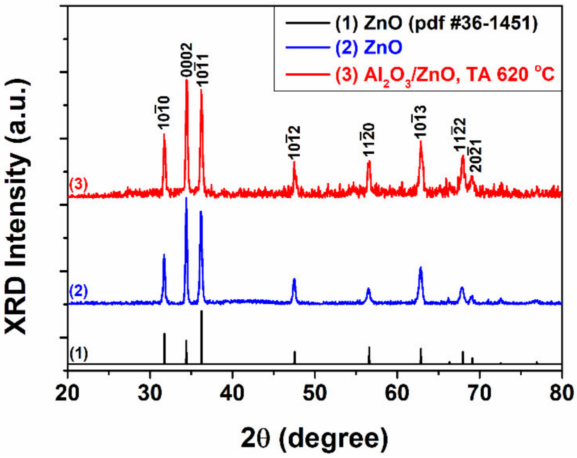

Fig. 3 XRD patterns of the: ZnO based on PDF #36-1451 (curve 1); ZnO (curve 2); and Al_2O_3/ZnO structures containing a nano-layer of Al_2O_3 with a thickness of 15 nm (curve 3).

The room temperature micro-Raman spectrum of the Al_2O_3/ZnO heterostructures with an Al_2O_3 thickness of 15 nm after thermal treatment at 620 °C for 40 min is shown in Figure 4. The high-intensity peaks at 100 and 437 cm^{-1} can be attributed to the $E_{2(low)}$ and $E_{2(high)}$ modes of ZnO, accordingly [22,23]. Additional peaks at 210, 331, 384, 407, 570 and 580 cm^{-1} can be assigned to the $2E_{2(low)}$ second-order mode $E_{2(low)}$-$E_{2(high)}$, multiphonon scattering, A_1(TO), E_1(TO), A_1(LO) and E_1(LO) (superposition) modes of ZnO, respectively [18,23,24]. The Raman spectrum of the Al_2O_3/ZnO heterostructures after thermally annealing the columnar ZnO samples at 550 and 650 °C and coating them with a nano-layer of Al_2O_3 with a thickness of 7 nm and further thermal treatment at 620 °C for 40 min, is presented in Figure 4b. No peaks associated with crystalline Al_2O_3 phases were detected, indicating that the exposed nanomaterial is an amorphous aluminum oxide layer.

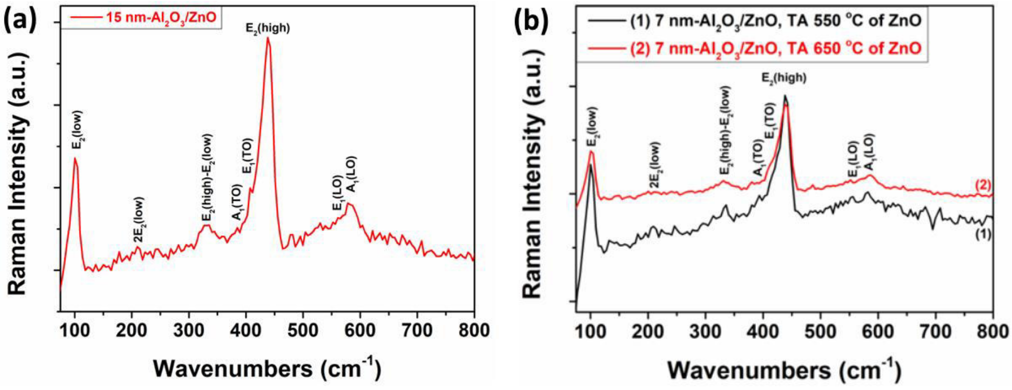

Fig. 4. (a) Room temperature micro-Raman spectrum of the annealed Al_2O_3/ZnO heterostructures containing a nano-layer of Al_2O_3 with a thickness of 15 nm. (b) Micro-Raman spectrum of the Al_2O_3/ZnO structures after thermal annealing of the ZnO underlayer at 550 °C (curve 1) and 650 °C (curve 2) followed by thermal annealing at 620 °C for 40 min of the Al_2O_3 nano overlayer with a thickness of 7 nm.

The sensing performances of the Au/Al_2O_3/ZnO heterostructures with the varying thicknesses of the Al_2O_3 layer ranging from 5-18 nm were investigated for several gases, including hydrogen, n-butanol, 2-propanol, ethanol, acetone and ammonia, at an operating/working temperature of 350 °C, as reported in Figure 5(a). The measured gas response values indicate that 12-15 nm of Al_2O_3 in the top layer leads to the highest response and largest selectivity towards 2-propanol vapor. The lowest response value to 2-propanol is 284%, which was measured for the sensor containing an Al_2O_3 coating layer with a thickness of just 5 nm, whereas the highest response to 2-propanol, in the order of 2000%, is achieved for the sensor containing an aluminum oxide layer with a thickness of 15 nm.

The same has been studied the influence of relative humidity on the 2-propanol response value at the operating temperature of 350 °C for ZnO films and Al_2O_3/ZnO heterostructures containing a nano-layer of Al_2O_3 with a thickness of 15 nm and are shown in Figure 6b, from which it can be seen that the Al_2O_3 layer over the ZnO films has a protective effect against the relative humidity compared to the ZnO films without Al_2O_3. Figure 5b also shows the response to other gases, such as hydrogen and ethanol, which can be detected at an OPT temperature as low as 200 °C, whereas the response to acetone vapors appears only at an OPT temperature of 250 °C. Figure 5c provides evidence that the dynamic response curves of the sensor recover completely at the operating temperature of 350 °C after stopping the flow of each of the tested gases, i.e., hydrogen, ethanol, 2-propanol, n-butanol, and acetone, with a concentration each of 100 ppm.

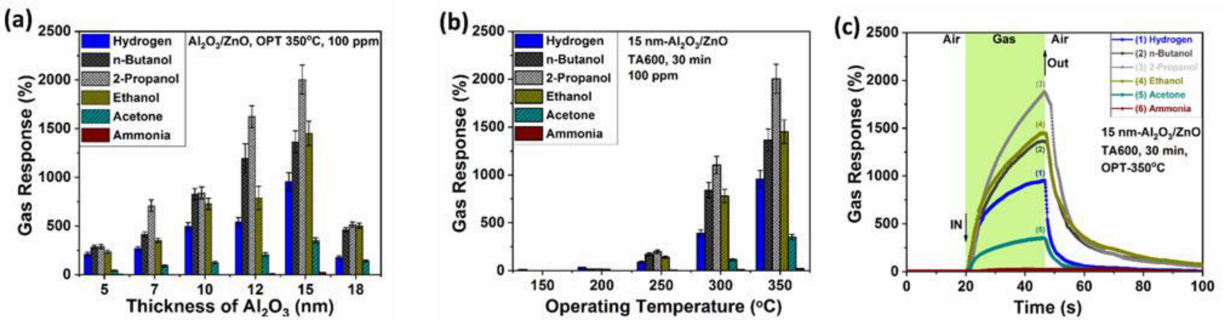

Fig. 5 (a) Gas response versus thickness of Al_2O_3 overlayer (5, 7, 10, 12, 15, 18 nm) on ZnO films. (b) Gas response versus operating temperatures, and (c) dynamic response of the Au/Al_2O_3/ZnO sample set containing a nano-layer of Al_2O_3 with a thickness of 15 nm.

Au/Al_2O_3/ZnO structures with a thickness of 15 nm of the top Al_2O_3 layer were measured several times over two years, and Figure 6a shows that the response is the same even after a long period of time, which is quite important for gas sensors. For thicker coatings, the gas response values decrease drastically, since 15 nm is the maximum thickness of the top Al_2O_3 layer which still allows the ZnO underlayer of the heterojunction to participate in the sensing mechanism to 2-propanol [25]. An explanation of the influence of Al_2O_3 layer thickness on the response value change can be explained by the initial resistance of the Au/Al_2O_3/ZnO heterostructure. Thus, Figure 6c, which shows the initial resistance of the Au/Al_2O_3/ZnO heterostructure depending on the thickness of the Al_2O_3 layer, shows that as the thickness of the aluminum oxide layer increases, the initial resistance of the heterostructure also increases. The lowest resistance was obtained to the top layer with a thickness of 5 nm, and the highest resistance to the layer with a thickness of 18 nm. When exposed to 2-propanol vapor, different responses are observed depending on the thickness of the Al_2O_3 layer. The highest response was obtained at a thickness of 15 nm. Sensors with smaller thicknesses have smaller responses, and at a thickness of 18 nm the same is a smaller response, respectively the optimal thickness is 15 nm. From the experimental data the gas response has *n*-type semiconductor oxide behavior, which assumes that the resistance to gas exposure decreases [26]. At a thickness of 5 nm, the resistance of structure with aluminum oxide is the lowest, which means that we have a smaller number of electrons that can participate in the detection of 2-propanol vapors [26]. As the thickness of the aluminum oxide increases, so does the number of electrons involved in detecting 2-propanol vapor. At thickness of 18 nm is the highest resistance, but the response is lower, this may be due to the fact that the tunnel life of the load carriers is longer compared to the smaller thicknesses [26]. Due to the higher number of load carriers and the shorter tunneling time, the thickness of 15 nm of the Al_2O_3 layer is optimal and at this given thickness the best 2-propanol vapor detection properties were found [25].

