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**ABABII NICOLAI**

# NON-PLANAR NANOMATERIALS AND HETEROJUNCTIONS BASED ON SEMICONDUCTING OXIDES

**233.01 NANO-MICROELECTRONICS AND OPTOELECTRONICS**

Summary of the doctoral thesisin engineering sciences

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The Ph. D. thesis has been elaborated within Department of **"Microelectronics and Biomedical Engineering"**, Center for Nanotechnologies and Nanosensors at **Technical University of Moldova**.
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**The defense will take place on 01 July 2022, at 15:00 in the meeting of the Doctoral Commission within the Doctoral School of the Technical University of Moldova (approved by the decision of the Scientific Council of TUM of May 23, 2022, protocol no. 4), 9/7 Studentilor street, study block no. 3, aud. 3-405, MD – 2068, Chisinau, Republic of Moldova.**

The doctoral thesis and the abstract can be consulted at the library of the Technical University of Moldova and on the ANACEC website (www.cnaa.md).

The summary was sent to „ 31 ” May 2022

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# RESEARCH CONCEPT GUIDELINES

**The actuality of the research.** Today, nanotechnologies have been envolved in many fields of science and engineering, from natural sciences to biomedicine, space innovation, oil industry, food industry, automotive. [1,2]. Today, a range of nanometer-scale materials and instruments can be developed and applied, thanks to nanomaterials and heterojunctions developed very intensively by the global scientific community, and an important area of application is gas sensor technology [3]. According to the latest data, the global sensor market will grow from 1.1 billion U.S. dollars in 2021 to 1.5 billion U.S. dollars by 2026 [4], because sensors are currently being used in all areas. Key factors driving the growth of this market include the high demand for gas sensors and volatile organic compounds (VOCs) in critical industries, the formulation and implementation of various global health and safety regulations, increasing the integration of gas sensors in heating systems, ventilation and air conditioning and air conditioning, air quality monitoring due to increasing air pollution and the need to monitor environment in smart cities [4]. A modern field in which gas and VOC sensors are widely used is biomedicine, addressing non-invasive methods for diagnosing various diseases by testing the content of exhaled air, such as detecting acetone as a biomarker for diabetes [5] or detecting hydrogen and/or methane following bacterial fermentation of sugar poorly absorbed in the intestines and followed by their absorption into the bloodstream and transported to the lungs [6]. The deployment of the Internet of Things (IoT), cloud computing and big data with gas sensors, the growing adoption of gas sensors in consumer electronics and the growing demand for miniaturized wireless gas sensors create a high demand for gas sensors and VOCs for efficient industrial operations [4]. Thus, obtaining micro- and nanometric 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, by developing new non-planar nanomaterials, heterostructures and heterojunctions based on semiconductor oxide which are excellent candidates to meet these challenges and provide real solutions.

**The importance of addressed issue.** Nanomaterials and individual oxides, such as CuO, $CuO/Cu_2O$, $TiO_2$ and ZnO, have certain disadvantages in sensors such as: low selectivity to a particular gas, degradation of nanostructures over time and/or the influence of relative humidity on the sensitivity value [7,8]. All these disadvantages are induced by the properties of individual materials used in the manufacture of gas sensors, and overcome can be done by addressing various efficient technological approaches of development, including combining them or even new methods of growth using modern nanotechnologies. It is known that the control of the sensitivity and selectivity of sensors based on semiconductor oxides can be achieved by such approaches as: control of morphology, crystallinity, porosity, diameter and their effective surface [9,10]. Another method is to combine two structures of the same type of electrical conductivity such as $In_2O_3$-NiO (*n-n*) [11], CuO-$Cu_2O$ (*p-p*) [12,13] or of different types (*p-n*) CuO-$TiO_2$, CuO-ZnO [12,14], thus obtaining heterostructures and heterojunctions with improved or even new sensory properties. There is also the method of doping semiconductor oxides with impurities, which results in changing the concentration of electric charge carriers in the structures of nanomaterials and heterostructures. [9,15]. Another quite effective approach of for controlling the performance of sensors is to functionalize the surface of nanostructures with nanoparticles of noble metals, polymers or other semiconductor oxides, thus forming heterojunctions, multilayer structures or core-shell structures, which modify the sensory properties due to the effects that occur on the surface and interface of nanomaterials or heterostructures [16–20].

One of the most recent approach used to obtain gas sensors with improved or absolutely new sensory performance is the method of 3D printing of oxide-based structures and heterostructures, which consists of layer-by-layer deposition of materials with very precise control of shape and size at the macroscopic level [21,22]. At present, not all approaches of oxide combining to obtain higher-performance sensitive nanomaterials and heterostructures for the detection of certain types of gases or volatile organic compounds have been identified. Based on current possibilities and the variety of combinations of semiconductor oxides, it is necessary to study and obtain gas or VOC sensors based on non-planar nanomaterials and heterostructures with improved and even new sensory properties, thus developing further the direction of gas sensors according to global requirements.

**The purpose and objectives of the research.** The doctoral thesis aims to: (i) obtain non-planar nanomaterials and heterostructures based on semiconductor oxides, CuO/$Cu_2O$, $TiO_2$/CuO/$Cu_2O$, $Fe_2O_3$ - CuO/$Cu_2O$, CuO-$Cu_2O$/ZnO:Al and $Al_2O_3$/CuO, through cost-effective methods and technologies; (ii) identification of nanomaterials and heterostructures with sensitivity and selectivity to gases ($H_2$) and volatile organic compounds (acetone, n-butanol, 2-propanol and ethanol); (iii) reducing the effect of high relative humidity on the sensory properties of the developed heterostructures.

**Proposed research objectives:**

- Increasing the sensitivity to UV radiation and changing the selectivity to $NH_3$ and ethanol of ultra-thin $TiO_2$ films by functionalizing surface with Ag, Ag-Au and Ag-Pt nanoparticles.
- Research on the stability over time of CuO/$Cu_2O$ and $TiO_2$/CuO/$Cu_2O$ heterostructures with sensitivity and selectivity to ethanol vapors by coating them with a top layer of $TiO_2$.
- Modification of $H_2$ and n-butanol selectivity of $TiO_2$/CuO/$Cu_2O$ heterostructures by functionalization with Pd, Ag and AgPt nanoparticles, respectively.
- Premiere research of the sensory properties of non-planar heterostructures of CuO/$Cu_2O$ and $Fe_2O_3$ - CuO/$Cu_2O$ obtained through 3D printing technology.

- Study of the sensory properties of $CuO/Cu_2O/Cu$ micro- and nanowires obtained by thermal oxidation with the possibility of manufacturing a 3-in-1 sensor device.
- Development of nanomaterials insensitive to high relative humidity based on $CuO$-$Cu_2O/ZnO:Al$ heterostructures with sensitivity and selectivity to n-butanol vapors and $Al_2O_3/CuO$ heterostructures with sensitivity and selectivity to $H_2$ gas.
- Detailed physico-chemical analysis of CuO, $TiO_2$ films and $TiO_2/CuO/Cu_2O$ heterostructures (functionalized with nanoparticles of noble metals (Au, Ag, Pd, Ag-Au and Ag-Pt)), $CuO$-$Cu_2O/ZnO:Al$ and $Al_2O_3/CuO$ via SEM, XRD, Raman, TEM, HRTEM, SAED, EDX and XPS techniques.

**Scientific research methodology.** In order to achieve the objectives of the thesis, technological methods and scientific research were used:

- the following methods were used to obtain nanomaterials and heterostructures: chemical synthesis from solutions (SCS), atomic layer deposition (ALD), spraying and 3D printing followed by conventional or rapid thermal annealing (RTA) in air;
- functionalization of nanomaterials and heterostructures with nanoparticles from Au, Ag, AgPt, Pd by vacuum deposition when spraying noble metal sources followed by heat treatments in air;
- scanning electron microscopy (SEM) and accelerated electron transmission microscopy (TEM), as well as high resolution transmission electron microscopy (HRTEM) for the analysis of morphological and crystalline properties.
- micro-Raman spectroscopy, selected area electron diffraction (SAED) and precision electron diffraction (PED), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and energy-dispersive X-ray spectroscopy (EDS or EDX) for advanced physicochemical analysis of crystalline nanostructures.
- Pre-calibrated regulators (MFC, Bronkhorst U.K.) were used to measure and control the target gas concentration.
- Electrical and sensory characterizations were performed using a computer-controlled programmable Keithley 2400 source-measurement unit via a graphical interface developed in LabView.

**The scientific novelty of the research results** consists in the development of sensor-type devices with a higher efficiency due to the involvement/formation of heterojunctions and based on the heterostructures of $TiO_2/CuO/Cu_2O$, $CuO$-$Cu_2O/ZnO:Al$, $Al_2O_3/CuO$, as well as obtaining for the first time of 3D printed $CuO/Cu_2O$ and $Fe_2O_3$ - $CuO/Cu_2O$ heterostructures. At the same time, the functionalization of heterostructures with nanoparticles of noble metals (Pd or Ag or Ag-Pt) allows the regulation of selective sensitivity to gases and volatile organic compounds, as well as reducing the power consumption of devices up to 1 nW. The $TiO_2/CuO/Cu_2O$ heterostructures allow to obtain the stability in time (105 days) of the performances, due to the self-cleaning effect of the $TiO_2$ film, and the formation of the $Al_2O_3/CuO$ junction, that ensures stability under relative humidity and long-term stability (for 70 days) when applying different concentrations of $H_2$ gas. These results elucidate the important relationship between sensor performance and the synergistic effects of combined nanomaterials, including catalytic properties and interface phenomena of heterojunctions and heterostructures formed.

**The scientific problem of solved research** is to identify nanomaterials and heterojunctions with sensitivity and selectivity to gases ($H_2$) and volatile organic compounds (acetone, n-butanol, 2-propanol and ethanol) and to obtain stability under relative humidity as follows: Cu-$Cu_2O$/ZnO:Al and $Al_2O_3/CuO$ heterostructures for the selective detection of n-butanol and $H_2$, respectively, with stability of device performances against relative humidity.

**The theoretical significance** consists in contributions to the development of physico-chemical mechanisms for the detection of gases/VOCs and UV radiation for nanomaterials and heterojunctions developed, based on the mechanisms existing in the literature at the moment. According to studies, the catalytic properties at the surface and the phenomena at the interface of nanomaterials and heterojunctions are a key factor for the sensory properties and performance of gas sensors. The theoretical meanings were developed from the calculations of the density functional theory (DFT) for these heterostructures, by simulating the interaction of gas/VOC molecules with the surface of heterojunctions modeled for the first time. Thus, the models of the proposed detection mechanisms and the calculations of the elaborated functional theory, in combination with the computational calculations of DFT type, have the essential purpose of understanding the effects and phenomena that take place at the surface and interface of the developed semiconductor oxide heterojunctions and heterostructures.

**The applicative value of the thesis** consists in the following:

- Functionalization of nanostructured ultra-thin $TiO_2$ films with Ag, Ag-Au or Ag-Pt nanoparticles (diameter 5 - 11 nm) allows to increase the response to UV radiation (by about an order of magnitude) and to change the gas selectivity to $NH_3$ vapors (by functionalizing the surface with Ag-Au nanoparticles);
- The deposition of the ultra-thin film of nanostructured $TiO_2$ (15 - 40 nm) on the surface of the CuO structure allows the sensitive and selective detection of ethanol vapors (with a response of ~140%) with a high stability in time (105 days), due to the self-cleanning effect;

- Functionalization of $TiO_2/CuO/Cu_2O$ heterostructures with Pd, Ag or AgPt nanoparticles allows modification of selectivity for $H_2$ and n-butanol, respectively, as well as reduction of power consumption up to 1 nW;
- 3D printing of $CuO/Cu_2O$ and $Fe_2O_3$ - $CuO/Cu_2O$ heterostructures allows the development of devices for the sensitive and selective detection of acetone vapors (~140%) with concentrations of only 0.5 ppm, as well as the reduction of consumption power up to 0.26 μW;
- Thermal annealing in the furnance of copper microwire (diameter 30 μm) allows obtaining sensitive and selective $CuO/Cu_2O$ microcrystals and nanowires to 2-propanol vapors (~25%) at room temperature, to ethanol vapors (~180%) in the operating temperature range of 150 ºC-250 ºC, at $H_2$ (~130%) in the operating temperature range of 275 ºC – 350 ºC;
- Sensitive and selective detection of n-butanol vapors (~200%) in the case of CuO-$Cu_2O$/ZnO:Al heterostructures and hydrogen gas (~140%) in the case of $Al_2O_3$/CuO heterostructures allows their use in bio-medical applications such as breath tests as a non-invasive method of diagnosis due to the reduction of the effect of high relative humidity.

