Romanian Academy
Institute of Physical Chemistry “Ilie Murgulescu”

PhD THESIS SUMMARY

CORRELATIONS BETWEEN STRUCTURAL AND PHYSICO - CHEMICAL PROPERTIES OF THE SEMICONDUCTOR OXIDES WITH OPTIC, SENSORISTIC AND MAGNETIC APPLICATIONS

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1. INTRODUCTION

During the last decades, major progress has been achieved in nanomaterial synthesis and characterization, leading to a great expansion in the field of nanoscience. Oxide semiconductors with nanometric sizes have great potential as basic materials in performant and modern applications.

Many scientific papers have dealt recently with the combination of SnO_2, ZnO and TiO_2 materials with improved structural, optical, electrical, photocatalytic or sensor properties in comparison with the simple materials.

The aims of this thesis were:

A. Study of the physicochemical properties of-systems listed above:

- The synthesis and characterization of SnO_2-TiO_2 modified with Zn and Pr thin films and powders for gas sensor applications.
- The study on the influence of Fe on the structure, morphology, surface chemistry, electrical and magnetic properties of SnO_2 thin films and powders containing Zn and Fe.

B. Obtaining of new oxide combinations with nanometric structures:

- Obtaining and characteriziation of TiO_2-SnO_2 films and correlation their optical and electronic properties with the structure, morphology and surface chemistry of these samples.
- Synthesis and characterization of ZnO films and powders modified with Fe and Ti for optoelectronic and gas sensor applications.

C. Supplementary studies on TCO materials with applications in gas sensors:

- Comparing ITO films obtained through chemical (sol-gel) and physical (sputtering) methods.
- Electric, microstructural and surface chemistry characterization of TiO_2 films doped with Nb as ~~a~~ CO sensor.

The Ph.D. thesis contains two parts: the introductory part which presents a literature study and the experimental part which highlights the original contributions of the Ph.D. student in the field.

Chapter 1 presents general considerations on the state-of-the-art in the field of the oxide semiconductors, focusing on the specific properties and applications of these materials.

Chapter 2 briefly describes the synthesis and characterization methods related to the oxide systems used in the thesis. Modern investigation techniques employed herein are: X-ray powder diffraction (**XRD**), scanning electron microscopy (**SEM**), energy-dispersive X-ray spectroscopy (**EDX**), adsobtion/desorbtion N_2 (**BET**), atomic force microscopy (**AFM**), X-ray photoelectron spectroscopy (**XPS**), spectral ellipsometry (**SE**), UV-Vis spectroscopy, vibrating sample magnetometry (**VSM**) and electrochemical impedance spectroscopy (**EIS**). The main specific objectives are also presented in this chapter.

All experimental results were presented in the Chapters 3 – 7 as follows:

- **Chapter 3 –** the SnO_2-TiO_2 system modified with Zn and Pr (films and powders),
- **Chapter 4** – the SnO_2 modified with Fe and Zn system (films and powders),
- **Chapter 5** – the TiO_2-ZnO system (films),
- **Chapter 6 –** the ZnO modified with Fe and Ti system (films and powders),
- **Chapter 7 -** auxiliary studies on sol-gel ITO and Nb doped TiO_2 for optical and sensors applications.

Chapter 8 summarizes the final conclusions based on the experimental data, followed by the original contributions and a dissemination list. At the end of the thesis the references and the abbreviation list are given.

2. EXPERIMENTAL RESULTS:

SnO_2 - TiO_2 modified with Zn and Pr - films and oxide powders

In this thesis were obtained films and oxide powders for the system SnO_2 - TiO_2 modified with Zn and Pr (Sn:Ti:Zn:Pr contents 60:20:15:5), in order to develop new materials with improved properties compared with separate components. Films were deposited by spin coating on the glass substrate, from gels of SnO_2 -TiO_2 system, modified with Zn and Pr obtained by a customized sol-gel method. The powder was obtained by calcination in air, at temperatures between 600 to 800°C.

XRD evidenced that the films were in amorphous phase, with an easy crystallization of SnO_2. The structural properties for the powders obtained at 600 ^{o}C showed only the presence of SnO_2-cassiterite and TiO_2-anatase phases with crystallites sizes of 24 nm for cassiterite and 9 nm for anatase. For the powders annealed at 800 °C, anatase phase is partially converted to rutile and the rest in titanate zinc and praseodymium (type crichtonite) phases (Fig. 1). The crystallite size is 40 nm for tin dioxide, 27 nm for the rutile and 28 nm the zinc titanate and praseodymium.

