IOSUD - Universitatea Politehnica Timişoara
Şcoala Doctorală de Studii Inginereşti

DEVELOPMENT OF HETEROSTRUCTURAL MATERIALS FOR SENSOR APPLICATIONS

PhD Thesis – Abstract

for obtaining the scientific title of doctor from

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INTRODUCTION

In the context of societal advancement and modern technological development, air pollution has become an increasingly significant concern, with substantial implications for the environment and global population health. The rising concentration of carbon dioxide (CO_2) in the atmosphere is one of the primary causes of global climate change. These changes can disrupt the ozone layer, leading to increased exposure to ultraviolet (UV) radiation on the Earth's surface. UV radiation can have harmful effects on human health, such as sunburn, premature skin aging, and an elevated risk of skin cancer.

Research justification

In recent years, environmental detection and monitoring technologies have made significant progress, continuing to evolve with the aim of ensuring environmental protection and human safety. Various sensors have been developed and implemented to detect and monitor both greenhouse gases and UV radiation intensity.

Nanostructured semiconductor metal oxides offer numerous advantages in sensor development. Their small size and high specific surface area make them highly sensitive to interactions with molecules of the analyzed substance, enabling precise detection and measurement. Another important aspect of nanostructured metal oxide semiconductors is their efficient absorption of light at specific wavelengths. By using oxide semiconductors with UV absorption capabilities, precise UV radiation monitoring devices with low production costs can be developed.

In the context of research dedicated to the development and improvement of various types of oxides for use in the sensor field, a special scientific interest has been generated by the method of combining these oxides to create oxide heterojunctions, thus paving the way for a new type of sensor. The development of these oxide heterojunctions aims to achieve more efficient and sensitive sensors, contributing to the advancement of environmental monitoring and control.

In the development of heterojunction sensors, different types of junctions are used, such as p-n, n-p, p-p, and n-n junctions, depending on the type of oxide used and its placement in the sensor module. At the same time, common experimental approaches include controlling the morphology and reducing the dimensions of crystallites. These experimental methods are used to improve sensor performance and sensitivity by optimizing the interaction between different semiconductor materials and controlling the nanoscale structure.

Amorphous metallic materials, due to their disordered atomic-scale nature and associated advantages, are suitable for use in sensor applications, either as a base substrate for obtaining high-specific-surface-area metal-oxide heterostructures or as flexible substrates on which oxide nanoparticles can be grown subsequently. Processes such as sputtering, or oxidation are used to functionalize amorphous metals. Using these processes, these amorphous metallic alloys become ideal candidates for next-generation flexible sensor applications.

The aim, objectives, and structure of the thesis

The purpose of this thesis is to obtain new nanostructured materials with morpho-structural, optical, and electrical properties that enable their integration into detection and monitoring devices used for the detection of CO_2 and UV radiation.

The specific objectives associated with this are as follows:

- developing technological processes for the deposition, growth, and processing of cost-effective nanostructured materials based on materials such as TiO_2, ZnO, Fe_2O_3, $CuMnO_2$, and NPC (nanoporous copper).
- obtaining oxide and/or nanoporous materials through sputtering and/or thermal oxidation of Cu-Zr-Al amorphous alloy strips and characterizing them in terms of morphology, structure, optical properties, electrical properties, and electrochemical properties.
- achieving cost-energy-efficient processes for obtaining nanostructured 1D, 2D, and 3D films and integrating them into heterojunction modules for the detection of CO_2 and UV radiation.
- developing sensors based on heterojunctions for the detection of CO_2 and UV radiation.

Consequently, the experimental program has focused on research aimed at both obtaining and physico-chemically characterizing nanostructured materials and integrating them into sensor devices based on oxide heterojunctions. These materials allow processing in these devices using the technologies identified and developed within the thesis.

CHAPTER 1. STATE OF THE ART

In the last decade, metal oxide-based semiconductors have gained increased scientific and technological interest. These semiconductors exhibit diverse electronic properties, ranging from insulators and semiconductors to superconductors, and find applications in a wide range of technological fields such as transparent electronics, solar cells, environmental monitoring sensors, catalysis, supercapacitors, and more.

The band theory describes the energy structure of a crystalline material and how electrons occupy energy levels within the lattice. This theory assumes that in a crystal, there are two main bands, the valence band and the conduction band, separated by an energy gap called the "band gap." [1]

These concepts of the band theory are fundamental to understanding the semiconductor properties of oxide materials and are of high importance in material development. Based on these considerations, materials are classified into three categories: insulators, semiconductors, and conductors. The schematic representation of the energy bands for these material classes is presented in Figure 1a. Depending on the majority charge carriers, oxide semiconductors are classified into two categories: n-type semiconductors and p-type semiconductors. Figure 1b depicts the band diagrams for an n-type semiconductor and a p-type semiconductor, using band theory. [2]

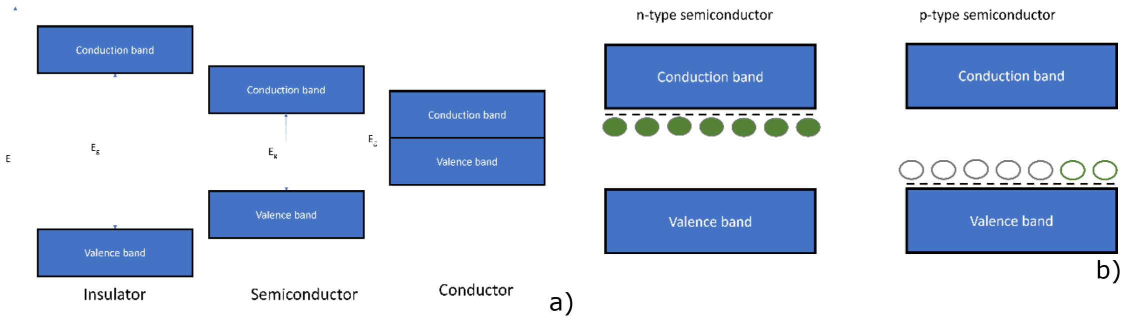

Figure 1. Band theory for: a) crystalline materials; b) semiconductor materials

The rapid technological progress in recent years has led to the spectacular development of new technological fields, including "sensory" technologies.

It is known that the human being gathers information about the surrounding environment through its five senses. This information is received by the nervous system, processed by the brain, and transmitted as electrochemical signals, manifesting as emotions and sensations. Our senses serve as a window to our reality.

Similarly, a "conceptual" sensor receives a signal that allows it to perceive a specific material or characteristic. This signal is then processed through analytical data and generates an appropriate response.

In recent years, complex research teams consisting of medical professionals, psychologists, engineers, and computer scientists have been studying ways to create sensors similar to biological ones or to model perception through sensory substitution. Sensor technology, as experts in the field predict, will become the interface between the world and our minds.

Semiconductor-based sensors have garnered increased interest in recent years, primarily due to their exceptional intrinsic properties, such as high catalytic efficiency, strong electron and photon adsorption capacity, and a very high surface-to-volume ratio. These attributes, coupled with their relatively low cost, make them highly attractive in the field of sensor technology. A clear example of this is the detection of gases and UV radiation, which are already considered typical applications in systems based on oxide semiconductors. These systems continue to evolve in both applied research and industry.

Given the considerable "abundance" of research based on the development of oxide sensors, classifying them becomes a complex task.