**Scientific theses submitted for defense:**

1. Obtaining $TiO_2/CuO/Cu_2O$ heterostructures allows the sensitive, selective and highly stable detection of ethanol vapors (~1.2%/ppm) at working temperature 300 ºC - 350 ºC due to the intensified catalytic oxidation activity of ethanol molecules by dehydrogenation.
2. The functionalization of the surface of $TiO_2/CuO/Cu_2O$ heterostructures with Ag, AgPt or Pd nanoparticles allows to change the selectivity from n-butanol (the case of the functionalization of the surface with Ag or AgPt nanoparticles and the working temperature range of 250 ºC - 350 ºC) to $H_2$ (case of functionalization with Pd nanoparticles and working temperature range 150 ºC - 300 ºC);
3. Obtaining $Fe_2O_3$ - $CuO/Cu_2O$ heterostructures by 3D printing allows sensitive and selective detection of acetone vapors with concentrations of only 0.5 ppm and low power consumption in the range of working temperatures of 250 ºC - 350 ºC;
4. Creating stability against high relative humidity for sensitive and selective detection of n-butanol vapors by developing CuO-$Cu_2O$/ZnO:Al heterostructures, due to the involvement in the detection mechanism of the interface between oxides CuO-$Cu_2O$ (*type p*) and ZnO:Al (*type n*);
5. The coating of CuO nanostructures with an ultra-thin layer of $Al_2O_3$ allows the sensitive and selective detection of $H_2$ gas and the achievement of stability against high relative humidity, including in breath tests, due to the formation of the heterojunction between $Al_2O_3$ and CuO.

**The scientific results have been partially implemented** in the instructive-educational process carried out within the Technical University of Moldova, as well as in the elaboration of undergraduate theses of students at the Department of Microelectronics and Biomedical Engineering, specialties

Microelectronics and Nanotechnology, and Biomedical Engineering. Subsequently, based on the scientific results, it was possible to obtain an implementing act at FCIM, TUM, as well as two patents.

**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, Department of Microelectronics and Biomedical Engineering, Technical University of Moldova (2016 - 2021); Scientific Seminar of the Department of Microelectronics and Biomedical Engineering of TUM (2021); reported, discussed, positively appreciated and presented at 14 international and national scientific conferences, including: SPIE, Oxide-based Materials and Devices VIII (March 07, 2017, San Francisco, California, United States); International Conference on Nanomaterials: Application & Properties (NAP), 2018 (Zatoka), 2019 (Odessa), Ukraine; International Conference on Nanotechnologies and Biomedical Engineering (ICNBME), 2019, Chisinau, Moldova and Central and Eastern European Conference on Thermal Analysis and Calorimetry (CEEC-TAC4), 2017, Moldova.

**Publications related to thesis subject.** The main results of the thesis were published in 27 scientific papers, namely in 2 patents of the Republic of Moldova; 10 articles reviewed in ISI and SCOPUS journals of international circulation, including **with an impact factor higher than 17** and one as first-author; 1 article in the JES magazine from the National Register of profile magazines; as well as 14 publications presented and published at National and International Conferences. (The list of publications and patents is attached at the end of the thesis and summary of Ph.D. thesis). The total number of publications is 70 scientific papers, including 29 listed ISI and SCOPUS. ***h*-index = 13** SCI Hirsch index. Number of international citations > 650 (according to SCOPUS).

**The volume and structure of the thesis.** The thesis consists of an introduction, five chapters, general conclusions and recommendations, a bibliography of 297 titles and 5 annexes, respectively. Contains 119 pages of basic text, 51 figures and 1 table.

**Keywords:** CuO, nanotechnologies, nanomaterials, heterojunctions, gas sensors.

## THESIS CONTENT

The ***Introduction*** argues the topicality and importance of the research in this field, gives an analysis of the current level of research and development on the topic, also sets out the purpose and objectives of the thesis, the scientific novelty of the results obtained, the main theses submitted for defense, certainty of results and list of conferences at which the basic results of the doctoral thesis were presented and approved.

The ***first Chapter*** presents different methods and approaches for obtaining non-planar nanomaterials and non-planar heterojunctions based on semiconductor oxides, as well as the concepts of improving their properties. A review of the fields of heterojunctions' application as sensors is performed. An analysis is made of the necessity to use nanomaterials and heterojunctions as gas sensors in medicine, food industry and environmental monitoring.

***Chapter 2*** describes the methods, experiments and devices used to characterize the properties of non-planar nanomaterials and heterostructures based on semiconductor oxides; atomic layer deposition of of $TiO_2$ and $Al_2O_3$ films, as well as of $TiO_2$ and $CuO/Cu_2O$ layers by spraying; obtaining 3D printed non-planar heterostructures of $CuO/Cu_2O$ and $Fe_2O_3$-$CuO/Cu_2O$; deposition of CuO and ZnO nanostructured films by the method of chemical synthesis from solutions SCS; functionalization with nanoparticles of noble metals such as Au, Ag, Pd, nanoalloys of Ag-Au and Ag-Pt.

***Chapter 3*** reports the results of research on the properties of $TiO_2/CuO/Cu_2O$ heterostructures as ethanol sensors with stability over time due to top $TiO_2$ film, as well as changing the selectivity to hydrogen and n-Butanol of gas sensors with low power consumption based on $TiO_2/CuO/Cu_2O$ heterostructures functionalized with nanoparticles of Pd (selective to hydrogen), Ag or AgPt (selective to n-Butanol).

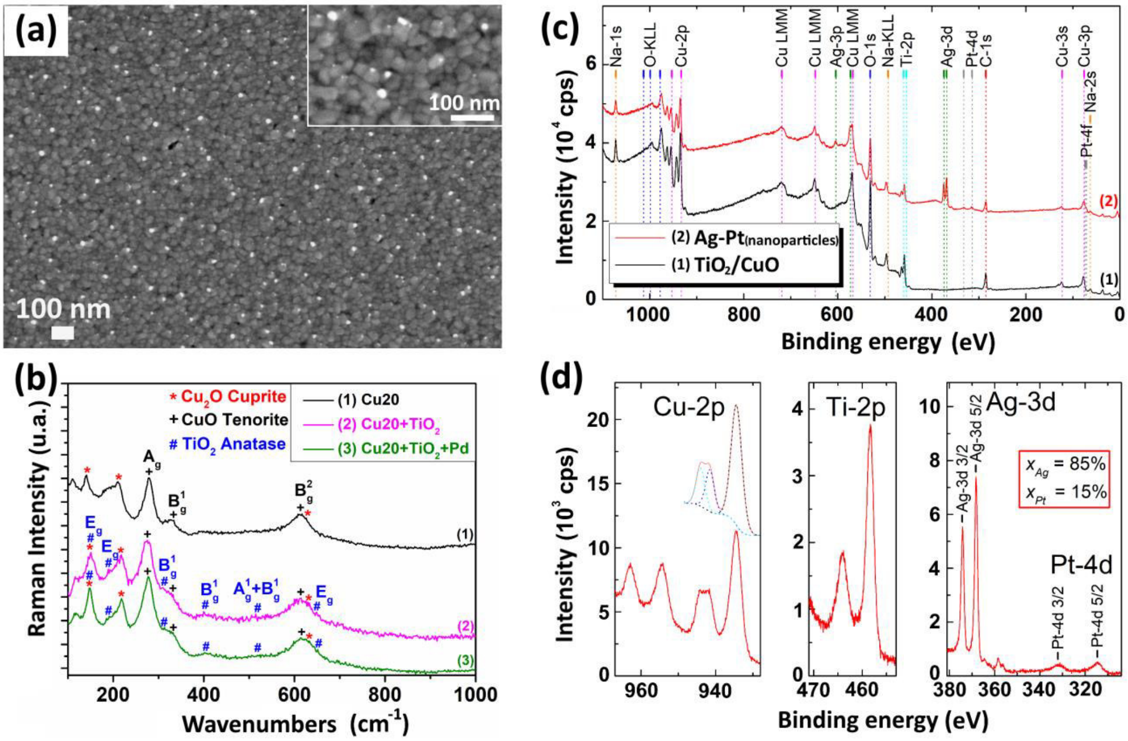


**Fig.1. (a) SEM images of nano-crystalline $CuO/Cu_2O$ samples treated at 420 °C for 30 min with a thickness of 20 nm (the insert shows an enlarged image). (b) Micro-Raman spectra for $CuO/Cu_2O$, $TiO_2/CuO/Cu_2O$ and $Pd/TiO_2/CuO/Cu_2O$ samples heat treated at 420 °C for 30 min. X-ray photoelectron (XPS) spectra of: (c) $AgPt/TiO_2/CuO/Cu_2O$ nano-heterostructure (curve 2) and non-functionalized $TiO_2/CuO/Cu_2O$ nano-heterostructure (curve 1); (d) high-resolution spectra of the Cu-2p and Ti-2p lines, as well as spectra for the Ag-3d and Pt-4d lines.**

Figure 1(a) shows the SEM image of the $CuO/Cu_2O$ sample, obtained by a reproducible spray/annealing approach, due to the ability to accurately control the rate of spray growth, forming interpenetrated nano-grains that completely the substrate surface.

The micro-Raman spectra of $CuO/Cu_2O$, $TiO_2/CuO/Cu_2O$ and $Pd/TiO_2/CuO/Cu_2O$ nanocomposites, which were investigated at room temperature in the range of 100-1000 $cm^{-1}$, are shown in Figure 1(b) and demonstrates three peaks at ~144 $cm^{-1}$, 212 $cm^{-1}$, 628 $cm^{-1}$, attributed to the crystalline phase of $Cu_2O$, three peaks at 298 $cm^{-1}$, 345 $cm^{-1}$ and 632 $cm^{-1}$ are attributed to the crystalline phase of CuO and six peaks at ~144 $cm^{-1}$, ~197 $cm^{-1}$, ~326 $cm^{-1}$, ~ 400 $cm^{-1}$, ~517 $cm^{-1}$ and ~635 $cm^{-1}$ are attributed to the crystalline phase of $TiO_2$. Figure 1(c) shows the X-ray photoelectron (XPS) spectra of non-functionalized and functionalized $TiO_2/CuO/Cu_2O$ heterostructures with AgPt nanoparticles, which demonstrated the detection of Cu, O, Ti, Na and C elements. Cu, O and Ti come from the base layer $TiO_2/CuO/Cu_2O$, while the signal C comes from the contamination of the surface with carbon in the atmosphere, for example, from carbohydrates [20].

Figure 1(d)) shows the high-resolution spectra of the Cu-2p, Ti-2p, Ag-3d, and Pt-4d lines, which show clear satellite peaks for both the Cu-$2p_{3/2}$ and Cu-$2p_{1/2}$, which are shifted to higher binding energies for the Cu-2p line. The Cu-$2p_{3/2}$ line, as well as the corresponding satellites, have been assigned to the nanocomposite - see the $2p_{3/2}$ deconvolution with the 3-peak satellite peaks. The observed satellite peaks are usually considered as a signature for the appearance of the $CuO/Cu_2O$ heterojunction with CuO exposed on the surface [23]. Consequently, the copper signal in the spectrum can be attributed to the presence of $CuO/Cu_2O$ in the base layer.

A Ti-$2p_{3/2}$ peak between 459.6 eV and 458.0 eV is commonly attributed to $Ti^{4+}$ in $TiO_2$. The evaluation of the XPS Ti-2p high-resolution connection energies shows that the Ti-$2p_{3/2}$ line is positioned around 458.3 eV. The peak positions of Ti-$2p_{3/2}$ and Ti-$2p_{1/2}$ and their separation of 5.6 eV indicate the presence of Ti in the form of $TiO_2$ in the base layer [24,25].

Ag and Pt were detected together with Cu, Ti, O and C in the heterostructure of functionalized $TiO_2/CuO/Cu_2O$, using AgPt nanoparticles. The high-resolution spectra of the Ag-3d and Pt-4d lines were recorded to quantify the composition of AgPt nanoparticles. Pt-4d lines were selected for quantification due to the overlap of Pt-4f with more intensive Cu-3p lines. In the case of the $AgPt/TiO_2/CuO/Cu_2O$ nanocomposite, the quantification of AgPt nanoalloy nanoparticles produces a platinum content of about 15% in the nanoparticles.

