



**MINISTRY OF EDUCATION  
AND  
RESEARCH**

**National University of Science and Technology  
POLITEHNICA Bucharest**

Blvd. Splaiul Independenței, nr. 313, sector 6, Bucharest  
**DOCTORAL SCHOOL MATERIALS SCIENCE AND  
ENGINEERING**

---



# **SUMMARY**

**of the doctoral thesis**

## **RESEARCH ON NANOSTRUCTURED OXIDE MATERIALS TO INCREASE THE PERFORMANCE OF PHOTOVOLTAIC CELLS**

**Scientific Coordinators**

Prof.univ.dr.Habil. Adriana-Gabriela ȘCHIOPU

Prof.univ.dr. Mohammed SALLAH

**Academic Guidance and Integrity Team**

Assoc. Prof. dr. Habil. Mihai OPROESCU

Assoc. Prof. dr. Cătălin DUCU

Assoc. Prof. dr. Ovidiu Constantin NOVAC

Drd. Valentin Marian CĂLINESCU

2025

## INTRODUCTION

The doctoral thesis is structured in 8 chapters:

**Chapter 1 – Introduction** highlights the strategic importance of solar energy in the global energy transition, due to its inexhaustible resources and low environmental impact. International and national trends to increase solar PV capacity, the role of nanomaterials in improving energy efficiency, and the continued need for innovation are presented. Solar energy, complemented by advanced nanotechnologies, represents a major solution for sustainability, requiring the integration of new materials to optimize photovoltaic performance.

**Chapter 2 – Working Hypothesis and General Objectives** proposes the use of additional nanostructured layers of metal oxides (MgO, ZnO) to reduce recombination losses and improve energy conversion. The objectives of the research include the elaboration of these layers, their characterization, the correlation of deposition parameters with energy efficiency and the realization of a complete test system. The chapter includes:

- Definition of the working hypothesis: reduction of energy losses by applying nanostructured oxide layers.
- Formulation of general objectives: synthesis and characterization of MgO and ZnO, development of a hardware-software test system and correlation of layers with energy yield.
- Presentation of a phased research delivery plan, including the Gantt chart.
- The implementation of oxide nanomaterials can increase the efficiency of solar cells, and a rigorous experimental methodology is essential for validating this hypothesis.

**Chapter 4 – General research methodology** details the experimental procedures:

- Preparation of solar cells.
- Selection and characterization of metal oxides (MgO and ZnO).
- Layer deposition using the spin-coating technique.
- Making and using solar emulators for testing.
- Development of a hardware-software measurement system for testing in laboratory and real conditions.

**Chapter 3 – Materials used in the manufacture of photovoltaic cells** analyzes the main photovoltaic cell technologies: monocrystalline/polycrystalline silicon, PERC, CIGS, CZTS, CdTe, DSSC. For each technology there are **advantages (efficiency, cost, flexibility) and limitations (cost, toxicity, instability)**. A detailed analysis of the materials used for various types of photovoltaic cells is also made: Monocrystalline/polycrystalline Si, PERC, CIGS, CZTS, CdTe, DSSC. The advantages, limitations and prospects of each technology are compared. Diversification of technologies is necessary, there is no universally ideal technology.

**Chapter 4 – General research methodology**, details the experimental procedures:

- Preparation of solar cells.
- Selection and characterization of metal oxides (MgO and ZnO).
- Layer deposition using the spin-coating technique.
- Making and using solar emulators for testing.
- Development of a hardware-software measurement system for testing in laboratory and real conditions.

Experimental protocols are developed for cell preparation, elaboration of oxide layers by spin-coating, advanced characterization (XRD, SEM, FTIR, UV-Vis) and performance testing by hardware systems. The methodology combines modern synthesis and characterization techniques, ensuring a rigorous assessment of the impact of nanolayers on solar cell performance.

**Chapter 5 – Contributions on the development and characterization of precursor metal oxides** presents the Structural and Morphological Characterization of MgO and ZnO, pure and Al-doped powders. XRD, SEM, EDS analysis and BET measurements for the determination of crystallite size and specific surface area complete the structural and morphological characterization. MgO and ZnO in the form of micro and nanoparticles are suitable for use in functional layers for photovoltaic cells. High-quality precursors (nano-MgO and nano-ZnO) obtained hydrothermally and by concentrating solar energy, provide the necessary material base for optimizing the surface layer of solar cells.

**Chapter 6 – Contributions regarding the elaboration and characterization of additional metal oxide layers.** The additional layers of MgO and ZnO were deposited by spin-coating and advanced characterization. The existence of a homogeneous morphology, with nanometric particles, and a good

integration on the surface of the cells was demonstrated. Compositional and structural analysis was performed by ATR-FTIR and UV-Vis spectroscopy.

Morphological characterization by SEM of different layer/surface combinations was performed to evaluate the uniformity and morphology of the deposits.

**Chapter 7 – Contributions on Testing the Energy Efficiency of Photovoltaic Cells** presents the testing of cells with additional oxide layers under laboratory conditions using solar emulators and in real lighting conditions.

Comparative analysis between the energy efficiencies of the starts submitted at different parameters. Tests have shown that the application of additional layers of MgO and ZnO results in an increase in energy efficiency of between 3% and 9% under laboratory and real conditions. Improvements in stability in bright lighting have also been observed. At the same time, further studies were carried out on the influence of particle synthesis, size and shape on performance.

In order to demonstrate the efficiency of the cell with additional start submitted, a technical-economic analysis of a residential photovoltaic system based on these cells was performed. The application of nanostructured oxide layers significantly optimizes the energy performance of photovoltaic cells, validating the working hypothesis and opening perspectives for industrial applications.

**The thesis** demonstrates that the integration of nanostructured oxide layers (MgO, ZnO) on photovoltaic cells based on polycrystalline silicon contributes decisively to improving the efficiency of converting sunlight into electricity. The experimental results validate the working hypothesis and provide an applied research direction for the development of new generations of high-performance and sustainable solar panels.

### **The impact of the results of the doctoral thesis highlighting the multi and inter-disciplinary character with the limits of the research carried out**

The research carried out within the doctoral thesis "*Research on nanostructured oxide materials to increase the performance of photovoltaic cells*" demonstrates a strong interdisciplinary character, at the intersection of two major areas of research and application: Materials Engineering and Electronic Engineering, Telecommunications and Information Technology.

#### **1. Contribution of materials engineering**

- **The development and characterization of nanostructured oxide layers** (MgO and ZnO) requires advanced expertise in materials synthesis, materials chemistry, as well as in spin-coating, hydrothermal synthesis and concentrated solar energy synthesis manufacturing processes.
- **The structural, compositional and morphological characterization** by XRD, SEM, EDS, FTIR, UV-Vis, BET methods uses analysis methods specific to modern materials engineering, essential for validating the physicochemical properties of the layers.
- **Optimization of active surfaces** and control of oxide layer microstructure to improve the energy performance of cells are fundamental activities in the field of advanced functional materials.

#### **2. Contribution of Electronic Engineering, Telecommunications and Information Technology**

- **The development of a hardware-software acquisition and control system** for testing photovoltaic cells in real time, using NI-USB 6211 acquisition boards and software applications developed in Python, belongs to the ETTI domain.
- **The design of solar emulators** and controlled electronic loads for measuring I–V and P–V curves require advanced knowledge of power electronics, instrumentation, and automation.
- **The acquisition, processing and analysis of experimental data** using modern computer techniques (statistical analysis, modeling, automatic graph generation) integrates information technology in the evaluation of the energy performance of the tested materials.

#### **3. Synergy between areas**

- **Materials Engineering** provides **the physical solution** by developing and characterizing optimized nanostructured oxide layers, while **Electronic, Telecommunications and**

**Information Technology Engineering** provides **the testing, measurement and analysis tools** that functionally validate the performance of these materials.

- The integration of the two areas allowed not only the passive testing of materials, but also their **active functional evaluation** under simulated and real conditions of use, in a holistic approach, oriented towards industrial applications.
- This complementarity between **material knowledge** and **the development of electronic assessment systems** is essential for the advancement of modern photovoltaic technologies and their adaptation to the complex requirements of the energy market.
- By combining expertise in advanced materials with modern electronics and information technology techniques, the research demonstrates a genuine interdisciplinary character. Thus, the use of ZnO and MgO helps to increase the performance of photovoltaic cells by maximizing light capture. By improving surface passivation, nano-ZnO and nano-MgO contribute to reducing energy losses and increasing the efficiency of photovoltaic cells. This not only validates the scientific results obtained, but also opens up concrete perspectives for **industrial applications, technology transfer** and **innovative product development** in the field of renewable energy materials.

*The working hypothesis* is thus constituted on the reduction of energy losses at the surface by developing an additional layer of nanostructured metal oxide on the anti-reflective layer of the photovoltaic cell based on polycrystalline Si in order to **additional passivation and protection**.

The **additional passivation** consists of:

- ✓ **Surface passivation:** Metal oxides help reduce **the recombination of charge carriers** (electrons and voids). This is a significant improvement in **conversion efficiency**. Without passivation, the efficiency of photovoltaic cells would be much lower, as many electrons and voids would recombine before they reach electrical contacts.
- ✓ **Improved fill factor (FF):** Passivation reduces **recombination losses**, which contributes to an **improvement in fill factor (FF)**, an essential parameter for solar cell performance.
- ✓ **Protection against degradation:** The metal oxide layer can **protect the silicon layer** from moisture and external contamination, preventing **oxidation** and other forms of long-term degradation.

The combination of Si<sub>3</sub>N<sub>4</sub> (anti-reflective coating) with a metal oxide layer for passivation has multiple advantages:

- Improved efficiency: Combining the two layers helps maximize light absorption and reduce recombination losses.
- Increased durability: Protects the cell against environmental factors and contributes to long-term stability.
- Improved low-light performance: The anti-glare and passivation coating allow the cells to perform better in diffuse lighting conditions.

The deposition of a metal oxide layer on the anti-reflective layer of silicon nitride (Si<sub>3</sub>N<sub>4</sub>) is aimed at improving the performance of silicon photovoltaic cells. It combines surface passivation with reduced optical and electrical losses, significantly contributing to increasing the conversion efficiency of solar cells. Also, this type of additional layer adds protection against long-term degradation, ensuring a more stable performance under real use conditions.

## General objectives

Within **photovoltaic (CF) cell research**, an important goal is to improve energy efficiency by implementing metal oxide layers. These layers are essential for improving light absorption and surface passivation with reduced optical and electrical losses, significantly contributing to increasing the conversion efficiency of solar cells. In this context, four main objectives (O1 - O4) are proposed aimed at developing, characterizing and optimizing these layers, as well as developing a system for monitoring the performance of photovoltaic cells.