Classifying oxide-based sensors can be approached by analyzing the specific type of oxide used as the base material. Some common examples of oxides used include zinc oxide (ZnO), titanium dioxide (TiO_2), tin oxide (SnO_2), copper oxide (CuO), aluminum oxide (Al_2O_3), nickel oxide (NiO), and others. Each type of oxide may have certain properties and characteristics that make it suitable for specific sensor applications. [3]

In addition to classification based on the type of oxide, an important approach is based on the size and geometric shape of oxide structures. This can include sensors based on thin films, nanoparticles, nanowires, nanotubes, and various other structural configurations. The size and geometric shape of these structures can significantly influence sensor sensitivity, selectivity, and overall performance.

Classification of sensors according to semiconductor type

Depending on the material used, oxide sensors can be classified as n-type or p-type sensors. The type of oxide semiconductor can occur naturally or can be modified through doping with different metal atoms. Figure 2 illustrates the distribution of scientific research in

2022 regarding oxide sensors, categorized by the type of semiconductor, for the most representative oxides. This figure was constructed using statistical data from publications available on the Scopus platform.

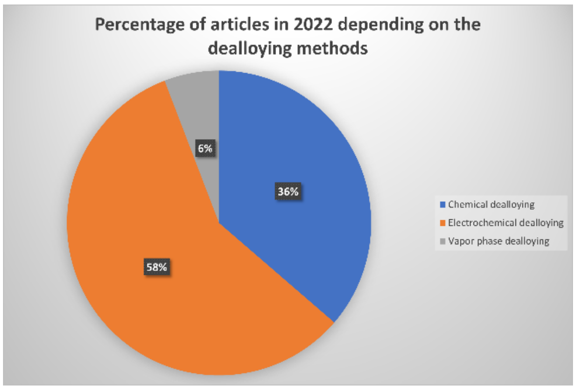

Figure 2: The Distribution of Scientific Studies on Oxide Sensors by Semiconductor Type in 2022 (The figure was created based on the results processed by the Scopus platform).

Sensor classification based on the shape and size of structures

In general, depending on the dimensions of oxide structures, nanostructured oxides can be classified as zero-dimensional structure (0D), one-dimensional structure (1D), and two-dimensional structure (2D). Additionally, sensors constructed with multiple overlapping reduced-dimensional structures are known as three-dimensional structures (3D). The classification of structures and their correlation with morphology is presented in Figure 2. [4]

Nano dimensional materials possess unique chemical, physical, and mechanical properties that are superior to bulk materials due to their high specific surface area and very large surface-to-volume ratio. Generally, the high surface-to-volume ratio of nanomaterials increases as the size of nanoparticles decreases. Furthermore, reducing the dimensions of materials gives rise to "quantum confinement" phenomena (observed when the size of a particle becomes so small that it can no longer be compared to the electron's wavelength), which alter their intrinsic properties. Nanomaterials can take various morphologies, such as nano-rods, nano-wires, nano-whiskers, nano-cubes, nano-spheres, and so on. [4]

Resizing materials at the nanoscale leads to the emergence of unique quantum phenomena for this class of materials. These phenomena result from the size restriction of particles and can significantly affect the behavior and properties of materials. For example, reducing particle size can lead to changes in the band gap, absorption spectrum, electrical conductivity, and other physical properties.

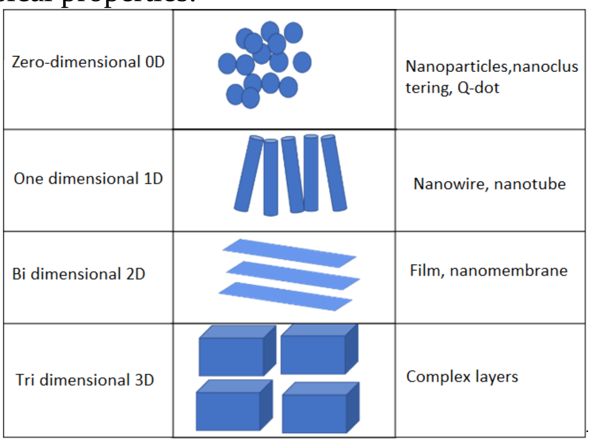

Figure 3. Classification of Nano and Microstructures based on their morphology

The study and development of nanomaterials have opened new perspectives in fields such as electronics, optoelectronics, chemical catalysis, medicine, and many others, as their unique properties and improved characteristics offer significant opportunities for innovation and advanced applications.

There are two main approaches to nanoparticle synthesis: the "top-down" approach and the "bottom-up" approach. In the "top-down" approach, bulk materials are reduced in size to obtain nanoparticles through various techniques such as lithography, milling, grinding, laser ablation, spray pyrolysis, sputtering, etc. [5]

On the other hand, in the "bottom-up" approach, nanoparticles are obtained through chemical, physical, or biological methods. These methods involve building nanoparticles at the atomic or molecular level, gradually constructing them to form nanoscale structures. Chemical synthesis and physical synthesis are the most common technological routes used in the "bottom-up" approach.

Chemical and physical synthesis methods offer advantages such as efficient production of significant quantities of nanoparticles. However, these approaches can be more costly and may involve the use of harmful chemicals. Nevertheless, these methods allow the production of nanoparticles with well-controlled properties and can be adapted to meet specific requirements for sensor applications. [5]

Figure 4 illustrates the methods for obtaining nanostructured oxides.

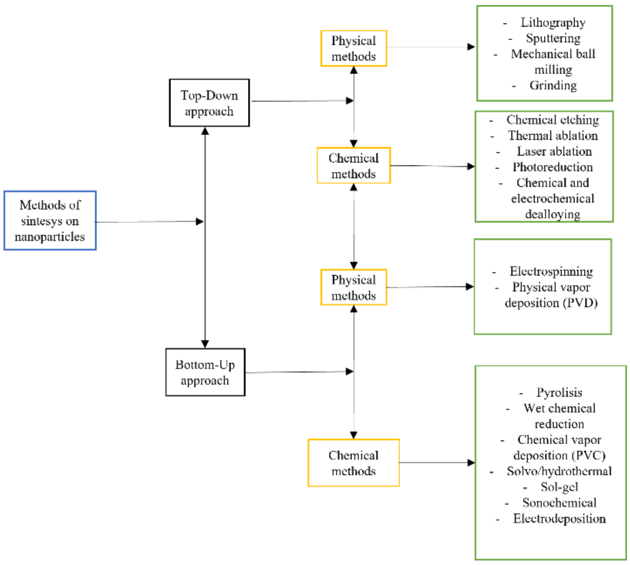

Figure 4. Classification of methods for producing nanostructured materials for integration in sensing applications

Heterostructured materials

Heterostructured materials (HS) are a new class of materials composed of heterogeneous regions with dramatically different mechanical or physical properties. The combination of multiple semiconductors in a device is referred to as a heterojunction. A heterojunction is an interface formed between two or more semiconductors with different chemical structures and energy levels.

D.R. Miller and his team [6] introduced a terminology to classify the structure and dispersion state of heterostructural semiconductor materials based on how they are represented: a hyphen for a simple mixture of two constituents (e.g., "CuO - SnO_2"), the "@" symbol for a base material on which a second material is deposited or grown (e.g., "SnO_2 @ PdO"), and a solid bar to indicate a clear partition or interface between two or more oxides, representing a "core-shell" or double-layer structure (e.g., "NiO/TiO_2").