Figure 2(a) shows the response of the $CuO/Cu_2O$ sample to various compounds ($H_2$, n-butanol, 2-propanol, ethanol, acetone and ammonia) at operating temperatures between 250 °C and 350 °C. For ethanol vapors, the sensor response at 350 °C is higher compared to the response to other test compounds. The test sets investigated at 250 °C, 300 °C and 350 °C have the highest response to ethanol of ~24%, ~121% and ~140%, respectively.

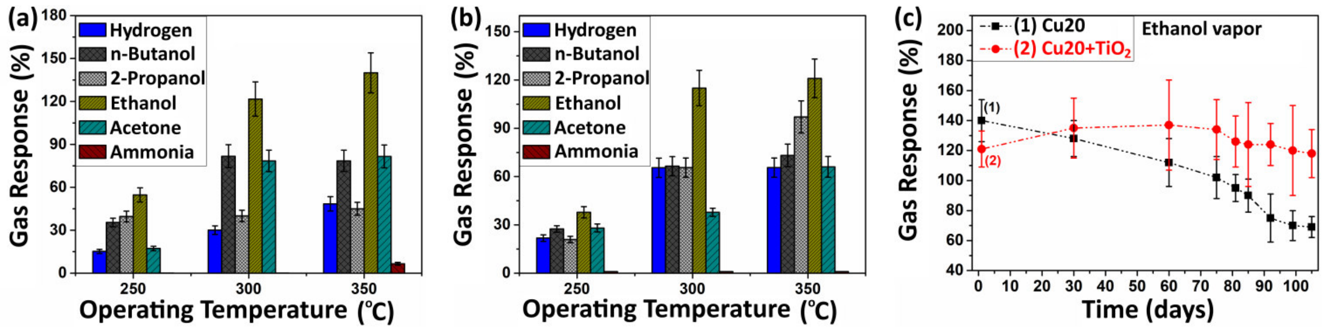


**Fig.2. Response to different gases and vapors depending on the working temperature of the samples of: (a) $CuO/Cu_2O$; and (b) $TiO_2/CuO/Cu_2O$ (Cu20). (c) Variation of ethanol vapor response over time for $CuO/Cu_2O$ and $TiO_2/CuO/Cu_2O$ samples.**

In the case of the $TiO_2/CuO/Cu_2O$ sample, it is observed that at 250 °C, 300 °C and 350 °C, the samples have the highest response to ethanol vapors with responses of ~38%, ~115% and ~121%, respectively (see Figure 2(b)). Comparatively (the data in Figure 2(a) and Figure 2(b)), the response value was improved with increasing working temperatures for the $TiO_2/CuO/Cu_2O$ nanomaterial. The maximum response is reached at a working temperature of 350 °C. Figure 2(c) shows the variation of the response of $CuO/Cu_2O$ and $TiO_2/CuO/Cu_2O$ samples to 100 ppm of ethanol vapor over 105 days, which shows that the response to ethanol vapor has decreased for $CuO/Cu_2O$ samples, and in the case of $TiO_2/CuO/Cu_2O$ samples it remained practically unchanged-stable. No significant changes in sensor performance were observed due to the self-cleaning effect of $TiO_2/CuO/Cu_2O$ samples covered with a thin $TiO_2$ film [26,27].

Figure 3(a) shows the response to $H_2$, n-butanol, 2-propanol, ethanol, acetone, ammonia and $CH_4$ of the functionalized samples of $Pd/TiO_2/CuO/Cu_2O$ at different operating temperatures. It demonstrates a high and selective response to $H_2$ gas with values of ~405%, ~487%, ~543% and ~371% at operating temperatures of 150 °C, 200 °C, 250 °C and 300 °C, respectively, thus identifying the optimum working temperature in the range of 200-250 °C. The dynamic response to different $H_2$ gas concentrations (5, 10, 50, 100, 500 and 1000 ppm) of $TiO_2/CuO/Cu_2O$ samples functionalized with Pd demonstrates a fairly high response of ~88% at a concentration of only 5 ppm of $H_2$ gas (Figure 3(b)). Figure 3(c) shows the response to different gases compared to the working temperature of $TiO_2/CuO/Cu_2O$ samples functionalized with Ag. It can be seen that at relatively low operating temperatures of 200 °C, the sample has *n*-type conductivity and has the performance of detecting only 2-propanol and ethanol vapors, because the electrical resistance decreases after molecular interactions, which can be explained by the fact that at relatively low working temperatures the mechanism of detecting only the $TiO_2$ layer (*n*-type) from the surface is involved, and at working temperatures of 250 °C, 300 °C and 350 °C, the sample already has a conductivity of *p*-type, due to the involvement of the heterojunction formed between $TiO_2$ (*n*-type) and $CuO/Cu_2O$ (*p*-type). Therefore, $TiO_2/CuO/Cu_2O$

heterostructures functionalized with Ag are selective for n-butanol, and the responses are ~54%, ~200% and ~163%, respectively. This phenomenon is due to the composition of the sample (Ag nanoparticles on the surface), which alters the surface activity and reaction products [13,19]. The dynamic response to different n-butanol concentrations for $TiO_2/CuO/Cu_2O$ samples functionalized with Ag demonstrates the detection of even lower concentration (5 ppm) of n-butanol vapors with a response of ~31% (Figure 3(d)).

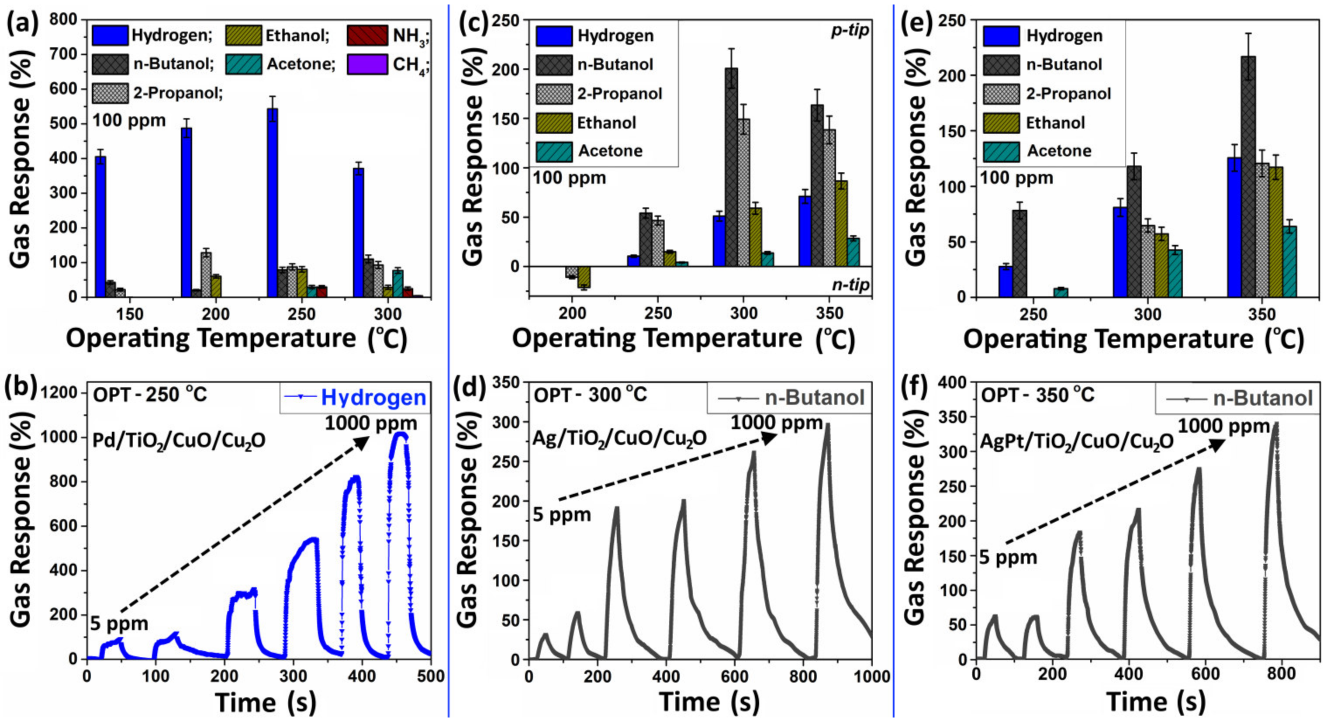


**Fig.3. (a) Response to various gases and VOC compounds of Pd-functionalized $TiO_2/CuO/Cu_2O$ samples at different working temperatures; (b) Dynamic response to different concentrations of hydrogen in Pd-functionalized $TiO_2/CuO/Cu_2O$ samples. (c) Response to different gases and compounds of Ag-functionalized $TiO_2/CuO/Cu_2O$ samples at different operating temperatures; (d) Dynamic response to different n-butanol concentrations of Ag-functionalized $TiO_2/CuO/Cu_2O$ samples. (e) Response to various gases and VOC compounds of AgPt-functionalized $TiO_2/CuO/Cu_2O$ samples; (f) Dynamic response to different n-butanol concentrations of $TiO_2/CuO/Cu_2O$ samples functionalized with AgPt nanoalloy**.

Figure 3(e) shows the response to hydrogen, n-butanol, 2-propanol, ethanol and acetone compared to the working temperature for AgPt-functionalized $TiO_2/CuO/Cu_2O$ samples, which show that at operating temperatures of 250 °C, 300 °C and 350 °C this sample is selective for n-butanol and the responses are ~78%, ~118% and ~216%, respectively, suggesting that the optimum working temperature is 350 °C. The dynamic response to 5, 10, 50, 100, 500 and 1000 ppm of n-butanol for AgPt-functionalized $TiO_2/CuO/Cu_2O$ samples shows a response of ~63% for only 5 ppm of n-butanol (see figure 3(f)). According to DFT computational calculations, it has been found that the selectivity of hydrogen for Pd-functionalized $TiO_2/CuO/Cu_2O$ samples is due to the lower adsorption energy of hydrogen molecules compared to the ethanol and n-butanol molecules on the sample surface, and in the case of Ag- or AgPt-functionalized $TiO_2/CuO/Cu_2O$ samples lower adsorption energy of n-butanol molecules compared to hydrogen and ethanol molecules.

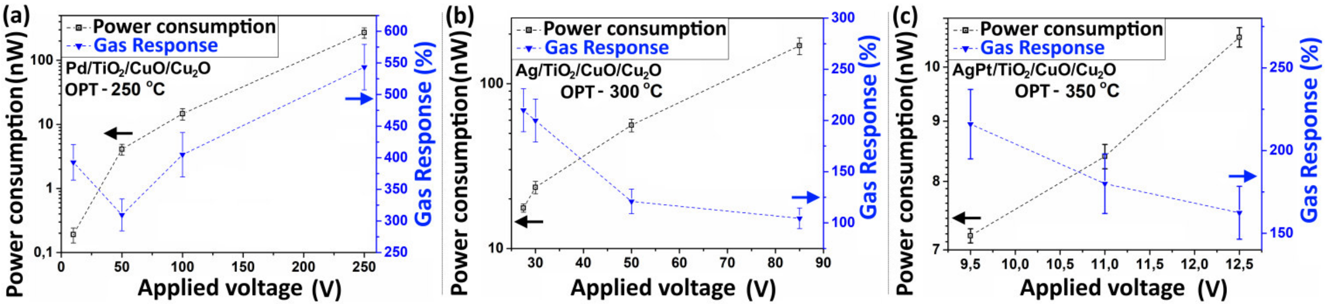


**Fig.4. Dependence of power consumption and gas response on the voltage applied to: (b) $Pd/TiO_2/CuO/Cu_2O$, (c) $Ag/TiO_2/CuO/Cu_2O$ and (d) $AgPt/TiO_2/CuO/Cu_2O$ heterostructures.**

The dependencies of the power consumption and the response to 100 ppm of $H_2$ gas depending on the voltage applied to the $Pd/TiO_2/CuO/Cu_2O$ samples (see Figure 4(a)), show that both the power consumed and the response to the $H_2$ gas decreased when the voltage applied to the sample decreases. However, it was also observed that for an applied bias voltage of 10 mV the response increased and the power consumption obtained was ~270, ~140, ~4.1 and ~0.19 nW, so the responses were ~588%, ~404%, ~310% and ~390% at the applied bias voltages of 250, 100, 50 and 10 mV, respectively. The dependencies of the power consumption and the response to 100 ppm of n-butanol vapor on the voltage applied to $Ag/TiO_2/CuO/Cu_2O$ heterostructures are shown in Figure 4(b), where it can be seen that the power consumption is ~170, ~56, ~23.5 and ~17.6 nW, and the respective responses are ~104%, ~121%, ~200% and ~210% at the applied bias voltages of 85, 50, 30 and 27.5 mV, respectively. For $AgPt/TiO_2/CuO/Cu_2O$ samples, the power consumption of n-butanol vapor is ~10.6, ~8.4 and ~7.2 nW, and the responses are ~162%, ~180% and ~216% at 100 ppm at applied bias voltages of 12.5, 11.0 and 9.5 mV, respectively (see Figure 4(c)).

