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THESIS SUMMARY

OXIDES WITH GAS SENSING PROPERTIES

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Introduction

In a laboratory the investigation of unknown gaseous species or gas mixtures is carried out accurately by analytical means such as mass spectrometry, chromatography, nuclear magnetic resonance, infrared or X-ray techniques or by combining these techniques. Unfortunately, these techniques are expensive and involve the use of qualified personnel. On the other hand some applications do not require a complete set of data for the analyzed sample. In such cases, the gas sensors are an appropriate solution. The sensors are small and they can be manufactured on a large scale with low costs [1].

Gas sensors have a wide range of applications in various sectors: automotive, medical, personal safety, nutrition, air quality control and environmental parameters control [2].

There are many types of chemical sensors that are based on different sensing materials and detection mechanisms. The most common types of chemical sensors in practice are: amperometric/voltammetric sensors, potentiometric sensors, resistive/conductive/impedance based sensors, optical sensors, mass sensors, biochemical sensors [1].

Resistive sensors are exclusively studied in this thesis, and the property is being changed in substance sensitive interaction with the gas of interest is present in the atmosphere analyzed the electrical resistance of the sensitive layer.

Sensors currently widely used resistive sensors are generally sensitive material deposited on a transducer.

This type of sensor has a number of advantages over classical sensors: small size, low power consumption, reduced manufacturing costs and the possibility of large-scale production. Electronic measuring and control circuit can also be included in microsensor, thus achieving *portability* of the entire assembly of sensors, data acquisition and control system.

Although sensors resistive were studied intensely in recent decades [3], there are some aspects that can be improved: the method of preparation/deposition of sensitive layer (in terms of cost and technology involved), the sensitivity and the selectivity sensors of certain gaseous species - to avoid triggering false alarms, degree of miniaturization of sensors and control devices.

So far many scientific papers were published on the topic of oxides with the role of sensitive material in a sensor. The most studied oxides in this category were: SnO_2, ZnO and TiO_2. Their choice was determined by the fact that they are very abundant in nature - leading to a reduced cost of these materials. On the other hand, the electrical properties of these semiconductors have been extensively studied in the past, so they are well-defined in the present.

Commercial gas sensors containing only one of these components present however a number of disadvantages among which we can mention [3]: high operating temperature (a strong economic disadvantage), expensive preparation techniques (CVD, PVD), low specificity for a certain gas (sensors are nonselective) - which may lead to false alarms being triggered resulting in panic at end-user level, lack of reliability and stability over time.

This thesis aimed to study various properties of oxide systems with gas sensor properties. To achieve these objectives several experimental installations were built and optimized for advanced sensors measurements. These setups are capable of data acquisition in alternating current (**AC**) and direct current (**DC**), being very versatile in working with oxide samples of various morphologies: powders, powder tablets (pellets) as well as films deposited on various supports (ceramic lamellas, miniaturized transducers, etc.). The other aim of this thesis was a study of oxide type sensitive materials, following a general trend towards miniaturization of sensors. Thus throughout the experimental part of this thesis the amount of material used for the sensitive detection of various gases was decreased gradually from one morphology to another: powders> pellets> films.

Thesis main objectives:

a) ***~~s~~ynthesis of the oxide materials based on TiO_2, ZnO and SnO_2, using cheap and ecological methods (co-precipitation, sol-gel).***
b) ***structural, morphological, optical and chemical characterization of the obtained oxide materials by specific analysis: X-ray Diffraction (XRD), scanning electron microscopy (SEM), electron spin resonance (ESR), X- ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM).***
c) ***testing the gas sensors properties of the oxide materials for the detection of the flammable/toxic gases and humidity: CO, C_3H_8, CH_4, CO_2, H_2O.***
d) ***developing sensing mechanisms for the systems based on TiO_2, ZnO and SnO_2.***

The thesis is structured into **5 chapters** which cover the thesis objectives.

Chapter 1 contains a review of recent progress in the field of resistive sensors. The basics of chemical sensors, their applications and detection mechanisms involved in the sensing process were defined. The most important methods of deposition of the oxide sensitive materials in a resistive sensor were analyzed and their advantages and disadvantages were presented. The factors affecting the electrical response of a chemical sensor have been identified.

Chapter 2 contains the experimental part of the thesis. This chapter is divided into chapters and sections.

Chapter 2.1 Based on the critical analysis carried out in the first chapter, aims and objectives were formulated for the doctoral program (listed above).

Chapter 2.2 This chapter presents a study on sensitive powder materials used for practical applications in the field of gas sensors.

The experimental setup, the sensing cell, the working protocol with this type of sensitive material are presented. In the sections of this chapter CO detection is studied in an anoxic atmosphere (carrier gas is He) in the concentrations range of 250-2000 ppm CO, using a commercial TiO_2 powder and mixed oxide SnO_2-CeO_2 powders as sensitive materials. The measurements are performed in **AC** current.