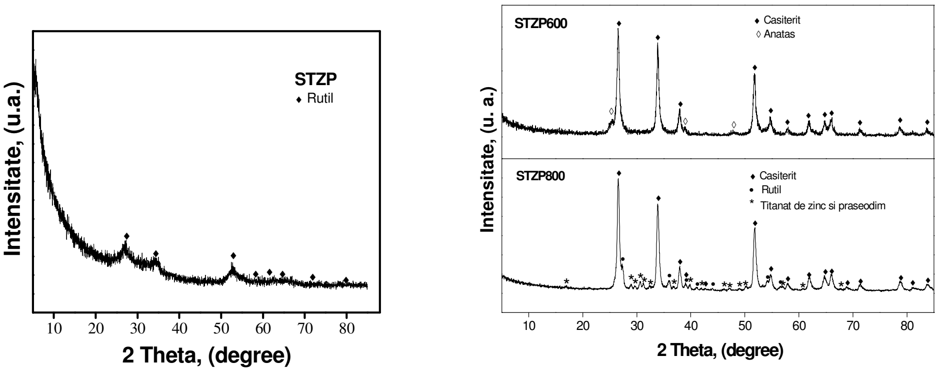

Fig. 1 X-ray diffraction patterns of films (left) and powders (right) STZP

SEM images showed the formation of a dense and uniform film (Fig. 2 left) and the formation of nanocrystalline powder particles (Fig.2 right).

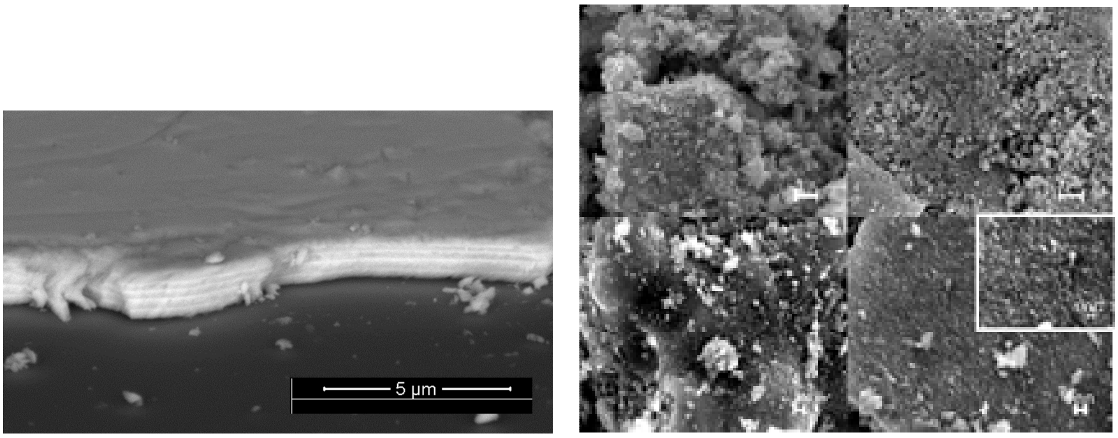

Fig. 2 SEM images of the two films (left) and powders (right) STZP

The CO sensing properties of the films and powders obtained were: the recovery time for returning to the initial film resistance is 25 minutes, and, in the case of powders is approximately 2 minutes, as can be seen in Fig. 3:

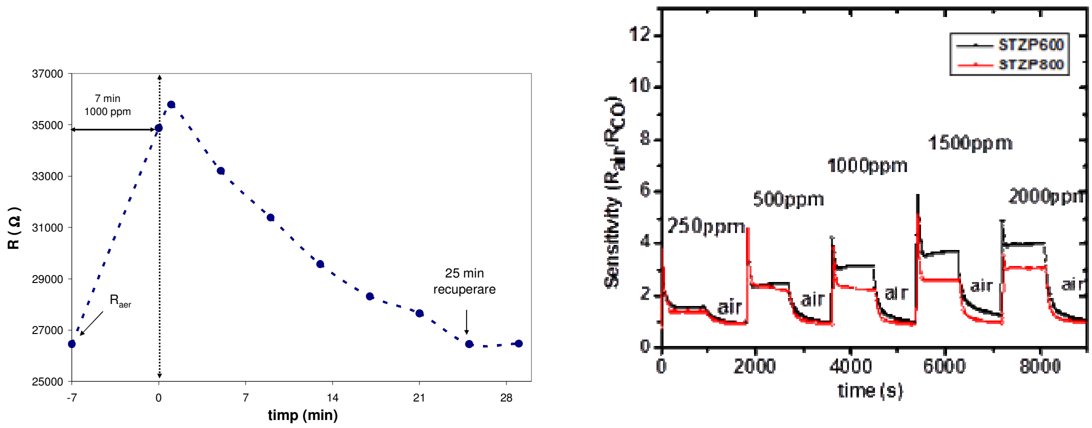

Fig. 3 Recovery time from the different concentrations of CO films (left) and powders (right) STZP

The most promising results in terms of sensitivity, but also in case of response time and recovery were obtained for the powders calcined at 600 °C, which recommended this material as the CO sensor.