D. Zapa and his team [7] further elaborate on the classification proposed by D.R. Miller.

Simple mixtures of materials forming mixed compounds lack a specific distribution, and the dispersion state is strongly influenced by production and processing routes. Overlaid layers exhibit well-defined interfaces, and heterojunctions based on bi- or multilayer films allow the investigation of thermal stability and mixed phases. Decorating with nanoparticles involves adding secondary particles to a base material, generating different detection mechanisms. In "core-shell" structures, complete coverage of the host material with a secondary phase is achieved, maximizing the interfacial area. This classification of heterojunctions is schematically presented in Figure 5. [7]

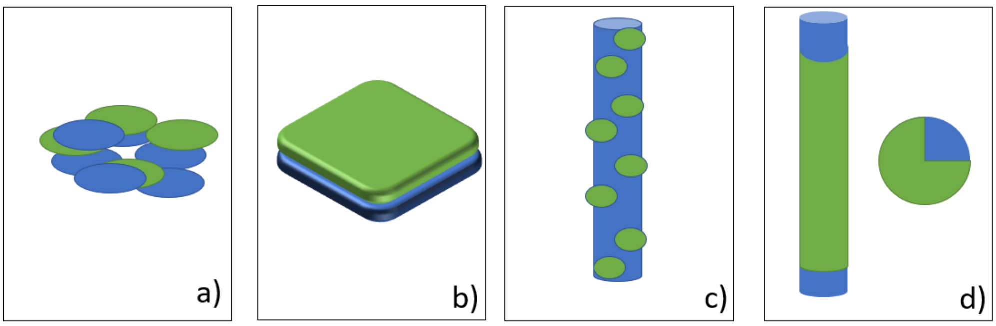

Figure 5. Schematic illustration of oxide-based heterojunctions, represented in different colors; a) mix oxides; b) multilayer stacked layers; c) oxides decorated with other oxides; d) "core-shell" type structures

Metal oxide heterojunctions

A heterojunction is a physical and electronic junction between two different semiconductor materials in a solid state. This junction allows for the connection of the Fermi levels of the materials and the active involvement of charge carriers of the same or different types in electronic processes. Silicon p-n junctions are the most popular heterojunctions and represent the fundamental elements of diodes, LEDs, and transistors.

Combining different oxide semiconductor materials aims to improve their morphological, structural, and functional properties, with the synergy between them aiming to enhance their electronic capabilities.

By connecting two materials into a heterostructure, an alignment of Fermi levels (EF) occurs, resulting in several interconnected phenomena. On one hand, electrons at higher energies migrate along the interface to unoccupied lower-energy states until the Fermi levels equilibrate, creating a depletion zone of charge carriers at the interface. On the other hand, an energy barrier potential forms at the interface due to band bending caused by the initial difference in Fermi levels of the materials. Consequently, charge carriers must overcome this potential energy barrier to cross the interface. In this context, oxide-oxide junctions play a crucial role in understanding gas sensing phenomena because, given the semiconductor nature of the materials, p-n, p-p, n-n, and n-p heterojunctions can be formed. [8]

The n-p junction within sensor applications is considered a reverse-biased p-n junction. Figure 6 illustrates the operation mechanism of oxide heterojunctions based on energy band diagrams.

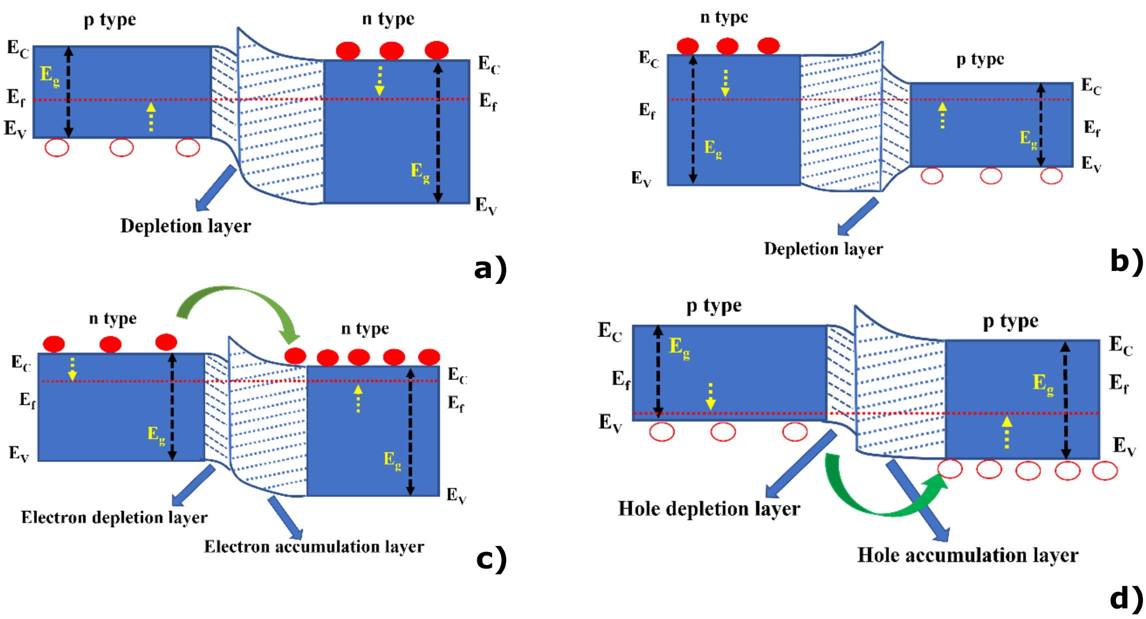

Figure 6. Schematic illustration of the operating mechanism of junctions based on energy band diagrams: a) p-n; b) n-p; c) n-n; d) p-p.

CHAPTER 2. GENERAL METHODS OF MATERIAL CHARACTERIZATION AND TESTING

During experiments and research, equipment from the following laboratories were used:

- Politehnica University of Timișoara
- Institute for Renewable Energy Research (ICER) Timișoara
- National Institute for Research and Development in Electrochemistry and Condensed Matter (INCEMC) Timișoara

These laboratories were classified according to the type of investigation into the following categories:

➢ Morphological and structural characterization methods:
- Scanning Electron Microscopy (SEM)
- Atomic Force Microscopy (AFM)
- X-ray Diffraction (XRD)

➢ Optical characterization methods:
- Ultraviolet-Visible Spectroscopy (UV-VIS)

➢ Electrochemical characterization methods:
- Mott-Schottky analysis

➢ Electrical parameter determination methods:
- Current-Voltage (I-V) characteristic
- Current-Time (I-T) characteristic

➢ Sensitivity testing methods for developed sensors
- UV radiation testing setup
- CO_2 testing setup

To test the sensitivity of heterojunction sensors for UV radiation and CO_2 detection, "home-made" setups were designed and implemented as part of the Advanced Micro and Nanomaterials Laboratory at INCEMC Timișoara. Figure 7 depicts the 3D design phase of the UV radiation and CO_2 testing setups.