Chapter 2.3 presents a study on pellet-type sensitive materials for practical applications in gas sensing.

In the sections of this chapter **DC** sensing measurements on ceramic composite (SnO_2, ZnO) pellets are presented. The working protocol differs, a new sensing cell and different mass-flow controllers being used (yielding investigated gas concentrations up to 5 ppm).

Chapter 2.4 presents a study on the use of thin film sensitive materials for practical applications in gas sensing.

In the sections of this chapter AC sensors measurements on the Nb-doped TiO_2 films deposited on a simple ceramic support are presented. The sensing cell used for the detection is the same cell used in the study of sensitive ceramic pellets, adapted to fit a sample containing a film deposited on a ceramic support. The studied gases are CO, CH_4 and C_3H_8 in the concentration range of 5-2000 ppm, under ambient conditions (the carrier gas is air).

Chapter 2.5 is dedicated to the DC study of micro-sensors using miniaturized transducers based on a porous alumina, containing a sensitive film of ZnO-SnO_2 (in various proportions). This chapter introduces a special working protocol for a new experimental setup. Among the elements of this installation the specially designed sensing cell is built in the frame of a cooperative project, in which the PhD student took part. The detection of: CO, CH_4, C_3H_8, CO_2 and H_2O is investigated under ambient conditions, over a range of concentrations of 5-2000 ppm - according to the requirements of a commercial sensor.

Chapter 3 formulates general conclusions of the thesis, obtained from the studies of the sensitive materials previously mentioned. Further research directions are presented by the PhD student.

Chapter 4 contains dissemination of the results presented in the thesis.

Chapter 5 presents the grants in which the PhD student is ~~a~~ member.

Results and discussions

I. Study on *powder-type* sensitive materials for practical applications in the field of gas sensors

a) The *degree of miniaturization* of the samples studied in this thesis gradually *increases*. Thus, the first samples studied were sensitive material in the form of powders, due to the PhD student experience in working with this kind of materials. The following tested samples were in the form of pellets (pressed powders), the thesis ending with the study of sensitive films deposited on various substrates.

Previous studies published in the literature on various oxide systems were used in the creation of the first experimental setup (Figure 1).

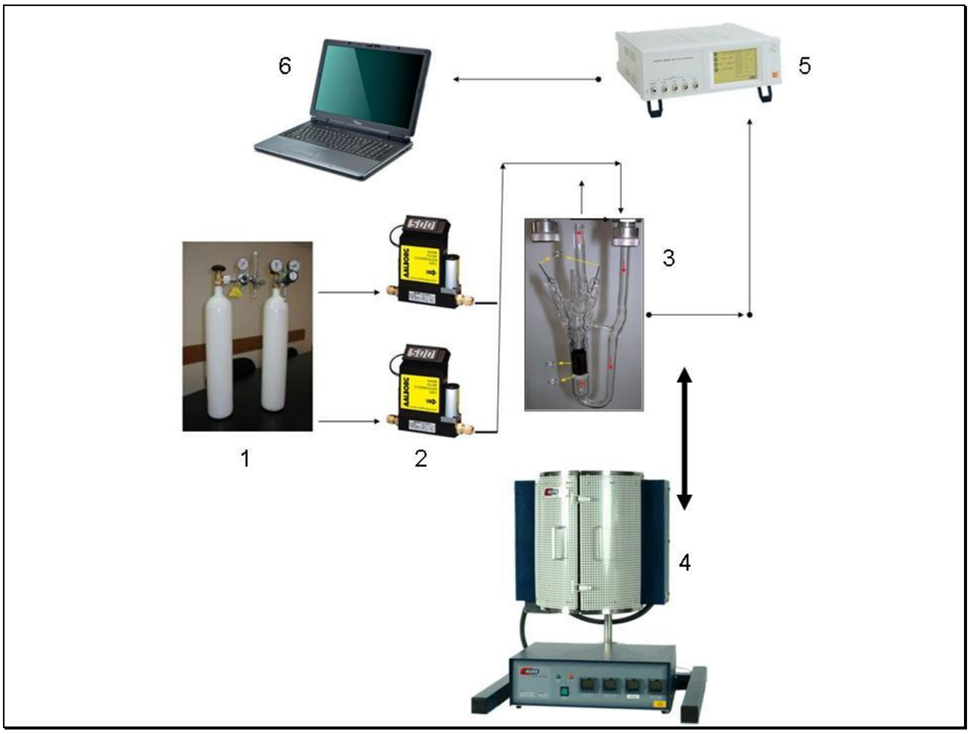

Figure 1 - Experimental setup for AC sensing measurements with:

1- gas tubes
2- mass-flow controllers (MFC)
3- sensing cell
4- electric oven
5- RLC Hioki bridge
6- data acquisition PC

The first sensing cell (Figure 2) was taken from an experimental setup having a different purpose (*in-situ* AC catalytic measurements on powder oxide samples).