The following correlations have been established:

- Structure and porosity are influenced by the annealing temperature (annealing at 800 °C promotes the highest level of crystallinity and leads to a drastic decrease of surface area and total pore volume).
- CO sensing is influenced by morphology through porosity which affects surface area.

SnO_2 modified with Zn and Fe - films and oxide powders

In the present study we have investigated the SnO_2 system modified with Zn and Fe (films and powders) in order to obtain a promising material for gas sensors and magnetic applications. In the literature, there is currently little data on this composite material, so the work included in this thesis is new and original. Films and oxide powders based SnO_2 modified with Zn and Fe (20 mol% Zn, 10 and 30 mol% Fe) were obtained by a sol-gel method.

The sensitivity of the sensor in an atmosphere of CO is shown in Fig. 4:

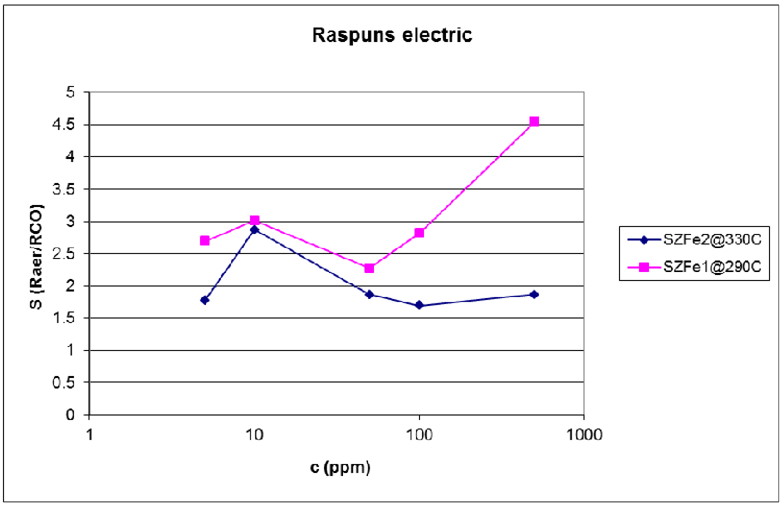

Fig. 4 Sensitivity to CO of sensors SZFe1 and SZFe2

Between those two films, the sensor SZFe1 (less Fe composition – 10 mol%) gives a better response to CO at low concentrations of 5 ppm and has a working temperature lower with 40 degrees (290 °C) than likely sensor SZFe2 (330 °C), which is an economic advantage. Recovery of the two films is comparable, being complete after approximately 180 seconds, the sensitivity returning to baseline after each injection (Fig. 5).

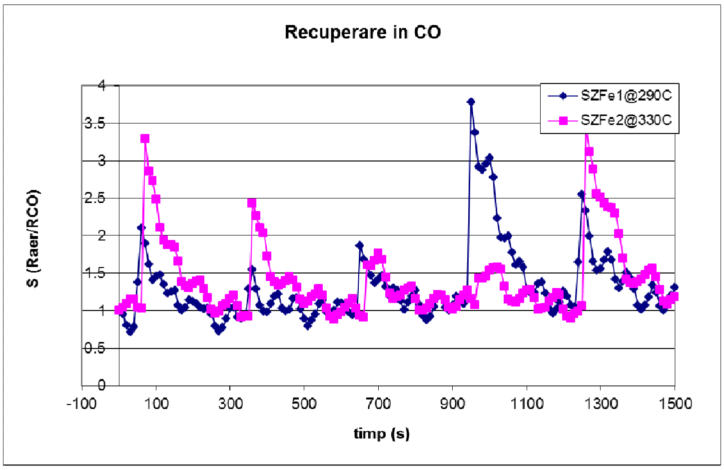

Fig.5 The recovery time of sensors SZFe1 and SZFe2

Following the favorable results of the sensors their selectivity was determined at a temperature of 290 ° C and a concentration of 500 ppm. To test the selectivity of the sensors the following gases were used: CO, CH_4 and C_3H_8.