To further evaluate the selectivity and sensitivity of $TiO_2(111)/CuO(\bar{1}11)/Cu_2O(111)$ heterostructures in the detection of hydrogen ($H_2$) gas, ethanol ($C_2H_5OH$) and n-butanol ($C_4H_9OH$) vapors, the modification of the heterojunction was calculated by adsorption of $Pd_7$, $Ag_7$ and $Ag_6Pt$ nanoparticles (see Figure 5). The purpose of these theoretical DFT calculations was to help interpret the gas response trends detected in experiments for functionalized heterostructures using noble metal nanoparticles.

Tunnel scanning microscopy images were calculated using HIVE code [28], which is based on the theory developed by Tersoff and Hamann [29] (see Figure 5(d-f)). The brightest spots on the surface of $TiO_2(111)/CuO(\bar{1}11)/Cu_2O(111)$ material functionalized with Pd nanoparticles correspond to noble metal groups. The almost perfect 5-fold symmetry of $Pd_7$, which is broken only by the Pd atom located away from the nanoparticle axis, can be clearly seen in Figure 5(d). After deposition, the $Ag_7$ nanoparticle divides into combined twin particles, each containing three metal atoms, connected by a bridge comprising an Ag atom (Figure 5(e)). Replacement of the axial and Pt-exposed Ag atom has a cohesive effect in the particles of the same type joined, which attach again in the form of pentagon, although they are still more distorted than $Pd_7$ (Figure 5(f)) [20].

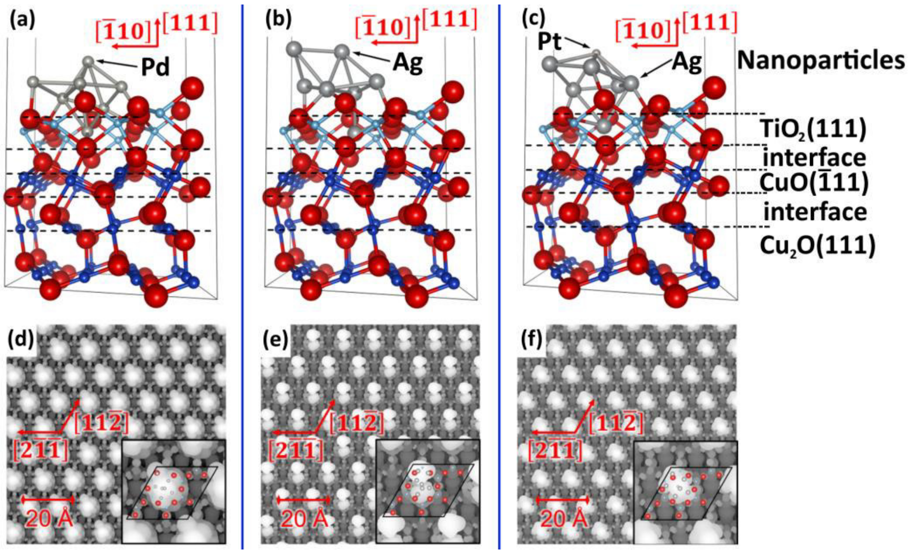


**Fig. 5. Side view (top images) and simulated scan (bottom row) scanning tunneling (STM) microscopy images of the heteroepitaxial junction of $TiO_2(111)/CuO(\bar{1}11)/Cu_2O(111)$ functionalized using nanoparticles of: (a and d) $Pd_7$; (b and e) $Ag_7$; and (c and f) $Ag_6Pt$. The insert shows the magnification of the STM image for the surface unit cell. The crystallographic directions are indicated in relation to the $Cu_2O$ substrate (111). *O* atoms are red, *C*u atoms are dark blue, *Ti* atoms are light blue, and *Pd*, *Ag*, or *Pt* atoms are gray [20].**

The mechanisms for detecting semiconductor oxides in the most common cases are based on the physico-chemical effects that take place on their surface [19,30]. Since nanoparticles of Pd, Ag or AgPt are added to the surface, several species of oxygen are adsorbed by the "spillover effect" [17]. The selectivity of hydrogen gas for $Pd/TiO_2/CuO/Cu_2O$ heterostructures can be explained by the fact that Pd is known to be an excellent catalyst for the dissociation of oxygen and hydrogen, as well as at a lower working temperature [18]. If the working temperature rises, the "spillover effect" is predominant, as it is a thermally activated event [20].

In such a case, the chemical sensitization is due to the dissociation of the hydrogen molecule over the reduced Pd nanoparticles, forming an atomic H with a better reactivity:

$$H_{2(gas)} \xrightarrow{Pd} H_{(ads)} + H_{(ads)}, \tag{1.1}$$

$$H_{(ads)} + H_{(ads)} \rightarrow 2H^{+}_{(ads)} + 2e^{-}, \tag{1.2}$$

indicating that the density of Pd nanoparticles on the surface of the material is an extremely important parameter [20].

As established in the XPS results of PdO-functionalized $WO_3$, the generated proton species ($H^+$) form palladium hydrides ($PdH_x$), which have lower working functions compared to pure Pd metal [20]:

$$xH^+_{(ads)} + xe^- + Pd_{(s)} \rightarrow PdH_{x(s)}. \quad (1.3)$$

$PdH_x$ formation simplifies the transfer of charge carriers from nanoparticles to $TiO_2/CuO/Cu_2O$ heterojunctions and decreases the electron depletion region, thereby improving gas detection properties.

During exposure of $Ag/TiO_2/CuO/Cu_2O$ or $AgPt/TiO_2/CuO/Cu_2O$ heterostructures to n-butanol vapors, they interact with adsorbed oxygen species to form $CO_2$ and $H_2O$ [14]. The improved vapor detection properties are due to the unique heterojunctions and spillover and catalytic effects of Ag and AgPt nanoparticles [17]. Electrons are released from oxygen species, reducing the size of the electron depletion region and potential barriers. This process produces an increase in electrical resistance and is described as such [14]:

$$(C_4H_9OH)_{gas} \leftrightarrow (C_4H_9OH)_{ads}, \quad (1.4)$$

$$(C_4H_9OH)_{ads} + 12O^{2-}_{ads} \rightarrow 4CO_2 + 5H_2O + 24e^-, \quad (1.5)$$

$$(C_4H_9OH)_{ads} + 12O^{-}_{ads} \rightarrow 4CO_2 + 5H_2O + 24e^-. \quad (1.6)$$

These concepts support the superiority of gas detection behavior by $Ag/TiO_2/CuO/Cu_2O$ or $AgPt/TiO_2/CuO/Cu_2O$ heterojunctions. Moreover, the large surface area of the crystals and the good catalytic performance of Ag and AgPt ensure a large number of active sites that facilitate the oxidation reaction of VOC vapors. The gas can diffuse into the pores of the sensor, which increases the value of the gas response.

***Chapter 4*** is based on the research of the morphological, vibrational, chemical, structural and sensory properties of 3D printed $Fe_2O_3$ - $CuO/Cu_2O$ and $CuO/Cu_2O$ non-planar heterostructures.

SEM images of copper oxide nano-microspheres showing large-scale details of the morphology of 3D printed $CuO/Cu_2O/Cu$ sensors on a glass substrate are shown in Figure 6(a, b, c). SEM images of neighboring microparticles coated with CuO nanowires with a length of 2-15 μm grown from $CuO/Cu_2O$ microparticles at different scales, demonstrate that these nanowires have a diameter of 35-50 nm and interpenetrate between two neighboring microparticles, thus forming electrical pathways. XRD diffractograms for the 3D printed $CuO/Cu_2O$ heterojunction nanowire array and subjected to heat treatment at 425 °C for 120 min in air, demonstrate good crystallinity of the samples, which can be attributed to the Cu and $Cu_2O$ structure with cubic face centered (cfc), monoclinic structure CuO, but also metallic Au from contacts (see figure 6(d)). The highest reflections (*hkl*) as shown in Figure 6(d) are of CuO (Tenorite) cupric oxide at 2θ values of 32.65°, 35.65°, 46.7°, 48.8°, 58.25°, 61.5°, 68.05°, 72.6°, 75.35°, 83.85°, 90.05° and 95.2°, respectively. The reflections 2θ at 36.5°, 42.35°, 52.75°, 73.35° and 77.7° are attributed to the $Cu_2O$ (Cuprite) phase. Due to the possibility of high-resolution measurement of the chemical composition, XPS photoelectron spectroscopy was used to determine the oxidation status of nanowires with greater accuracy. The XPS spectrum overview of $CuO/Cu_2O/Cu$ microparticles with nanowire network is shown in Figure 6(e), from which the presence of *Cu*, *O* and *C* can be inferred.

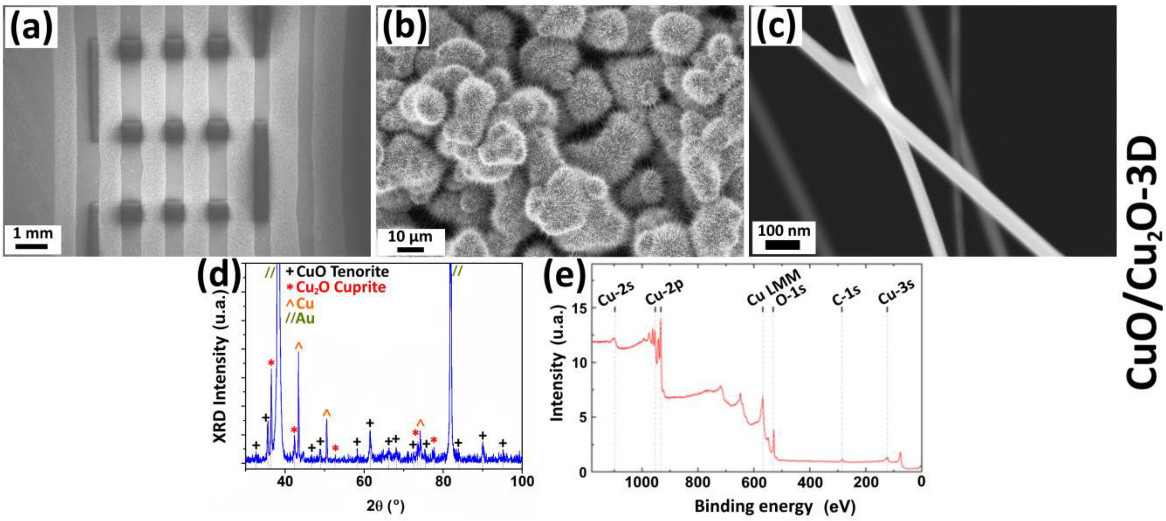


**Fig. 6. (a) SEM image of 3D printed $CuO/Cu_2O/Cu$ microspheres on the sensor substrate directly on the interdigital Au contacts. SEM images of nano-microspheres coated with $CuO/Cu_2O$ nanowires representing details of morphology at the scale of: (b) 10 µm; and (c) 100 nm. (d) XRD diffractogram of 3D printed $CuO/Cu_2O/Cu$ nanostructure nanowire arrays and thermally treated at 425 °C for 120 min in air. (e) Overview XPS spectrum in general indicating the presence of *Cu*, *O* and *C*.**

Morphological details of interpenetrated $Fe_2O_3$-CuO nanowires on the surface of $CuO/Cu_2O$ and $Fe_2O_3$ microparticles are presented by SEM images obtained at different scales (see Figure 7(a, b, c)). The morphologies of each sample are described as nanowires and nanospheres of different thicknesses and lengths, which are composed of CuO and $Fe_2O_3$, respectively. The nanostructures are arranged in an open, easily accessible, network-like microstructure, which is difficult to obtain for planar structures of thin films manufactured by standard techniques.

For a more advanced physico-chemical analysis of the properties, micro-Raman measurements were performed on 3D printed $CuO/Cu_2O$ –$Fe_2O_3$ strips at room temperature in the range of 100-1000 $cm^{-1}$, which demonstrated the presence of CuO as Tenorite and $Cu_2O$ as Cuprite in microparticles, as well as the existence of α-$Fe_2O_3$ (Hematite) confirmed by the detection of vibrational modes (figure 7(d)). Transmission electron microscopy investigation of the crystal structure and chemical details was performed on CuO nanowires and $Fe_2O_3$ nanowires with the morphologies described above (see Figure 7(a, b, c)) and are shown in the STEM image in Figure 7(e).