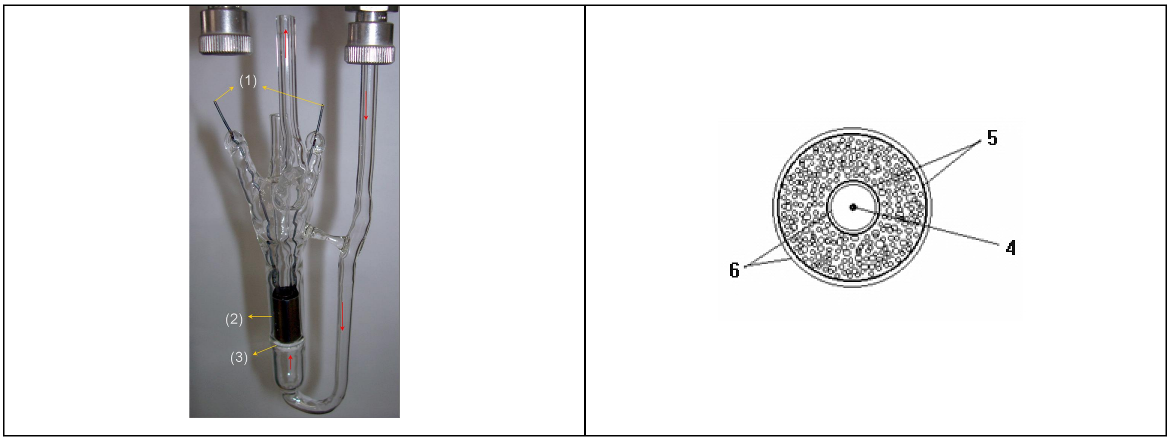

Figure 2 - Sensing cell for AC powder measurements [4] with*:*

1- Tungsten wires;
2- Tantalum cylinder coaxial electrodes;
3- Ceramic frit;
4-Thermocouple;
5- Tantalum cylinder coaxial electrodes (slice view);
6- Glass walls (slice view);

The electrons released during the catalytic oxidation process are used by the RLC bridge in the experimental setup to reveal the presence of target gas in the sensing cell.

Sensing mechanism:

$$\boxed{TiO_2 + CO \xleftrightarrow{K} TiO + CO_2 + 2e^- + 2V_O{}^+}$$

$$R_s = \frac{R_{gp}}{R_{ga}}$$

where $\boldsymbol{R_s}$ is the response of the sensitive material for the tested gas, $\boldsymbol{R_{gp}}$ is the electrical resistance of the sample in the carrier gas, $\boldsymbol{R_{ga}}$ is the electrical resistance of the sample in the tested gas. The response of the sensitive material can also be a function of the sample conductance, $\boldsymbol{G}$ (Figure 3).

$$G = \frac{1}{R}$$

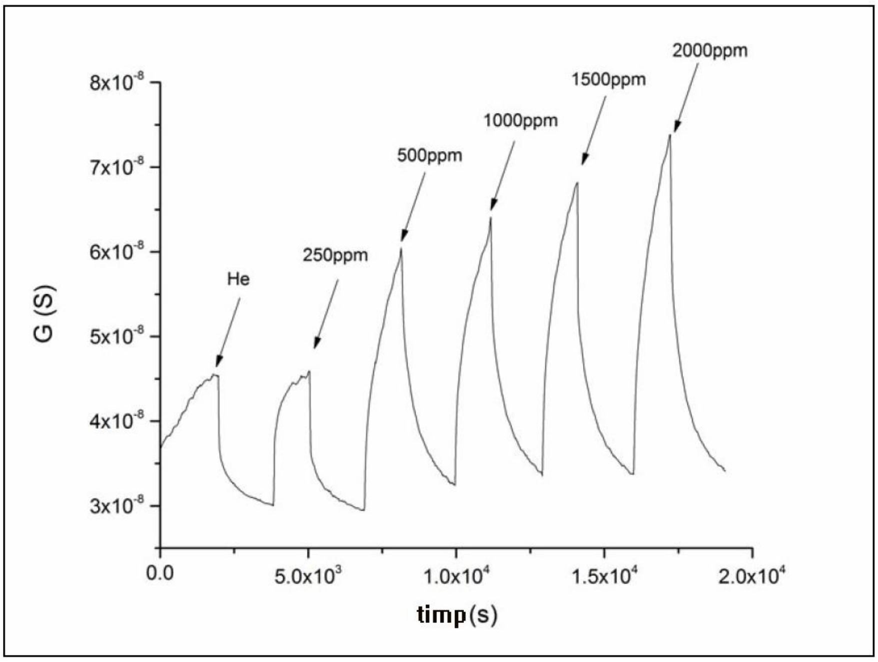

Figure 3 - The response/recovery characteristic of the TiO_2 sample at 400^0C (G=Conductance) [4]

The results obtained using as sensitive material the commercial TiO_2 powder, led to the following conclusions:

• The response of the sensitive material (Figure 3) is in good agreement with results previously reported in the literature [5, 6].