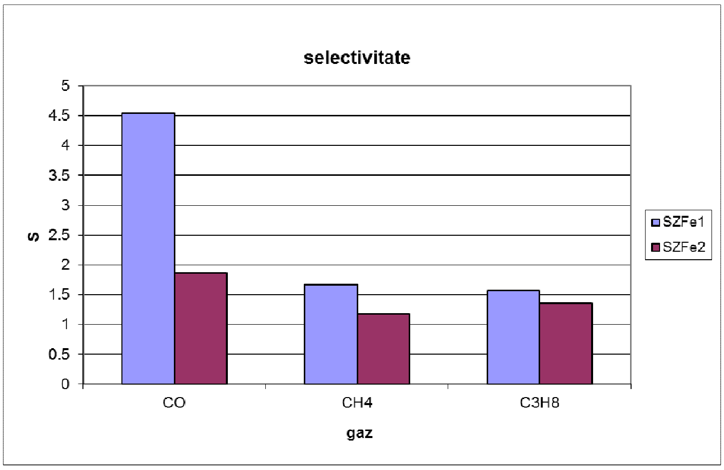

Fig. 6 Selectivity of sensors SZFe1 film and SZFe2 film

We observed that sensor SZFe1 is more selective than sensor SZFe2. The response of the SZFe1sensor to CO is three times higher than for methane and propane (Fig. 6). The electrical property improvement due to the percent of Fe introduced in the composition recommends it as a promising sensing material.

The magnetization behavior of the studied samples is presented in Fig. 7:

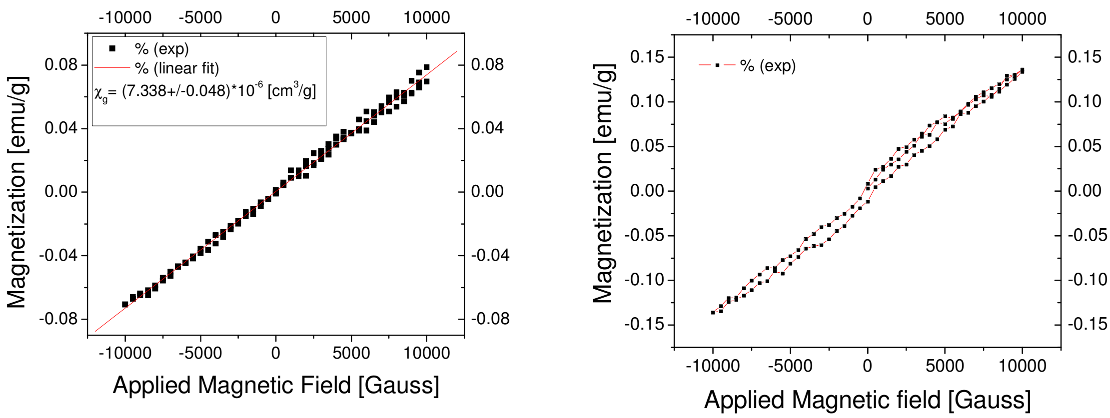

Fig 7. Magnetization of the sample: SZFe1 (left)and SZFe2(right)

The incipient formation of $ZnFe_2O_4$ in the SZFe1 sample can be visualized in Fig. 7 (left), confirming the XRD results. Zinc ferrite is too small to be felt, so the magnetism is not manifested, SZFe1 remaining a paramagnetic sample. In SZFe2 (Fig. 7 right) deviations from a linear behavior in M vs. H are evidenced. The magnetization of SZFe2 sample is composed from a ferromagnetic phase with a superparamagnetic-like behavior and a paramagnetic one (see Fig. 8).

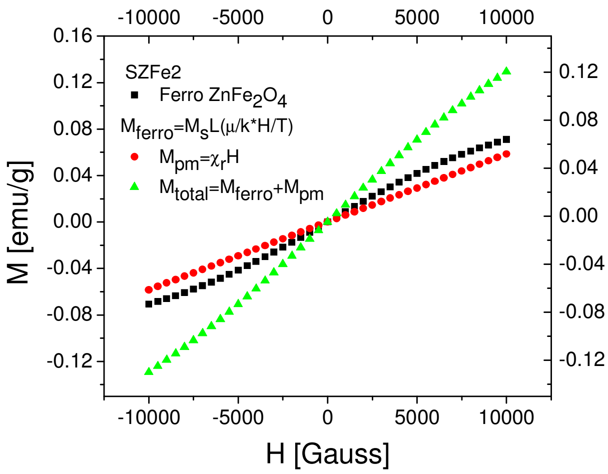

Fig. 8. Magnetization of the SZFe2 sample: ferro, para and total calculated contributions

Sol-gel method is proved to be an encouraging technique for the preparation of low-cost composite materials used for obtaining of CO gas sensors and soft magnetic materials. The following correlations have been established:

- The magnetic properties are influenced by the increasing of Fe content (sample SZFe2 has a superparamagnetic behavior).
- Morphology (uniformity, homogeneity) influences the properties of the sensor.
- CO sensing depend on the content of Fe in the matrix (SZFe1 sensor has a better response).

TiO_2 - ZnO – films

Films were obtained by spin-coating, from TiO_2 - ZnO gels (40 mol% Zn and 20 mol% Zn), synthesized by sol-gel method. The films were deposited on glass substrates.