### **O1: Elaboration and characterization of nanostructured layers**

The first objective focuses on the elaboration and characterization of nanostructured layers of pure and doped MgO and ZnO, using spin-coating technology. This is a method of controlled deposition of materials in

the form of thin films on commercial photovoltaic cell substrates, which allows to obtain uniform layers with nanostructure dimensions (pure or doped zinc oxide) by centrifugation in the *Research Laboratory* of Nanomaterials, Biomaterials and Advanced Functional Materials/NanoBioMat, within the Faculty of Mechanics and Technology and in the *CRC&D-Auto* center from the Pitesti University Center.

### **O2: Design and development of a hardware & software system for parameter control**

The second objective (**O2**) focuses on the design and development of a hardware and software system for monitoring and controlling the operating parameters of photovoltaic cells. The system includes:

- ✓ a data acquisition system for measuring the electrical parameters of the CF, such as no-load voltage, on-load voltage, and short-circuit current.
- ✓ Software application for the analysis of the fusion of data from ambient parameters (temperature, lighting) and functional parameters of photovoltaic cells. It will allow real-time monitoring of the performance of the cells and their adjustment according to external conditions.

This component is implemented within the Power Electronics and Microcontroller Systems Laboratories within the Faculty of Electronics, Communications and Computers and in NanoBioMat.

### **O3: Correlation of nanostructured layers with the energy yield of CF**

The O3 objective aims to correlate the development parameters of nanostructured layers (layer thickness, material type, etc.) with the energy efficiency of photovoltaic cells. This will include studying the effect of nanostructures on conversion efficiency, by testing photovoltaic cells under different operating conditions (variable lighting, temperature, dynamic electric load). The information obtained will allow the optimization of the elaboration parameters in order to maximize energy performance.

The last objective (**O4**) focuses on finalizing an experimental model for the construction of an energy-efficient photovoltaic cell. This model will include:

- Development of effective nanostructured layers to maximize light absorption through additional passivation.
- Monitoring and control of the electrical parameters of the photovoltaic cell, with the aim of improving its overall performance and stability.

The implementation of this model will provide a functional prototype that can be tested under different conditions, to validate the impact of nanostructures on energy performance. The achievement of these objectives also leads to the dissemination of research results through the publication of articles in journals or conferences with ISI indexed volumes.

**The novelty of the research** consists in:

- ✓ Identification and implementation of technologies for obtaining photovoltaic structures with active surfaces increased by the effect of nanostructures, which allows optimizing the performance of photovoltaic cells.
- ✓ Improving efficiency by optimizing the thickness of nanostructured layers and adapting them to various environmental conditions and energy requirements.
- ✓ Interdisciplinary characterization of photovoltaic layers, specific to the fields of **Materials Engineering and Electronic Engineering, Telecommunications and Information Technologies**, in order to obtain a high-performance and energy-efficient final product.

## **Specific objectives**

The stages and activities specific to doctoral research, in correlation with the deliverables associated with each activity are presented in the table below.

*Stages and activities specific to the doctoral project*

No.	Stage / activity	Available
<b>1.</b>	<b>Stage E1 - Analysis</b> , elaboration and characterization of nanostructured layers	
1.1	Study of technologies for the manufacture of photovoltaic cells	Report on the process of developing oxide nanostructured layers
1.2	Determination of metal oxides and precursor materials	
1.3	Elaboration and characterization of metal oxides	

No.	Stage / activity	Available
1.4	Manufacture of nanostructured layers by spin-coating technique	
1.5	Morphological and structural analysis of the obtained layers	
2.	Stage E2 - Design and development of a hardware & software system	
2.1.	Creation of the hardware device for monitoring and controlling CF parameters at laboratory level	Report on the hardware device for monitoring and controlling CF parameters and the implemented software solution
2.2.	Development of the software application for monitoring and controlling CF parameters	
2.3.	Realization of the hardware system and software application for monitoring and controlling CF parameters at laboratory level	Parameter monitoring and control system report
3.	Step E3 - Correlation of nanostructured layers with the energy yield of CF	
3.1	Characterization of nanostructured oxide layers by monitoring the electrical parameters of CF	Database with the experimental results obtained
3.2.	Analysis of the relationship between the parameters of layer elaboration and the electrical efficiency of the CF under different operating conditions	Report on correlation analysis
3.3.	Dissemination activities	articles in journals or conferences with ISI indexed volumes
4.	Stage E4 - Definition and validation of the experimental construction model of an energy-efficient CF	
4.1.	Establishment of the experimental model for the manufacture of nanostructured oxide layers	System Test and Optimization Report
4.2.	Development of the experimental model for monitoring and controlling the electrical parameters of the CF	
4.3.	Validation of the integrated and functionalized system	
4.4.	Dissemination activities	articles in journals or conferences with ISI indexed volumes

The distribution of activities by month is shown in the following Gantt chart.

## Gantt Chart

	Activity Month											
	1-4	5-8	9-12	13-17	18-21	22-25	26-29	30-34	35-37	38-40	41-44	45-48
<b>E1</b>												
A 1.1.												
A 1.2.												
A 1.3.												
A 1.4.												
A 1.5.												
<b>E2</b>												
A 2.1.												
A 2.2.												
A 2.3.												
<b>E3</b>												
A 3.1.												
A 3.2.												
A 3.3.												
<b>E4</b>												
A 4.1.												
A 4.2.												
A 4.3.												
A 4.4.												

Following the comparative analysis of the main types of photovoltaic cells, it can be concluded that the evolution of technologies in this field reflects a clear trend of diversification and specialization according to application, efficiency, cost and ecological impact. Crystalline silicon cells, especially monocrystalline and those optimized with PERC structures, continue to dominate the commercial sector due to their high efficiency, long-term reliability, and maturity of manufacturing processes. In parallel, thin-film technologies, such as CdTe and CIGS, offer significant advantages in terms of flexibility, low-light performance and the possibility of integration on alternative substrates, but are limited by aspects related to the sustainability of raw materials (tellurium, indium, gallium) and the complexity of processing. CZTS technology emerges as a promising, environmentally friendly and scalable option, but low efficiency and compositional instability remain major challenges [1-4]. Similarly, DSSC cells, although characterized by low cost, versatile aesthetics, and good behavior in diffuse light, are still restricted to niche applications due to limitations on stability and efficiency. In this context, the development perspectives aim at integrating hybrid architectures (tandem) and moving towards safer, more abundant and recyclable materials, in a global effort to reduce the ecological footprint and increase energy sustainability.

## COMPARATIVE ANALYSIS OF PHOTOVOLTAIC CELLS

Photovoltaic cells are devices that directly convert solar energy into electricity through the photovoltaic effect. Depending on the materials used and the internal structure, PV cells are classified into several types, each with specific advantages, disadvantages, and applications.

Current commercially available photovoltaic cells are not very efficient in converting solar energy into electricity, and their production is expensive[5]. This is because they rely on very pure materials, require very high manufacturing temperatures, and often require expensive "doping" materials.

Polycrystalline photovoltaic cells generally have a lower temperature coefficient compared to monocrystalline photovoltaic cells. Recently, new photovoltaic cell structures have been designed using nanomaterials that can be flexible and lightweight [6], [7]. This is because the new structures have a very large specific surface area for capturing sunlight. Crystalline silicon cells, especially monocrystalline and those optimized with PERC structures, continue to dominate the commercial sector due to their high efficiency, long-term reliability and maturity of manufacturing processes. In parallel, thin-film photovoltaic cell technologies such as CdTe and CIGS offer significant advantages in terms of flexibility, low-light performance and the possibility of integration on alternative substrates, but are limited by aspects related to the sustainability of raw materials (tellurium, indium, gallium) and the complexity of processing. CZTS technology emerges as a



promising, environmentally friendly and scalable option, but low efficiency and composition instability remain major challenges. Similarly, DSSC cells, although characterized by low cost, versatile aesthetics, and good behavior in diffuse light, are still limited to niche applications due to stability and efficiency limitations. In this context, the development prospects aim at integrating hybrid architectures and moving towards safer, more abundant and recyclable materials, in a global effort to reduce the ecological footprint and increase energy sustainability.

The efficiency of converting solar energy into electricity through photovoltaic cells is between 7% and 26% for semiconductor material. Thus, the technological development of photovoltaic cells is very important. This is because material and conversion efficiency are directly related. Nanomaterials have revolutionized the field of photovoltaic cells by improving conversion efficiency, reducing costs, and increasing the flexibility of devices. Their optical, electrical and structural properties, which are difficult to achieve with traditional materials, allow the exploitation of advanced mechanisms for converting solar energy into electricity.

The PhD thesis explores the types of nanostructured metal oxides used in photovoltaic cell manufacturing technology, performance improvement mechanisms, current challenges, and future research directions.

Among the most used nanomaterials are: metallic nanoparticles (e.g. Ag, Au), which intensify the absorption of light through plasmonic effects; quantum dots (CdSe, PbS), which offer adjustable bandgap and much higher conversion potential than traditional cells; carbon nanotubes and graphene, which contribute to the rapid transport of electrons and the realization of transparent electrodes with low resistance. Also, perovskitic materials with nanometer morphology have attracted the attention of researchers through high conversion efficiencies and the possibility of manufacturing on flexible substrates.

The improvement mechanisms introduced by these materials include: increasing absorption by efficiently capturing photons (due to textured surfaces and electric field localization effects), efficient separation of charge carriers (through interfaces with well-controlled potential) and rapid transport of them to electrodes. All these advantages contribute to reducing losses and, implicitly, to increasing the efficiency of energy conversion.

However, the use of nanomaterials also comes with a number of technical and environmental challenges. The stability over time of the materials (especially in the case of perovskites and quantum dots), the toxicity of some compounds (e.g. Cd, Pb), as well as the difficulties in the industrial reproduction of laboratory results are major obstacles to commercialization. Moreover, some synthesis methods require special conditions or hazardous solvents, which makes the scaling process difficult.

The current research directions focus on the development of hybrid nanocomposites (organic/inorganic), the integration of low-temperature printing technologies, the exploration of nanostructures inspired by nature, which combine performance with additional functionalities (self-cleaning, anti-reflection, etc.), as well as on strategies to minimize electron-void recombination. Strategies to minimize recombination consist of:

- use of **passivation layers** (e.g.  $\text{Al}_2\text{O}_3$ ,  $\text{SiN}_x$ ,  $\text{TiO}_2$ ). Thus, the interface between the active material and the electrodes can be optimized to repel minority carriers, directing them to the right contacts. This control of energy barriers significantly reduces SRH (Shockley-Read-Hall) recombination; [14, 15]
- the use of **nanostructures** such as nanowires, nanocolumns or quantum dots, which create directed pathways for the transport of wearers. In such geometries, electrons and voids are spatially separated, reducing the probability of recombination in volume [16-20].
- the use of **nanomaterials** such as perovskites or selenide and tellurium-based compounds, which have long carrier lifetimes ( $>1 \mu\text{s}$ ), providing sufficient time for collection before recombination [21-24].