• By performing the tests in an anoxic atmosphere a mechanism was formulated to reveal the detection on the surface of the sensitive material.

• It was found that on the surface of the commercial TiO_2 a catalytic oxidation of CO to CO_2 occurs, using the oxygen from the TiO_2 lattice.

• The elaborated mechanism was verified by a good correlation with the data obtained from the measurements of partial pressure of CO.

b) After successful testing of the setup a composite oxide sample of SnO_2-CeO_2 synthesized by co-precipitation method was used as a sensitive material, in the form of powder. The basic idea was to improve the sensing properties of the sensitive material containing a known semiconductor oxide by the addition of the second oxide component having specific properties. The material with known properties is in this case SnO_2 - with a small specific surface area, a feature that adversely affects the adsorption of gases and thus the electric conduction/detection. The second component taken into consideration was CeO_2, an oxide with a large specific surface area, thermally stable, with high porosity and having a specific property: the ability to store oxygen in its bulk (acts as an oxygen tank). The obtained composite material (Table 1) has superior surface area and improved sensing properties for CO detection comparing to individual oxide components: SnO_2 and CeO_2.

Table 1- Composition, surface area and experimental adsorption data (from ref. [7])

Sample	***Abbreviation***	***S_{BET} m^2/g***	***SnO_2 (*wt %) ICP-AES (volume)***	***SnO_2 (wt %) SEM-EDX***	***SnO_2 (wt%) XPS***
CeO_2	CeO_2	46	-	-	-
SnO_2	SnO_2	13	-	-	-
5% SnO_2-CeO_2	Sn5Ce	105	5,4	5,3	4,2
10% SnO_2-CeO_2	Sn10Ce	99	10,7	11,3	8,4
20% SnO_2-CeO_2	Sn20Ce	93	21,3	21,4	17,3

Sensing mechanism:

Step I: $\boxed{CO_{(ads)} + O^*_{surf} \xleftrightarrow{K} CO_2 \uparrow + V_O^+ + e^-}$

Step II: $\boxed{O^*_{bulk} \xrightarrow{difuzie} O^*_{surf}}$

$$\boxed{R_S = \frac{G_{CO}}{G_{He}}}$$

where $\boldsymbol{R_s}$ is the response of the sensing material for the tested gas and $\boldsymbol{G}$ is the electric conductance (Figure 4).

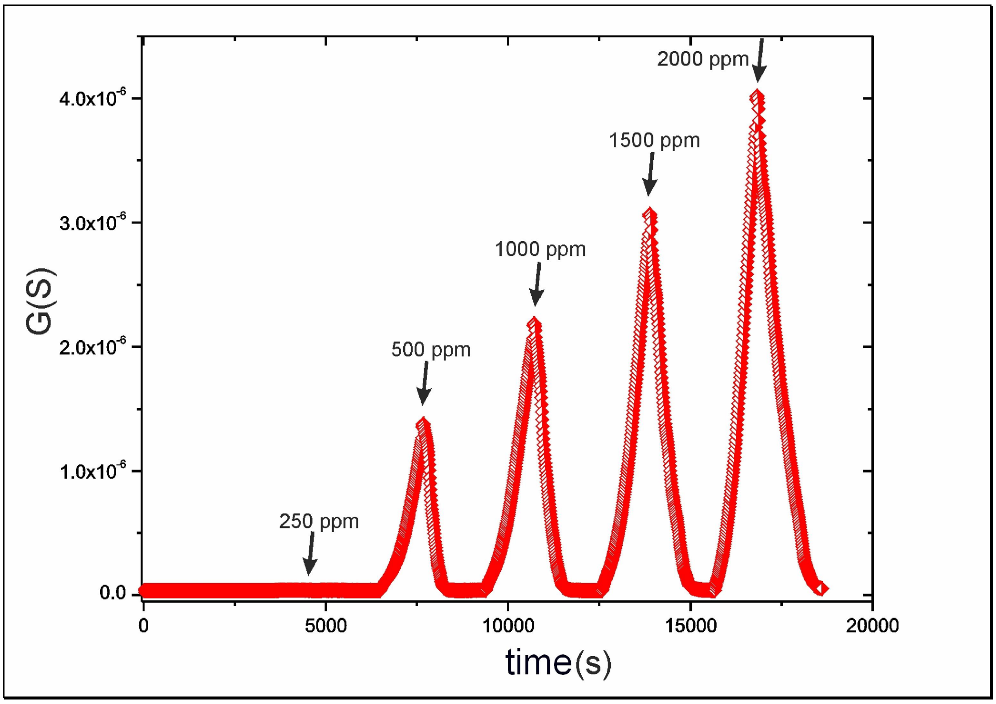

Figure 4 - The response of the Sn5Ce sample, at 400°C, for all the tested CO concentrations [7]