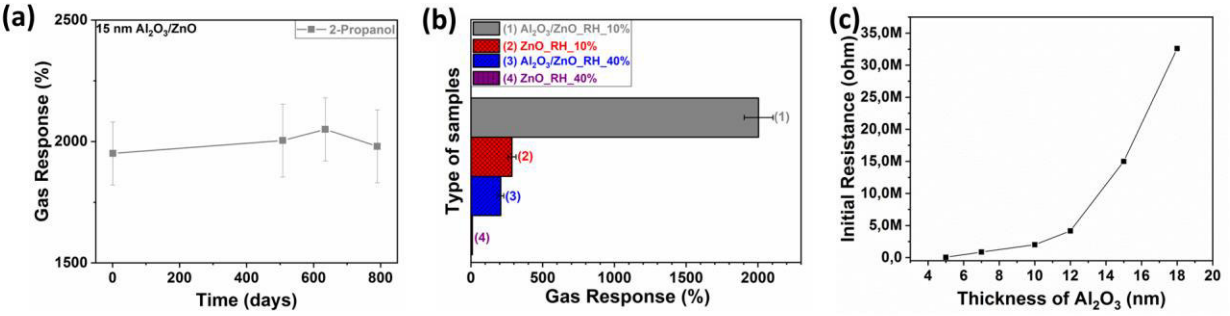

Fig. 6. (a) Variation of the gas response to 2-propanol vapors over time for the Au/15nm-Al_2O_3/ZnO structures. (b) The influence of relative humidity to 2-propanol response at different relative humidities of the ZnO films and Al_2O_3/ZnO structures. (c) Initial resistance of the Au/Al_2O_3/ZnO heterostructure depending on the thickness of the Al_2O_3 layer.

The mechanisms for detecting structures based on semiconductor oxides are based on the physico-chemical effects occurring on its surface.

Aluminum oxide (Al_2O_3), which is known for its excellent surface passivation properties [27], with a number of forbidden band lengths, depending on the particular metastable polymorph, including γ, η, δ, θ and χ [28]. Zou et al. [29] demonstrated that the amorphous aluminum oxide coating alters the conductivity of the mAl_2O_3/WO_3 composite heterostructure, which raises the number of catalytic reactions that take place on the surface, where oxygen species O^{2-}, O_{2-} and O^- are adsorbed [29–31].

Previous reports show that Al_2O_3 dissociates according to the following relation:

$$2Al_2O_3 \rightarrow 4Al^{3+} + 4O + O_2 + 6e^- \quad (3.1)$$

The Al_2O_3 and ZnO oxide phases of the heterostructure were deposited by combining the SCS approach with the ALD method respectively. The interface region or junction formed between these two semiconducting oxides plays an important role in the gas detection mechanism. The adsorption of atmospheric oxygen, on the surface of the heterojunction leads to a transfer of electrons from the conduction band to the different oxygen species (O^{-2}, O^{-}, O_2^{-}) formed at the surface [34]. Removing these oxygen species leads to the onset of spatial charge at the surface of the heterojunction. Exposing our heterostructures to the VOCs and inorganic gases trigger various surface reactions, leading to the dehydrogenation and the formation of various oxygen species. The commonly accepted [35] mechanism for the detection of gases and VOCs using zinc oxide (ZnO)-based devices, involves adsorption and desorption reactions causing the formation of oxygen (O^{2-}) following the extraction of an electron, $e^{-}$from the semiconducting oxide. This process can be represented as follows [35]:

$$O_{2(\mathrm{gas})} + e^- \rightarrow O_{2(\mathrm{ads})} + e^- \rightarrow O_{2(\mathrm{ads})}^-. \qquad (3.2)$$

The oxygen species O(ads) that form on the surface of oxide when the sensor is exposed to air interact with the applied C_3H_8O vapor according to the relation:

$$C_3H_8O + 9O_{(ads)}^- \rightarrow 4H_2O + 3CO_2 + 9e^- \qquad (3.3)$$

We can see in equation (3.3) that the number of electrons increase in the accumulation layer after H_2O and CO_2 are formed, which also increases the electric current that can be detected by the structure [23].

Al_2O_3 dissociates into Al^{3+}, oxygen species and free electrons, which catalyse efficiently the dehydrogenation reactions on the heterostructures surface and are responsible for the high response to 2-propanol gas, as mentioned by Zou et al. [29].

The Au/Al_2O_3/ZnO structures were tested for volatile compounds in electric batteries.

Figure 7a shows the gas response of the Au/Al_2O_3/ZnO sample to $C_3H_6O_2$, $C_4H_{10}O_2$, E1 and LP30 (100 ppm) for different thicknesses of 5, 7, 10, 12, 15 nm of the Al_2O_3 films at an operating temperature of 350 °C. The selectivity for $C_3H_6O_2$ is achieved for all thicknesses of the Al_2O_3 layer, with the sample containing the 10 nm layer generally showing the highest response of ~25.19%.

Figure 7b indcates that the operating temperature has a strong impact on the gas response, which increases with temperature for 100 ppm of $C_3H_6O_2$, $C_4H_{10}O_2$, E1 and LP30.

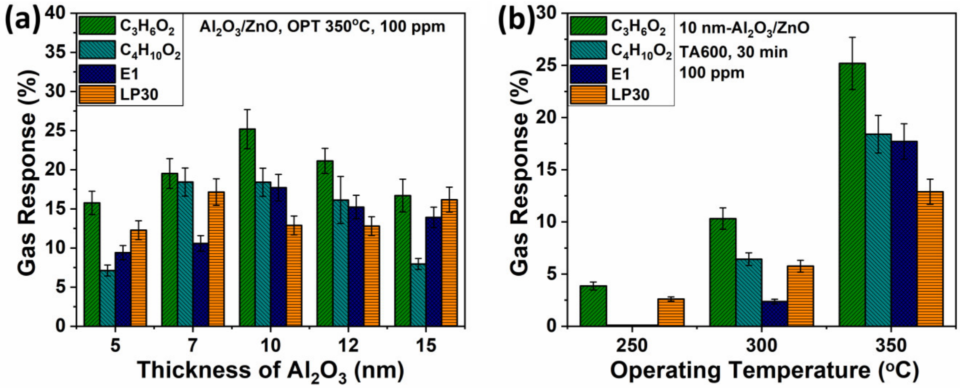

Fig. 7 (a) Gas response versus different thickness of 5, 7, 10, 12, 15 nm of the Al_2O_3 overlayer. (b) Gas response versus operating temperatures of the Au/Al_2O_3/ZnO sample set containing the 10 nm overlayer of Al_2O_3 after thermally annealing (TA) at 600 °C for 30 min.

At an operating temperature of 250 °C, there is only response for $C_3H_6O_2$ and LP30 vapors with values of ~ 4% and ~ 2.5%, respectively. However, by raising the operating temperature to 300 °C, a response occurs for all vapors with evident selectivity for $C_3H_6O_2$ with a value of ~10.31%, and for $C_4H_{10}O_2$ with a value of ~6.43%. By elevating the operating temperature by 50 °C, up to the value of 350 °C, we found that the response to all vapors increases further, while the selectivity remains the same for the $C_3H_6O_2$ vapor.