Technology	Advantages	Limitations	Main applications	Perspectives
<b>Monocrystalline silicon (mc-Si)</b>	- High efficiency (20–23%) - High durability - Wide industrial availability	- Higher costs - Sensitive to shading - Rigidity	- Residential systems - Large solar parks - Grid-connected systems	- Optimizations through HJT, bifacial technologies



<b>Polycrystalline silicon (pc-Si)</b>	<ul style="list-style-type: none"> <li>- Low costs</li> <li>- Decent efficiency (15–18%)</li> <li>- Good reliability</li> </ul>	<ul style="list-style-type: none"> <li>- Lower efficiency compared to c-Si</li> <li>- Sensitivity to high temperatures</li> </ul>	<ul style="list-style-type: none"> <li>- Commercial and residential panels</li> <li>- Off-grid systems</li> </ul>	<ul style="list-style-type: none"> <li>- Progressively replaced by monocrystalline and PERC</li> </ul>
<b>PERC</b>	<ul style="list-style-type: none"> <li>- Increased efficiency (up to 22%)</li> <li>- Easy to implement on existing lines</li> <li>- Moderate costs</li> </ul>	<ul style="list-style-type: none"> <li>- Light-induced degradation (LID)</li> <li>- Limited performance at high temperatures</li> </ul>	<ul style="list-style-type: none"> <li>- Solar farms</li> <li>- Large commercial applications</li> </ul>	<ul style="list-style-type: none"> <li>- Integration with bifacial, N-type, HJT for efficiencies &gt;24%</li> </ul>
<b>CdTe</b>	<ul style="list-style-type: none"> <li>- Low costs</li> <li>- Good performance in diffuse light</li> <li>- Yield &gt;18% (industrial)</li> </ul>	<ul style="list-style-type: none"> <li>- Cadmium toxicity</li> <li>- Scarcity of tellurium</li> <li>- Ecological limitations</li> </ul>	<ul style="list-style-type: none"> <li>- Ground-mounted systems</li> <li>- Large industrial projects (First Solar)</li> </ul>	<ul style="list-style-type: none"> <li>- Optimization of rear contact</li> <li>- Alternative to silicon in warm environments</li> </ul>
<b>CIGS (CuInGaSe<sub>2</sub>)</b>	<ul style="list-style-type: none"> <li>- High efficiency (&gt;23% in the laboratory)</li> <li>- Flexibility</li> <li>- Adjustable bandgap</li> </ul>	<ul style="list-style-type: none"> <li>- High cost of raw materials (In, Ga)</li> <li>- Complex processing</li> </ul>	<ul style="list-style-type: none"> <li>- Portable applications</li> <li>- Smart textiles</li> <li>- Flexible systems</li> </ul>	<ul style="list-style-type: none"> <li>- Research for replacing In/Ga with Zn/Sn</li> <li>- Tandem technologies</li> </ul>
<b>CZTS</b>	<ul style="list-style-type: none"> <li>- Non-toxic and abundant materials</li> <li>- Ideal bandgap (1.4–1.5 eV)</li> <li>- Thin-film compatibility</li> </ul>	<ul style="list-style-type: none"> <li>- Low efficiency (~12% max)</li> <li>- Structural defects that are difficult to control</li> </ul>	<ul style="list-style-type: none"> <li>- Green systems</li> <li>- BIPV Applications</li> <li>- Off-grid systems</li> </ul>	<ul style="list-style-type: none"> <li>- Replacing CdS with eco-friendly alternatives</li> <li>- Technological process stabilization</li> </ul>
<b>DSSC</b>	<ul style="list-style-type: none"> <li>- Low cost</li> <li>- Variable aesthetics</li> <li>- Good efficiency in stray light</li> <li>- Flexibility</li> </ul>	<ul style="list-style-type: none"> <li>- Low efficiency (7–12%)</li> <li>- Low stability</li> <li>- Problems with liquid electrolyte</li> </ul>	<ul style="list-style-type: none"> <li>- Portable electronics</li> <li>- Active windows</li> <li>- Sensors, IoT</li> </ul>	<ul style="list-style-type: none"> <li>- Solid/gel electrolytes</li> <li>- Perovskite integration</li> <li>- Indoor applications</li> </ul>

Thus, it does not outline a universally applicable "ideal" photovoltaic cell technology, but rather a portfolio of complementary solutions, the optimal selection of which depends on the technological, economic and geographical context of each application.

## METHODOLOGY FOR DEVELOPING ADDITIONAL LAYERS

### Development of additional oxide layers on photovoltaic cells

#### *Preparation of photovoltaic cells*

Polycrystalline Si-based photovoltaic cells, purchased from **Guangzhou Runxi Trading**, China, are cleaned in the ultrasonic bath, at 42 KHz, ethyl alcohol and deionized water. The cleaning process aims to remove impurities (e.g. grease, dust). The duration of the process was 180s for each cleaning agent. Characteristics of the solar cell used for experimental activities EAN model: 35, power 0.16W, dimensions 5.2 cm\*1.9 cm, thickness 200±20µm. The characteristics given by the manufacturer are presented in the following table [69].

Characteristics of Si-polycrystalline photovoltaic cells

Efficiency	Intensity (A)	Voltage (V)	Power(W)
17,4%	0,3	0,5	0,16

### ***Establishment of oxides***

MgO, in the form of white powder, is an inorganic compound, very stable at high temperatures in oxidizing atmospheres up to 2300°C and reducing to, respectively 1700 °C, and crystallizes in the form of the crystalline cubic structure. MgO is generally also "relatively inert" being a metal oxide. The hygroscopic nature of MgO and its transition to Mg(OH)<sub>2</sub> [70, 71] is often mentioned in experimental research with the mention that MgO is generally stable. MgO (magnesium oxide) is a semiconductor material with interesting optical and electrical properties, which has considerable potential for applications in solar cells. Although it is not as widely used as ZnO, MgO has certain advantages that make it an attractive option for research and development. It features a bandgap width of 7.8 eV, which allows it to absorb a wide range of sunlight, including ultraviolet (UV) radiation. MgO is a promising material for the passivation of photovoltaic cell surfaces due to its ability to reduce the recombination of charge carriers at the interface of the semiconductor material (usually silicon) with adjacent layers[72-75]. By forming a thin layer of MgO, a field passivation effect can be created, which helps to block minority carriers (electrons and voids), thus improving the energy yield of photovoltaic cells [75].

### **Justification for the use of MgO as a precursor material for layers on photovoltaic cells**

#### ***Reduction of recombination of charge carriers***

MgO has a very high bandgap (~7.8 eV), making it an excellent electrical insulator.

In multilayer structures, it can be used to control the alignment of energy bands, facilitating the separation of charges and blocking of minority carriers, which reduces unwanted recombination. MgO helps to decrease surface defects that favor the recombination of charge carriers, which leads to increased efficiency of converting sunlight into electrical energy [71, 73].

#### ***The effect of nanostructures and the increase of the active surface area***

MgO used in the form of nanostructures (e.g. nanocrystals or thin films) to increase the active surface area of photovoltaic cells. This allows for better light capture and expansion of absorption capacity, which are essential for improving the energy performance of solar cells [76].

#### ***Increased durability and stability***

The MgO layer not only improves energy performance, but also contributes to extending the life of photovoltaic cells, due to its high resistance to environmental conditions and degradation. This is especially important for long-term applications of photovoltaic cells, which need to maintain high efficiency over a long period of time [63, 68].

#### ***Interfacial passivation layer***

MgO is used as a passivation layer between the substrate and the active layer or between the transport layers (electrons or voids). This layer reduces interface defects that can lead to recombination of charge carriers, which significantly improves cell efficiency.

Example: in perovskitic cells, MgO is sometimes deposited between the glass substrate coated with conductive oxide (e.g. ITO) and the electron transport layer [45].

#### ***Controlled reflection***

In some cases, MgO is also used as a controlled reflection layer behind the active layer, to redirect unabsorbed photons back into the cell, maximizing light absorption [76].

Zinc oxide (ZnO), in white powder form, is an inorganic compound, insoluble in water. It has a wide range of uses, but important in current research is the use of ZnO as an n-type semiconductor [77]. Also, noteworthy properties are good transparency, high electron mobility, 3.37eV bandgap and strong luminescence at room temperature. All of these properties make zinc oxide valuable for a variety of emerging applications: transparent electrodes in liquid crystal displays, energy-saving or heat-shielding windows, and electronics such as thin-film transistors and light-emitting diodes. Due to its excellent electrical conductivity and transparency properties, ZnO plays an important role in improving the performance and energy efficiency of photovoltaic cells. Moreover, it can also be used as a passivation material or anti-reflective coating in various types of solar cells, including CIGS, DSSC, and amorphous silicon [78, 79].

Zinc oxide being an important semiconductor material with unique optical and electronic properties becomes promising for various applications in the field of solar cells [77, 81].

### Justification for the use of ZnO as a precursor material for layers on photovoltaic cells

#### *Transparent Conductive Oxide (TCO)*

Aluminum-doped ZnO (AZO) or gallium-doped ZnO (GZO) is used as an alternative to ITO (indium-tin oxide), due to: high optical transparency (UV-VIS), good conductivity, low cost and efficient processing methods. AZO is often integrated into commercial solar panels where reducing the cost of raw materials is essential [82].

#### *Anti-reflective and transparent coatings*

The ZnO layer often covers the surface of photovoltaic cells as an anti-reflective coating. It helps maximize light absorption by reducing reflection to the cell surface. In incident light, a thin layer of ZnO can help orient and scatter light, increasing the absorption time in the active material. Due to its transparency in the visible and UV spectrum, ZnO allows light to penetrate the active layer (e.g., silicon, CIGS, or perovskite), increasing the efficiency of capturing solar energy [83-85].

#### *Surface passivation*

ZnO, when used in combination with passivation layers, reduces the recombination of charge carriers at the surface. It can protect the surface of the semiconductor from surface defects that favor recombination (in the case of silicon cells, for example). Thus, ZnO contributes to the improvement of open circuit voltage ( $V_{oc}$ ) and fill factor (FF), essential parameters for the overall efficiency of the cell [86].