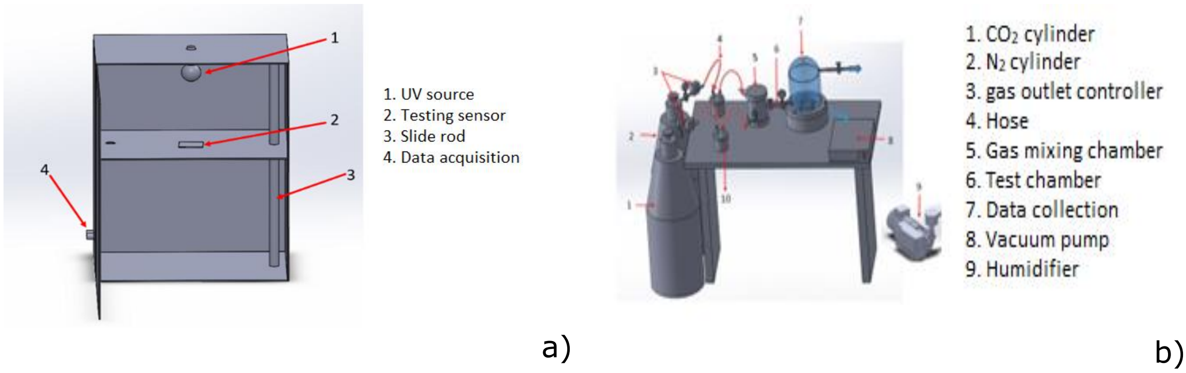

Figure 7. Three-dimensional (3D) design of the sensor testing setup; a) UV setup; CO_2 setup.

CHAPTER 3. DEVELOPMENT OF HETEROSTRUCTURED SENSORS FOR UV AND GAS DETECTION

Within this doctoral thesis, the goal was to develop heterostructured oxide materials that could be integrated into oxide heterojunction sensors of the n-p type. To optimize both the targeted detection applications and the construction of the sensors, several n-p heterojunction devices were fabricated, varying the substrate on which the heterojunction was formed. Below, a brief summary of the results related to their fabrication and integration into heterostructural modules for environmental detection and monitoring applications is presented.

Developing the n-TiO_2/p-$CuMnO_2$ Junction constructed on Au Substrate

Within these experiments, the synthesis of oxide materials in the form of powders, both n-type and p-type, was pursued using various synthesis methods such as sol-gel and sonochemical techniques. Additionally, pastes were prepared for the deposition of thin films with the purpose of integrating these materials into heterojunction devices. Furthermore, both the obtained powders and the deposited layers were characterized from a physico-chemical standpoint.

To create the heterojunction device, deposition techniques such as "magnetron sputtering" (for the Au layer), "Doctor-Blade" (for the TiO_2 layer), and "spin-coating" (for the $CuMnO_2$ layer) were employed. These methods were chosen to facilitate the construction and testing of the obtained heterojunctions, as depicted in Figure 8.

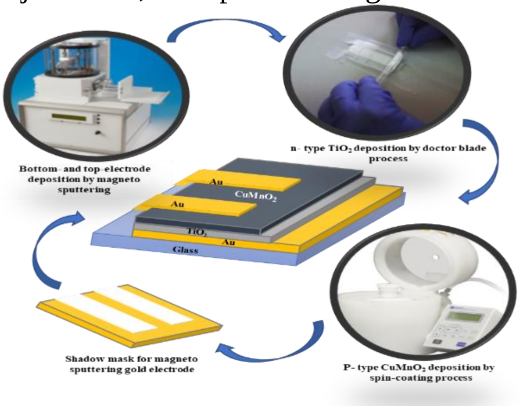

Figure 8. Schematic diagram of the deposition processes for making the heterojunction device

The obtained results demonstrate the potential and opportunities offered by the n-TiO_2/p-$CuMnO_2$ heterojunction, which serves as a significant platform for the development of new devices for the detection of UV radiation or targeted gases. The n-TiO_2 and p-$CuMnO_2$ materials synthesized through sol-gel methods and ultrasound-assisted co-precipitation were used to develop and test an n-p heterojunction for the first time using these materials.

The structural and morphological characteristics of both oxide powders and $CuMnO_2$ and TiO_2 films used for the development of heterojunction modules were investigated using XRD and SEM/EDX techniques. These investigations confirmed the phase stability, material purity, and layer uniformity after the performed heat treatments.

The oxide semiconductor layers were electrochemically investigated using Mott-Schottky measurements. Through these measurements, the electrochemical functionality of the heterojunctions was demonstrated for the first time by analyzing the Mott-Schottky directly on the formed n-TiO_2/p-$CuMnO_2$ heterostructure. Additionally, results such as the flat-band potential V_{FB} for TiO_2 (-0.28 V vs. NHE) and $CuMnO_2$ (0.98 V vs. NHE), the type of conductivity (n-type for TiO_2 and p-type for $CuMnO_2$), and the carrier concentration for both materials were obtained, calculated as 2.19 x 10^{18} cm^{-3} for the TiO_2 film and 1.74 x 10^{18} cm^{-3} for $CuMnO_2$.

Electrical parameters such as the ideality factor and reverse saturation current of the junction were also extracted using the theory of thermionic emission from current-voltage (I-V) measurements. The reverse saturation current and ideality factor for this junction at room temperature were obtained as 8.30 and 4.1 nA, respectively. The current-voltage measurement confirms the formation of the junction between n-TiO_2 and p-$CuMnO_2$, with a low turn-on voltage of 0.72 V (Figure 9). Furthermore, a decrease in resistivity with increasing temperature was observed for the Au/n-TiO_2/p-$CuMnO_2$ heterostructure compared to Au/TiO_2, which is generated by the interface mechanisms of the formed n-p heterojunctions. [9]

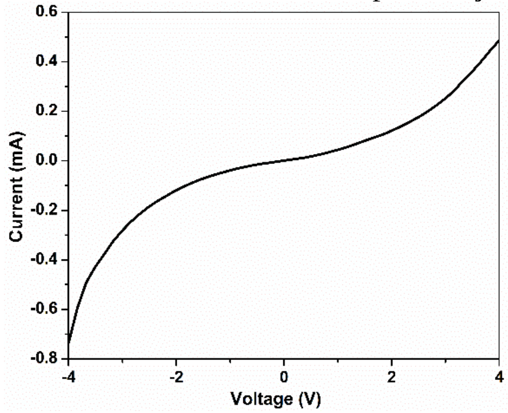

Figure 9. I-V Curve of the Au/n-TiO_2/p-$CuMnO_2$ Oxide Junction

Development of self-powered sensors based on the n-TiO_2/p-$CuMnO_2$ heterojunction on an FTO glass substrate.

By using a layer-by-layer technique and coating methods like "Dr. Blade" and "spin coating" (see Figure 8), a successful fabrication of a self-powered n-TiO_2/p-$CuMnO_2$ heterojunction photodetector was achieved for the first time. The device was built on a conductive glass substrate known as FTO (fluorine-doped tin oxide).

The structural and morphological characteristics of the FTO/n-TiO_2/p-$CuMnO_2$ heterostructures confirmed the stability and purity of the phases, as well as the uniform and crack-free coverage of the thin and transparent layers.

To confirm the transparency feature of the oxide heterojunction-based devices, UV-VIS spectroscopy analysis was performed for FTO-TiO_2 and FTO-TiO_2-$CuMnO_2$ (see Figure 10). The UV-VIS spectra indicate the transparency of the devices in the visible light region. The average light transparency in the visible region is 60%, with a 10% decrease compared to FTO-TiO_2, which is caused by the increased total thickness of the layers.

