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FACULTY OF MATERIALS SCIENCE AND ENGINEERING

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PhD THESIS

-Abstract-

MULTIFUNCTIONAL ZnO NANOSTRUCTURES

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« MULTIFUNCTIONAL ZnO NANOSTRUCTURES »

Phd Student : Raluca Anca MEREU
Scientific Supervisor: Prof. Dr. Eng. Lelia CIONTEA

The present thesis entitled Multifunctional ZnO nanostructures follows the research line of the Superconductivity, Spintronics and Surface Science Centre C4S, Faculty of Materials and Environmental Engineering within the Technical University of Cluj-Napoca, Roumania. The main aspects of this thesis are focusing on the synthesis and characterization of zinc oxide nano-structures (powders and thin films). The thesis presents the research results on ZnO thin films which subscribe to the challenging topics concerning the alternative energies.

The public defence of the thesis will take place on the 14th of December 2012.
The jury members are:

Prof. Dr. Phys. Traian PETRISOR – President of the jury
Prof. Dr. Eng. Lelia CIONTEA- Scientific Supervisor
Prof. Dr. Eng. Rodica PODE – Referee
Assoc. Prof. Dr. Eng. Monica VENTER - Referee
CR1 Dr. Eng. HDR Coriolan TIUSAN- Referee

Keywords: *zinc oxide, nanopowders, thin films, sputtering, chemical solution deposition.*

CONTENT

Abstract of the thesis

Global energy consumption is continuously increasing. Currently, electricity is the most versatile of all forms of energy we use for a growing number of applications. The human development index (HDI) is a measure of life quality in the countries all around the world and significantly depends on the electricity consumption (kWh/ year) in each country.

The need of alternative energy sources comes from the necessity and the need to reduce dependence on fossil fuels. The gradual depletion of oil, coal and natural gas industry research leads to increasing efforts for using alternative energy sources. One of the most important alternative energy sources is the sun. It represents a natural source of energy, clean, free and, most important, inexhaustible.

In the global context of the new materials development, the nanostructured materials present an increasing interest from a scientific and technological point of view. Crystalline and/ or amorphous oxide materials, under various forms (powders, films, fibers) are suggestively illustrated by the research aimed to obtain materials with prerequisite properties.

Multifunctional ZnO semiconductor is a potential candidate for electronics and optoelectronics applications and can be commercialized due to its excellent electrical and optical properties, inexpensiveness, relative abundance and chemical stability towards air. The semiconducting and piezoelectric properties of environmentally friendly ZnO are extremely important for energy harvesting devices.

The research performed within this thesis addresses to zinc oxide based materials, both as nano-powders and thin films.

The main thesis objectives are:

- The synthesis of ZnO nano-powders starting from different precursors and using different synthesis methods;

- The chemical deposition and the characterization of ZnO and ZnO:M (M=Al and/or Ho) thin films;
- The sputtering deposition of ZnO, ZnO:Al, ITO thin films on large substrates (9cm × 9cm);
- ZnO heterostructures deposition: AZO/*i*-ZnO/glass, ITO/*i*-ZnO/glass and ITO/*i*-ZnO/CdS/glass for the Cu(InGa)Se_2 photovoltaic solar cells.

In this context, we have investigated the influence of various preparation parameters: the precursor type, the concentration, the use of surfactant agents, temperature on the structural and morphological characteristics of powders. The characterization of the obtained ZnO nanostructures has been performed by using X-ray diffraction, IR, Raman and PL spectroscopy, and transmission electron microscopy.

The research focused on the synthesis and characterization of zinc oxide thin films aims the preparation of the thin films by two methods: chemical and physical methods (sputtering deposition). The structural characterisation of the thin films was performed by X-ray diffraction and the morphology was evaluated by Atomic Force Microscopy. The optical properties of the ZnO thin films were determined by UV-VIS and fluorescence spectroscopy.

The thesis is structured in two parts: "Literature review" and "Original contributions to the synthesis of ZnO powders and thin films". In addition, a general introduction and conclusions are included.

The ***first part*** presents a literature review focusing on zinc oxide based nanostructures, synthesis and characterization of powders and thin films. This part is divided into three chapters:

***Chapter** 1* - is dedicated to the general characterization of zinc oxide and updating the literature information regarding the potential applicability of ZnO.

Chapter 2 - is dedicated to the review of the main synthesis methods specific for both powder and oxide thin films with tailored properties.

Chapter 3 - presents the specific characterization methods and techniques used in this work for both powders and oxide thin films.

Part two includes the scientific contributions on obtaining and characterization of ZnO nano-powders and thin films and is divided into four chapters.

Chapter 4 - describes the results of the research regarding the obtaining and characterization of ZnO nano-powders using different organometallic precursors (mercapto-thiadiazole carboxylate, oxalate or propionate) and different methods (combustion or hydrothermal synthesis). ZnO nano-powders were obtained with acicular morphology (rods) with the size of 150-290 nm by the hydrothermal synthesis using an original approach, using propionic acid as a chelating agent. We have demonstrated the ability of mercapto-thiadiazole carboxylate to form ZnO and ZnS powders and potentially ZnO-ZnS or doped ZnO, under controlled thermal treatment/atmosphere. The influence of the preparation parameters, such as: the thermal treatment atmosphere (N2, humid oxygen, air), heat treatment temperature (700-1000 °C), precursor solution concentration, the nature of the surfactant agents on the solvothermal reaction synthesis was also studied. We have synthesized ZnO nanopowders with crystallites size of about 50 nm.

Chapter 5 - in a first part, we present studies regarding the synthesis and the characterization of the ZnO and ZnO: M (M = Al and/or Ho) thin films chemically deposited from precursor solutions on different substrates. Two synthesis methods were discussed: one based on aqueous solutions environmentally friendly and another one based on the trifluoroacetate method. Special attention was given to the study of precursors; their nature can be responsible for the characteristics of the obtained oxide films. The stability of the precursor solution has been investigated in order to ensure a good reproducibility of the films (6 months stability). Undoped, and Al and/or Ho -doped ZnO thin films were obtained at 400°C. The optical properties of the thin films were investigated by UV-VIS and PL measurements.

Chapter 6 - describes the experimental technique used for the deposition of oxide films (ZnO, ZnO:Al and ITO) by physical methods - sputtering. A special attention was given to the global parameters to better describe the physical properties of transparent conducting oxide thin films (TCO). Thus, we have studied the influence of

pressure, power, frequency, film thickness, substrate temperature on the optical and electrical properties of TCO films. The TCO thin films deposition was performed on Pyrex glass substrates with 9cm × 9cm in size. Electrical (4 contacts method) and optical (UV-VIS spectroscopy) measurements have been performed for the characterization of TCO thin films. We have ensured the compatibility of the deposition techniques elaborated for the mono-layers thin films with the rest of the deposition techniques involved in the elaboration of the multi-layer architecture deposition.

Chapter 7 - is dedicated to the obtaining and characterization of bi-layered heterostructures of ZnO:Al/i-ZnO/glass and ITO/i-ZnO/glass type, as well as ITO/i-ZnO/CdS/glass tri-layers obtained both by chemical and physical methods, using large substrates (9cm × 9cm). The ZnO heterostructures have been characterized in terms of optical and electrical properties in order to use them in CIGS solar cells.

The thesis is completed with general conclusions and original contributions. It should be noted that some of the results presented in this thesis were performed in the mobility stages. The results obtained during the three years of doctoral training were published, communicated or are on pending. The articles developed and dedicated to thesis topic are attached at the end of the work.