#### *Doping with additional elements*

ZnO can be doped with various elements (e.g., aluminum - Al:ZnO), thus improving electrical conductivity and making it a transparent conductive material. This is especially important in thin-film photovoltaic cells, as it can reduce resistance losses and ensure efficient current collection [42, 79, 87].

#### *Layers of protection and stability*

ZnO plays an important role in protecting photovoltaic cells from external factors, such as humidity, air, and UV, which can cause photovoltaic materials to degrade. ZnO layers are often used to improve the durability and longevity of photovoltaic cells [88].

An overview of the use of MgO and ZnO in photovoltaic cells is given in the following table [39, 62, 73, 89].

Use in photovoltaic cells			
Advantages	Disadvantages	Advantages	Disadvantages
MgO		ZnO	
Large bandgap width (7.8eV)	The efficiency of MgO solar cells is still relatively low and requires significant improvements	High electron mobility, which allows efficient charge transport (3.37eV)	The efficiency of ZnO solar cells is still lower than that of traditional silicon-based solar cells
It can be used in silicon photovoltaic cells and advanced structures such as PERC due to its passivation properties.	MgO is opaque in the visible spectrum, so it is not suitable for use as an anti-reflective coating or TCO (Transparent Conductive Oxide).	Aluminum-doped ZnO (Al:ZnO) is a transparent conductive material widely used in TCO layers for photovoltaic cells, allowing for efficient electron collection and light transmission to the active material.	Under certain conditions, ZnO can induce recombination at the interface with the active material, especially if the ZnO layer is not of good enough quality or is not correctly passivated.
It creates an electric field that repels	MgO is more difficult to dope to achieve	ZnO is used in anti-reflective coatings to reduce light loss,	ZnO is not always the best material for

Use in photovoltaic cells			
Advantages		Disadvantages	
MgO		ZnO	
minority carriers, improving the performance of photovoltaic cells.	significant electrical conductivity compared to other materials, which limits its applications in certain types of solar cells.	thereby improving the overall efficiency of photovoltaic cells.	passivation layers in the case of p-type silicon photovoltaic cells (especially in monocrystalline cells), where materials such as Al <sub>2</sub> O <sub>3</sub> may be more efficient.
Highly chemically stable, resistant to degradation in the environment	Lower electron mobility than other semiconductor materials, limiting the performance of solar cells	ZnO is chemically and thermally stable, having good resistance to UV radiation and temperature changes, which improves the performance and durability of photovoltaic cells in the long term.	Some ZnO deposition techniques, such as sputtering or CVD, may involve additional costs compared to other passivation materials, although ZnO is generally considered an affordable material.
Cheap material Pure MgO Prices: 1 kg: 20-50 USD 10kg: 15-40USD/kg 100kg: \$10-30/kg		Relatively inexpensive material, making it an attractive option for mass production. Pure ZnO Pricing: 1 kg: 50-100 USD 10kg: USD 40-80/kg 100 kg: 30-70 USD/kg	
Research to overcome the current limitations of photovoltaic cells with oxide layers			
<div>➤ Development of novel doped nanostructural materials to increase electron mobility</div> <div>➤ Study of the engineering of the interfaces between MgO, ZnO and other semiconductor materials.</div> <div>➤ Optimizing manufacturing processes to achieve high-quality starts.</div>			

Mg and Zn oxides are purchased in powder form, of analytical purity. MgO is from Honeywell, and ZnO is from Sigma Aldrich. The ZnO powder is from Sigma Aldrich, CAS 1314-13-2,  $\rho=5.61 \text{ g/cm}^3$ . The MgO powder is from Honeywell, CAS 1309-48-4,  $\rho=3.58 \text{ g/cm}^3$ .

The 1M zinc nitrate solution was used as a precursor for obtaining undoped powders, and in the case of doped powders, zinc nitrate, Zn(NO<sub>3</sub>)<sub>2</sub>, and aluminum chloride, AlCl<sub>3</sub> dissolved in distilled water, were used. As a hydrolysis agent, the KOH solution of 1M concentration was used. The elaboration reactor used is the Cortest autoclave with a capacity of 2l, in collaboration with the National Institute of Non-Ferrous and Rare Metals. The elaboration of pure and ZnO-doped powders was carried out by hydrothermal synthesis at 200<sup>o</sup>C, 4.5 bar, for 40 minutes.

Nano-ZnO and nano-MgO offer significant advantages due to their small size and nanometer characteristics. These materials can form nanostructured layers, which have an increased active surface area, which:

**Improves light absorption** – Nanostructures can capture more light and help maximize the efficiency of absorbing sunlight.

**Increased interaction with photons** – Nanolayers can sustain photons in the photovoltaic material for longer, which increases the likelihood that they will be absorbed

**Reduction of charge carrier recombination** – Nano-ZnO and nano-MgO are efficient in passivating the surface of photovoltaic cells, reducing the recombination of charge carriers (electrons and voids) that occurs at the interface of the active material with adjacent layers. These nanostructured layers can:

- It blocks surface defects that are responsible for the recombination of charge carriers, thus improving the energy yield of cells.
- It increases the open circuit voltage ( $V_{oc}$ ) and fill factor (FF), two essential measures of the performance of photovoltaic cells.

The large area-to-volume ratio that characterizes nanostructured materials, compared to that of micrometric materials, confers unique properties such as optical, magnetic, electrical, and chemical-specific. The application of nanomaterials and nanotechnology is very attractive in energy. A Business Wire report confirmed that the global nanotechnology market is poised to grow at a compound annual growth rate of 18.1% in the coming years, to a market size of USD 173.95 billion by 2025 [4, 90, 91].

The synthesis of magnesium oxide and zinc oxide nanostructures by physical vapor phase deposition (PVD) is performed using solar energy, in the PROMES Odeillo laboratory, France, within the projects NANOMAGLAY, Synthesis and characterization of nanostructured magnesium oxide powders for composite layers, N° SURPF1904040032, and NOSC: Nanostructured oxides layers by SPVD for enhance Solar Cell efficiency, No. SURPF2201300023, <https://sfera3.sollab.eu/wp-content/uploads/2022/05/>.

### Making additional oxide layers by centrifugation

Spin coating is a procedure used to apply uniform thin films to flat substrates. A typical process involves depositing a small amount of solution in the center of a substrate and then rotating the substrate at high speed (usually around 3000 rpm). It is highly used in the manufacture of photovoltaic cells, especially for [95]:

- passivation layers,
- buffer layers,
- Active layers in perovskite, organic or quantum dot cells.

#### The critical parameters of the process are:

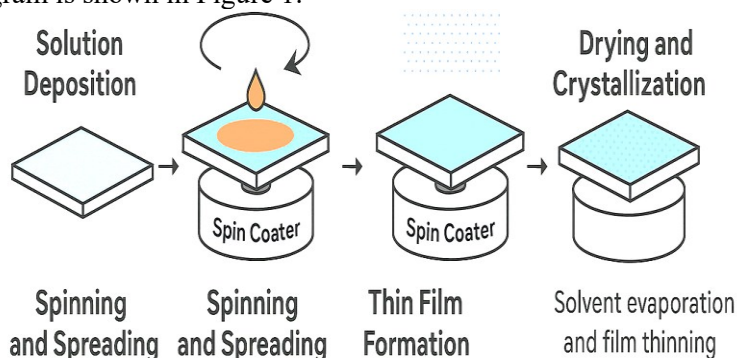
- **Rotational speed** (rpm): controls the thickness of the film (higher speeds produce thinner films).
- **Rotation time**: influences the uniformity and degree of evaporation of the solvent.
- **Solution concentration**: determines how much material remains on the substrate after evaporation.
- **Solvent type**: affects the evaporation rate and final morphology of the film.

The centrifugal force causes the solution to spread towards the edge of the substrate, leaving a thin film on the surface [55, 96-98].

#### Stages of the process:

- **Preparation of the solution**: A precursor solution containing the metal oxide compounds dispersed in a volatile solvent is prepared.
- **Solution deposition**: A small amount of the solution (100  $\mu$ l–200  $\mu$ l) is dripped onto the center of the substrate (polycrystalline Si photovoltaic cell).
- **Substrate rotation**: The substrate is rotated rapidly (usually between 1000 and 3000 rpm), centrifugal forces stretch the solution towards the edges, forming a uniformly thin film.
- **Solvent evaporation**: During rotation, the solvent evaporates, and the layer thickness stabilizes.
- **Heat treatment**: To convert the amorphous or pre-organic film into a crystalline metal oxide, heat treatment (drying, calcining or annealing) is applied between 100 and 180 °C.

The process diagram is shown in Figure 1:



**Figure 1.** Schematic representation of the spin-coating process

## CHARACTERIZATION METHODS AND TECHNIQUES

### Structural characterization by X-ray diffraction

X-ray diffraction (XRD) analysis is an essential method for characterizing the crystal structure of thin layers, providing qualitative and quantitative information on the phases present, the degree of crystallinity, the preferential orientation (crystal texture), as well as the average size of the crystallites. In the case of deposited layers, the interpretation of the diffractograms allows the highlighting of possible phase transitions induced by heat treatments, the identification of possible impurities or secondary phases, as well as the evaluation of the structural homogeneity in the normal direction of the substrate. Also, the comparison of the relative intensities of the experimental peaks with those in the standard sheets allows the estimation of the existence of a preferential crystalline orientation, which is essential in optoelectronic or functional applications. Therefore, the XRD technique is a basic tool in optimizing synthesis processes and validating the structural quality of thin layers of metal oxides. The morphological characterization of the ZnO powders developed within the international research project was carried out in the PROMES Odeillo laboratory, with the PW1710 diffractometer (Philips). The structural characterization of MgO was performed in the Advanced Materials laboratory, the Research and Development Center for Innovative Materials, Products and Processes for the Automotive Industry (CRC&D-Auto), Pitesti University Center, with the Ultima IV diffractometer (Rigaku).

### Morphological and compositional characterization

Scanning electron microscopy (SEM) is used for morphological characterization. It allows morphological determinations at the nanometer and subnanometer scale, microstructural determinations (identification of crystalline phases by electron diffraction and high-resolution electron microscopy) as well as compositional determinations (elemental chemical analysis by EDS technique, composition mapping by EDS mapping). SEM-EDS analysis is performed using the Hitachi SU5000 electron microscope equipped with secondary and backscattered electron detectors, coupled with the X-ray fluorescence spectrometry module. In order to observe the morphology of the surfaces, SEM images were acquired in secondary electrons (SE) and backscattered electrons (BSE), as well as at variable pressure (30Pa) at different sizes. The morphological characterization of the ZnO powders developed within the international research project was carried out in collaboration with the Institute of Physics, Polish Academy of Sciences, with the Leo microscope (Zeiss). The morphological and compositional characterization of MgO and the elaborated layers was performed in the Advanced Materials laboratory, CRC&D-Auto, Pitesti University Center, with the SU 5000 microscope (Hitachi).