The selectivity and response to $C_3H_6O_2$ vapor was characterized at a concentration of 100 ppm, which showed the highest response for the Au/Al_2O_3/ZnO heterostructured layers with a thickness of 10 nm for the Al_2O_3 overlayer. Subsequently, gas response measurements were performed at different concentrations of $C_3H_6O_2$ vapor (1, 5, 10, 100, 500 and 1000 ppm), which are reported in Figure 8a. The highest response of ~58% was detected at a vapor concentration of 5 ppm of $C_3H_6O_2$. Increasing the concentration of the $C_3H_6O_2$ vapor decreases the gas response, with a value of only ~24% at the highest concentration of 1000 ppm. It can be explained by the saturation of the surface with adsorbed species. Figure 8b illustrates the dynamic response to $C_3H_6O_2$ vapor of different concentrations from which the times of response and times of recovery were calculated. The response times τ_r are 21.74, 21.91 and 10.29 s, and the recovery times τ_d are >50.20, >50, and 23.83 s for the vapor concentrations of 5, 10 and 100 ppm, respectively. Figure 8b also shows that at the concentrations of 5 and 10 ppm, there is a partial recovery, but at the concentration of 100 ppm there is a total recovery after the supply of the target vapors has been stopped. Figure 8c shows the variation of the response to 5 ppm of $C_3H_6O_2$ vapor over time for the sample containing the 10 nm overlayer of Al_2O_3, where we can observe that the response remains essentially constant.

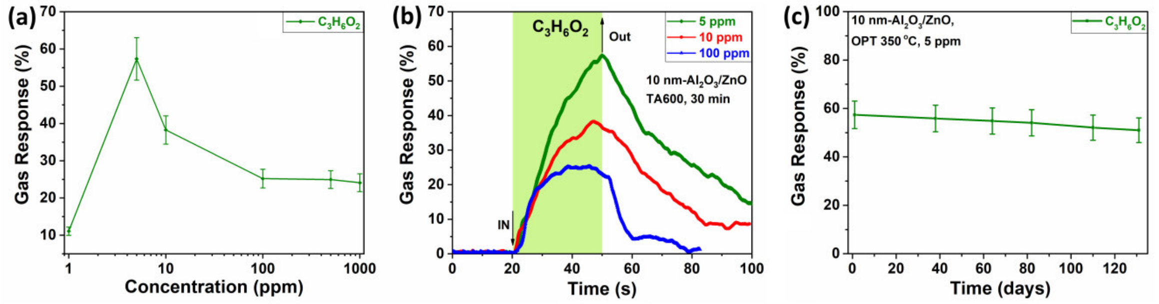

Fig. 8. (a) Response to different concentrations of $C_3H_6O_2$ of the Au/Al_2O_3/ZnO samples set with a thickness of 10 nm of the Al_2O_3 overlayer thermally annealled (TA) at 600 °C for 30 min. (b) Dynamic response to concentrations of 5, 10 and 100 ppm of the Au/Al_2O_3/ZnO sample set with a thickness of 10 nm of the Al_2O_3 overlayer thermally annealed (TA) at 600 °C for 30 min. (c) Variation of the gas response to 5 ppm of $C_3H_6O_2$ vapors over time for the sample containing the 10 nm overlayer of Al_2O_3.

The detection mechanism for volatile compounds in electric batteries is proposed as follows.

Heterojunctions based on metal oxides can lead to new properties, such as improved sensitivity and selectivity, as reported in previous studies [18,36]. One of the main reasons for this behavior is the interface or junction between two semiconductor metal oxides, which plays an important role in gas detection, due to the adsorption of atmospheric oxygen at the heterojunction surface. In the case of zinc oxide (ZnO) structures, this leads to the transfer of electrons from the oxide surfaces to a certain oxygen species (O^{2-}, O^-, O_2^-) formed on the surface [36,37], according to the reaction:

$$O_{2(\mathrm{gas})} + e^- \rightarrow O_{2(\mathrm{ads})} + e^- \rightarrow O^-_{2(\mathrm{ads})}. \qquad (3.4)$$

In the case of aluminum oxide (Al_2O_3), dissociation [32,33] can occur according to the equation:

$$2Al_2O_3 \rightarrow 4Al^{3+} + 4O + O_2 + 6e^- \qquad (3.5)$$

Upon exposure to 1,3-dioxolane gas, due to the presence of oxygen species on the surface, a low-conductivity depletion region is formed on the surface, and as a result, the current channels in the Au/Al_2O_3/ZnO structure are narrowed. Thus, dioxolane molecules can interact with surface oxygen ions. The given process can be described using the following chemical reaction [38,39]:

$$C_3H_6O_2 + 7O^-_{(ads)} \rightarrow 3H_2O + 3CO_2 + 7e^- \qquad (3.6)$$

Reaction (3.6) shows that a rise in the number of electrons leads to an increase in the electric current flowing through the heterojunction, explaining the large sensitivity obtained for $C_3H_6O_2$ vapor.

The high selectivity towards 1,3-dioxolane of the Au/Al_2O_3/ZnO heterostructure with a 10 nm thick aluminum oxide layer can also be explained by the Debye length effect for ZnO [40–42], which can is calculated:

$$\lambda_D = \sqrt{\frac{\varepsilon k T}{q^2 n_c}} \qquad (3.7)$$

where ε, k, T, q, and n_c are the static dielectric constant, Boltzmann constant, absolute temperature, electric charge, and charge carrier concentration, respectively.

The Debye length for n-type semiconductors can be controlled by the concentration of donors within the lattice. The Al^{3+} ions, obtained in equation (3) allow the control of the Debye length for ZnO [43]. We found that 10 nm of thickness of aluminum oxide (Al_2O_3) is equal to the Debye length, leading to an electron-depleted region with a strong change in resistance when the gas mixture is applied, resulting in a high response. For thicknesses of aluminum oxide larger than 10 nm, the Debye length changes, which reduces the region depleted of electrons and the electrical resistance and the response to the gases.

The high selectivity of the Au/Al_2O_3/ZnO heterostructure for 1,3-dioxolanes can be rationalized as follows:

The Debye length only becomes equal to the thickness of Al_2O_3, when the latter has 10 nm, which allows the formation of a large electron depletion region, resulting in a high selectivity towards 1,3-dioxolanes [44].

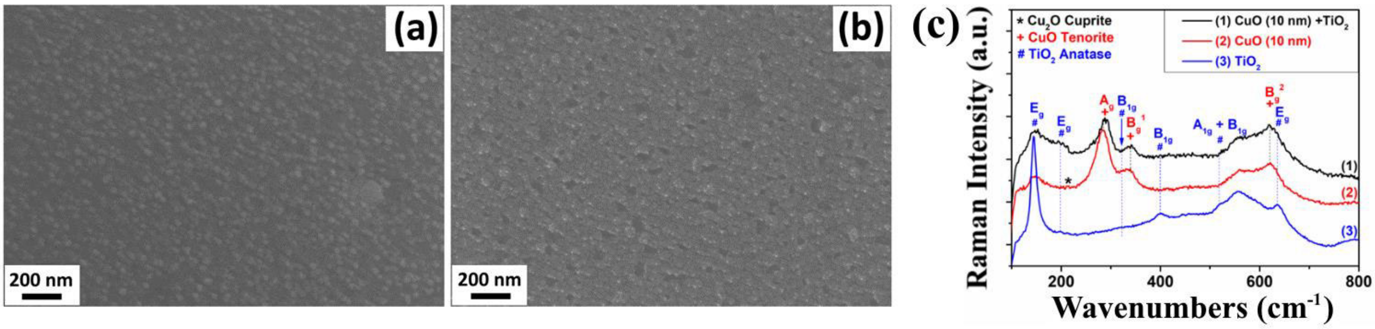

Fig 9. SEM images of the: (a) nanocrystallite CuO/Cu_2O samples; and (b) TiO_2/CuO/Cu_2O structures with thickness of the CuO layer of 10 nm (Cu10). (c) Micro-Raman spectra of thin nanocrystalline layers of (1) TiO_2/CuO structures (Cu10), (2) CuO/Cu_2O films (Cu10) and (3) TiO_2 layer.

Figure 9a presents the SEM micrograph of the nano-crystalline Au/CuO/Cu_2O specimens with a thickness of 10 nm (sample set labeled as Cu10) grown on a glass substrate using a reproducible ALD/sputtering/annealing approach [45], followed by thermal annealing at 420 °C for 30 min in air. The layered thin films adhere strongly to the microscopic glass substrates and appear with a morphology of films composed of nano-crystallites. Figure 9b presents the SEM images of the Au/TiO_2/CuO/Cu_2O heterostructures, which reveal that the nano-crystallites shown in Figure 9a are coated with a layer of TiO_2, consisting of nano-granules/dots.