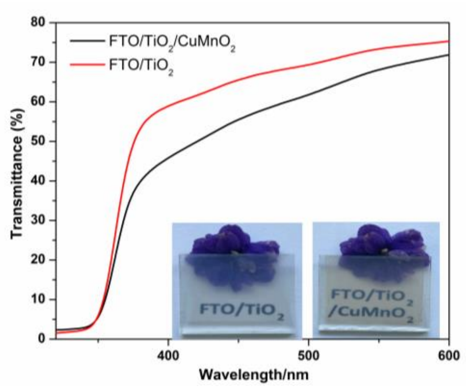

Figure 10. Transmission spectra with inset macroscopic images of FTO-TiO_2 and FTO-TiO_2-$CuMnO_2$ transparent devices

Through the I-V analysis presented in Figure 11a in the range of -1V to +1V, conducted in both dark conditions and under UV illumination, we observe an increase in current in the forward bias when the device is illuminated with UV radiation, from 196 nA (dark state) to 283 nA (UV illumination state). Additionally, under UV illumination, we can observe a significant reduction in the turn-on voltage, from 0.43 V in the dark state to 0.24 V. These results confirm that the heterojunction, under UV illumination, has lower power consumption, indicating a more efficient behavior of the device.

To evaluate the photodetector characteristics in both self-powered and externally powered modes at 1V, current-time (I-T) measurements of photocurrent were conducted in dark conditions and under UV illumination. Figure 11b presents the I-T measurements in the self-powered mode. It was demonstrated that the n-p junction-based device operates without the need for an external voltage. The device exhibits an excellent on/off ratio at 0 V bias, approximately 48.3, much higher than the one obtained at 1 V bias, which is approximately 1.4. Moreover, good values of UV light response were obtained in both operating modes. Although the response and recovery times are relatively slower for both modes, due to the reduced mobility of photogenerated holes in the n-p depletion layer, when a 0 V bias is applied, these times improve and become faster. All the results obtained indicate that the transparent n-TiO_2/p-$CuMnO_2$ heterojunction-based device functions as a self-powered ultraviolet photodetector with high sensitivity. [10]

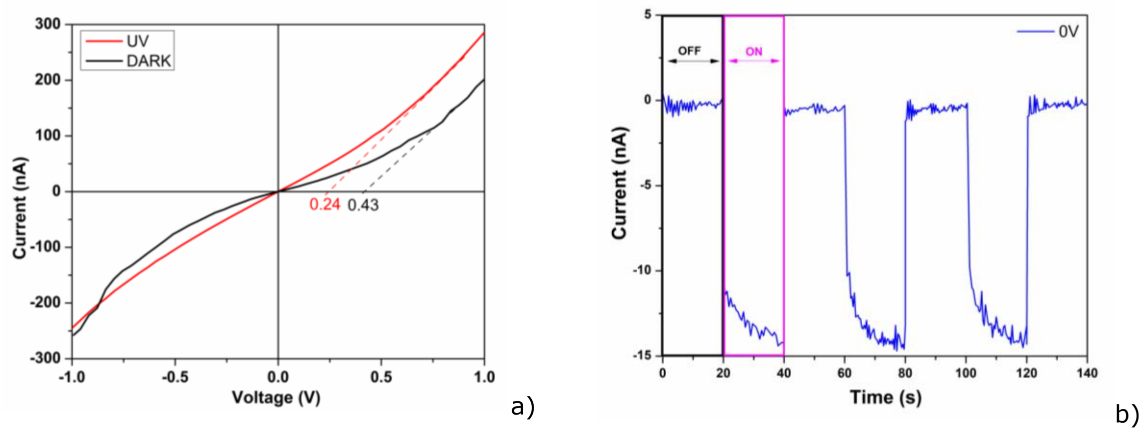

Figure 11. Detection characteristics of the heterojunction sensor: a) IV curve; b) Self-powered I-T analysis

Development of sensors based on n-TiO_2/p-$CuMnO_2$ heterojunction constructed on Ti substrate

The UV photodetectors based on the n-TiO_2/p-$CuMnO_2$ oxide heterojunctions were successfully obtained through two simple and cost-effective steps. In the first step, the TiO_2 layers were grown on a Ti foil through thermal oxidation (Ti-TiO_2), and then the $CuMnO_2$ layers were deposited onto the TiO_2 layers' surface using the Doctor Blade method. Additionally, in this subsection, changes in the detection performance were observed based on the chemical corrosion time of the Ti plates before the oxidation process. The plates were immersed in an aqueous solution with a molarity of 0.5M, hydrofluoric acid (HF) at immersion times ranging from 1 to 3 hours.

Structural analyses confirmed the purity and stability of the materials, and morphological analyses showed the growth and orientation of the TiO_2 layers. Figure 12 presents the morphological characteristics of the Ti/TiO_2 and Ti/TiO_2/$CuMnO_2$ heterostructures at a holding time of 2 hours. The TiO_2 layers were grown in the form of polyhedra with curved surfaces, resembling the appearance of a broken stone, and the $CuMnO_2$ layer covered the entire surface of the TiO_2 layer, following the polyhedral shape. This morphology allows for a larger surface area light absorption due to the surface scattering phenomenon.

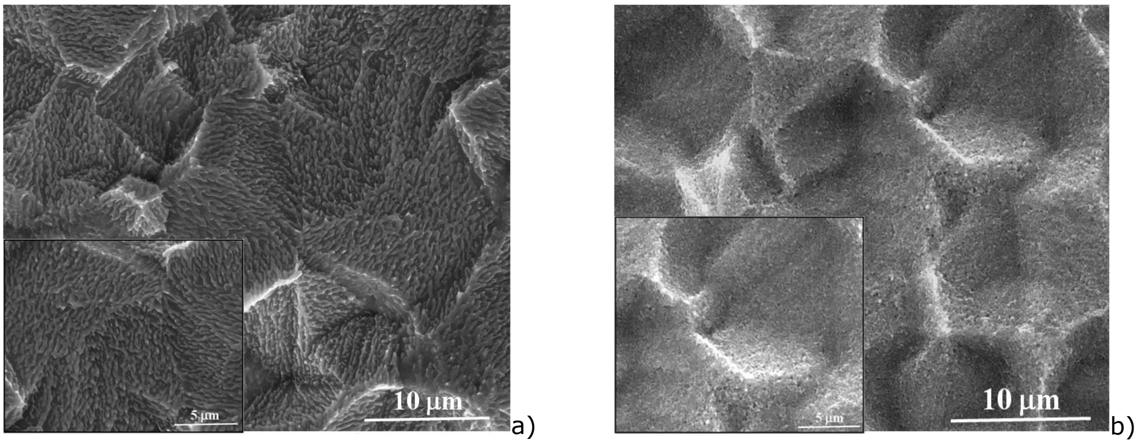

Figure 12. SEM images of the heterostructures obtained after 2 hours of immersion: a) Ti-TiO_2; b) Ti-TiO_2-$CuMnO_2$

The current-voltage (I-V) properties of the n-p oxide heterojunctions were investigated at room temperature under dark conditions, visible light illumination, and UV illumination, and the results are presented in Figure 13a for the heterojunction sensor obtained through immersion for 2 hours. The n-TiO_2/p-$CuMnO_2$ heterojunction exhibits rectifying behavior in all three tested cases, both in the dark and under UV illumination. Furthermore, all current-voltage measurements conducted in the range of -2 to +2 V showed increased current and reduced turn-on voltage under UV illumination compared to dark conditions. This phenomenon can be attributed to an increase in the concentration of charge carriers as a result of UV excitation.