### Structural and compositional characterization by absorption spectroscopy

UV-VIS absorption spectroscopy is the chemical and structural analysis method that exploits the absorption that occurs at frequencies corresponding to the electronic transitions from the fundamental state to the excited state. The analysis is performed with UV-Visible spectroscopy with Ocean Optics HR2000+ in the range of 200-800 nm [69].

IR absorption spectroscopy with Fourier transform is a vibrational spectroscopy technique based on the phenomenon of selective absorption of radiation at specific frequencies in IR, which correspond to the frequencies of their normal modes of vibration of molecules. The infrared spectrum represents a "fingerprint" of the sample and is recorded with the FTIR spectrometer, model Tensor 27 (Bruker Optics), with total attenuated reflection (ATR) accessory, in the spectral range 4000-400  $\text{cm}^{-1}$ , spectral resolution 4  $\text{cm}^{-1}$  [69].

### Characterization of the specific surface

BET (Brunauer–Emmett–Teller) surface characterization is an essential analysis for porous or nanostructured materials, providing information related to the specific surface area, pore volume and porosity distribution. BET is a physicochemical method of nitrogen adsorption (usually at 77 K), used to determine the specific surface area of a solid material.

The specific area represents the total available adsorption area per gram of material and is expressed in  $\text{m}^2/\text{g}$ . Typical values:

<10  $\text{m}^2/\text{g}$ : compact, low-porous materials

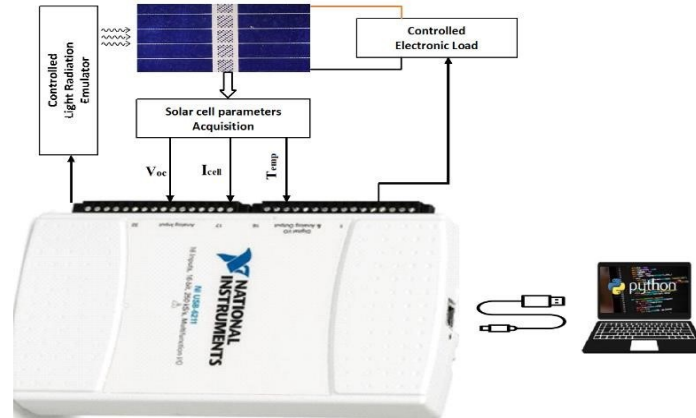


10–100 m<sup>2</sup>/g: common powders

100 m<sup>2</sup>/g: materials with high porosity (e.g. aerogels, MOFs, nanomaterials).

## REALIZATION OF THE SOLAR CELL TEST SYSTEM WITH ADDITIONAL LAYERS

Each layer of metal oxide, obtained by centrifugation on solar photovoltaic cells, is tested in two solar simulators. The proposed system for the control and acquisition of parameters influencing the operation of a solar cell is shown in Figure 2.



**Figure 2.** *Solar Cell Test System Using Solar Emulators*

The system consists of:

- Solar cell block: in this block we find the solar cells of type UFY002914 [69].
- Solar radiation emulation block: with this block we want to ensure a light radiation as uniform as possible and with the same parameters all for the solar cells tested.
- Controlled electronic load block – implemented by means of a current source that fixes the current through the solar cell in the range 0-30mA.
- Acquisition and control block
- Stabilized, controlled power supply – this power supply provides the DC voltages used by the other component blocks. At the same time, the start and stop of the operation of the solar radiation emulation block is controlled, being synchronized with the start/end of the acquisition of parameters from the tested solar cell.

## Solar Radiation Emulator Construction

The solar emulators were made as part of the doctoral research, in the NANOBIOMAT research laboratory. They are software controlled to operate for different power ranges by applying a continuous voltage between 1 and 10 V with the step of 1 V (LIS- Light Illumination Set) [69].



**Figure 3.** *Solar Radiation Emulator*



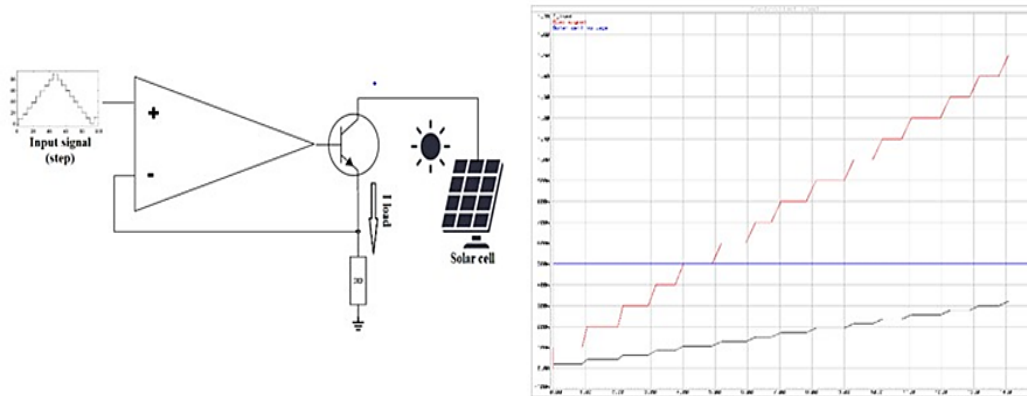
The construction features of solar emulators in the lab are summarized in the following table.

Solar Emulator Type	Features
Solar Simulator 1	150W, 200 lm/watt, spreading angle 1200, intensity Adjustable luminous, operating temperature -250-500 C, diameter 350 mm, wavelength light radiation $\lambda=405$
Solar Simulator 2	200W, 200 lm/watt, spread angle 900, intensity adjustable luminous, operating temperature -250-500 C, diameter 400 mm, wavelength light radiation $\lambda=470$

The degree of illumination (measured with the Optimus AT X81 lux meter), at a distance of 1 m from the light source, for the 2 emulators is shown in the following [69].

Step	Solar Simulator 1	Solar Simulator 2
	Lighting [LUX]	
LIS 1 – 1 V	2700	3460
LIS 2 – 2 V	2700	3470
LIS 3 – 3 V	5200	6100
LIS 4 – 4 V	8000	9600
LIS 5 – 5 V	10800	13000
LIS 6 – 6 V	13500	16400
LIS 7 – 7 V	16200	19700
LIS 8 – 8 V	18850	21500
LIS 9 – 9 V	20200	24500
LIS 10 – 10 V	22400	27200

To obtain the I-V characteristic of the solar cells, a controlled electronic load is connected to the output of the circuit, according to the diagram in Figure 4.



**Figure 4.** *Dynamic Load*

The electronic load functions as a current source circuit. The value of the current through the solar cell is given by the ratio of the analog input voltage on the non-inverting pin (+) of the operational amplifier to the resistance R [69].

Since the maximum current that can be supplied by the solar cells is 32mA, and the analog voltage applied to the input of the electronic load circuit is in the range  $[0 \div 1.5V]$ , we chose for R the value of  $33\Omega$ . Analyzing the results obtained by simulating the proposed circuit, it is observed that regardless of the set load current, the voltage supplied by the solar cells is not influenced [69].

## Control of the proposed test system and acquisition of photovoltaic cell parameters

The entire management of setting the parameters of the illumination level, the level of the electronic load and the acquisition of the parameters of the solar cells (V, I) in accordance with the set parameters, is carried out with the help of the NI USB 6211 acquisition and control board [69].

The NI-USB 6211 acquisition interface has, according to the manufacturer's data, the following input/output ports:

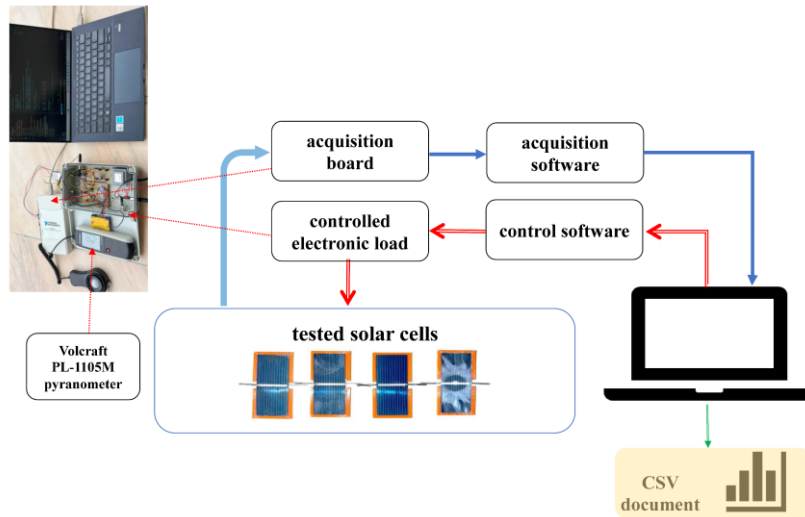
- 16 analog input channels (16-bit, 250 kS/s)
- 2 analog output channels (250 kS/s)
- 8 digital input/output channels

Of these, in the case of the experiments carried out, the following are used: 2-analog inputs for the acquisition of the voltage of the solar cell, 2 analog outputs, one for the control of the lighting level of solar simulators and one for the control of the output electrical load, 1 digital output for the synchronized control of the solar radiation emulation block is controlled.

At the same time, the connection to the Python software application is made through NI USB 6211 [69]. To plot the comparative graphs between the parameters of 2, 3 or more solar cells, Python was also used, the loaded vectors already having the optimal structure [99].

## Realization of the solar cell test system in real lighting conditions

Starting from the solar cell test system using solar emulators and having as the main objective of experimental research the optimization of energy efficiency by integrating solar cells covered with advanced optoelectronic layers, a second hardware-software system was designed and implemented for real-time monitoring and precise control of cell operating parameters [22]. For this purpose, an integrated acquisition and control system was developed, assisted by a software application capable of correlating the data obtained from the variation of environmental parameters (temperature, lighting) with the characteristic electrical parameters of solar cells, such as no-load voltage, voltage under load and short-circuit current [100-104].