Micro-Raman spectroscopy was conducted to determine the chemical composition of the sensor materials and to study the lattice dynamics (electron−phonon interaction) of the CuO/Cu_2O and TiO_2/CuO nanomaterials at the nanoscale. The micro-Raman spectra were obtained at room temperature in the range 100−1000 cm^{-1} for the TiO_2/CuO, CuO/Cu_2O and TiO_2 nanomaterials, as shown in Figure 9c. The copper oxide films (Cu10) (curve 2) exhibit both the CuO tenorite phase and the Cu_2O cuprite phase (marked with an asterisk "*"), but in the TiO_2/CuO heterostructures (Cu10) (curve 1) the cuprite phase vanishes since the CuO/Cu_2O layer has a thickness of only 10 nm (Cu10). After the deposition of the TiO_2 layer, the heterostructures undergo another annealing process that transforms the cuprite phase into the tenorite phase [46].

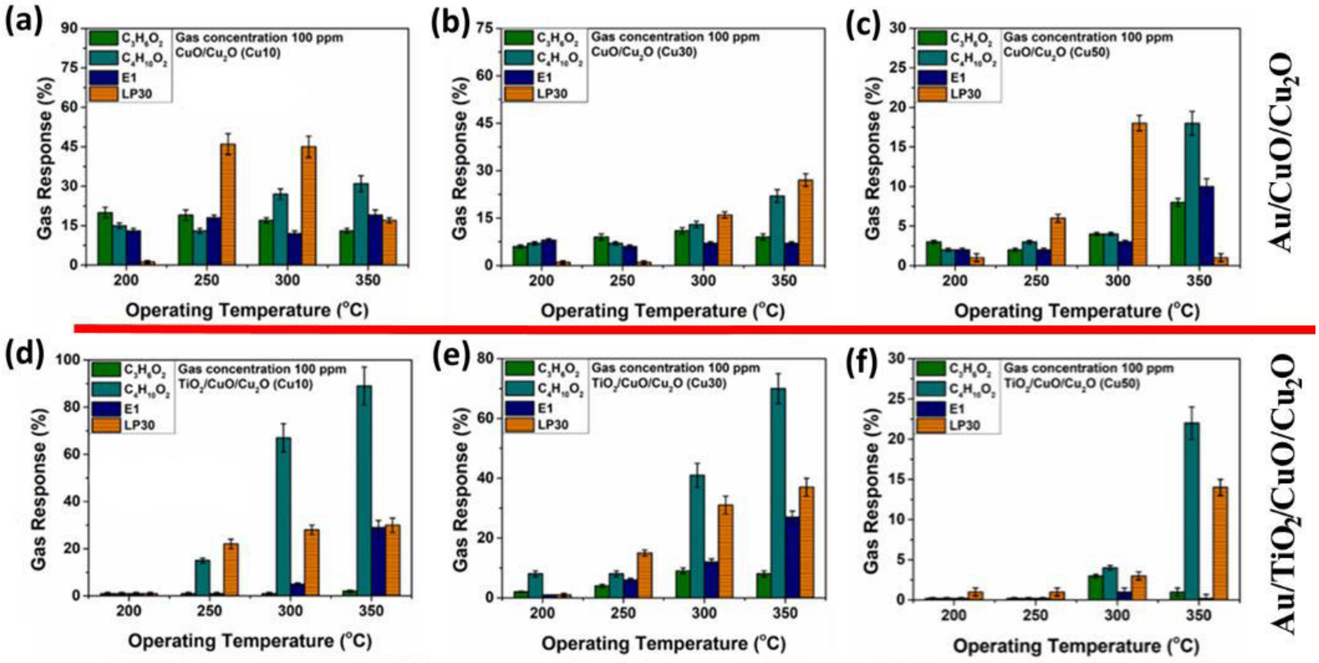

Fig. 10. Gas response (to $C_3H_6O_2$, $C_4H_{10}O_2$, E1 and LP30) versus operating temperatures for: (a, b, c) Au/CuO/Cu_2O samples and (d, e, f) Au/TiO_2/CuO/Cu_2O samples with different thicknesses of 10 nm (Cu10), 30 nm (Cu30) and 50 nm (Cu50).

Figure 10 shows the response of CuO/Cu_2O (Figure 10a,b,c) and $TiO_2/CuO/Cu_2O$ samples (Figure 10 d,e,f) with thicknesses of 10 nm (Cu10), 30 nm (Cu30) and 50 nm (Cu50) to 100 ppm of $C_3H_6O_2$, $C_4H_{10}O_2$, E1 and LP30 as a function of operating temperatures. Figures 10a,b,c show that all thicknesses of the $Au/CuO/Cu_2O$ samples respond to all gases, with a higher selectivity towards LP30, especially for $Au/CuO/Cu_2O$ specimens with 10 nm thickness (Cu10) at OPTs 250 °C - 300 °C with responses of ~46%, and ~45%, respectively. For the $Au/TiO_2/CuO/Cu_2O$ samples (Figures 10d,e,f), the selectivity changes to $C_4H_{10}O_2$ with the highest responses observed at operating temperatures of 300 and 350 °C. At 300 °C, the response values are ~67 %, ~41 % and ~4 % for Cu10, Cu30 and Cu50, respectively, while at 350 °C, the response values are ~89 %, ~70 % and ~22 % for the same samples.

Chapter 4 is based on the development and study of $PV/CuO/Cu_2O/ZnO:Fe$ structures and ZnO nanowires hydrothermally treated for sensing vapor from electric battery electrolytes, ethanol and hydrogen gas at different concentrations and relative humidities.

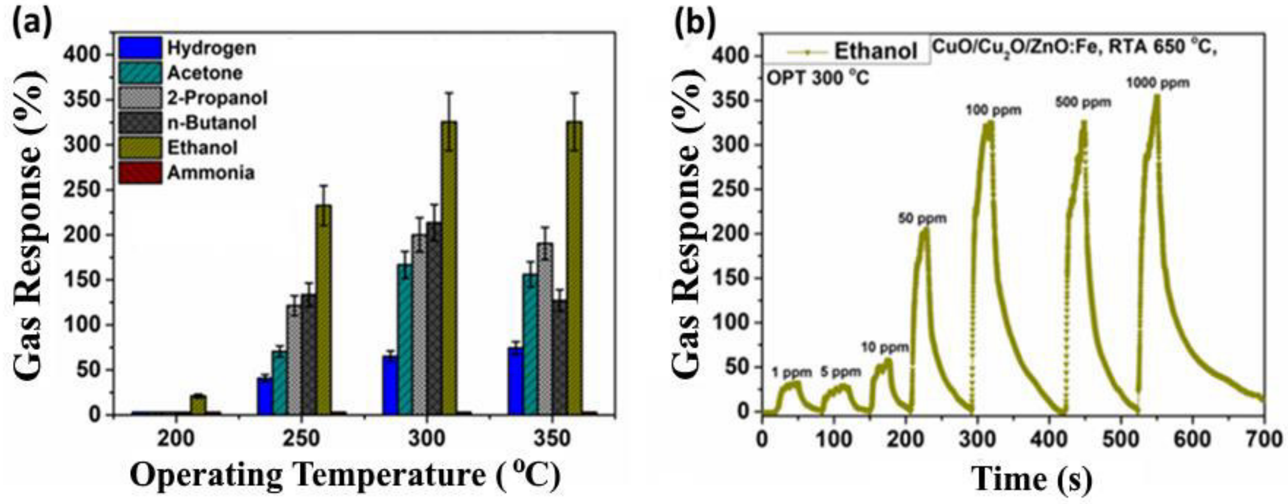

Fig. 11. (a) The dependence of the gas response (to hydrogen, acetone, 2-propanol, n-butanol, ethanol and ammonia) versus operating temperature of the $Au/CuO/Cu_2O/ZnO:Fe$ structures with RTA 650 °C. (b) Dynamic response to ethanol vapors at different concentrations (1, 5, 10, 50, 100, 500 and 1000 ppm) of the $Au/CuO/Cu_2O/ZnO:Fe$ heterostructures with RTA treatment at 650 °C.