Based on opto-electrical and gas sensing applications, a complex electrical characterization of TiO_2 - ZnO thin films was achieved:

The crystalline structure was revealed by X-ray diffraction and confirmed that the films have a crystal form of anatase TiO_2; other phases of ZnO and TiO_2-ZnO combinations are not identified. The films were uniform, homogeneous and porous, with micron thickness. Surface chemistry evaluated by XPS, revealed the presence of all the material on the surface and their oxidation states: Ti^{4+} and Zn^{2+}. Experimental stoichiometry is in agreement with XRD results. The high transmission obtained on these samples (around 80%) make them attractive for optical applications.

The sensing properties of the films obtained were evaluated for CO (in air). The increase in Ti content lowers the temperature at which it is transformed from a n-type in p-type semiconductor (Fig. 9).

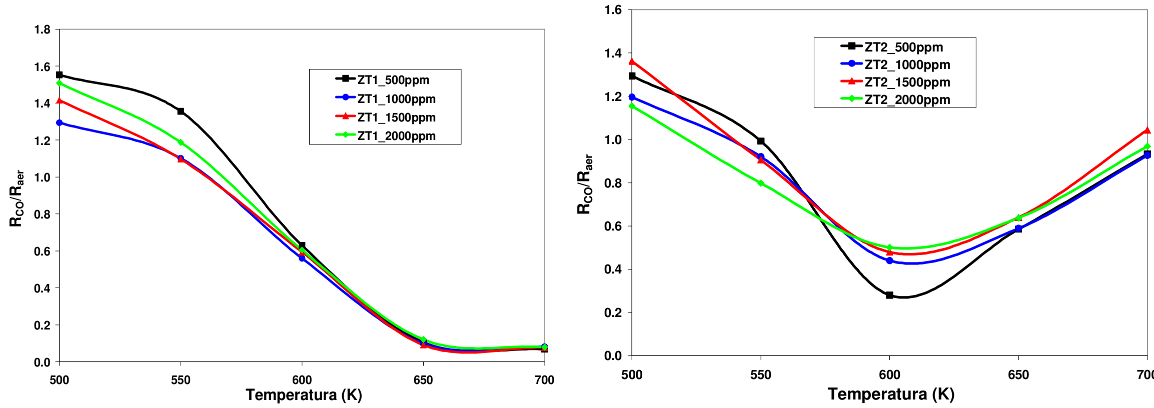

Fig. 9 The sensitivity of the films ZT1 (left) and ZT2 (right) at different concentrations of CO in air

ZnO modified with Ti and Fer - films and oxide powders

Crystalline structure and chemical surface composition of the manufactured materials have been investigated in order to be correlated with electrical and dielectrical properties. Films and powders with different Fe content (10, 15 and 20 mol%) were prepared by sol–gel method. The XRD data show that Zn-Ti-Fe-O system contains two phases, Iron Zinc Titanium Oxide ($FeZnTiO_4$) and Zincite (ZnO) is also confirmed by SEM analysis. Iron Zinc Titanium Oxide crystallizes in a cubic inverse spinel structure, but with increasing of Fe content, the degree of inversion is reduced due to the tendency of Fe (III) to prefer the octahedral coordination.

The XPS analysis (Fig.10) shows a continuous modification in the Fe surface chemistry with the increase of Fe content. For ZTFe1 and ZTFe2 samples, Fe is found as a mixture between Fe^{3+} as majority phase and Fe^{2+}, while in ZTFe3 there is a mixture of the oxidation states 3+ and 2+.

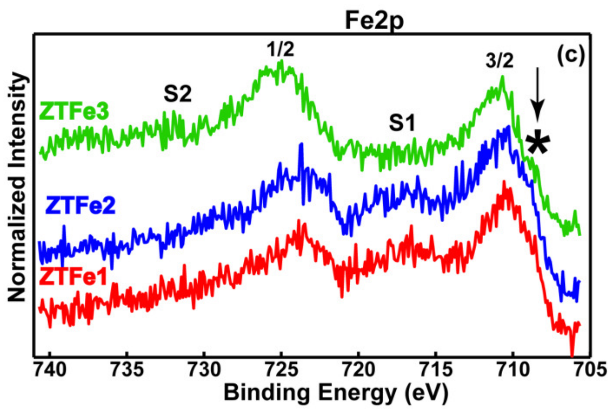

Fig. 10 The superimposed XPS spectra of Fe2p for samples ZTFe1, ZTFe2 and ZTFe3

XPS showed also that the increase of Fe content is accompanied by a corresponding decrease in Zn while the Ti content remains constant (Table 1).