The results obtained using a series of composite powders of SnO_2-CeO_2 as sensing materials, led to the following:

- A detection mechanism for the detection of CO on the surface of the oxide was formulated, which showed that CO detection is based on a process of catalytic oxidation of CO to CO_2 (with release of electrons) using the oxygen from CeO_2 lattice.
- The oxide surface recovers in the absence of gaseous oxygen by diffusion of oxygen from CeO_2 bulk.
- Testing of the proposed mechanism was achieved using a number of techniques: XRD, ESR, SEM, XPS, which showed that the sensor surface morphology does not change and that CeO_2 is reduced at Ce_2O_3 during the test with CO.
- The proposed mechanism is in good correlation with data obtained from the partial pressures of CO experiments carried out on samples.
- Sensitive composite powders materials have high stability over time, provide a strong response to the presence of CO and have total recovery (Figure 4), thus they are eligible for the development of a sensor used to detect CO in an anoxic atmosphere, with applications such as fuel cells.

II. Study on *pellet-type* sensitive materials for practical applications in the field of gas sensors

The next type of sensitive materials tested in this thesis was the ceramic composite pellets (based on SnO_2-ZnO). These ceramic composites introduce in the thesis a new working method and thus a second experimental setup (Figure 5), for measurements under ambient conditions (carrier gas is air) in DC current, using a standard impedance measurements cell as a sensing cell. Obtaining ceramic pellets involves a simple synthetic method: mixing the wet component oxides, followed by the final heat treatment of the pellets.

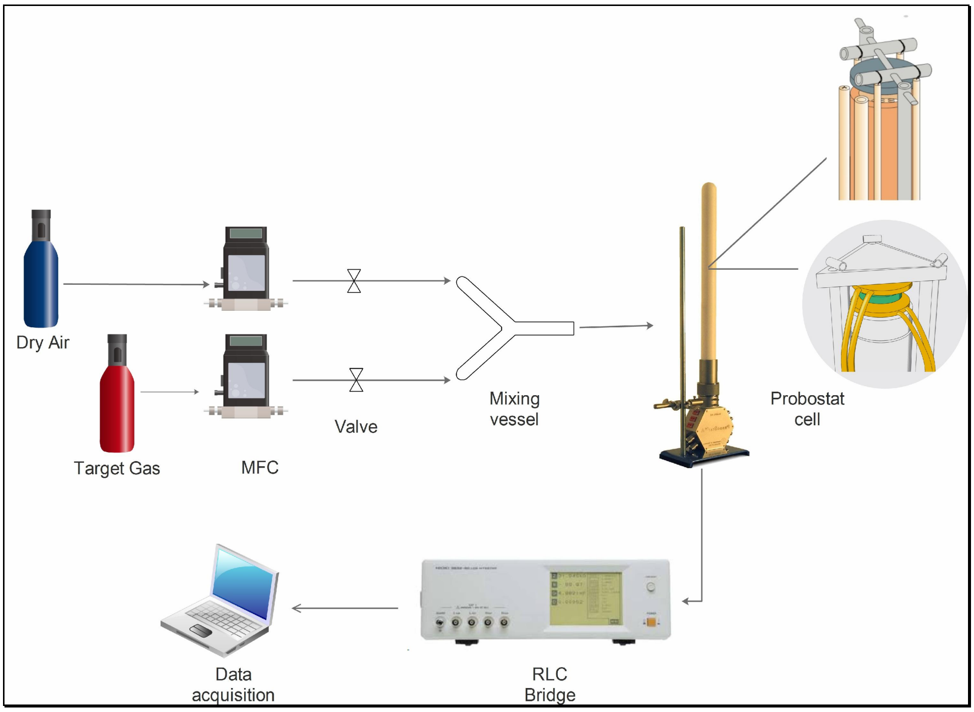

Figure 5 - Experimental setup for AC/DC sensing measurements using the Probostat sensing cell for films/pellets [8]

Tabel 2 - Sample composition and characteristics

Sample	**Content**		**Thermal treatment (^oC)**	**Phase composition***	**Ceramic characteristics**	
	ZnO (mol %)	SnO_2 (mol %)			Porosity (%)	Shrinkage (%)
S_1	100	-	1100	ZnO	0.2	12
S_2	97.5	2.5	1100	ZnO, Zn_2SnO_4	2	11
S_3			1300	ZnO, Zn_2SnO_4	1.9	11
S_4	67	33	1100	Zn_2SnO_4	7.5	0
S_5	50	50	1100	Zn_2SnO_4, SnO_2	7	-1
S_6			1300	Zn_2SnO_4, SnO_2	4.5	-5.9