Figure 11a indicates that from all used operating temperatures, i.e., 200 °C, 250 °C, 300 °C and 350 °C, the optimum operating temperature is 300 °C or 350 °C. The response to ethanol vapours at these operating temperatures is ~21%, ~232%, ~325% and 325%, respectively. The response is type-*p* because the resistance of the heterojunctions at the time of the test gas application is increased. Figure 11b presents the dynamic response to ethanol vapours at different concentrations at OPT 300 °C for the Au/CuO/Cu_2O/ZnO:Fe heterostructures with RTA at 650 °C. It can seen that at low concentrations of 1 and 5 ppm the response is quite high with ~30%. It is increasing with the increase in concentration. The respective gas responses at 10, 50, 100, 500 and 1000 ppm, are: ~57%, ~204%, ~322%, ~324% and ~355%, respectively.

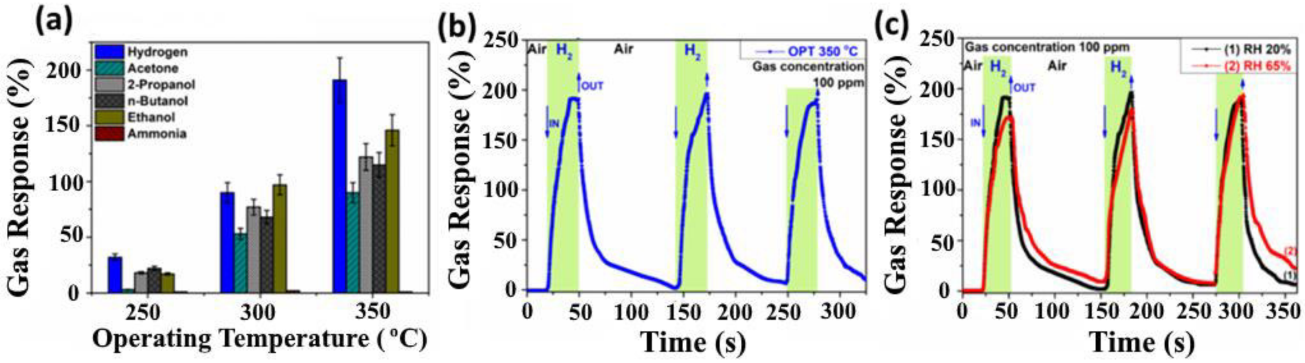

Fig. 12. (a) The gas response dependences (to hydrogen, acetone, 2-propanol, n-butanol, ethanol and ammonia) versus operating temperature of the Au/CuO/Cu_2O/ZnO:Fe structures coated with PV3D3 annealed RTA 650 °C. (b) Dynamic response to hydrogen gas at OPT 350 °C of the Au/CuO/Cu_2O/ZnO:Fe heterostructures coated with PV3D3. (c) Dynamic response to hydrogen gas with 100 ppm concentration at different relative humidity of the Au/CuO/Cu_2O/ZnO:Fe heterostructures coated with PV3D3 at OPT 350 °C, sample annealed RTA at 650 °C.

Figure 12a shows that after the deposition of the PV polymer layer over the CuO/Cu_2O/ZnO:Fe structures, hydrogen selective sensors were obtained at all operating temperatures. The hydrogen responses at operating temperatures (250 °C, 300 °C and 350 °C) are ~32%, ~90% and 191%, respectively. Figure 12b shows the dynamic response to hydrogen at the operating temperature of 350 °C for PV polymer coated Au/CuO/Cu_2O/ZnO:Fe structures. From this graph, it can be seen that for all types of structures coated with PV polymer the response to hydrogen is ≈200%. The results confirm fairly good repeatability and full recovery of the response after turning off the test gas at each pulse. Figure 13c shows the response to hydrogen with the concentration of 100 ppm at different relative humidities, where we observe that the response remains unchanged.

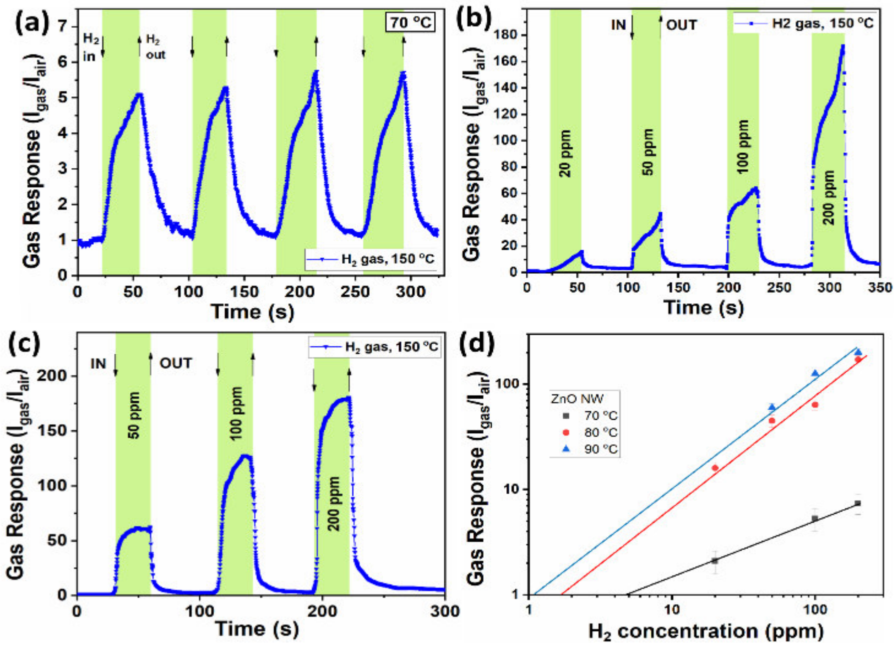

Fig. 13. (a) Dynamic gas response at 150 °C of individual ZnO nanowire synthesized at 70 °C to multiple exposures of H_2 gas with 100 ppm, as well as to different concentrations of hydrogen gas for a single ZnO nanowire synthesized at: (b) 80 °C and (c) 90 °C. (d) Dependence of gas response on gas H_2 concentration at 150 °C for individual ZnO nanowire synthesized at 70 °C, 80 °C and 90 °C, respectively.

In Figure 13, the dynamic gas response at 150°C of individual ZnO nanowire NW synthesized at 70 °C to multiple exposures of H_2 gas with 100 ppm is presented. Here, the good repeatability of the fabricated sensors is demonstrated. The residual standard deviation of the gas response for all samples is limited to 10%. In Figures 13a and 13b the dynamic response to H_2 gas with different concentrations at an operating temperature of 150°C for individual ZnO nanowire synthesized at 80°C and 90°C is presented. A complete recovery of the signal to the starting electrical baseline after evacuating the H_2 gas from the testing chamber is observed. This is very important for real-time application in monitoring of hydrogen gas concentrations. The response time and recovery times for detecting 100 ppm H_2 gas is 26 s and 35 s for nanowire grown at 70 °C, 21 s and 20 s for nanowire grown at 80°C, 17 s and 16 s for nanowire grown at 90°C. Therefore, Figures 13a-c indicate that nanowires grown at higher temperatures have a faster saturation of the gas response and a faster recovery of the signal in comparison to samples ECD at lower temperature.

Figure 13d shows the gas response value versus hydrogen gas concentration at 150 °C for individual ZnO nanowire synthesized at 70°C, 80°C and 90°C, demonstrating a power law dependence of gas response on hydrogen concentration. [43] The I_{gas}/I_{air} >1.2 criterion was used to determine the lower detection limit (LDL) of the nanosensor. [42] For nanowires grown at 70°C, 80°C and 90°C the estimated LDL value is ~5 ppm, ~1.8 ppm and ~1.1 ppm, respectively. Overall, the presented results show that the use of ZnO nanowire grown at the higher temperatures, especially at 90°C, are preferable to fabricate gas nanosensors with higher performances, including gas response, response/recovery time and lowest detection limit. Hydrothermally treated ZnO nanowires showed a higher gas response and a faster recovery, as well as better performances as reported in our works [48].

Next, the methodology for creating a PSpice model of a gas sensor as realistic as possible is presented. To describe the gas sensor we will use the analytical model based on physical processes and some experimental data obtained in the laboratory on developed structures of semiconducting oxides. For this it is necessary that the sensor we want to simulate meets certain requirements. Among them we can list the following requirements: 1) The results obtained from the simulation must be as close as possible to the experimental ones; 2) The sensor should have an optimal number of pins (the number of inputs-outputs); 3) Imposing as few usage restrictions as possible; 4) A simple mode of use. The schematic for the simulation is shown below.