Table 1 Data XPS: the binding energy (eV) and relative atomic concentrations (at.%)

Sample	**Binding energy, eV**			**Atomic concentrations, at.%**			
	Zn2p3/2	Ti2p3/2	Fe2p3/2	O	Ti	Fe	Zn
ZTFe1 (10 mol%Fe)	1021.8	458.5	710.6 709.3	54.20	6.69	5.03	34.08
ZTFe2 (15 mol%Fe)	1021.8	458.5	710.7 709.4	54.10	6.80	7.00	32.10
ZTFe3 (20 mol%Fe)	1021.8	458.5	711.0 709.4	54.19	6.73	10.06	29.03

For the analyzed samples dielectric behavior was investigated (Fig. 11). We can see that the dielectric constant decreases with increasing frequency from 100Hz to 3MHz. The high value of the dielectric constant indicates that the exchange of the electrons between Zn^{2+} and Fe^{3+} ions is predominant at lower frequencies. At higher frequencies, the dielectric constant reaches a constant value because beyond a certain frequency electron exchange between Zn^{2+} and Fe^{3+} occurs more slowly than the frequency of the applied electric field.

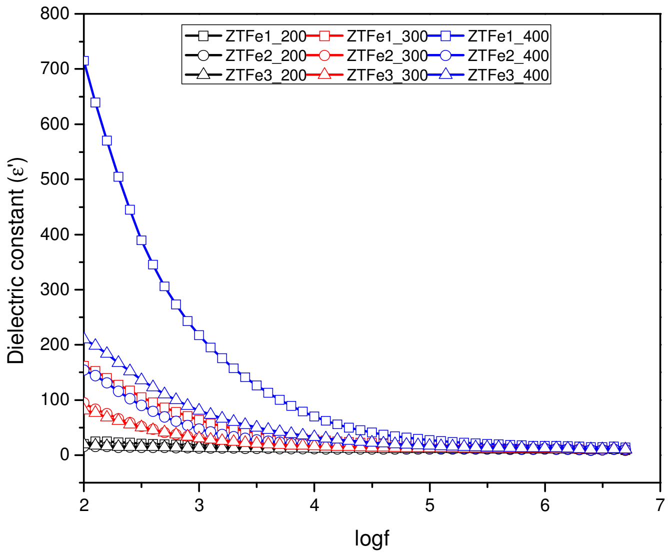

Fig. 11 The variation of the dielectric constant with frequency for the samples ZTFe, 1 ZTFe2 and ZTFe3 at different temperatures

Fig. 12 shows the change in dielectric constant (ε) and loss tangent (tanδ) at different frequencys (1 kHz, 10 kHz and 100 kHz).

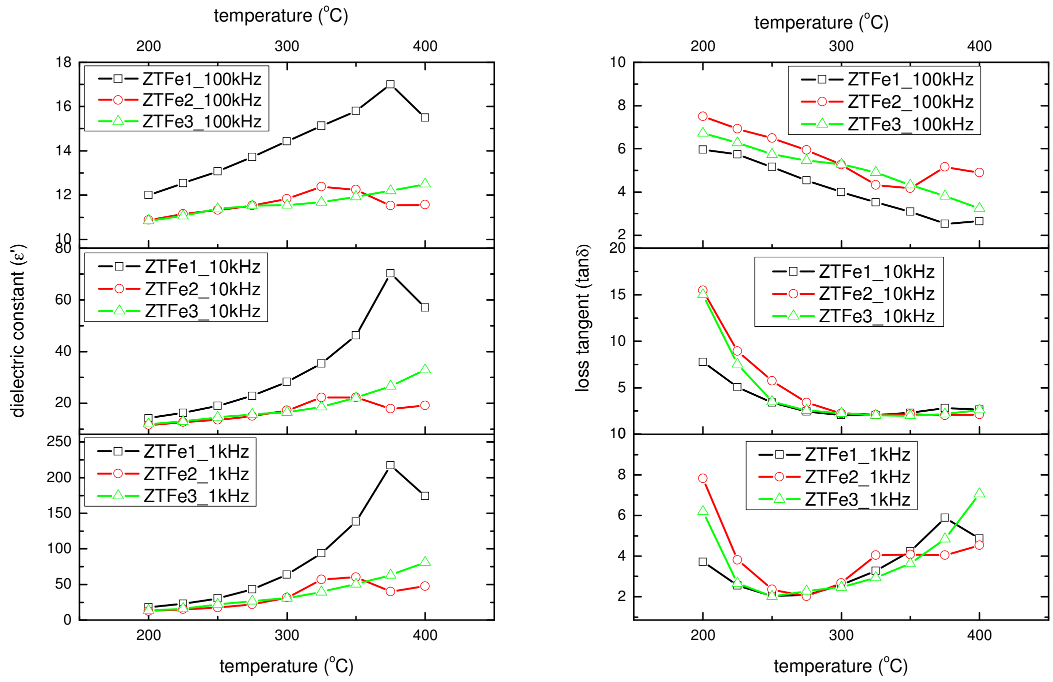

Fig. 12 Variation of dielectric constant (left) and loss tangent (right) of samples ZTFe1, ZTFe2 and ZTFe3 with frequency at different temperatures

The increase of Fe in the analyzed samples leads to a decreasing of dielectric constants. The loss tangent values (quality the dielectric is inversely proportional to the loss tangent value) are high for all samples, probably due to defects associated with intergranular boundaries. Good dielectric properties of these materials recommends them as sensors, transducers and actuators.