To evaluate the photodetector characteristics when powered at 2V, current-time (I-T) measurements of the photocurrent were performed under dark conditions and under UV and visible (Vis) illumination (Figure 13b). It was demonstrated that the response time of the heterostructured sensor to UV illumination varies linearly with the corrosion time, but the sensor immersed for 2 hours exhibits maximum sensitivity and selectivity. The number in the code of the developed heterojunction sensors represents the immersion time in the solution. Additionally, it can be observed in Figure 13a that the sensors have demonstrated their potential as selective UV photodetectors with good rejection of visible light.

By correlating the electrical analyses with morpho-structural and electrochemical analysis, a dependence on the voltage of the Ti-TiO_2 layer structure and a direct correlation between sensitivity to UV illumination and the measured "flat band" band values were presented. [11]

This novel approach provides a simple and promising method for the development of efficient UV sensors. This research has opened up new directions for future research in the field of using metal substrates for depositing metal oxides in combination with another oxide for the development of heterojunction sensors for detecting target gases.

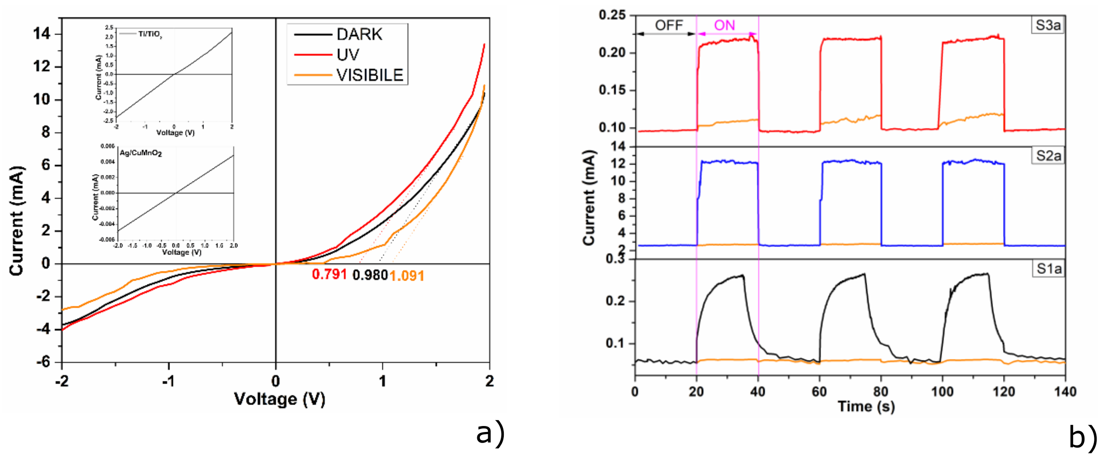

Figure 13. Characteristics of the heterojunction sensor: a) IV curve; b) I-T analysis for UV radiation detection in the experimental program

Development of sensors based on n-ZnO and p-$CuMnO_2$ heterojunctions constructed on a Zn substrate

In this subsection, gas sensors for CO_2 detection in gas form were successfully obtained by growing ZnO nanowires (NW) layers through thermal oxidation of a Zn foil, followed by depositing $CuMnO_2$ layers on the surface of Zn-ZnO(NW) heterostructures using the "spin-coating" process (as shown in Figure 8). After the deposition of the $CuMnO_2$ layer, the heterojunction sensors are referred to as $ZnO_{NW@}CMO$. Additionally, in this subsection, changes in gas detection were monitored based on thermal oxidation parameters for obtaining ZnO nanowires (holding time and oxidation temperature).

The structural, morphological, and electrical properties of the Zn-ZnO(NW) and $ZnO_{NW@}CMO$ structures were investigated. X-ray analysis identified the hexagonal structure of zinc oxide and specific peaks for $CuMnO_2$. SEM morphology revealed the gradual transition from ZnO nanoparticles to ZnO nanowires on the surface of the Zn foil, depending on the time and temperature. Additionally, different coverage of the $CuMnO_2$ layer on the Zn-ZnO(NW) structures was observed due to the density and random growth of ZnO nanowires. At a treatment temperature of 350 °C, the nanowires were completely covered. This incomplete coverage can enhance the detection properties due to the higher specific surface area and the operation of the heterojunction as both n-p and p-n depending on the oxide in contact with the gas. Figure 14 presents SEM morphological analyses for samples oxidized at a temperature of 400°C for 6 hours.

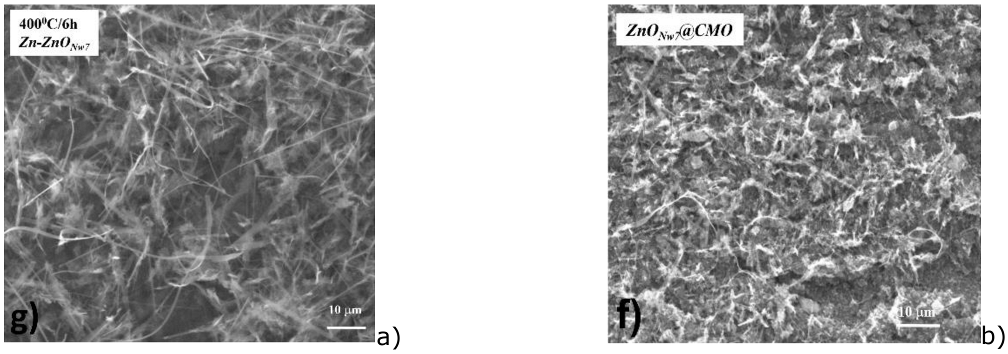

Figure 14. SEM images of the samples from the experimental program, samples oxidized at 400°C for 6 h: a) Zn-ZnO(NW); b) Zn-ZnO@CuMnO2

The I-V measurements of the heterojunctions indicated a correlation between ideality factors, reverse saturation current, and the thermal oxidation process parameters of the Zn foil.

To evaluate the gaseous CO_2 detection characteristics of the heterojunction sensor, I-T measurements were conducted at different holding temperatures ranging from 25 to 200°C and at a CO_2 concentration of 400 ppm in the carrier gas.

Figure 15a represents the correlation between the testing temperature and the responses of the $ZnO_{Nw@}CMO$ sensors, where the ZnO nanowires were grown at 350°C. The graph reveals that at temperatures below 100°C, the sensor response is very low, significantly lower than at higher temperatures. As the testing temperature increases, the sensor response increases rapidly. The maximum response values are achieved at 200°C for all tested sensors. In particular, the $ZnO_{Nw3@}CMO$ sensor exhibits a high response at temperatures below 150°C, with the highest response recorded at approximately 77.5%. This indicates a dependency between the operating parameters and the testing temperature at a concentration of 400 PPM CO_2.