<u>Sensing mechanism:</u>

In carrier gas:

$$\begin{cases} O_{2gas} \rightarrow O_{2ads} \\ O_{2ads} + e^{-}{}_{(MOS)} \rightarrow O_2^{-}{}_{ads} \Rightarrow R_s \text{ increases} \end{cases}$$

In target gas

$$\begin{cases} CO_{gas} \rightarrow CO_{ads} \\ CO_{ads} + O_2^{-}{}_{ads} \rightarrow CO_{2gas} + e^{-} \Rightarrow R_s \text{ decreases} \end{cases}$$

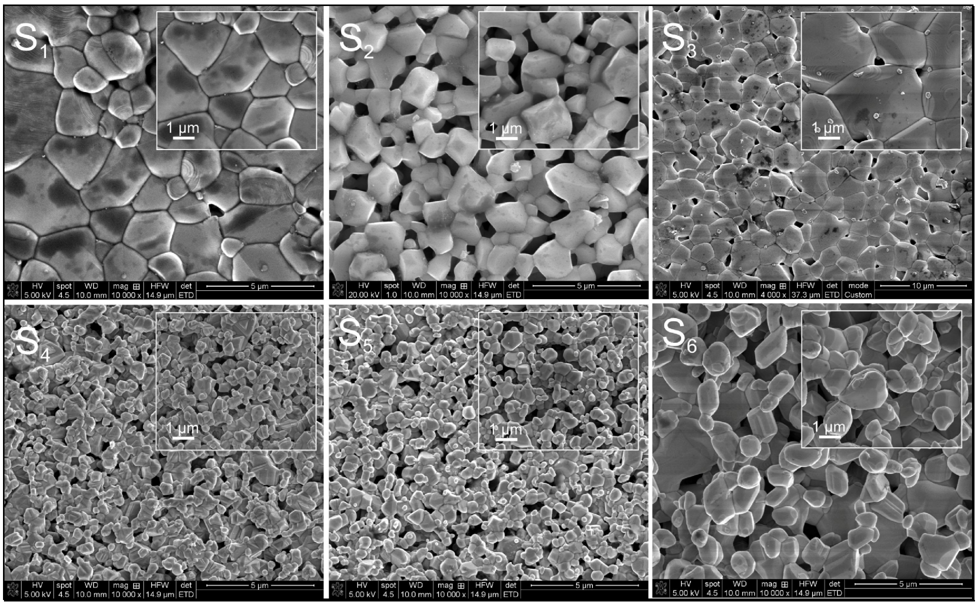

Figure 6 - SEM Images of $\boldsymbol{S_{1\text{-}6}}$ [8]

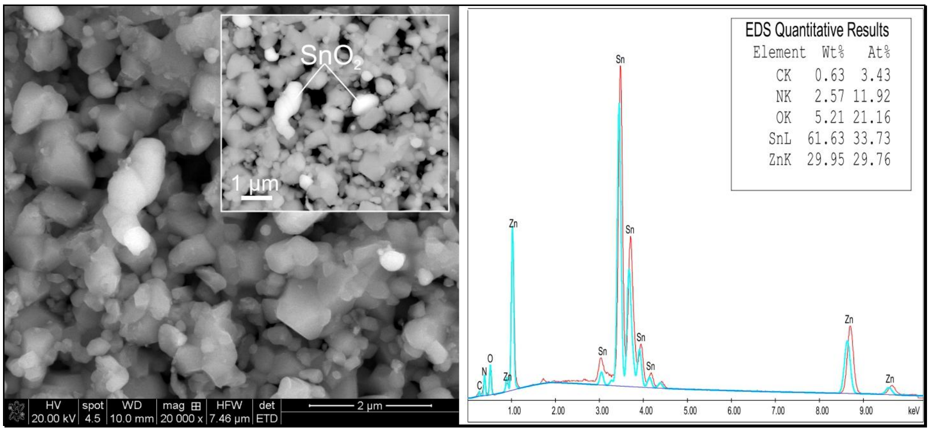

Figure 7 - SEM-EDX of $\boldsymbol{S_5}$ *sample* [8]

$$S_R = \frac{R_{aer}}{R_{CO}}$$

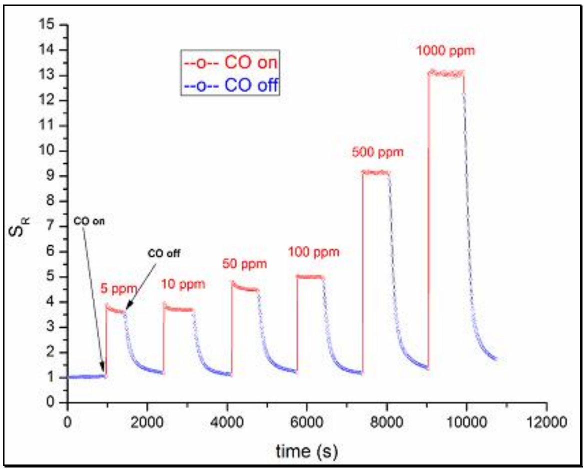

Figure 8 - Response recovery characteristic for ***S_{5Ag}*** *at T_W = 500°C* [8]