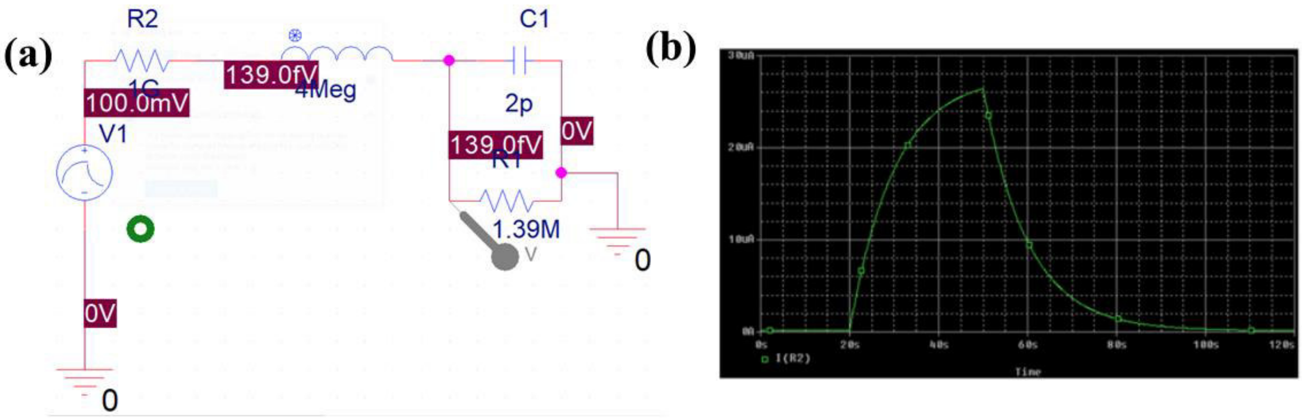

Fig. 14. (a). Scheme for simulation of developed sensor. (b). Simulation of the response to 2 -propanol vapors of the Au/Al_2O_3/ZnO structure.

Following the simulation of the scheme presented in figure 14, the following results were obtained

At the end of each chapter, a summary of the main results obtained is presented, and the conclusions and recommendations show the practical and theoretical value of the research carried out.

GENERAL CONCLUSIONS AND RECOMMENDATIONS

Following the research proposed for the detection of volatile organic compounds, electrolyte vapors from electric batteries and H_2, different structures were obtained that can detect these compounds. Thus, based on the results obtained, the following general conclusions can be formulated:

1. The structures based on $Au/Al_2O_3/ZnO$ obtained by combining the SCS and ALD methods allowed to obtain selective sensors against 2-propanol vapors stable for more than 2 years, where it is demonstrated that the response to 2-propanol remains unchanged [25].
2. The $Au/Al_2O_3/ZnO$ structures obtained by combining the SCS and ALD methods, but using different temperatures and durations of the heat treatment allowed to obtain new time-stable sensors that will allow the detection of the components of electric batteries, of LIBs. In this way, selective sensors against $C_3H_6O_2$ vapors were obtained, the highest response being shown for the structure with an Al_2O_3 layer thickness of 10 nm [44].
3. The 10 nm thick $Au/CuO/Cu_2O$ structures, which were obtained using heat treatment at 420 °C for 30 minutes over ZnO:Fe, resulting in the $Au/CuO/Cu_2O/ZnO$:Fe structure are selective to ethanol vapor with the highest response of 325% at operating temperatures of 300 °C - 350 °C [13].
4. The deposition of the PV polymer state on top of the $CuO/Cu_2O/ZnO$:Fe structures allowed to achieve a change in selectivity from ethanol vapor to hydrogen gas, as well as a reduced influence of high relative humidity on the sensor response [13].
5. Structures obtained by sputtering metallic copper followed by heat treatment in a CuO/Cu_2O furnace can detect LP($LiPF_6$) vapors at low operating temperatures, and by depositing an ultrathin layer of TiO_2, selective structures against the $C_4H_{10}O_2$ compound have been obtained even and at the concentration of 1 ppm [46].
6. Steam/water vapor treatment has been shown to be an efficient method to obtain single ZnO nanowires for H_2 vapor detection at the lowest concentrations with the lowest response time and recovery times [48].
7. The development of sensor models will allow to approximate some measurements that can be obtained from gas testing of different structures from different semiconductors.

Following the analysis of the obtained results, the following recommendations can be formulated:

1. It is recommended to use $Au/Al_2O_3/ZnO$ structures with Al_2O_3 layer thickness of 15 nm for the time detection of 2-propanol vapors.

2. It is recommended to use Al_2O_3/ZnO structures with Al_2O_3 layer thickness of 10 nm for the detection of $C_3H_6O_2$ vapors in the composition of electric batteries.

3. For hydrogen detection at high humidity it is recommended to use CuO/Cu_2O/ZnO structures coated with a thin layer of PV polymer.

4. It is recommended to use Au/CuO/Cu_2O structures for detecting $LiPF_6$ vapors, and Au/TiO_2/CuO/Cu_2O structures for detecting the lowest concentrations of $C_4H_{10}O_2$ vapors in the composition of electric batteries.

5. It is recommended to use hydrothermally treated ZnO nanowires to rapidly detect the smallest concentrations of hydrogen gas.

6. It is recommended to use PSpice to develop some models for gas sensors.

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LIST OF THE AUTHOR'S PUBLICATIONS ON THE SUBJECT OF THE Ph.D. THESIS

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1. SANTOS-CARBALLAL, D., LUPAN, O., **MAGARIU, N.,** KRÜGER H., ABABII, N., BODDULURI, M. T., LEEUW N. D., HANSEN, S., ADELUNG R. Al_2O_3/ZnO Composite-Based Sensors for Battery Safety Applications: An Experimental and Theoretical Investigation, În: *NanoEnergy*, Volume 109, May 2023, 108301 ISSN 22112855, (**Impact Factor: 19.069**)
2. LUPAN, O., SANTOS-CARBALLAL, D., **MAGARIU, N.**, MISHRA, A.K., ABABII, N., KRÜGER, H., WOLFF, N., VAHL, A., BODDULURI, M.T., KOHLMANN, N., ADELUNG, R., LEEUW, N. D., HANSEN, S. Al_2O_3/ZnO Heterostructure-Based Sensors for Volatile Organic Compounds in Safety Applications. În: *ACS Appl. Mater. Interfaces* 2022, 14, pp. 29331–29344, ISSN 1944-8244. (**Impact factor: 10.3**).
3. LUPAN, O., **MAGARIU, N.**, KHALEDIALIDUSTI, R., MISHRA, A.K., HANSEN, S., KRÜGER, H., POSTICA, V., HEINRICH, H., VIANA, B., ONO, L.K., CUENYA,B. R., CHOW, L., ADELUNG, R., PAUPORTÉ, T. Comparison of Thermal Annealing versus Hydrothermal Treatment Effects on the Detection Performances of ZnO Nanowires. În: *ACS Appl. Mater. Interfaces* 2021, 13, pp. 10537–10552, ISSN 19448252 (**Impact factor: 10.3**).
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7. SCHRÖDER, S., **MAGARIU, N**., STRUNSKUS, T., ABABII N., LUPAN, O., FAUPEL, F. New Vapor Deposited Dielectric Polymer Thin Films For Electronic Applications, În: *Journal of Engineering Science* Vol. XXIX (3) 2022, pp. 34-44 ISNN 2587-3482;

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8. **MAGARIU, N.** Effects of Heat Treatment on Palladium-Doped Zinc Oxide on Sensory Selectivity. În: *4th International Conference on Nanotechnologies and Biomedical Engineering*, 2019 p.259-262 ISBN 978-9975-45-588-6;
9. **MAGARIU, N**., ABABII, N., ZADOROJNEAC, T., KRÜGER, H., BODDULURI, M. T., PAUPORTÉ, T., ADELUNG, R., HANSEN, S., LUPAN O. Semiconducting Oxide-Based Micro- and Nano-Sensors for Environmental and Biomedical Monitoring, În *IEEE 11th International Conference Nanomaterials: Applications & Properties (NAP)*, 05-11 September 2021, ISBN 978-1-6654-3907-7, pp.1-4;
10. LUPAN, O., **MAGARIU, N**., KRÜGER, H., SEREACOV, A., ABABII, N., RAILEAN, S.,I ZIMOCH, L., ADELUNG, R., HANSEN, S. Nano-Heterostructured Materials - Based Sensors for Safety and Biomedical Applications În *IEEE 12th International Conference "Nanomaterials: Applications & Properties" (IEEE NAP-2022)*, Krakow, Poland, Sep. 11-16, 2022, ISBN 978-1-6654-8982-9, pp.1-4;

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11. **MAGARIU**, N., PAUPORTÉ, T., LUPAN, O., TiO_2/ZnO columnar heterostructures În: *International Conference on Electronics, Communications and Computing*, October 23–26, 2019, Chisinau, Moldova, pp. 66, ISBN 978-9975-108-84-3.