Figure 15b shows the sensor response as a function of the testing temperature based on the heterojunction where the nanowires were grown at 400°C. It can be observed that the response is reduced at temperatures below 100°C, with all tested sensors showing response values of approximately 17%. For the $ZnO_{Nw5@}CMO$ sensor, the maximum response value is reached at 150°C, after which the response decreases. In contrast, for the $ZnO_{Nw6@}CMO$ and $ZnO_{Nw7@}CMO$ sensors, the maximum response values are recorded at 200°C, and these values increase linearly with the testing temperature. The maximum response is obtained for the $ZnO_{Nw7@}CMO$ sensor, with a value of approximately 95.4%, suggesting that a high surface-to-volume ratio of ZnO(NW) nanowires enhances the sensor response values. [12]

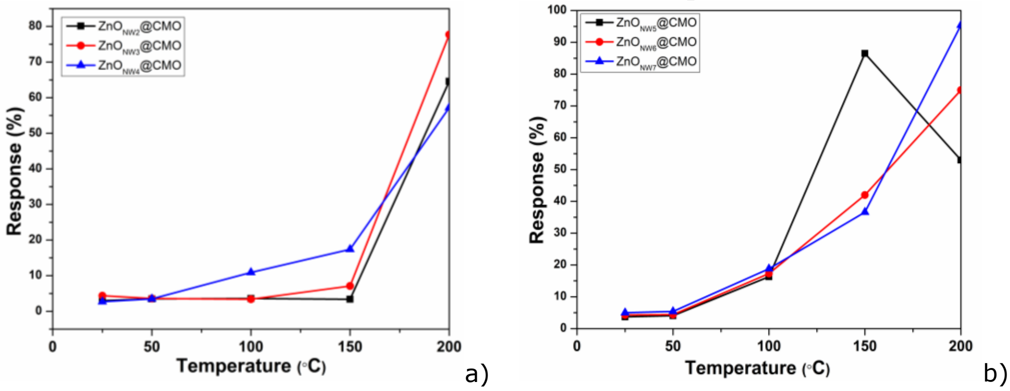

Figure 15. Characteristics of the heterojunction sensor: a) ZnO(NW) obtained at 350°C; b) ZnO(NW) obtained at 400°C

The development of flexible sensors based on n-Fe_2O_3/p-$CuMnO_2$ heterojunctions constructed on amorphous Fe-based alloy substrate.

In this research, the use of metallic ribbons with amorphous structure as a flexible substrate for heterostructured gas sensors was presented. An easy and cost-effective method for obtaining porous iron oxide (Fe_2O_3) particles on the surface of these bands was described using a chemical oxidation process. The p-type semiconductor layer of $CuMnO_2$ was deposited on the surface of the Fe-Fe_2O_3 heterostructures through the "Doctor Blade" process (shown in Figure 8).

XRD structural analyses confirmed the formation of hexagonal Fe_2O_3 oxide on the surface of the amorphous bands, crystallized as a result of the chemical oxidation of the amorphous bands. SEM morphological analyses show that the chemical oxidation process on the surface of the bands leads to the formation of oxide structures in the shape of "hollow" oxide spheres, similar to a tangled ball of thread. After the deposition of the $CuMnO_2$ layer, it can be observed that the "p"-type semiconductor particles surround the "n"-type particles, thus forming a heterostructural arrangement. Figure 16 presents SEM images of the surfaces of the Fe-Fe_2O_3 and Fe-Fe_2O_3/$CuMnO_2$ heterostructures.

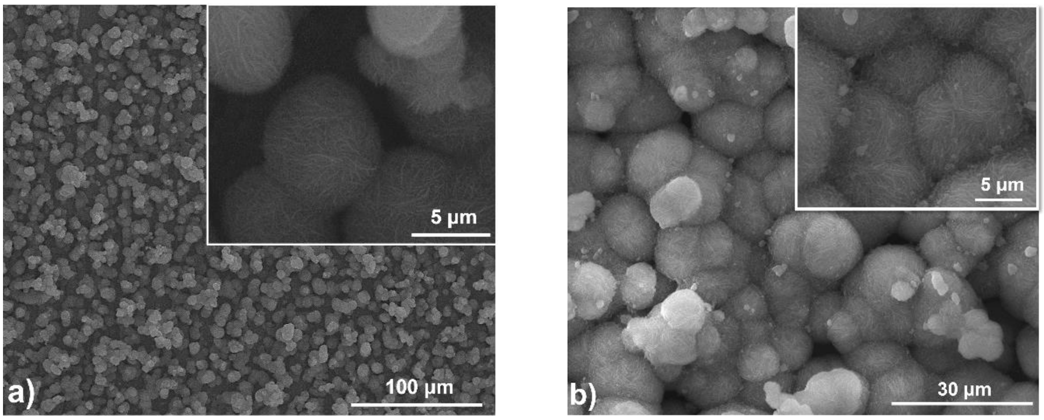

Figure 16. SEM morphologies of flexible ribbons decorated with oxide nanoparticles: a) Hexagonal Fe_2O_3 oxide; b) $CuMnO_2$ layer deposited over the grown Fe_2O_3 layer

Additionally, the oxide semiconductor layers were electrochemically investigated using Mott-Schottky measurements. In this case, for the electrode decorated with Fe_2O_3 particles, which is the novelty in this subsection, the positive slope of the line suggests n-type conductivity of the synthesized material. The flat-band potential V_{FB} for Fe_2O_3 oxide was determined to be 0.59 V vs. NHE, and the carrier concentration was determined to be 4.16×10^{17} cm^{-3}.

I-V measurements confirm the formation of n-Fe_2O_3/p-$CuMnO_2$ heterojunctions with a low turn-on voltage of 0.816 V (Figure 17a).

Figure 17b provides a graphical illustration of the testing temperature and the response of the flexible heterojunctional sensor tested at a concentration of 400 ppm CO_2 in the carrier gas.

The graph shows a correlation between increased sensitivity and testing temperature. Sensors constructed using Fe_2O_3 oxide semiconductors exhibit high sensitivity at high temperatures, around 400°C. By using the n/p-type oxide heterojunction, sensors were successfully developed to provide a response at lower temperatures, down to 200°C. Figure 17b shows that the sensor response increases exponentially from 100°C, with the maximum detection recorded at a temperature of approximately 200°C, reaching around 30%. Due to technological limitations and the possibility of the $CuMnO_2$ compound changing its structure from crednerite to spinel, tests were not conducted at temperatures higher than 200°C.

These promising results provide a solid foundation for further research to improve the performance of heterostructured gas sensors and their practical applications. These devices can contribute to the development of advanced gas monitoring systems, with the potential to bring significant benefits in areas such as security, the environment, and health.

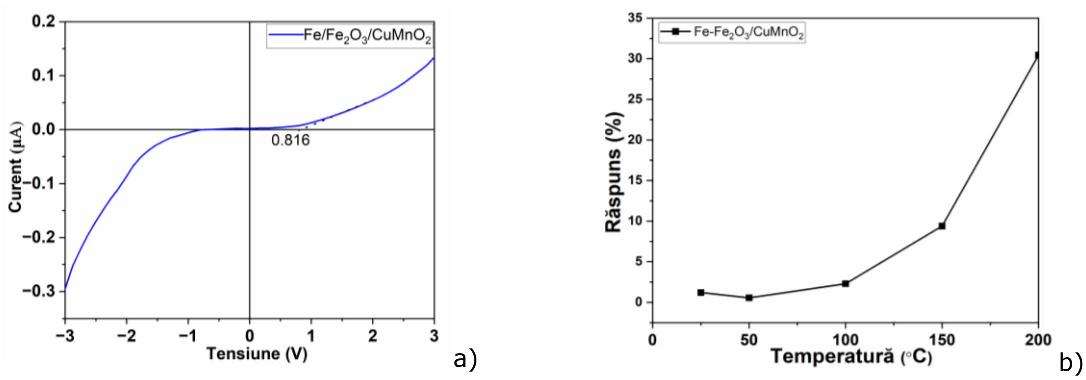

Figure 17. Characteristics of the heterojunction sensor: a) IV curve; b) I-T analysis for CO_2 detection as a function of temperature

Development of oxide materials and/or nanoporous materials obtained through dealloying and thermal oxidation of amorphous CuZrAl alloy ribbons

In this subsection, research on the potential applications of amorphous alloys fabricated in the form of micrometer-thick strips is presented. Using the processes of dealloying and/or thermal oxidation on amorphous CuZrAl-based alloy ribbons, highly usable oxide and/or nanoporous materials have been produced for sensor applications.