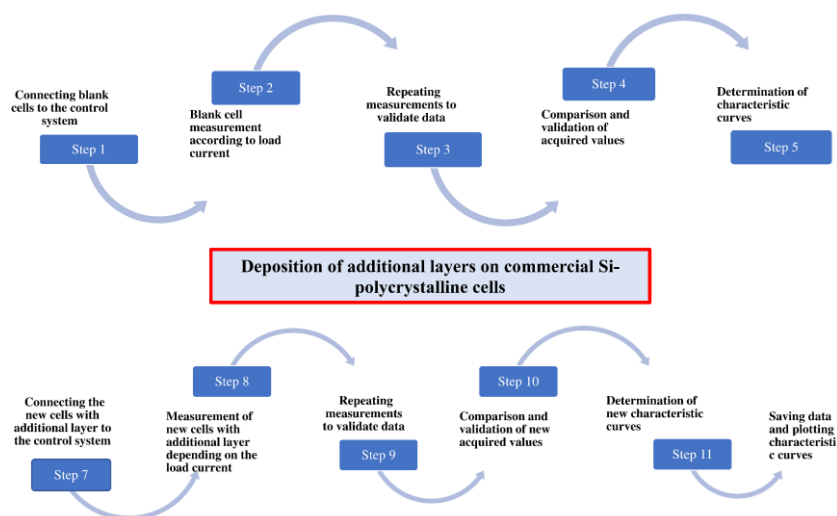


**Figure 5.** *Electronic Solar Cell Test System*

The general structure of the test system used is shown in Figure 5 and integrates several essential functional blocks (many of them similar to the previous test system): the block of tested solar cells, made up of commercial type UFY002914 cells; the controlled electronic load block, made of 4 or 5 (as the case may be) programmable current sources, which allow the regulation of the current through each cell; the acquisition and control block, responsible for two-way communication with the dedicated software and for interfacing with electronic elements; a stabilized power supply, which provides the continuous voltages necessary for the operation of the assembly; as well as a Volcraft PL-1105M pyranometer, used to monitor the level of incident lighting on the cells during testing.

Experimental data acquisition is performed through the same NI USB-6211 interface. In the configuration used for the tests carried out, eight / ten analog input channels were exploited for monitoring the

voltages of the four / five solar cells (both in idle mode and under load), as well as an analog output channel dedicated to the control of the electronic load. The interface is connected to a software application developed in Python, which is responsible for the complete management of the system: task control, acquisition, processing and saving data in a CSV file.



**Figure 6.** *Diagram for the software application*

At the same time, the application allows the automatic generation of comparative graphs for the analysis of the electrical performance of two or more cells, using data vectors structured in an optimal format for interpretation.

Each solar cell is connected to a controlled electronic load. All electronic loads are controlled synchronously, using the same control parameters. For the experiments, 100 values were imposed for the load current through each solar cell, between 0mA (open circuit) and 50 mA. After each set current value, wait 1 second and then start the purchase. For each set current value, 50 values for the voltage of the solar cell and 50 values for the current absorbed by the solar cell are purchased.

## STRUCTURAL AND MORPHOLOGICAL CHARACTERIZATION OF THE LAYERS

**Chapter 6** presents a detailed study on the development and characterization of additional layers of metal oxides (mainly MgO and ZnO) deposited on polycrystalline silicon-based photovoltaic cells, in order to optimize their performance. The research aimed both at the technological optimization of the deposition process and at investigating the compositional, structural and morphological characteristics of the obtained layers.

The elaboration of the MgO and ZnO layers was carried out using the spin-coating technique, a method that involves the controlled application of a precursor solution on the surface of the photovoltaic substrate, followed by the evaporation of the solvent and heat treatments to stabilize the deposited layer. Experimental parameters included variable solution volumes (between 0.3 and 1.1 ml), rotational speeds adjusted in stages (1500 rpm initially, then 2000 rpm), application times in 30-second increments, as well as drying at temperatures between 85°C and 120°C. The solvents used were ethanol (EtOH), ethanolamine (EA) and ethylene glycol (EG), each having a distinct role in controlling the size and morphology of the particles obtained.

For compositional characterization, ATR-FTIR and UV-VIS spectroscopic methods were applied. The ATR-FTIR spectroscopy revealed the presence of chemical bonds specific to oxidic materials and organic residues from solvents. The spectra confirmed the formation of Mg–O and Zn–O bonds, along with organo-metallic interactions at the oxide-solvent interface. The comparative analysis of the spectra showed the differences between the MgO dispersion in EtOH, EA and EG, highlighting the intensity of the characteristic vibrations O–H, C–H, C–O, N–H, as well as the presence of complexation in the solution. UV-VIS spectroscopy demonstrated the differences in optical absorption between dispersions, with a maximum absorption observed in the case of MgO dispersed in ethylene glycol, suggesting stronger interactions and the possible formation of coordinated organo-metallic structures.

For ZnO, the absorption threshold detected by UV-VIS was around 376 nm, indicating good quality of the synthesized nanoparticles and a corresponding dispersion in solution. ZnO doping with Al (10% at.) was analyzed by ATR-FTIR, confirming the structural changes induced by doping on the crystal lattice.

The morphological characterization was performed by scanning electron microscopy (SEM) and elemental analysis (EDS). The SEM analyses highlighted in detail the internal structure of the photovoltaic cells, including the anti-reflective layer of Si<sub>3</sub>N<sub>4</sub>, the upper electrode of Ag and the lower electrode of Al. The anti-reflective layer was confirmed to have a string morphology, specific to pyramidal texturing, and the electrodes exhibited a spherical (Al) and compact (Ag) morphology, characteristic of metallic materials deposited by standard commercial processes.

The additional oxide layers showed distinct morphologies depending on the solvent used. In the case of MgO deposited from EtOH solutions, thin needle structures with nanometric diameters, but unevenly distributed, were obtained. Instead, the use of ethylene glycol allowed the production of spherical particles, with sizes between 53–78 nm, evenly distributed, with a denser coating and controlled porosity. The layers deposited with higher volume solutions (1 ml) showed smaller particles and more compact distributions compared to those obtained from small volume solutions (0.3 ml), confirming the direct influence of the deposition parameters on the final microstructure.

For ZnO, the morphology was dominated by the formation of prismatic columns or polyhedral structures, characteristic of the hexagonal wurtzite phase, with dimensions between 100–500 nm. Spin-coating deposition generated dense layers with uniform coverage, especially when using large volumes of solution and appropriate heat treatments. The EDS compositional maps confirmed the uniform presence of Zn and O in the deposited layers, without significant contamination, and highlighted the compatibility of the oxide layer with the Si<sub>3</sub>N<sub>4</sub> substrate and the Ag electrode.

An important aspect highlighted in the study was the direct influence of technological parameters on the performance of the final layer. Adjusting the rotational speed and solution volume allowed the particle size and uniformity to be optimized, reducing the risk of excessive agglomeration and ensuring consistent coverage of the photovoltaic surface. The heat treatments contributed to the complete removal of the solvent, the mechanical stabilization of the layer and the strengthening of the chemical bonds at the interface.

The functional analysis of the oxide layers revealed that they fulfill multiple roles: they improve light absorption by reducing reflection, thus increasing the efficiency of photoconversion, and they contribute to the passivation of surfaces, reducing the recombination processes of charge carriers. In the case of the ZnO layer, a protective effect on the migration of Ag ions was also observed, suggesting an additional benefit in the long-term stability of cells.

By comparison, the MgO layers demonstrated better control over nanostructuring, but required further adjustments to the centrifugation process to avoid uneven distribution and coffee-ring edge effects. In contrast, ZnO showed an orderly growth, favorable for optoelectronic applications, but with sensitivity to Al doping, which can alter the structure of the crystal lattice.

In conclusion, the chapter demonstrates, through a coherent set of experiments and analyses, the feasibility of using additional layers of metal oxides (MgO, ZnO) for the functional optimization of photovoltaic cells. The obtained results validate the proposed technological approach and open perspectives for the large-scale application of these nanostructures in the renewable energy industry.

**The personal contributions that derive from Chapter 6 are as follows:**

- Optimization of the spin-coating process parameters for the elaboration of MgO and ZnO layers on photovoltaic cells.
- Comparative investigation of the influence of solvents (EtOH, EA, EG) on the morphology and distribution of oxide particles.
- Realization and interpretation of ATR-FTIR and UV-VIS spectra for compositional and structural confirmation of the elaborated layers.
- Detailed morphological analysis by SEM microscopy of the oxide layer deposited on Si<sub>3</sub>N<sub>4</sub> substrates and Ag electrodes.
- Correlation of synthesis parameters with the functional performance of layers, highlighting the impact on optical absorption and surface passivation.
- The protective role of the ZnO layer against Ag ion migration has been demonstrated, helping to increase the stability of the photovoltaic cell.
- Validation of the integration of oxide layers in commercial photovoltaic configurations, with potential for industrial application.

- Theoretical and experimental contributions to the understanding of organo-metallic interactions at the oxide-solvent-substrate interface.
- Development of a complete multi-technical characterization methodology (spectroscopic, morphological, compositional) for nanostructured oxide layers.
- Formulating conclusions and directions of technological optimization for the subsequent implementation of these layers in high-efficiency photovoltaic cells.

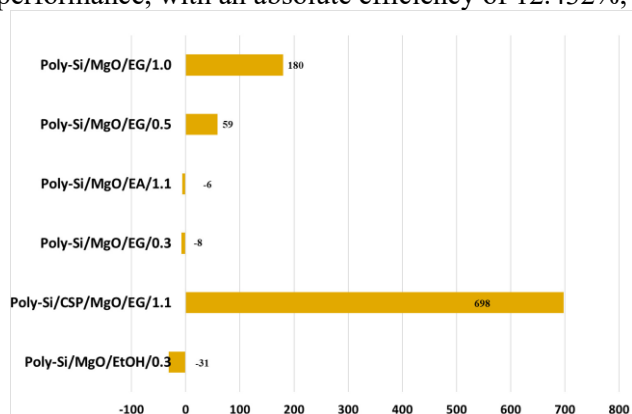
## ENERGY EFFICIENCY TESTING OF PHOTOVOLTAIC CELLS WITH ADDITIONAL LAYERS

**Chapter 7** of the paper analyzes in detail the testing of the energy efficiency of photovoltaic cells, with a focus on rigorous experimental methods and obtaining relevant quantitative results. The study focuses on testing solar cells both in laboratory conditions, using solar simulators, and in real atmospheric conditions, applying additional layers of MgO and ZnO, synthesized by various methods. The analysis is carried out on several levels: I-V and P-V characteristics, current density, output power, energy efficiency and the impact of particle morphology and size on cell performance.