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12. **MAGARIU, N.**, SEREACOV, A., ULFA, M., Efectele formării nano-heterojoncţiunilor non-planare a oxizilor de titan şi zinc asupra selectivităţii senzoriale. În: *Conferinţa Tehnico-ştiinţifică A Studenţilor, Masteranzilor şi Doctoranzilor* 26-29 martie 2019 ISBN 978-9975-45-588-6 pp.364-368;
13. **MAGARIU, N.**, SEREACOV, A., BODDULURI, M. T., GAPEEVA, A. Al2O3/ZnO Non-Planar Heterostructures For UV Radiation Sensor Applications, În: *Conferința Studenților Masteranzilor si Doctoranzilor* UTM, 1-3 aprilie 2020. ISBN 978-9975-45-633-3, pp. 277-280;
14. ZADOROJNEAC T., ABABII N., **MAGARIU** N., Sensing Studies of Copper Oxide-Zinc Oxide Heterojunctions to Volatile Organic Compounds, În: *Conferința Studendilor Masteranzilor si Doctoranzilor UTM*, 1-3 aprilie 2020 ISBN 978-9975-45-633-3, pp. 293-296;
15. ZADOROJNEAC, T., **MAGARIU, N.** Cercetarea structurilor pe bază de oxizi semiconductori pentru monitorizarea mediului În *Conferinţa tehnico-ştiinţifică a Studenţilor, Masteranzilor şi Doctoranzilor*, 23-25 martie 2021 ISBN: 978-9975-45-700-2, pp. 315-318
16. **MAGARIU, N.**, ABABII, N., POSTICA, V., BODDULURI, M.T., LUPAN, O., ADELUNG R., HANSEN S. Al_2O_3/CuO non-planar heterostructures for VOCs vapors detection În *The 11th International Conference on Electronics, Communications and Computing*, 21-22 octomber 2021, ISBN: 978-9975-45-776-7, pp. 97-100;
17. SCHRÖDER, S., **MAGARIU**, N., STRUNSKUS, T., ABABII N., LUPAN, O., FAUPEL, F New Vapor Deposited Dielectric Polymer Thin Films for Electronic Applications *În The 11th International Conference on Electronics, Communications and Computing*, 21-22 octomber 2021, ISBN: 978-9975-45-776-7, pp. 94-96;

Patents and other intellectual property objects (IPO):

18. LUPAN, O., **MAGARIU, N.**, TROFIM, V. Procedeu de obținere a senzorului de n-Butanol pe baza heterojoncțiunii ZnO-Al_2O_3 Hotărâre pozitivă nr.10155 din 04.11.2022.

ADNOTARE

MAGARIU Nicolae, „ Proprietățile fizico-chimice și modelele senzorilor în baza semiconductorilor oxidici nanometrici ”, teză de doctor în științe inginerești, Chișinău, 2023

Structura tezei: Teza este scrisă în limba română și constă din introducere, 4 capitole, concluzii generale și recomandări, bibliografie din 421 de titluri, 118 pagini text de bază, 57 figuri și 4 tabele. Rezultatele obținute au fost publicate în 35 de lucrări științifice dintre care 18 lucrări sunt la tema tezei, inclusiv: 1 brevet de invenție; 6 articole recenzate în reviste cotate ISI și SCOPUS (dintre care unul cu Factor de Impact 19.069 și trei cu Factor de Impact: 10.3); 1 articol în reviste din Registrul Naţional al revistelor de profil, JES; 10 lucrări prezentate, recenzate și publicate la Conferinţe Naţionale şi Internaţionale.

Cuvinte-cheie: oxid de zinc, oxid de aluminiu, oxid de cupru, nanotehnologii, structuri, electroliți, senzori de gaze, baterii, semiconductori.

Scopul lucrării: constă în obținerea structurilor $Au/Al_2O_3/ZnO$, $Au/CuO/Cu_2O/ZnO:Fe$ $Au/CuO/Cu_2O$ și $Au/TiO_2/CuO/Cu_2O$ prin metode și tehnologii cost-eficiente; identificarea structurilor și a nanofirelor cu sensibilitate și selectivitate la gaze (H_2) și compuși organici volatili (COV) (2-propanol și etanol), testați comparativ și la alte gaze din categoria COV; obținerea structurilor senzor stabili la umiditatea relativă; detectarea compușilor din componența bateriilor electrice; elaborarea unor modele a senzorilor pe baza structurilor semiconductoare.

Obiectivele cercetării: cercetarea proprietăților fizico-chimice, inclusiv senzoriale, ale structurilor în bază de: (i) $Au/Al_2O_3/ZnO$ cu diferite grosimi ale oxidului de aluminiu; (ii) $Au/CuO/Cu_2O/ZnO:Fe$ și cu depunerea polimerului PV; (iii) $Au/TiO_2/CuO/Cu_2O$ cu diferite grosimi ale oxidului de cupru; (iv) tratamentul în vapori a nanofirelor de ZnO; (v) propunerea unui model de simulare a senzorilor.

Noutatea și originalitatea științifică: asigurarea stabilității caracteristicilor pe termen lung, reglarea sensibilității selective, precum și îmbunătățirea răspunsului față de compușii organici volatili (COV), H_2 și compușii din componența bateriilor electrice a structurilor $Au/Al_2O_3/ZnO$, $Au/CuO/Cu_2O/ZnO:Fe$, $Au/TiO_2/CuO/Cu_2O$ și a nanofirelor de ZnO. Cu ajutorul echipamentelor moderne au fost studiate proprietățile morfologice, structurale, vibraționale: XRD, SEM, Raman, HRTEM, TEM, SAED, EDX și XPS pentru demonstrarea calității și caracteristicilor fizico-chimice ale structurilor obținute. Pentru a simula interacțiunea moleculelor de gaz cu suprafața structurilor studiate au fost efectuate calculele teoriei DFT, ce permite de a simula/modela mecanismele de detectare a gazului ce au loc la suprafaţa structurilor elaborate.

Problema științifică și de cercetare soluționată constă în obținerea structurilor și nanofirelor sensibile și selectivitate la gaze: (H_2), compuși organici volatili (COV: 2-propanol și etanol) și compușiilor din componența bateriilor electrice ($C_3H_6O_2$, $C_4H_{10}O_2$ și $LiPF_6$) stabile în timp și la umiditatea relativă înaltă.

Semnificația teoretică și valoarea aplicativă a lucrării are ca scop de a propune și elabora mecanismele fizico-chimice de detectare a gazelor, a COV și a compușilor din componența bateriilor electrice de către structurile obținute pe bază de $Au/Al_2O_3/ZnO$, $Au/CuO/Cu_2O/ZnO:Fe$, $Au/TiO_2/CuO/Cu_2O$ și pe baza nanofirelor de ZnO tratate hidrotermal, precum și exemplificarea aplicațiilor pentru detectarea gazelor și a diferitor vapori de COV (2-propanol și etanol) care sunt stabile în timp și imune/stabile la umidități înalte. Mecanismele de detectare propuse au fost susținute de calculele teoriei funcționale și simulările DFT, ce permit de a simula procesele de interacțiune a gazelor sau vaporilor COV la suprafața structurilor elaborate din semiconductori oxidici nanometrici.

Implementarea rezultatelor științifice. Rezultatele științifice obținute au fost utilizate parțial în procesul educativ, la elaborarea tezelor de licență și masterat la departamentul MIB, din cadrul UTM. Apoi în baza rezultatelor științifice elaborate a fost obținut un act de implementare a cercetărilor inovaționale la Facultatea CIM, UTM, precum și un brevet de invenție.

ABSTRACT

MAGARIU Nicolae, „Physico-chemical properties and models of sensors based on nanoscale oxide semiconductors", the scientific degree of Doctor in Engineering Sciences, Chisinau, 2023

Structure of the thesis: The thesis is written in Romanian language and consists of an introduction, 4 chapters, general conclusions and recommendations, a bibliography of 421 titles, 118 pages of basic text, 57 figures and 4 tables. The obtained results were published in 35 scientific papers, 18 of which are on the topic of the thesis, including: 1 invention patent; 6 peer-reviewed articles in ISI and SCOPUS rated journals (one of which with Impact Factor 19.069 and three of which with Impact Factor: 10.3); 1 article in journal from the National Register of professional journals, JES; 10 publications were presented, reviewed and published at National and International Conferences.