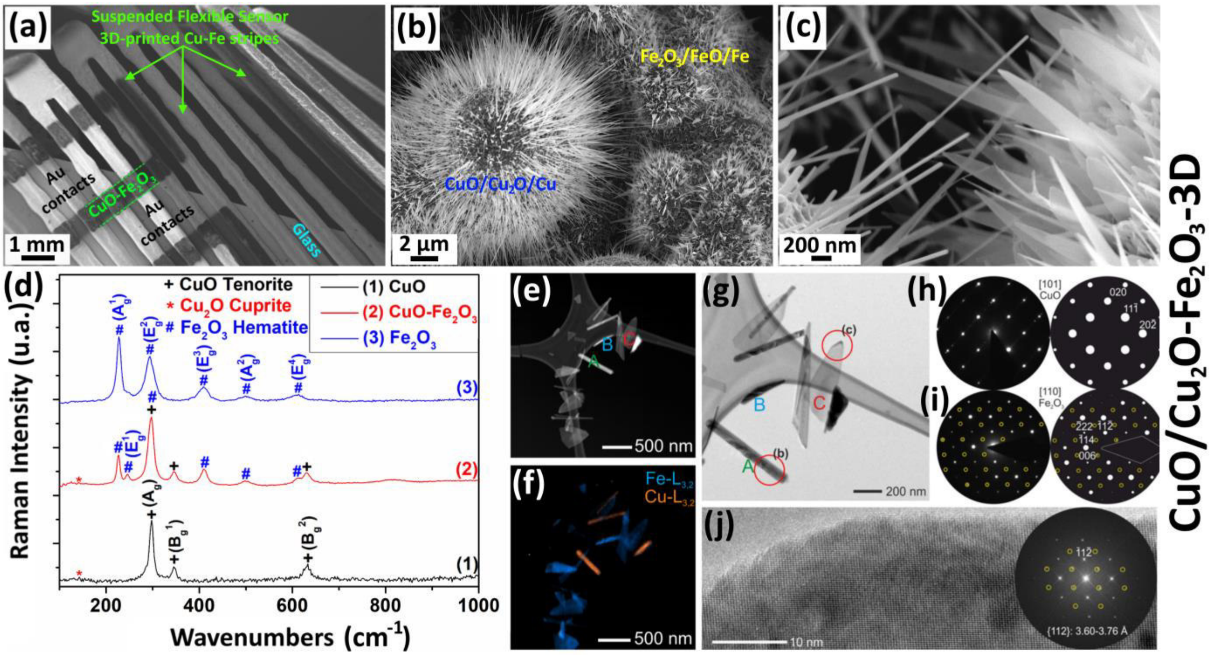


**Fig. 7. SEM images of the sensor element with 3D-printed Cu-Fe microparticles: (a) printed strips suspended on the edge of the glass substrate with flexible strips with Au contacts at the top; (b) the junctions between CuO/$Cu_2O$ and $Fe_2O_3$ at the smaller magnification of the microparticles coated with nanowires-spikes; (c) enlarging the area between the printed microparticles, highlighting the CuO/$Cu_2O$ nanowires and $Fe_2O_3$ nanospikes between the microparticles. Micro-Raman spectra of 3D printed strips: (d) spectrum (1) CuO/$Cu_2O$ nanowires; curve (2) CuO/$Cu_2O$ nanowires - $Fe_2O_3$ nanospikes; and $Fe_2O_3$/Fe nanospikes curve (3). (e) TEM images; the positions of the EELS measurements are indicated in capital letters A-C [22]. (f) EFTEM mapping showing the spatial distribution of basic Fe and Cu loss signals. (g) TEM light-field image showing the respective oxide nanostructures, indicating locations for high-resolution electronic diffraction and imaging experiments. (h) Monoclinic CuO electronic diffraction pattern in [101] orientation and simulated model. (i) Electron diffraction pattern of a $Fe_2O_3$ nanospike in [110] orientation. (j) High resolution TEM images and FFT analysis of the area highlighted in (i).**

Direct identification of copper and iron-containing nanostructures was activated by using electronically transmitted electron microscopy (EFTEM) using electrons from *L*-loss functions to create element-specific contrast images. Overlapping and colored EFTEM images are shown in Figure 7(f). In order to validate the results of single-point spectroscopic measurements with crystallographic data, electron diffraction (ED) measurements were further performed on structures marked with inscriptions *A* and *C*. These investigations are summarized by showing a filtered image with a zero lossy peak spectrum, including indicators for virtual diffraction aperture positions (see Figure 7(g)).

Indeed, the ED models are assigned to the monoclinic CuO zone [101] axis model and the trigonal $Fe_2O_3$ [110] model, which is in agreement with the EELS results (see Figure 7(h) and Figure 7(i)). The ED model of the CuO nanowire shows diffuse strings along the reciprocal direction [11-1]*, an effect that occurs due to a structural disturbance (Figure 7(h)) [22]. For the $Fe_2O_3$ model, additional reflections appear in discrepancy with the trigonal spatial group of hematite *R*-3*c* (yellow circles) (see Figure 7(i)). A representative HRTEM image together with a Fast Fourier Transformation (FFT) model suggests local variations, most likely in the distance range 3.60 Å - 3.76 Å measured for the {-11-2} planes (in hematite 3.68 Å) (see see figure 7(j)) [22].

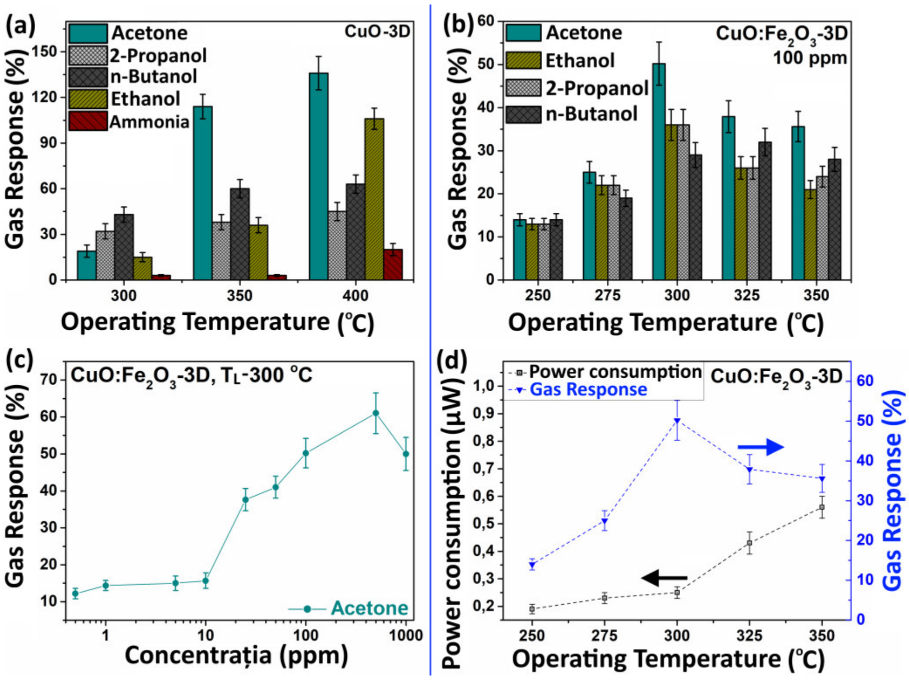


**Fig. 8. Response to different gases (100 ppm) versus working temperature for 3D printed sensors based on: (a) $CuO/Cu_2O$ and (b) $CuO/Cu_2O-Fe_2O_3$. (c) Response to acetone vapor concentration at 300 °C working temperature of $CuO/Cu_2O-Fe_2O_3$-3D samples. (d) Dependence of power consumption and response to acetone versus working temperature of $CuO:Fe_2O_3$-3D samples.**

The response to different gases (100 ppm) versus working temperature for $CuO/Cu_2O$-3D sensors demonstrates a sensitivity and selectivity for acetone vapors, and the highest response of ~140% is at the operating temperature of 400 °C (see Figure 8(a)). The response to various volatile organic compounds (acetone, ethanol, 2-propanol and n-butanol) with a gas concentration of 100 ppm for the 3D printed sensor structures of $CuO/Cu_2O-Fe_2O_3$ is shown in Figure 8(b). Thus, the data obtained show that at all operating temperatures the 3D printed sensor structures are selective for acetone vapor at 100 ppm and the optimum operating temperature is 300 °C with a response of approximately 50% (see Figure 8( b)). Figure 8(c) shows the response versus concentration of acetone vapor from 0.5 ppm to 1000 ppm at a working temperature of 300 °C, from which it can be seen that at low concentrations the response is quite high and increases with concentration. The dependence of the power consumption and the response to acetone versus working temperature of the samples of $CuO:Fe_2O_3$-3D, demonstrates that the working temperature of 300 °C leads to the highest response of ~50% with the consumption power of about 0.26 µW, which is the optimum working temperature for developed devices (see Figure 8(d)). This is most likely due to the processes established on the surfaces of the nanowires during the experiment.

Also, the properties of non-planar heterostructure based on micro- and nanowires of $CuO/Cu_2O$ elucidate the possibility of obtaining a 3-in-1 sensor, due to the possibility of detecting 2-propanol vapor only at room temperature and ethanol vapor in the range of operating temperatures of 150 - 200 °C and hydrogen gas at the operating temperatures of 250 - 350 °C (see Figure 9).

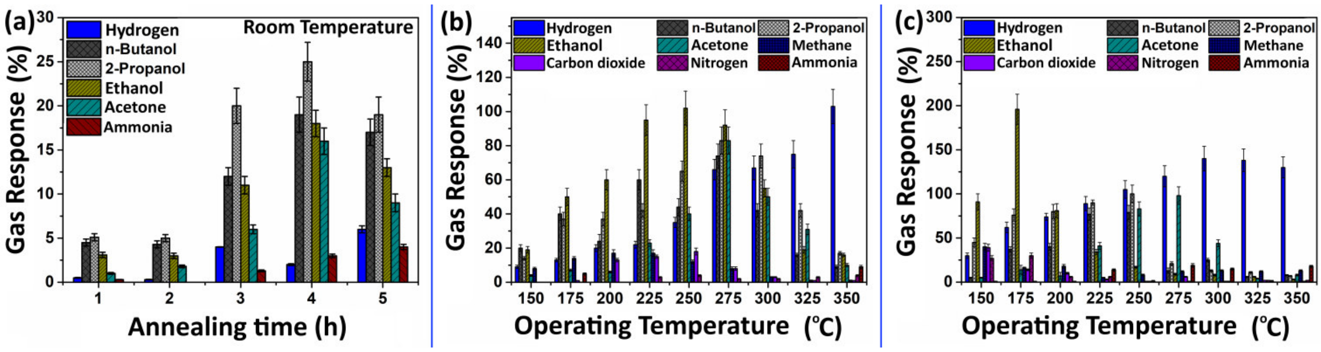


**Fig. 9. (a) The response of the $CuO/Cu_2O/Cu$ microwire completely coated with CuO nanowires thermally treated at 425 °C tested for different gases (100 ppm) versus treatment duration. Response to different gases versus working temperature for the $CuO/Cu_2O/Cu$ microwire thermally treated at 425 °C for: (b) 2 hours and (c) 4 hours, respectively.**

***Chapter 5*** elucidates the research of $CuO-Cu_2O/ZnO:Al$ heterostructures for the detection of volatile organic compounds due to the formation of the *p-n* junction near the sensor surface. The results of the research on $Al_2O_3/CuO$ heterostructures for $H_2$ gas detection applications, including in breath tests, are then presented. Thus, obtaining a very simple and cost-effective method for the manufacture of heterostructures of $CuO-Cu_2O/ZnO:Al$ with increased selectivity to n-butanol vapors, and of $Al_2O_3/CuO$ for the detection of $H_2$ gas with stability of sensory properties at higher relative humidity.

The sensory properties have been studied in several types of samples. Response to 100 ppm n-butanol vapor at operating temperature of 350 °C for sensor structures based on $CuO-Cu_2O$, ZnO:Al and $(CuO-Cu_2O)/ZnO:Al$ (in all cases the Al content is approximately 0.1 at%) are shown in Figure 10(a). ZnO:Al samples showed a response with *n-type* behavior - a decrease in resistance after exposure to reducing gases, while other samples ($CuO-Cu_2O$ and $(CuO-Cu_2O)/ZnO:Al$) showed a response of *p-type* (representing an increase in electrical resistivity after exposure to reducing gases).