The following correlations have been established:

- Opto-electrical properties depend on the structure, morphology and chemical composition.
- Porosity plays an important role in the variation of dielectric constant (higher porosity lead to a lower dielectric constant).
- The iron content influences the dielectric constants and CO sensitivity.

Transparent conducting oxides (TCO)

Among the materials most commonly used as TCO is indium oxide doped with tin (ITO) due to its outstanding properties. Within this experiment we have developed two sets of ITO nanostructured films namely prepared by physical methods (r.f. sputtering, deposited in nitrogen atmosphere of N_2 75% şi 100%) and films by chemical deposition (sol-gel, concentration 0.1 M and 0.25 M) on glass substrates (coated with a layer of SiO_2). The aim of this study is the replacement of the sputtering method with a cheaper one, namely sol-gel. Diversification deposition parameters have influenced the morphology and electrical behavior. The morphology of films obtained by sputtering is affected by RTA temperature less than the atmosphere deposition. Sol-gel films morphology is influenced by the initial concentration of the solution, 0.25 M solution leads to films with low surface roughness and porosity comparable to those of films sputtering (Fig. 13 a, b).

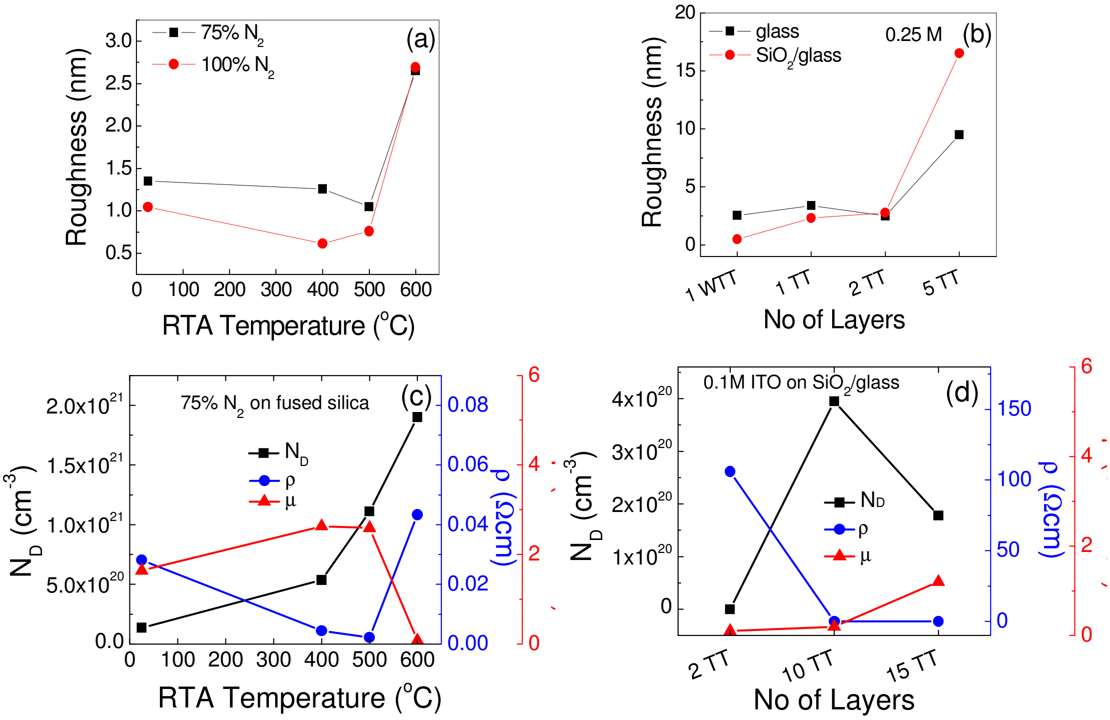

Fig. 13 Roughness (a, b), carrier concentration, resistivity and mobility (c, d) of sputtered (left) and sol–gel films (right)

The yield comparable values for properties of interest between the films deposited by physical method in 75% N_2 atmosphere and heat treated by RTA at 500 °C with the films deposited by chemical solution 0.1M, the SiO_2/glass (Fig. 13 c, d). The electrical properties of both films series were influenced mainly by morphology (roughness and porosity). The behavior of films produced by sol-gel deposition is similar to those deposited by sputtering semiconductor degenerate.