Key words: zinc oxide, aluminum oxide, copper oxide, nanotechnologies, structures, electrolytes, gas sensors, batteries, semiconductors.

The aim of the work: consists in obtaining layered structures $Au/Al_2O_3/ZnO$, $Au/CuO/Cu_2O/ZnO:Fe$ $Au/CuO/Cu_2O$ and $Au/TiO_2/CuO/Cu_2O$, through cost-effective methods and technologies; identification of structures and nanowires with sensitivity and selectivity to gases (H_2) and volatile organic compounds (VOCs) (2-propanol and ethanol); obtaining sensor structures stable at relative humidity; detection of compounds in electric batteries.

Research objectives: research on the physico-chemical properties, including sensory, of heterostructures based on: (i) $Au/Al_2O_3/ZnO$ structures with different thicknesses of aluminum oxide; (ii) $Au/CuO/Cu_2O/ZnO:Fe$ and with PV polymer deposition; (iii) $Au/TiO_2/CuO/Cu_2O$ with different copper oxide thicknesses; (iv) hydrothermal treatment in water vapor of ZnO nanowires; (v) proposing a sensor simulation model.

Scientific novelty and originality: ensuring the long-term stability of the characteristics and adjusting the selective sensitivity, as well as improving the response to volatile organic compounds (VOCs), H_2 and compounds in the composition of electrical batteries of layered structures $Au/Al_2O_3/ZnO$, $Au/CuO/Cu_2O/ZnO:Fe$, $Au/TiO_2/CuO/Cu_2O$ and hydrothermally treated ZnO nanowires. Using the modern equipment were studied the morphological, structural, chemical and vibrational properties: by using XRD, SEM, Raman, HRTEM, TEM, SAED, EDX and XPS to demonstrate the quality and physico-chemical characteristics of the obtained structures oxide semiconductors. In order to simulate the interaction of gas molecules with the surface of the studied structures, the calculations of the DFT theory were chosen, which allows to simulate/model the gas detection mechanisms that take place on the surface of the structures.

The scientific and research problem solved consists in obtaining sensitive oxide semiconductor-based structures and nanowires and selectivity to gases: (H_2), volatile organic compounds (VOC: 2-propanol, and ethanol) and compounds from the composition of electrical batteries ($C_3H_6O_2$, $C_4H_{10}O_2$ and $LiPF_6$) stable over time and at high relative humidity.

The theoretical significance and applied value of the work consist in the proposed physico-chemical characteristics and mechanisms for the detection of gases, VOCs and compounds from the composition of electrical batteries by the structures obtained on $Au/Al_2O_3/ZnO$, $Au/CuO/Cu_2O/ZnO:Fe$, $Au/TiO_2/CuO/Cu_2O$ and based on hydrothermally treated ZnO nanowires, as well as exemplifying applications for sensing gases and various VOC vapors (2-propanol and ethanol), that are highly stable over time and to high humidities. The proposed detection mechanisms were supported by functional theory calculations and DFT simulations, which allow simulating the interaction processes of VOC gases or vapors on the surface of the structures made from developed nanometric oxide semiconductors.

The scientific results The obtained scientific results were partially used in the educational process, in the elaboration of bachelor's and master's theses at the MIB department, FCIM within the UTM. Then, based on the scientific results obtained, an invention patent was obtained and an act of implementation of innovative research at the Faculty of CIM, UTM.

АННОТАЦИЯ

МАГАРИУ Николае, „ Физико-химические свойства и модели сенсоров на основе наноразмерных оксидных полупроводников ", Кандидатская диссертация по техническим наукам, Кишинев, 2023

Структура диссертации: Диссертация написана на румынском языке и состоит из введения, 4 глав, общих выводов и рекомендаций, библиографии из 421 наименований, 118 страниц, 57 рисунков и 4 таблицы. Результаты опубликованы в 35 научных статьях, из них 18 научных работах по теме диссертации, в том числе: 1 патент на изобретение; 6 статьи в рецензируемых журналах ISI и SCOPUS (один из которых с импакт-фактором 19.069; три из которых с импакт-фактором 10.3); 1 статья в журналах из Национального реестра профильных журналов, JES; 10 докладов представлены, рассмотрены и опубликованы на национальных и международных конференциях.

Ключевые слова: оксид цинка, оксид алюминия, оксид меди, нанотехнологии, структуры, электролиты, газовые сенсоры, аккумуляторы, полупроводники.

Цель работы: заключается в получении структур $Au/Al_2O_3/ZnO$, $Au/CuO/Cu_2O/ZnO:Fe$, $Au/CuO/Cu_2O$ и $Au/TiO_2/CuO/Cu_2O$ с помощью экономичных методов и технологий; идентификация чувствительности и селективности к газам (H_2) и летучим органическим соединениям (ЛОС) (2-пропанол и этанол); получение сенсорных наноструктур, устойчивых к относительной влажности; обнаружение соединений в электрических батареях с помощью полупроводниковых оксидных структур.

Задачи исследования: исследование физико-химических свойств, в том числе сенсорных, структур на основе: (i) $Au/Al_2O_3/ZnO$ с различной толщиной оксида алюминия; (ii) $Au/CuO/Cu_2O/ZnO:Fe$ и с осаждением полимера; (iii) $Au/TiO_2/CuO/Cu_2O$ с различной толщиной оксида меди; (iv) обработка паром нанонитей ZnO для наносенсора; (v) предложение модели датчика.

Научная новизна и оригинальность: повышение долговременной стабильности за счет улучшения характеристик, регулирование селективной чувствительности, а также улучшение отклика на летучие органические соединения (ЛОС), H_2 и соединениях в составе электрических батарей гетероструктуры $Au/Al_2O_3/ZnO$, $Au/CuO/Cu_2O/ZnO:Fe$, $Au/TiO_2/CuO/Cu_2O$ и нанонитей ZnO. С помощью современного оборудования были изучены морфологические, структурные и вибрационные свойства: XRD, SEM, Raman, HRTEM, TEM, SAED, EDX и XPS для определения качества и физико-химических характеристик полученных структур. Для моделирования взаимодействия молекул газа с поверхностью исследуемых структур были выбраны расчеты по теории функционала электронной плотности DFT, позволяющей моделировать механизмы обнаружения газа, происходящие на поверхности структур разработаные из нанометрических оксидов полупроводников.

Решаемая научно-исследовательская задача заключается в получении чувствительных структур и нанонитей и их селективности по отношению к газам: (H_2), летучим органическим соединениям (ЛОС: 2-пропанол и этанол) и соединениям из состава электрических батарей ($C_3H_6O_2$, $C_4H_{10}O_2$ и $LiPF_6$) которые стабильны во времени и при высокой относительной влажности.

Теоретическая значимость и прикладная ценность работы заключаются в том, чтобы предложить и разработать физико-химические механизмы обнаружения газов, ЛОС и соединений из состава электрических батарей с помощью структур, полученными на основе $Au/Al_2O_3/ZnO$, $Au/CuO/Cu_2O/ZnO:Fe$, $Au/TiO_2/CuO/Cu_2O$ и на основе гидротермально-обработанных нанонитей ZnO, а также примеры применения для измерения газов и различных паров ЛОС (2-пропанола и этанола), которые стабильны во времени и не чувствительны к высокой влажности. Предложенные механизмы обнаружения были подкреплены расчетами функциональной теории и моделированием DFT, которые позволяют моделировать процессы взаимодействия газов или паров ЛОС на поверхности структур.

Внедрение научных результатов. Полученные научные результаты частично использовались в учебном процессе, при разработке бакалаврских и магистерских диссертаций на департаменте МБИ, в рамках ТУМ. Затем на основе полученных научных результатов был получен патент на изобретение и акт о проведении инновационных исследований на факультете ЦИМ, ТУМ.

MAGARIU NICOLAE

PHYSICO-CHEMICAL PROPERTIES AND MODELS OF SENSOR BASED ON NANOSCALE OXIDE SEMICONDUCTORS

233.01 NANO-MICROELECTRONICS AND OPTOELECTRONICS

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