So, the respone in the case of heterostructure ($(CuO-Cu_2O)/ZnO:Al$) is dominated by the $CuO-Cu_2O$ layer and the formed junction.

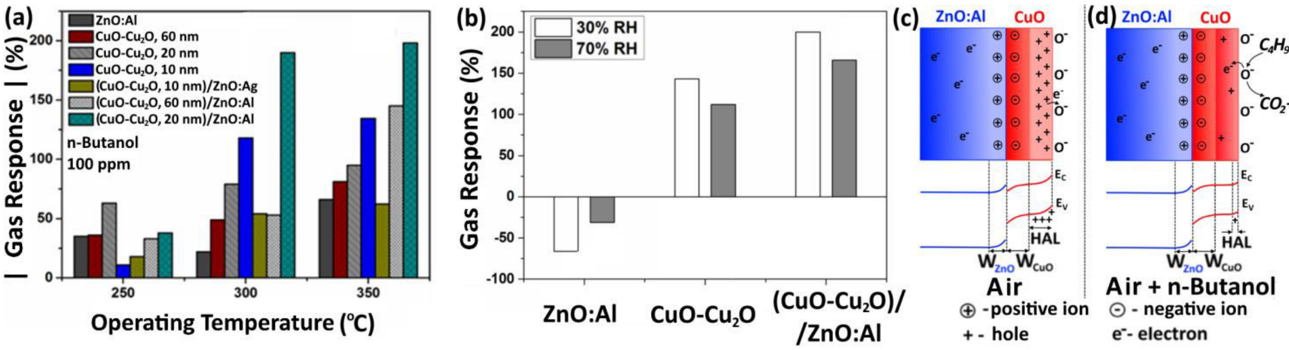


**Fig. 10. (a) Sample response of $CuO-Cu_2O$, ZnO:Al and (CuO-Cu2O)/ZnO:Al at 100 ppm of n-butanol at different working temperatures. (b) Response to 100 ppm of n-butanol at the operating temperature of 350 °C for different types of sensors: ZnO:Al untreated with 0.1 at% of Al, $CuO-Cu_2O$ films with a thickness of 20 nm and ($CuO-Cu_2O$, 20 nm)/ZnO:Al. Schematic illustration of the gas detection mechanism based on the CuO/ZnO:Al heterostructure under exposure to ambient air (c) and n-butanol vapors (d).**

From Figure 10(a) it can be seen that the ZnO:Al samples have the lowest response to 100 ppm of n-butanol vapor (-66%) and the $CuO-Cu_2O$ layers with a thickness of 10 nm, 20 nm and 60 nm showed a higher response than ~134%, ~95% and ~81%, respectively. The same situation is for ($CuO-Cu_2O$)/ZnO heterostructures. For sensors based on $CuO-Cu_2O$-(60 nm)/ZnO/glass, the response is comparable to that of the $CuO-Cu_2O$/glass layer with a thickness of 60 nm (~144%), and the highest response was obtained for ($CuO-Cu_2O$)/ZnO:Al heterostructures with a thickness of 20 nm of the upper layer of $CuO-Cu_2O$ (denoted as ($CuO-Cu_2O$, 20 nm)/ZnO:Al), namely ~200%. The effect of moisture, which decreases the performances of gas detection oxides due to the decrease in the concentration of adsorbed oxygen on the surface [7,8], is a well-known problem and is a limiting factor for commercialization and use in practical applications. Thus, the gas detection properties of metal oxide sensors in the presence of humidity were investigated, see Figure 10(b). The response to 100 ppm of n-butanol was measured at a working temperature of 350 °C. Humid environment (response was measured in the presence of humidity at 30% and 70% RH at 23 °C, respectively). The results for ZnO:Al, $CuO-Cu_2O$(20 nm) and ($CuO-Cu_2O$, 20 nm)/ZnO:Al based sensors show that in the case of ZnO:Al nanostructured films, the decrease in response is ~53% (from -66% to -31%), and for the $CuO-Cu_2O$ and ($CuO-Cu_2O$)/ZnO:Al samples, the decrease in response is ~22% and ~17%, respectively (see Figure 10(b)). These results demonstrate that in the case of copper oxide sensors, the higher RH value has a smaller influence on the response value of heterostructured sensors, which is very attractive for real VOC detection applications.

The proposed gas detection mechanism is based on the ionosorption effects that occur at the surface of the heterostructure. Under exposure to ambient air, oxygen species in the atmosphere will adsorb on the surface of the CuO-$Cu_2O$ layer (see Figure 10(c)) and ZnO:Al granules. At temperatures above 150 - 200 °C, oxygen species are adsorbed mainly in atomic form ($O^-$) [14,31]:

$$O_{2(gas)} \leftrightarrow O_{2(ads)} + 2e^- \leftrightarrow O^-_{2(ads)} + e^- \leftrightarrow 2O^-_{(ads)}. \quad (1.7)$$

At lower temperatures, molecular species ($O_2^-$) are mainly adsorbed, which are known not to be reactive and react very slowly with gaseous species [14]. The result is the absence/low response of metal oxides at operating temperatures <150 °C. Due to the capture of electrons on a surface state, in the case of *p-type* metal oxides, the adsorption of oxygen species leads to the formation of a hole accumulation layer (HAL - with lower electrical resistivity) near the surface. In the case of *n-type* metal oxides, an electron depletion layer (EDL - with higher electrical resistivity) is formed [31]. Under exposure to n-butanol vapor ($C_4H_9OH$), n-butanol molecules react with adsorbed oxygen species [14]:

$$C_4H_9OH_{(gas)} + 12O^-_{(ads)} \rightarrow 4CO_2 + 5H_2O + 12e^-. \quad (1.8)$$

As a result, electrons are donated to metal oxide structures. In the case of *p-type* materials, this leads to a narrowing of the HAL region, namely there is an increase in electrical resistivity, and in the case of *n-type* materials, this leads to a narrowing of the EDL and a decrease in electrical resistivity [31].

In the case of (CuO-$Cu_2O$)/ZnO:Al heterostructures, the improved detection properties must be explained using additional mechanisms. While the ionosorption mechanism remains the main mechanism, it is the (CuO-$Cu_2O$)/ZnO:Al interface that has the greatest influence on the detection performance. Results from the literature on hybrid core-coating materials as well as nanostructured CuO/$Cu_2O$ films have shown that if the top layer is in the range of tens of nanometers (~20 nm), which is comparable to the Debye length ($\lambda_D$) [32], the interface of materials can also be affected by surface reactions and can significantly increase the detection properties depending on various factors [13,32,33].

The width of a depletion region can be calculated using the following relation [33]:

$$W_{CuO} = \left[\frac{2\varepsilon_{CuO}\varepsilon_{ZnO}N_{ZnO}V_0}{qN_{CuO}(\varepsilon_{CuO}N_{CuO}+\varepsilon_{ZnO}N_{ZnO})}\right]^{1/2}, \quad (1.9)$$

where $V_0$ (~ 1.5 eV) is the contact potential difference between ZnO and CuO [34], $\varepsilon_{ZnO}$ (~4) and $\varepsilon_{CuO}$ (~25) is the permittivity of ZnO and CuO [9,35], respectively, $N_{ZnO}$ (~$10^{18}$ $cm^{-3}$) and $N_{CuO}$ (~$10^{19}$ $cm^{-3}$) are the electron and hole concentrations of ZnO and CuO, respectively [9,35], and $q$ is the charge of an electron. The estimated $W_{CuO}$ is ~12 nm. On the other hand, previous calculations showed that the upper HAL width for CuO is in the range of ~10 nm [13,33]. Therefore, the optimum thickness of the top layer is ~$HAL + W_{CuO}$, so is ~ 20 nm. Exposure to oxidizing gaseous species (such as VOC vapors) will result in more pronounced resistance modulation (see Figure 10(d)). Thus, the lower ZnO:Al layer greatly improves the gas detection performance by narrowing the active region of the CuO layer to a value comparable to the HAL region, providing a greater change in electrical resistance [35].

In the case of $Al_2O_3$/CuO heterostructures excellent stability to relative humidity has been demonstrated with an increased ratio of $H_2$ interference/humidity/sensitivity and the ability to detect low concentrations of hydrogen gas, obtaining a response of ~27% at a concentration of only 1 ppm.

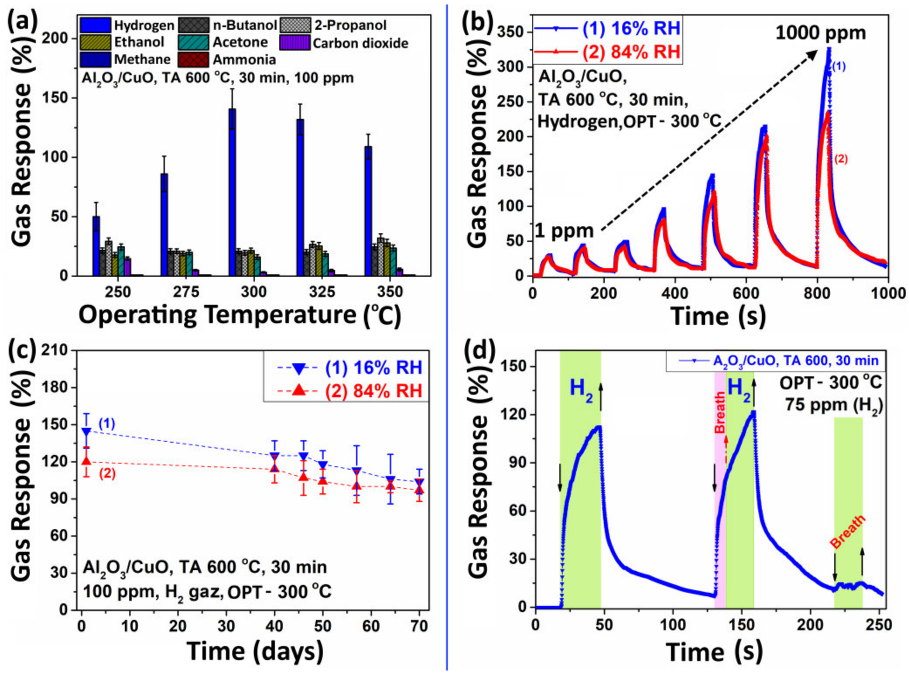


**Fig. 11. (a) Response to different gases (100 ppm) and working temperatures of $Al_2O_3$/CuO heterostructures with a thermal treatment at 600 °C for 30 min. (b) Dynamic response to multiple hydrogen concentrations (1, 5, 10, 50, 100, 500 and 1000 ppm) at 300 °C working temperature of $Al_2O_3$/CuO heterostructures treated at 600 °C for 30 min for low and high relative humidity. (c) Long-term stability of $Al_2O_3$/CuO heterostructures for low and high relative humidity at 300 °C working temperature and response to $H_2$ gas at concentrations of 100 ppm. (d) Influence of the expiration of a healthy person on the hydrogen response, pulse 3.**

From the measurements of the sensory properties at different gases (hydrogen, n-butanol, ethanol, 2-propanol, acetone, carbon dioxide, methane and ammonia) with concentrations of 100 ppm of $Al_2O_3$/CuO heterostructures at different working temperatures, a high and selective response to $H_2$, thus obtaining the values of ~50%, ~86%, ~140%, ~131% and ~109% at working temperatures of 250 °C, 275 °C, 300 °C, 325 °C and 350 °C, respectively, resulting in an optimum operating temperature of 300 °C (see Figure 11(a)). Dynamic response to different concentrations of hydrogen (1, 5, 10, 50, 100, 500 and 1000 ppm) at working temperature of 300 °C for $Al_2O_3$/CuO heterostructures with heat treatment at 600 °C for 30 min under low relative humidity value (16% RH) and high relative humidity (84% RH) demonstrate that concentrations of 1 ppm of $H_2$ can be detected with a response of ~27% (see Figure 11(b)). Similarly, the response difference for low and high relative humidity values can be observed for 1, 5, 10, 50, 100, 500 and 1000 ppm of $H_2$, indicating changes of ~10%, ~11%, ~13%, ~17 %, ~16%, ~7% and ~28%, respectively, of the maximum response for each tested concentration. The long-term stability of $Al_2O_3$/CuO heterostructures at low (16%) and high (84%) relative humidity values and $H_2$ response at 300 °C working temperature at 100 ppm concentrations for 70 days demonstrates that during this time the gas response is approximately constant/stable, varying by only 10-15%, demonstrating the long-term stability of the developed sensors (see Figure 11(c)). Breath tests were performed as follows: at a working temperature of 300 °C, a flow of $H_2$ gas with a concentration of 75 ppm was applied to the sample (first pulse, figure 11(d)), at the same time as the flow of $H_2$ gas also breath test from a person for 10s (second pulse, figure 11(d)), and the third pulse in this figure is obtained only from the expiration of air from a person to record the influence of the response depending on the breath. It can be seen that the first pulse, where only hydrogen gas with a concentration of 75 ppm is applied at a working temperature of 300 °C, leads to a response of 112%. A second pulse, consisting of 75 ppm hydrogen gas and a breath test applied for 10s, leads to a maximum response of 121%. Expiration test showed no effect on the response, which proves the excellent stability of the sensor. Only in the third pulse, when the expiration is applied, there is a negligible response of about 5%, explaining the high response to the second pulse of 121%.