Experimental results have shown the possibility of replacing the sputtering method with the sol-gel method, because the chemical method can yield a film of electrically competitive with those produced by physical method.

Nb-doped TiO_2 for applications as sensor CO

The study aimed Nb doped TiO_2 for applications as gas sensor. The samples were analyzed in the reducing average of CO. Also it was monitored the possibility of replacing ITO with Nb-doped TiO_2 (which has higher availability and lower cost).

Structural and morphological analyzes revealed that the multilayered films contain anatase grains surrounded by amorphous areas The films, containing fine grains of anatase have small thickness and roughness (less than 1 nm). From analysis of atomic force microscopy (AFM) surface topography can be seen that Nb-doped TiO_2 films has one layer thermally treated with 1, 10 layers annealed:

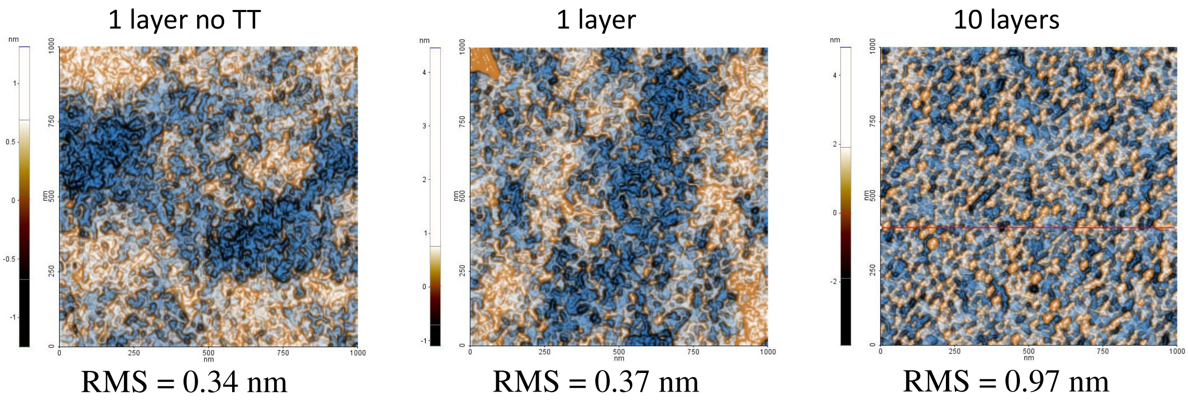

Fig. 14 AFM 2D images (in high contrast format) of Nb-doped TiO_2 films

AFM 2D images ("enhanced contrast") claim that a single layer films are amorphous. Crystallinity increases with the number of layers deposited, in good agreement with XRD results. The films from this series cannot be used to replace ITO material n-type conduction TCO, but could be used as a CO sensor due to large specific surface.

Final conclusions

Considering the research results obtained in the frame of this doctoral thesis we can conclude that optical, sensorsistic and magnetic properties of selected oxide semiconductors depend on their structure, morphology and chemical composition.

The study has lead to the following conclusions:

- New semiconductor materials have been obtained with nanometric sized particles.
- The systems studied in this work were obtained by sol-gel and the r.f. sputtering methods.

- The solution concentration and the deposition number of sol-gel films affect the level of crystallinity.
- The annealing temperature can modify the structure (high temperatures induce the highest degree of crystallinity), but does not influence the chemical composition.
- More promising as CO sensor despite films are the powders.
- The tested materials behave as n-type and p-type semiconductor.
- Optical properties prove to be attractive since it was able to obtain a high transmission.
- Opto-electronic properties of the samples were influenced by structure (crystallinity level) rather than morphology (porosity, homogeneity).
- Introduction of Fe in oxide matrix affect the structure, morphology, specific surface area, the magnetic and electrical properties.
- Samples have ferromagnetic properties with increasing of Fe content, but the conduction is better in the samples with low Fe content.
- Replacing an expensive deposition (r. f. sputtering) with a cheap deposition method (sol-gel) proved to be encouraging.

Original contributions and future research

Original aspect of this work is to obtain new oxide materials with potential applications in various fields, which is in line with proposed objectives. The systems SnO_2-TiO_2 modified with Zn and Pr and SnO_2 modified with Zn and Fe, were studied for the first time in this thesis.

The experimental results made an important contribution for specialized literature by determining the electrical properties of materials used for gas sensor applications.

The most important result of this study is the deposition of modified SnO_2 films with Zn and Fe on microtraductors in the sensors fabrication. For measurement of CO adsorption, this sensor presents low detection limit, selectivity, stability and very good reproducibility.

In the future the studies will focus on improving optoelectronic and magnetic properties of oxide materials used in microelectronics, sensor and solar cells production.