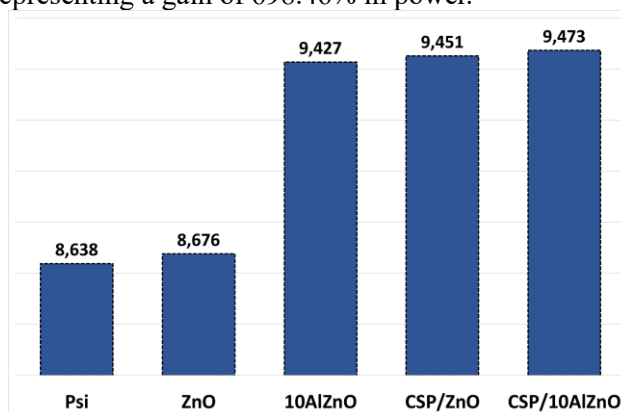
Initially, the author investigated six solar cells, including one commercial reference cell and five cells coated with different layers of magnesium oxide (MgO), tested using two solar simulators. The parameters purchased included voltage, current per load, output power and current density, under standard laboratory conditions. In the first phase, insignificant differences were observed between the standard cells without coatings, but subsequent comparative tests showed clear effects of the deposited layers. The use of solvents such as ethanol, amine ethanol and ethylene glycol had a significant impact on layer uniformity and energy efficiency, with results correlated with the volume of the solution applied. The increase in volume to 1 mL led to a significant improvement in efficiency, especially in the case of ethylene glycol, where there was an average increase in power of 77.42% (simulator 1) and 108.26% (simulator 2), compared to the control cell.

Comparative analyses revealed that the solvent ethanol does not promote the formation of uniform layers of MgO, which limits the improvement of energy efficiency. In contrast, the use of ethanol amine and ethylene glycol, in corresponding volumes, demonstrated a positive effect, with significant increases in current intensity and output power, especially in the case of ethylene glycol, where power differences of up to 100.13% were recorded for certain lighting levels.

During the tests under real conditions, the author applied MgO layers on polycrystalline silicon cells, analyzing the effect of the synthesis and volume of the solution on the electrical performance. Compared to control cells, MgO-coated cells obtained by using ethanol amine and ethylene glycol demonstrated remarkable increases in potency and efficiency, especially at larger volumes (1 ml). In particular, cells treated with MgO synthesized in ethylene glycol showed an average output power 182% higher than commercial cells, and layers made with powders obtained by concentrated solar vapor condensation (CSP) recorded exceptional performance, with an absolute efficiency of 12.432%, representing a gain of 698.46% in power.



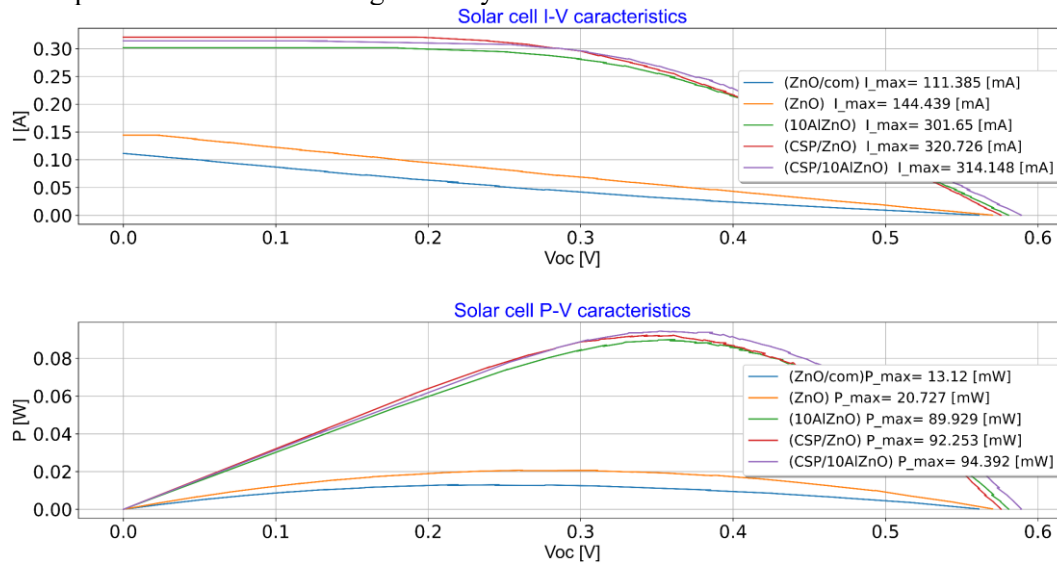
**Figure 7.** *Change in the percentage of energy efficiency of cells with MgO layer compared to the average efficiency value of uncoated cells*



**Figure 8.** *Technical and economic analysis for a residential photovoltaic system - the annual energy production of the residential system according to the type of solar cells used*

For the ZnO layer, the tests included four commercial cells, analyzed before and after the application of the additional layers, using hydrothermal synthesis, aluminum doping and CSP synthesis. The results

indicated that commercial ZnO powders do not bring significant improvements, generating a modest efficiency of 2.408%. In contrast, the application of aluminum-doped ZnO and hydrothermal synthesis resulted in an increase of almost 600% in power, and the use of CSP synthesis allowed to achieve maximum values of over 625% improvement in power compared to the control cell. The synergistic impact of doping and CSP synthesis was evident, considerably increasing the active surface and mobility of the charge carriers, reducing recombination processes and maximizing overall yield.



**Figure 9.** Current-voltage (*I-V*) and power-voltage (*P-V*) characteristics of commercial photovoltaic cells after deposition of additional layers

A key aspect of the research is the analysis of the influence of particle size and shape. Reducing particle size from the micrometer to nanometer level and optimizing their shape (from spheres and nanorods to whiskies) has been shown to significantly improve cell performance. The layers of doped nanometric particles, made by CSP, allowed to obtain structural networks with much larger specific areas, facilitating the efficient transport of charges and the absorption of light. This morphological progression has generated performance leaps of over 350%, confirming the superiority of advanced structures compared to commercial ones.

The technical-economic analysis carried out extended the research from the individual cell level to the photovoltaic panel level, respecting the specifications of a commercial JA Solar JAP72S10 350/SC panel. By configuring a 5.6 kW system, using software simulations and extrapolating the experimental results, it was estimated that the application of optimized layers (CSP/10AlZnO) can increase the daily energy production from 1.75 kWh (basic Psi) to 2.58 kWh, equivalent to an annual increase of approximately 300 kWh. From an economic point of view, this translates into annual savings of between €667 and €879 per system with 10 modules, demonstrating not only the technical feasibility but also the financial sustainability of integrating advanced materials into the photovoltaic cell architecture.

The author demonstrates with academic rigor how the careful selection of chemical precursors, the optimization of the volume of the deposited solutions, the choice of synthesis methods and the control of the layer morphology profoundly influence the performance of solar cells. The methodology used combines standardized experimental testing, detailed acquisitions of electrical parameters and solid comparative analyses, the results obtained validating the central hypothesis of the research: advanced materials and innovative technologies can fundamentally transform the efficiency of solar photoconversion, with direct benefits both technologically and economically.

The main conclusions of Chapter 7 are:

- Tests carried out with two solar simulators built in the laboratory showed that the application of additional layers of MgO and ZnO results in an average increase in energy efficiency of between 3% and 9% compared to commercial cells without additional oxide layers.
- Comparative analysis of the *I-V* and *P-V* curves confirmed improvements in short-circuit current and open-circuit voltage for the treated cells.
- MgO layers applied from ethylene glycol (EG) solutions provided the best results in terms of energy efficiency.



- Tests carried out in real atmospheric conditions, using pyranometer for lighting monitoring, validated the trends observed in the laboratory.
- The efficiency increase in real conditions was between 2.5% and 7%, varying depending on the solvent used for the dispersion of the oxides and the nature of the oxide layer.
- The MgO-based coatings showed better stability of long-term operating performance.
- The MgO layers had a major contribution to reducing the recombination of minority carriers and increasing the open-circuit voltage ( $V_{OC}$ ).
- The ZnO layers, due to their high optical transparency and good conductivity, favored the increase of the short-circuit current (ISC).
- The use of Al-doped ZnO brought further improvements.
- The synthesis of ZnO powders by vaporization and solar-assisted condensation produced materials with favorable morphologies (whiskers/nanorods) that led to additional efficiency increases compared to conventional oxides.
- The size of the particles and their shape significantly influence the performance of the layer: smaller nanoparticles and elongated morphologies favored increased efficiency through extended light capture.

## CONCLUSIONS OF THE DOCTORAL THESIS AND PERSONAL CONTRIBUTIONS

This doctoral thesis entitled "*Research on nanostructured oxide materials to increase the performance of photovoltaic cells*" makes significant contributions both theoretically and applied in the field of renewable energy, with a focus on optimizing photovoltaic conversion through the use of nanostructured oxide layers. The research, at the intersection of **Materials Engineering** and **Electronic Engineering**, demonstrates the potential of oxide nanomaterials (such as Al-doped MgO, ZnO and ZnO) in improving the energy efficiency of polycrystalline Si-based solar cells.

The work followed a well-founded logical structure, starting with the elaboration and characterization of nanostructured materials using advanced techniques (XRD, SEM, FTIR, UV-Vis, BET), continuing with their integration into the architecture of photovoltaic cells, and culminating with the testing of electrical parameters in laboratory and real conditions. The conclusions obtained are relevant both from the fundamental perspective of understanding the mechanisms of transport and recombination of load carriers, and from the practical perspective of applicability in commercial systems.

The results clearly showed that the MgO layer contributes majorly to reducing the recombination of minority carriers, increasing the open-circuit voltage ( $V_{oc}$ ), while ZnO, due to its transparency and conductivity, favors the increase of short-circuit current ( $I_{sc}$ ). Doping ZnO with Al led to further improvements, resulting in remarkable increases in energy yield, with conversion efficiencies exceeding 10%, compared to about 1.5% in the case of the untreated control cell.

The statistical analysis correlated the morphology of the particles (nanometer sizes, rod-like shapes or whiskers) with the optoelectronic performance of the cells. The synthesis of materials through advanced methods, such as solar-assisted vapocondensation, allowed to obtain structures with porosity and optimal active surface for photon capture and efficient charge transport.

From an economic *point of view*, the thesis demonstrated that the integration of these layers can generate an additional annual energy production of approximately 300 kWh per module, which, compared to a residential system of 10 modules, can mean an annual saving of 667–879 euros, contributing to the rapid amortization of the investment. Thus, the research offers not only a scientific breakthrough, but also a sustainable application model, with a direct impact on the renewable energy market.