Advances in such a competitive field could contribute to the development of a cost-effective, low-power, reproducible power heterojunction for the widespread detection of $H_2$ gas in portable battery applications, not just for gas analysis, but also for security, environment, breath testing and food safety applications.

Each chapter of the thesis ends with conclusions of research and a summary of the main results obtained. **The final conclusions and recommendations** express the main results, published in journals, which justify the theoretical and practical value of research on non-planar nanomaterials and heterojunctions based on investigated semiconductor oxides.

## GENERAL CONCLUSIONS AND RECOMMENDATIONS

The proposed field of research aimed to identify nanomaterials, heterostructures and heterojunctions with sensitivity and selectivity to gases ($H_2$) and volatile organic compounds (acetone, n-butanol, ethanol and 2-propanol) and to obtain stable nanomaterials at high relative humidity, including in breath tests. Based on the research and the results obtained, the following general conclusions can be drawn:

1. The functionalization of ultra-thin $TiO_2$ films with noble metal nanoparticles (Au, Ag, Ag-Au and Ag-Pt) results in a considerable improvement in the sensory properties of hydrogen gas and ultraviolet radiation (approximately by one order of magnitude) [16,19].

2. Formation of $TiO_2/CuO/Cu_2O$ heterostructures demonstrated the possibility of obtaining long-term stability (for 105 days) of the sensor due to the self-cleaning effect after deposition of the thin layer of $TiO_2$ on top [12].

3. Formation of $TiO_2/CuO/Cu_2O$ heterostructures and functionalization with Pd, Ag or Ag-Pt nanoparticles demonstrated the regulation of selective sensitivity with ultra-low power consumption, thus obtaining in the cases of functionalization with: of Pd nanoparticle a hydrogen response of ~543%; Ag nanoparticles a n-butanol vapor response of ~200% and with Ag-Pt nanoparticles a n-butanol vapor response of ~216%. The change in selectivity depending on the nanoparticles types of Pd, Ag or Ag-Pt is due to the lower adsorption energies at the surface of the heterostructure of the hydrogen or n-butanol molecules, respectively [20].

4. The formation of $CuO/Cu_2O$ heterostructures through the technology of 3D printing in a single stage, demonstrated the obtaining of the network of dense array of nanowires with diameters of 20 nm. The gas detection properties showed excellent selectivity to acetone vapor at operating temperature 350 °C with a response of ~150% at 100 ppm. The high response is attributed to the formation of $CuO/Cu_2O$ heterojunctions due to the increase in the large number of nodes in the nanowire network [21].

5. Formation of $Fe_2O_3$-$CuO/Cu_2O$ heterostructures through 3D printing technology, demonstrated sensory properties to volatile organic compounds and high selectivity to acetone vapors with concentrations up to 1 ppm as well as reduced power consumption of up to 0.26 µW. The high response is attributed to the formation of $Fe_2O_3$-$CuO/Cu_2O$ heterostructures with an increase in the number of nodes between CuO nanowires and $Fe_2O_3$ nanospikes [22].

6. The formation of non-planar heterostructures based on a $CuO/Cu_2O/Cu$ microwire fixed with microparticles converted to $CuO/Cu_2O$ crystals and completely covered with CuO nanowire networks has demonstrated the possibility of manufacturing a 3-in-1 sensor, due to the control of the sensitive and selective detection of 2-propanol vapors at room temperature, of ethanol vapors in the working temperature range of 150 $^oC$ - 250 $^oC$ and of $H_2$ gas in the working temperature range of 275 $^oC$ - 350 $^oC$. The change in selectivity is attributed to the catalytic properties of the $CuO/Cu_2O/Cu$ heterojunctions to completely oxidize 2-propanol at room temperature, ethanol in the working temperature range of 150 $^oC$ - 250 $^oC$ and $H_2$ gas in the working temperature range of 275 $^oC$ - 350 $^oC$ [36].

7. The formation of $CuO$-$Cu_2O/ZnO$ heterostructures demonstrated sensitivity and selectivity to n-butanol vapors of ~200% with a concentration of 100 ppm at a working temperature of 350 °C with

low dependence on the response to humidity, which is extremely attractive for practical applications, due to the involvement in the detection mechanism of heterojunction interface between CuO-$Cu_2O$ (*p-type*) and ZnO:Al (*n-type*) [14].

8. Formation of $Al_2O_3$/CuO heterostructures by deposition of the ultra-thin layer of $Al_2O_3$ on the surface of the nanostructured CuO film demonstrated high selectivity to $H_2$ gas with a value of ~140%, at the working temperature of 300 °C and the ability to detect low hydrogen concentrations, obtaining a response of ~27% at a concentration of 1 ppm, as well as stability at high concentrations of relative humidity of 84%, namely with the practically unchanged gas response value [6].

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

1. The use of ultra-thin $TiO_2$ films (15 nm thick by ALD method and 40 nm by spray method) is recommended for sensitive and highly selective detection of hydrogen gas.
2. It is recommended to functionalize ultra-thin $TiO_2$ films with noble metal nanoparticles (Au, Ag, Ag-Au and Ag-Pt) in order to increase the response to UV radiation and change the selectivity to ammonia and ethanol vapors.
3. For the long-term stability of the ethanol vapor-sensitive and selective CuO/$Cu_2O$ sensor, it is recommended to deposit the ultra-thin layer of $TiO_2$ on top.
4. Functionalization of $TiO_2$/CuO/$Cu_2O$ heterostructures with noble nanoparticles, in order to obtain the tunning of the selective sensitivity as well as the reduction of the consumption power of up to 1 nW; Pd/$TiO_2$/CuO/$Cu_2O$ to obtain selectivity for hydrogen gas at the operating temperature of 250 °C; Ag/$TiO_2$/CuO/$Cu_2O$ to obtain selectivity for n-butanol vapors at a working temperature of 300 °C; AgPt/$TiO_2$/CuO/$Cu_2O$ to obtain n-butanol vapor selectivity at 350 °C.
5. It is recommended to obtain non-planar heterostructures of CuO/$Cu_2O$ and $Fe_2O_3$-CuO/$Cu_2O$ by 3D printing technology, in order to obtain a high selectivity to acetone vapors with concentrations up to 1 ppm and low power consumption.
6. It is recommended to use CuO nanowire networks based on a CuO/$Cu_2O$/Cu microwire fixed with CuO/$Cu_2O$ microparticles to obtain a 3-in-1 sensor device, by controlling the sensitive and selective vapor detection of 2-propanol (at room temperature), ethanol vapor (at working temperature of 150 °C - 250 °C) and $H_2$ (at working temperature of 275 °C - 350 °C).
7. To obtain CuO-$Cu_2O$/ZnO heterostructures for sensitivity and selectivity to n-butanol vapors at a working temperature of 350 °C and stability of the response to relative humidity.
8. Deposition of the ultra-thin layer of $Al_2O_3$ on the top surface of the CuO film to obtain the $Al_2O_3$/CuO heterostructures as a detector of $H_2$ gas with stability at high concentrations of relative humidity.

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

### Articles in international journals listed ISI and SCOPUS:

1. LUPAN, O., **ABABII, N.**, SANTOS-CARBALLAL, D., TERASA, M.-I., MAGARIU, N., ZAPPA, D., COMINI, E., PAUPORTE, TH., SIEBERT, L., FAUPEL, F., VAHL, A., HANSEN, S., DE LEEUW, N. H., ADELUNG, R. Tailoring the selectivity of ultralow-power heterojunction gas sensors by noble metal nanoparticle functionalization. În: *Nano Energy*. 2021, vol. 88, pp. 106241. ISSN 2211-2855. (**Impact Factor: 17.881**).
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23. **ABABII, N.** Creșterea localizată și cercetarea proprietăților senzoriale ale nanostructurilor oxizilor mixti de Fe-Cu. În: *Conferința Tehnico-Ştiinţifică a Studenţilor, Masteranzilor și Doctoranzilor, UTM*, 26-29 Martie, 2019, Chisinau, Moldova, vol. I, pp. 357-360, ISBN 978-9975-45-588-6.
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**Patents and other intellectual property objects (IPO):**

26. **ABABII, N.,** POSTICA, V., TROFIM, V., LUPAN, O., *Senzor de etanol pe bază de oxid de cupru*, Brevet de invenţie MD 4495. Nr. depozit: A 2016 0101. Data depozit: 2016.09.09. Publicat 2017.06.30. În: BOPI. 2017, nr. 6.
27. LUPAN, O., **ABABII**, **N.,** TROFIM, V. *Procedeu de obţinere a senzorului de hidrogen stabil la umiditate*, Brevet de invenţie MD 1588. Nr. depozit: s 2020 0110. Data depozit: 2020.09.10. Publicat 2021.12.31. În: BOPI. 2021, nr. 12.

## ADNOTARE

la teza cu titlul ”**Nanomateriale și heterojoncțiuni non-planare în bază de oxizi semiconductori**”, înaintată de competitorul **ABABII Nicolai**, pentru conferirea gradului științific de doctor în științe inginerești, la specialitatea 233.01 ”Nano-Microelectronică și Optoelectronică”.

**Structura tezei:** Teza a fost realizată în cadrul Universității Tehnice a Moldovei (UTM), Centrul de Nanotehnologii și Nanosenzori (CNN), Departamentul Microelectronică și Inginerie Biomedicală (DMIB). Este scrisă în limba română și constă din introducere, 5 capitole, concluzii generale și recomandări, bibliografie din 297 de titluri, 119 pagini text de bază, 51 figuri și 1 tabel. Rezultatele obținute au fost publicate în 27 lucrări științifice, inclusiv: 2 brevete de invenție; 10 articole recenzate în reviste cotate ISI și SCOPUS (dintre care două cu Factor de Impact: 17.881); 1 articol în reviste din Registrul Naţional al revistelor de profil; 14 lucrări prezentate, recenzate și publicate la Conferinţe Naţionale şi Internaţionale.

**Cuvinte-cheie:** CuO, nanotehnologii, nanomateriale, heterojoncțiuni, senzori de gaze.

**Scopul lucrării:** constă în obținerea nanomaterialelor, heterojoncțiunilor și heterostructurilor non-planare în bază de oxizi semiconductori, $CuO/Cu_2O$, $TiO_2/CuO/Cu_2O$, $Fe_2O_3$ - $CuO/Cu_2O$, $CuO$-$Cu_2O/ZnO:Al$ și $Al_2O_3/CuO$, prin metode și tehnologii cost-eficiente; identificarea nanomaterialelor și heterostructurilor cu sensibilitate și selectivitate la gaze ($H_2$) și compuși organici volatili (COV) (acetonă, n-butanol, etanol și 2-propanol); obținerea structurilor senzor stabili la umiditatea relativă înaltă în baza nanomaterialelor și heterojoncțiunilor elaborate.

**Obiectivele cercetării:** cercetarea proprietăților, inclusiv senzoriale, ale nanomaterialelor și heterojoncțiunilor în bază de: (i) pelicule de $TiO_2/CuO/Cu_2O$ și funcționalizarea lor; (ii) heterostructuri non-planare de $Fe_2O_3$ - $CuO/Cu_2O$ imprimate 3D; (iii) heterostructuri de $CuO$-$Cu_2O/ZnO:Al$; (iv) heterostructuri de $Al_2O_3/CuO$ cu un răspuns stabil la umiditatea relativă; (v) analiza fizico-chimică avansată și caracterizarea proprietăților; cercetarea stabilității caracteristicilor la umiditatea relativă înaltă.