The thermal oxidation of amorphous ribbons allows for the creation of heterostructured metal oxides with low production costs, avoiding the use of hazardous chemicals and the production of polluting by-products such as exhaust gases and chemical pollutants. This approach can be extended to other amorphous metal alloys to synthesize nanostructured mixed oxides. The absorption spectra of the mixed Cu-Zr oxide samples treated at different temperatures show an absorption band at 217 nm and intense absorption characteristics in the 320-500 nm region, suggesting possible improved photocatalytic activity and an extension of the absorption wavelength from UV to the visible light region. [13]

By using a relatively simple method, the process of chemical dealloying in a 0.5 M HF aqueous solution has successfully produced nanoporous copper decorated with Cu_2O nanocubes and silver nanoparticles. In the study conducted, nanoporous structures with pore sizes ranging from 50 to 500 nm were synthesized for the $Cu_{48}Zr_{47}Al_5$ alloy and between 10 and 500 nm for the $Cu_{45}Zr_{45}Al_5Ag_5$ alloy. With a high Ag content, the $Cu_{40}Zr_{45}Al_5Ag_{10}$ alloy does not form an interconnected pore network but results in craters with sizes ranging from 50 nm to 3 μm. The formation of copper oxide nanocubes during the dealloying process has a positive impact on electrochemical applications due to their semiconductor properties. The addition of Ag to the alloy leads to a linear evolution of the Cu crystallite size, and the increase in the size of Cu crystallites in the $Cu_{45}Zr_{45}Al_5Ag_5$ alloy can lead to a reduction in the space between pores and, consequently, a decrease in the overall pore size. [14]

Dealloying and thermal oxidation of amorphous strips are interesting approaches for obtaining 3D networks of CuO nanoparticles (NP-CuO) with varied morphologies and low production costs. The absorption spectra of NP-CuO samples show a broad absorption band in the 350-800 nm region and a high surface-to-volume ratio, which can lead to improved photocatalytic activity for environmental remediation. NP-CuO could be used as an ideal collector of solar radiation due to its extended absorption spectra. Additionally, by extending the holding time to 24 hours, one-dimensional nanowires are successfully synthesized on the surface of NP-CuO. An important aspect of these experiments is the reporting of a high bandgap energy value in the range of 3.30 eV to 3.68 eV for CuO nanoparticles obtained through dealloying and thermal oxidation of amorphous ribbons, representing a novel achievement.

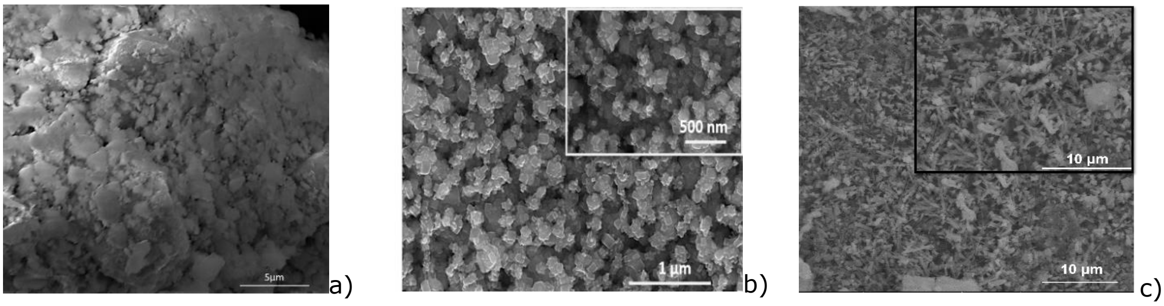

Figure 18. SEM Morphology of Synthesized Oxide Materials: a) Cu-Zr mixed oxide obtained by thermal oxidation; b) Cu_2O nanocubes on NPC substrate synthesized by dealloying process; c) CuO nanowires obtained by dealloying and oxidation

The results obtained highlight the possibility of using amorphous metal alloys, in this case, those from the Cu-Zr-Al family, for the production of oxide and/or nanoporous materials for sensor applications. The viability and ease of obtaining these materials are emphasized. The integration of these materials into sensor modules represents a developing application that will be further explored in ongoing doctoral scientific research.

CHAPTER 4. GENERAL CONCLUSIONS AND FUTURE RESEARCH DIRECTIONS

General conclusion

The research conducted in this thesis focuses on identifying and developing nanotechnological processes necessary for efficiently depositing, growing, and processing nanostructured materials based on TiO_2, ZnO, Fe_2O_3, $CuMnO_2$, and NPC, NPC/oxide. The main goal is to obtain materials with morpho-structural, optical, and electrical properties that can be integrated into oxide heterojunction-based detection devices of the n/p type.

In this context, structural investigations and physico-chemical analyses were carried out to characterize the oxide semiconductor layers, both before and after processing. The mechanisms at the interfaces allowing the operation of these heterojunction devices in the detection of CO_2 and UV radiation were identified and understood.

Based on the results obtained, it can be concluded that a series of oxide heterojunctions - some unprecedented in the specialized literature - have been realized with significant potential for their use in the field of sensor technology.

Thus:

- A n-TiO_2/p-$CuMnO_2$ heterojunction was successfully obtained and characterized for the first time, using a gold conductor substrate, highlighting the potential and opportunities offered by this heterojunction for future research.
- For the first time, a self-powered and transparent photodetector was developed using n-TiO_2/p-$CuMnO_2$ heterojunctions on an FTO substrate for UV sensor development.
- For the first time, a UV photodetector was obtained using n-TiO_2/p-$CuMnO_2$ heterojunctions on a titanium substrate.
- A CO_2 sensor was created using n-ZnO/p-$CuMnO_2$ heterojunctions on a Zn substrate.
- A flexible CO_2 sensor was developed using n-Fe_2O_3/p-$CuMnO_2$ heterojunctions on an

amorphous metal alloy substrate.

Additionally, significant contributions were made, including the production of oxide and/or nanoporous materials obtained from the chemical etching and thermal oxidation of amorphous CuZrAl-based alloy ribbons and the use of thermal and chemical oxidation processes of metallic ribbons in optimizing sensor construction.

The conclusions presented have demonstrated that this field is current and of interest, with n-p oxide heterojunction-based environmental monitoring sensors being successfully applicable in various detection and monitoring applications due to their low production cost and high energy-efficient production efficiency.

Future Research Directions

The studies and experiments conducted have led to the identification of new research directions in this field, including:

- Integration of the developed oxide heterostructured materials from this thesis into electrochemical applications, such as electrochemical sensors and supercapacitors.
- Exploration of integrating the sensors developed in this thesis into devices that can function both as sensors and as energy storage elements, contributing to the development of self-sustaining and/or self-powering gas sensors.

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