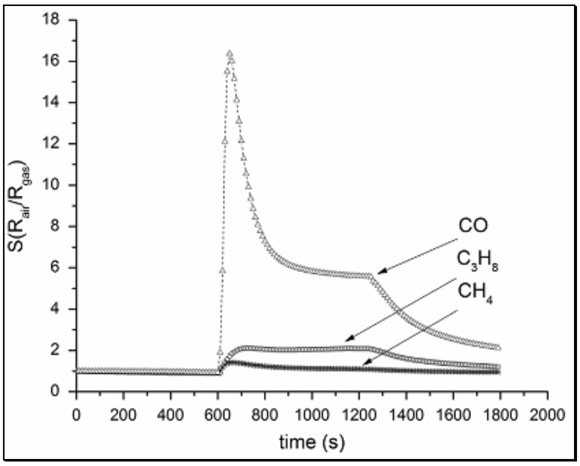

Figure 9 - ***S_{5Ag}*** *response for 50 ppm CO, CH_4, C_3H_8, at Tw = 500°C* [8]

The results obtained using a series of SnO_2-ZnO composite sensitive materials, led to the following conclusions:

- Sensitive materials obtained by combining the two oxide components in different proportions contain different phase mixtures: ZnO, SnO_2, Zn_2SnO_4, which were identified using SEM-EDX and XRD (Figure 7). These phases influence the sensor response to various tested CO concentrations.
- The surface of the samples is different. A different degree of porosity was identified by SEM (see Figure 6), depending on the amount of SnO_2 present in the sample.
- The composite samples with high content of SnO_2 were found to have the highest electrical conductivity. These samples are porous, proving that composite sensitive materials are more efficient for sensing applications.
- With the introduction of metal-metal contact between the electrode and the pellet the sensitivity increased from 250 ppm to 5 ppm CO (Figure 8).
- Selective detection of CO was proven by testing the sensitive material for the detection of several gases: CH_4, C_3H_8 and CO (Figure 9).
- The samples were extremely stable, maintaining their sensor properties even 3 years after the synthesis process, a rare property for any sensitive material used in gas detection.

III. Study on *thin film* sensitive materials used for practical applications in the field of gas sensors

The next experimental stage of this thesis was to study Nb-doped TiO_2 films deposited on a glass substrate. The idea behind this study was based on the fact that in the literature [9-11] are only preliminary data regarding CO sensitivity of Nb-doped TiO_2 films, and a thorough study of this problem would be particularly necessary and useful in the field of gas detection. Doping is one way of improving the sensing properties of TiO_2 films, Nb^{5+} acting as a stabilizer for the anatase phase (preferred phase in gas detection due to lower electrical resistance than rutile phase) and electron donor, thus stimulating the sensing process. Another idea was that in literature Nb-doped TiO_2 films are obtained by the economically challenged ways, in this thesis being presented an alternative method of preparing/depositing sensitive films, cheaper and environmentally-friendly, namely sol-gel & dip-coating. Multi-layered samples were obtained (with 2-10 deposited sensitive layers) using these techniques.

The results showed in Figure 11 were obtained using the same sensing cell used for measuring ceramic composite pellets from the previous study, equipped with a kit for film samples deposited onto ceramic substrates.