*The limitations* identified in the research include the stability of nanostructured materials over time, the potential risks of toxicity (especially in the case of Cd, Pb-based dopants), as well as the challenges related to the large-scale industrial replication of laboratory processes. Future studies are needed on scaling synthesis processes, developing low-temperature printing techniques, and integrating hybrid organic/inorganic materials to achieve additional functionalities (e.g., self-cleaning, moisture resistance, anti-reflective).

The *interdisciplinary* impact of the research is obvious: on the one hand, it contributes to the field of advanced functional materials, providing essential experimental data on the structure, morphology and electrical behavior of oxide nanomaterials; on the other hand, it brings value in electronic engineering, through the development of innovative hardware and software solutions for monitoring and optimizing the performance of solar cells. The hardware-software system implemented for real-time testing of photovoltaic cell parameters,



using NI-USB acquisition boards and Python applications, demonstrates the successful integration of modern digital tools in experimental research.

Among *the original contributions* of the thesis are:

- development and characterization of efficient nanostructured oxide layers, using innovative synthesis methods;
- Demonstrating the synergistic effect of aluminum doping and solar vapocondensation on energy performance;
- correlation of the morphology of nanostructures with the electrical parameters of cells;
- Realization of an experimental model for the construction of an energy-efficient cell, validated through extensive testing;
- Development of a robust hardware-software system for real-time monitoring, with the potential to expand into commercial applications.

*The general conclusions* of the thesis show that oxide nanomaterials represent a strategic research direction for improving the performance of photovoltaic cells, with major implications for the energy transition and global sustainability. The integration of these advanced solutions can contribute not only to maximizing energy efficiency, but also to reducing the carbon footprint, supporting European and international renewable energy goals.

*Future proposed research directions* include expanding studies on the stability over time of nanolayers, exploring hybrid materials, and implementing scalable manufacturing technologies. At the same time, it is recommended to strengthen international collaborations and participate in interdisciplinary projects, in order to accelerate the transfer of technology from the laboratory to industry.

In conclusion, the doctoral thesis is part of a cutting-edge research framework, capitalizing on multidisciplinary expertise to provide concrete and innovative solutions in the photovoltaic field. The results obtained demonstrate not only the viability of the proposed approach, but also its potential to contribute significantly to the development of a sustainable energy future.

## PROSPECTS FOR FUTURE RESEARCH

Based on the results obtained and the conclusions formulated, a series of recommendations for future research directions are outlined, aimed at amplifying the scientific and applicative impact of the current study:

1. **Stability of nanostructured materials:** It is necessary to investigate the stability over time of the applied oxide layers, especially under real operating conditions, in order to assess possible degradation or loss of long-term performance.

2. **Exploration of hybrid materials:** The combination of organic and inorganic materials could bring further improvements in terms of flexibility, light weight, and production costs. Studies on hybrid interfaces and chemical compatibility are essential.

3. **Scalable manufacturing techniques:** It is recommended to test industrial methods, such as inkjet or roll-to-roll printing, to assess the feasibility of scaling up lab-developed solutions to commercial scale.

4. **Sustainability analyses:** An important direction is the assessment of the ecological footprint of the entire manufacturing and use process, including the recycling of materials and the disposal of toxic components.

5. **Optimization of hardware-software systems:** The development of more advanced monitoring systems, the integration of smart sensors, and the use of machine learning algorithms could improve the overall efficiency of photovoltaic systems.

6. **Interdisciplinary studies and international collaborations:** It is recommended to strengthen collaborations with research teams in the fields of chemistry, physics, electrical engineering and computer science, in order to accelerate the development of innovative solutions.

7. **Participation in European and international projects:** Involvement in international consortia and programs such as Horizon Europe can provide financial resources, access to state-of-the-art equipment and increased visibility of research results.

These perspectives are oriented towards maximizing the scientific and commercial impact of research and ensuring an efficient transfer of innovative technologies from academia to industry.

*The articles published* within the doctoral studies reflect an intense, coherent and focused scientific activity in the field of nanostructured materials and their application in increasing the performance of photovoltaic cells. The analysis of the works reveals a clear evolution of the research directions, but also a maturation of the methodological approaches and the complexity of the studies carried out.

First, articles published in ISI-listed journals, such as *Materials*, *Archives of Metallurgy and Materials*, *Engineering Technology & Applied Science Research*, and *Crystals*, show a constant concern for investigating the morphology, structure, and optoelectronic properties of nanostructured metal oxides. The paper published in *Materials*, for example, details the synthesis and characterization of ZnO particles produced by solar ablation, highlighting manufacturing method innovation and the potential of nanostructured particles.

The publications produced together with the team coordinated by Prof. Mihai Oproescu show a fruitful collaboration, with a clear contribution of the doctoral student in the experimental aspects, synthesis and characterization, but also in the interpretation of the results. The fact that I am the main author or co-author in leading positions confirms the direct contribution to the development and completion of this research.

On the other hand, the articles presented at the IEEE conferences (ECAI 2022) confirm the openness to the international community and the interest in validating the ideas and prototypes developed within the doctoral thesis. The papers presented at ECAI address topics such as the development and characterization of nanostructured layers, the proposal of hardware systems for testing the efficiency of solar cells and the analysis of energy alternatives for current consumption requirements.

**Analyzing the publications thematically**, one can observe a clear complementarity between the theoretical and the applied articles. On the one hand, fundamental studies on the characterization of nanostructures provide a solid basis of knowledge, and on the other hand, the application of these structures in real systems (such as photovoltaic cells) validates the practical relevance of the research. This two-way approach – theory and practice – is essential in the field of advanced materials, where only the synergy between **Materials Engineering and Electronic Engineering is possible**.

In terms of **scientific impact**, articles published in ISI-rated journals, even those in Q4, are valuable because they reflect original contributions and provide international visibility. Publication in journals from Q1 (*Materials*) and Q2 (*Crystals*) demonstrates the quality of the research and the ability to align with the high standards of the international community. The constant presence in IEEE publications completes the image of a researcher concerned with both the academic side and innovation.

An important aspect of the analyzed articles is **the interdisciplinary** approach. The doctoral student's research is not limited to a narrow field, but integrates knowledge and methods from engineering, physics, chemistry and electronics. This is clear from the combination of chemical synthesis, structural characterization (XRD, SEM, FTIR) and electrical testing techniques. Moreover, the development of hardware-software solutions for monitoring energy parameters shows an openness to the engineering of integrated systems.

Another relevant direction is **the potential for commercial applicability** of published research. The articles are not limited to theoretical aspects, but include concrete proposals for functional systems with possible applications in the renewable energy industry. Thus, doctoral research has not only an academic impact, but also an applicative potential, supporting the idea of a technology transfer from the laboratory to industry.

In conclusion, the published articles used in the thesis demonstrate a robust scientific activity, oriented towards innovation and applicability, with an impact on both fundamental knowledge and emerging technologies in the photovoltaic field. The contribution to scientific research is significant, and the publication of the results in prestigious journals and conferences is not only an academic validation, but also an important step towards developing a solid career in research and innovation.

The scientific activity carried out is distinguished not only by the articles published in prestigious journals and conferences, but also by its active participation in relevant international projects. This involvement reflects a double strategic direction: on the one hand, **deepening fundamental research through international collaborations**, and on the other hand, validating the results by disseminating them within broad scientific communities. Analyzing the correlation between published articles and involvement in international projects, a mutual amplifying effect can be observed. The results obtained within the international projects were disseminated through publications, increasing their visibility and impact, while the published articles strengthened the position of the research team in competitions to attract new funding.

The international projects in which the author participated, such as the European initiatives Horizon Europe or Erasmus+, bilateral projects with Mansoura University in Egypt and research institutes in Poland, had an essential role in providing material, logistical and human resources to carry out complex experiments

### Papers in ISI Rated Journals

1. A-G. Schiopu, M. Oproescu, V.G. Iana, C.M. Ducu, S.G. Moga, D.S. Vilcoci, G.Cirstea, V.M. Calinescu., Ahmed O. Synthesis and characterization of ZnO-Nanostructured Particles Produced by Solar Ablation. *Materials*. 2023, Vol. 16, Issue 19, no. 6417, WOS:001094705200001, <https://doi.org/10.3390/ma16196417>, FI. 3.1 (Q1)
2. Valentin Marian Calinescu, Mihai Oproescu, Vasile Gabriel Iana, Marian Catalin Ducu, Adriana Gabriela Schiopu, Morphological Changes of Metal Oxides Through the Solar Physical Vapor Deposition Process, International Conference on Innovative Research Iasi, 11th–12th of May 2023, published in *Archives of Metallurgy and Materials*, Vol.69, Issue 2, p.535-540, WOS:001296371200027 , DOI10.24425/amm.2024.149780, FI.0,7 (Q4)
3. Mihai Oproescu, Adriana-Gabriela Schiopu, Valentin Marian Călinescu, Vasile Gabriel Iana, Nicu Bizon, Mohammed Sallah, Influence of Supplementary Oxide Layer on Solar Cell Performance, *Engineering Technology & Applied Science Research*, Vol. 14, No.2, pag. 13274-13282, WOS: 001198238800021, DOI: 10.48084/etasr.6879, FI.0.55 (Q2)
4. M. Oproescu, A.-G. Schiopu, V.-M. Calinescu, and J. D. Fidelus, "Enhanced Efficiency of Polycrystalline Silicon Solar Cells Using ZnO-Based Nanostructured Layers," *Crystals (Basel)*, vol. 15, no. 5, p. 398, Apr. 2025, doi: 10.3390/cryst15050398, FI. 2.4 (Q2)

### IEEE Indexed Papers

1. V. Calinescu, M. Oproescu, V. G. Iana and V. A. Stan, "Overview on elaboration and characterization of nanostructured oxides for solar cells," 2022 14th International Conference on Electronics, Computers and Artificial Intelligence (ECAI), Ploiesti, Romania, 2022, pp. 1-8, doi: 10.1109/ECAI54874.2022.9847476.
2. V. Calinescu, M. Oproescu, G. -V. Iana, O. C. Novac and M. C. Novac, "Efficiency of Nanostructured Layers Deposited on Solar Cells - hardware system proposal," 2022 14th International Conference on Electronics, Computers and Artificial Intelligence (ECAI), Ploiesti, Romania, 2022, pp. 1-6, doi: 10.1109/ECAI54874.2022.9847309.
3. V. Calinescu, M. Oproescu, G. V. Iana and V. A. Stan, "Solar Cells - Alternative for Energy Demand," 2022 14th International Conference on Electronics, Computers and Artificial Intelligence (ECAI), Ploiesti, Romania, 2022, pp. 1-5, doi: 10.1109/ECAI54874.2022.9847417.