**Noutatea și originalitatea științifică:** asigurarea stabilității caracteristicilor pe termen lung, reglarea sensibilității selective, precum și îmbunătățirea răspunsului la gaze și compuși organici volatili (COV) a nanomaterialelor și heterostructurilor de $TiO_2$, $CuO/Cu_2O$, $TiO_2/CuO/Cu_2O$, $CuO$-$Cu_2O/ZnO:Al$ și $Al_2O_3/CuO$. Pentru prima dată s-au obținut heterostructuri de $CuO/Cu_2O$ și $Fe_2O_3$ - $CuO/Cu_2O$ prin metoda imprimării 3D și cercetate proprietățile lor. Prin intermediul tehnicilor SEM, XRD, Raman, TEM, HRTEM, SAED, EDX și XPS s-au efectuat cercetările pentru determinarea calității și caracteristicile nanomaterialelor și heterostructurilor elaborate. Calculele teoriei funcționale a densității (DFT) a heterojoncțiunilor, prin simularea interacțiunii moleculelor de gaz/COV cu suprafața nanomaterialelor modelate, au fost efectuate pentru modelarea mecanismelor de detectare propuse și de a înțelege efectele și fenomenele care au loc la suprafața și interfața heterojoncțiunilor elaborate.

**Problema științifică și de cercetare soluționată** constă în identificarea nanomaterialelor și heterojoncțiunilor cu sensibilitate și selectivitate la gaze ($H_2$) și compuși organici volatili (COV: acetonă, n-butanol, etanol și 2-propanol) și obținerea stabilității lor la umiditatea relativă înaltă.

**Semnificația teoretică și valoarea aplicativă a lucrării** se bazează pe aprofundarea și elaborarea mecanismelor fizico-chimice de detectare a gazelor/COV și a radiației UV de către nanomaterialele și heterostructurile obținute pe bază de $TiO_2$, $CuO/Cu_2O$, $TiO_2/CuO/Cu_2O$, $Fe_2O_3$ - $CuO/Cu_2O$, $CuO$-$Cu_2O/ZnO:Al$ și $Al_2O_3/CuO$, precum și prezentarea aplicațiilor practice de detectare sensibilă și selectivă a gazelor/vaporilor de hidrogen, etanol, acetonă, n-butanol și 2-propanol cu stabilitate în timp și la umiditatea relativă înaltă ale acestora. Modelele mecanismelor de detectare propuse au fost susținute de calculele teoriei funcționale a densității elaborate, în combinație cu simulările DFT, prin simularea interacțiunii moleculelor de gaz/COV cu suprafața heterojoncțiunilor.

**Implementarea rezultatelor științifice.** Rezultatele științifice au fost implementate parțial în procesul instructiv-educativ desfășurat în cadrul UTM, la elaborarea tezelor de licență ale studenților din cadrul departamentului MIB. Ulterior, în baza rezultatelor științifice a fost posibilă obținerea unui act de implementare a cercetărilor inovaționale la Facultatea CIM, UTM, precum și a două brevete de invenție.

**ABSTRACT**

of the thesis with title ”**Non-planar nanomaterials and heterojunctions based on semiconducting oxides**” presented by **ABABII Nicolai**, for conferring the scientific degree of Doctor in Engineering Sciences at speciality 233.01 "Nano-Microelectronics and Optoelectronics"

**Thesis structure:** The thesis was realised at the Technical University of Moldova (TUM), Center for Nanotechnologies and Nanosensors (CNN), Department of Microelectronics and Biomedical Engineering (DMBE). It is written in Romanian language and consists of introduction, 5 chapters, general conclusions and recommendations, bibliography with 297 references, 119 pages of basic text, 51 figures and 1 table. The obtained results were published in 27 scientific papers, including: 2 patents; 10 peer-review papers in international journals listed ISI and SCOPUS database (two of which have an Impact Factor: 17.881); 1 article in journals from the National Register of specialized journals; 14 papers presented, revised and published in proceeding of National and International Conferences.

**Keywords:** CuO, nanotechnologies, nanomaterials, heterojunctions, gas sensors.

**Aim of the study:** consists in obtaining non-planar nanomaterials, heterostructures, and heterojunctions based on semiconductor oxides, $CuO/Cu_2O$, $TiO_2/CuO/Cu_2O$, $Fe_2O_3$ - $CuO/Cu_2O$, $CuO$-$Cu_2O/ZnO$:Al and $Al_2O_3/CuO$, through cost-effective methods and technologies; identification of nanomaterials and heterostructures with sensitivity and selectivity to gases ($H_2$) and volatile organic compounds (VOC: acetone, n-butanol, ethanol and 2-propanol); obtaining sensor structures stable at high relative humidity based on developed nanomaterials and heterostructures.

**Objectives:** research of the sensor properties of nanomaterials and heterostructures based on: (i) $TiO_2/CuO/Cu_2O$ films and their functionalization; (ii) 3D printed $Fe_2O_3$ - $CuO/Cu_2O$ heterostructures; (iii) $CuO$-$Cu_2O/ZnO$:Al heterostructures; (iv) $Al_2O_3/CuO$ heterostructures with a stable response at high relative humidity; advanced physico-chemical analysis and characterization of properties; stability research at high relative humidity.

**Scientific novelty and originality:** ensuring long-term stability of response, regulating selective sensitivity, as well as improving the gas and VOC response of $TiO_2$, $CuO/Cu_2O$, $TiO_2/CuO/Cu_2O$, $CuO$-$Cu_2O/ZnO$:Al and $Al_2O_3/CuO$ nanomaterials and heterostructures. For the first time, heterostructures of $CuO/Cu_2O$ and $Fe_2O_3$ - $CuO/Cu_2O$ were obtained by the 3D printing method and investigated their properties. Through the techniques of SEM, XRD, Raman, TEM, HRTEM, SAED, EDX and XPS, research was performed to determine the quality and characteristics of obtained nanomaterials and heterostructures. Calculations (DFT) of heterojunctions, by simulating the interaction of gas/VOCs molecules with the surface of modeled structures were performed to model the proposed detection mechanisms and to understand the effects and phenomena that occurs at the surface and interface of heterojunctions developed in this thesis.

**The solved scientific and research problem** is to identify nanomaterials and heterojunctions with sensitivity and selectivity to gases ($H_2$) and VOCs (acetone, n-butanol, ethanol and 2-propanol) and to obtain stability at high relative humidity.

**The theoretical significance and applicative value of the work** are based on the deepening and elaboration of physico-chemical mechanisms for detecting gases/VOCs and UV radiation by nanomaterials and heterostructures developed based on $TiO_2$, $CuO/Cu_2O$, $TiO_2/CuO/Cu_2O$, $Fe_2O_3$ - $CuO/Cu_2O$, $CuO$-$Cu_2O/ZnO$:Al and $Al_2O_3/CuO$, as well as the presentation of practical applications for sensitive and selective detection of hydrogen, ethanol, acetone, n-butanol and 2-propanol gases/vapors with stability of response over time and at high relative humidity. The models of the proposed detection mechanisms were supported by the calculations of the elaborated functional theory, in combination with DFT simulations, by simulating the interaction of gas/VOCs molecules with the surface of heterojunctions.

**Implementation of scientific results.** The scientific results were partially implemented in the instructive-educational process carried out within TUM, and in the elaboration of the undergraduate theses of the students within the MBE Department, Subsequently, based on the acquired scientific results, it was possible to obtain an act for the implementation of innovative research at the Faculty of CIM, TUM, as well as two patents.

## АННОТАЦИЯ

к диссертации „ **Непланарные наноматериалы и гетеропереходы на основе полупроводниковых оксидов**”, представленной соискателем **АБАБИЙ Николай,** для присуждения ученой степени доктора технических наук по специальности 233.01 ”Нано-микроэлектроника и оптоэлектроника”.

**Структура диссертации:** диссертация была выполнена в Техническом Университете Молдовы (ТУМ), Центр Нанотехнологий и Наносенсоров (ЦНН), Департамент Микроэлектроники и Биомедицинской Инженерии (ДМБИ). Написана на румынском языке и состоит из введения, 5 глав, общих выводов и рекомендаций, библиографии из 297 наименований, 119 страниц основного текста, 51 рисунков и 1 таблица. Полученные результаты опубликованы в 27 научных работах, в том числе: 2 патента; 10 статей, рецензируемых в журналах ISI и SCOPUS (две из которых имеют импакт-фактор: 17.881); 1 статья в журналах из Национального реестра профильных журналов; 14 докладов представлены и опубликованы на национальных и международных конференциях.

**Ключевые слова:** CuO, нанотехнологии, наноматериалы, гетеропереходы, газовые сенсоры.

**Цель работы:** получение непланарных наноматериалов, гетероструктур и гетеропереходов на основе полупроводниковых оксидов, $CuO/Cu_2O$, $TiO_2/CuO/Cu_2O$, $Fe_2O_3$ - $CuO/Cu_2O$, $CuO$-$Cu_2O/ZnO$:Al и $Al_2O_3/CuO$, экономичными методами и технологиями; идентификация наноматериалов и гетеропереходов с чувствительностью и селективностью к газам ($H_2$) и летучим органическим соединениям (ЛОС: ацетон, н-бутанол, этанол и 2-пропанол); получение сенсорных структур стабильных при высокой относительной влажности на основе разработанных наноматериалов и гетероструктур.

**Задачи исследования:** исследование свойств, включая сенсорные, наноматериалов и гетероструктур на основе: (i) пленок $TiO_2/CuO/Cu_2O$ и их функционализации; (ii) 3D-печатные гетероструктуры $Fe_2O_3$ - $CuO/Cu_2O$; (iii) гетероструктуры $CuO$-$Cu_2O/ZnO$:Al; (iv) стабильные гетероструктуры $Al_2O_3/CuO$ к относительной влажности; расширенный физико-химический анализ и определение свойств; исследование стабильности гетероструктур при высокой относительной влажности.

**Научная новизна и оригинальность:** обеспечение долговременной стабильности, регулирование селективной чувствительности, а также улучшение газового и ЛОС-отклика наноматериалов и гетероструктуры $TiO_2$, $CuO/Cu_2O$, $TiO_2/CuO/Cu_2O$, $Cu_2O/ZnO$:Al и $Al_2O_3/CuO$. Впервые были получены гетероструктуры $CuO/Cu_2O$ и $Fe_2O_3$ - $CuO/Cu_2O$ методом 3D-печати и исследованны их свойства. С помощью методов SEM, XRD, Raman, TEM, HRTEM, SAED, EDX и XPS были проведены исследования для определения качества и характеристик полученных наноматериалов и гетеропереходов. Расчеты (DFT) гетеропереходов путем моделирования взаимодействия молекул газа/ЛОС с поверхностью моделируемых структур были выполнены для моделирования предложенных механизмов обнаружения и понимания эффектов и явлений, которые происходят на поверхности и на границе раздела разработанных гетеропереходов.

**Решенная научно-исследовательская задача** заключается в идентификации наноматериалов и гетероструктур обладающих чувствительностью и селективностью к газам ($H_2$) и ЛОС (ацетон, н-бутанол, этанол и 2-пропанол) и получению стабильности отклика при высокой относительной влажности.

**Теоретическая значимость и прикладная ценность работы** основана на углублении и разработке физико-химических механизмов обнаружения газов/ЛОС и УФ-излучения наноматериалами и гетероструктурами разработанных на основе $TiO_2$, $CuO/Cu_2O$, $TiO_2/CuO/Cu_2O$, $Fe_2O_3$ - $CuO/Cu_2O$, $Cu_2O/ZnO$:Al и $Al_2O_3/CuO$, а также презентация практических приложений для чувствительного и селективного обнаружения газов/паров водорода, этанола, ацетона, н-бутанола и 2-пропанола со стабильностью характеристик во времени и при высокой относительной влажности. Модели предложенных механизмов обнаружения были подтверждены расчетами разработанной функциональной теории в сочетании с DFT-моделированием путем моделирования взаимодействия молекул газа/ЛОС с поверхностью гетеропереходов.

**Внедрение научных результатов.** Научные результаты были частично внедрены в учебно-образовательном процессе, проводимом в рамках ТУМ, и при разработке дипломных работ студентов Департамента МБИ. На основании научных результатов удалось получить акт внедрения инновационных исследований на факультете КИМ, ТУМ, а также два патента.

**ABABII NICOLAI**

# NON-PLANAR NANOMATERIALS AND HETEROJUNCTIONS BASED ON SEMICONDUCTING OXIDES

**233.01 NANO-MICROELECTRONICS AND OPTOELECTRONICS**

Summary of the doctoral thesis in engineering sciences

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