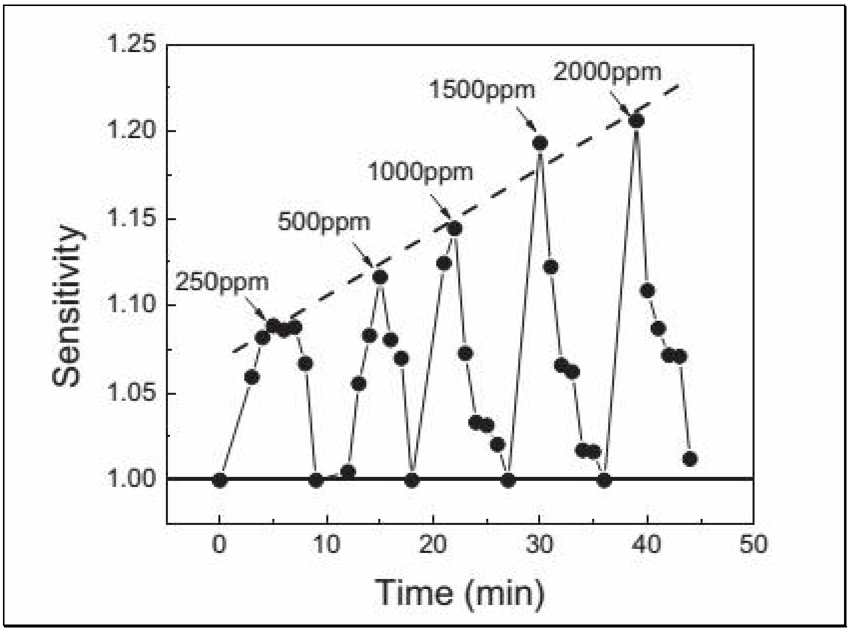

Figure 11 - Response/recovery characteristic for 10TiO_2:Nb sample (with 10 deposited layers) at various tested CO concentrations and a Tw = 400°C [12]

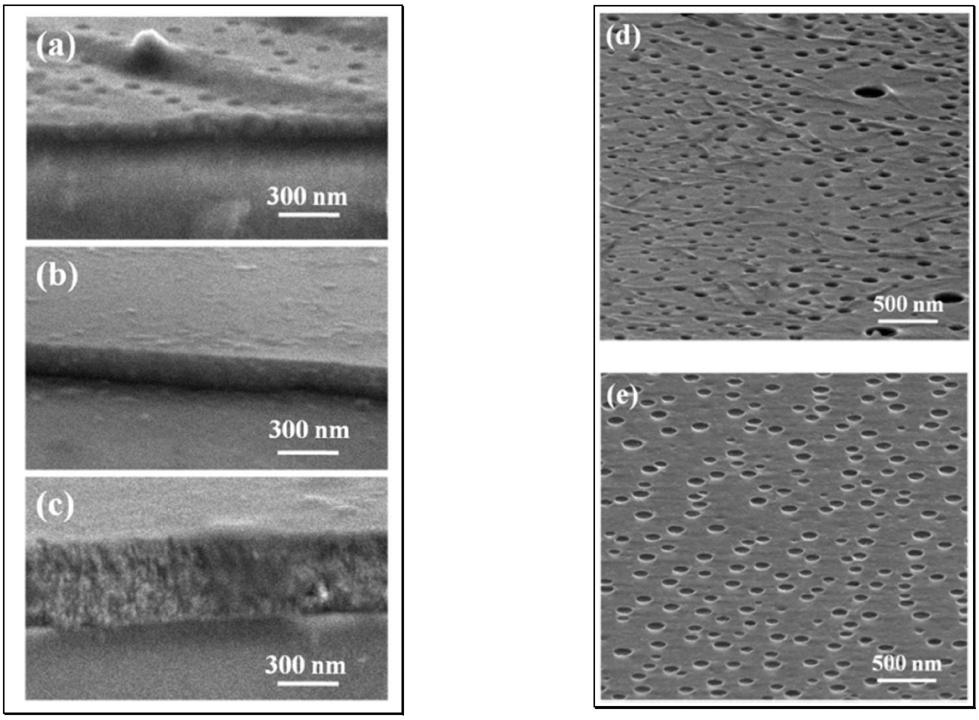

Figure 10 - SEM Images of: a) $2TiO_2$:Nb, b) $5TiO_2$:Nb, c) $10TiO_2$:Nb d) $2TiO_2$:Nb, e) $10TiO_2$:Nb thin film samples [12]

<u>Sensing mechanism:</u>

$$\begin{cases} CO_{(g)} + O^-{}_{(ads)} \rightarrow CO_2{}^-{}_{(ads)} \rightarrow CO_{2(g)} + e^- \\ Nb_2O_5 \rightarrow 2Nb^{\bullet}{}_{Ti} + 4O^x{}_O + \frac{1}{2}O_{2(g)} + 2e^- \text{(electron donor)} \end{cases}$$

It has been shown that:

- The doping positively influence CO detection under ambient conditions; Nb-doped films are more sensitive to CO than undoped ones.
- The number of deposited sensitive layers do not greatly influence the sensitivity to CO, morphology and structure of films with various thickness (2, 5, 10 layers) being identical.
- All obtained sensitive films are nanostructured, fact highlighted using SEM (maximum thickness of thin films 370 nm - Figure 10) and AFM techniques (a particle size of 13 nm was obtained).
- The films containing 2, 5 and 10 sensitive layers contain only TiO_2 anatase phase, a substantially improved material is thus obtained due to smaller electrical resistance than for the rutile phase.

Good response values were obtained when CO is present, under ambient operating conditions (R_s = 1.25). Total recovery of sensitive material achieved in a relatively short time (5 minutes) and fair stability are particularly important factors ensuring later development of a commercial sensor using as sensitive materials thin films of Nb-doped TiO_2, obtained by alternative sol-gel method.

IV. ***Micro-sensors*** based on nanostructured SnO_2-ZnO films and porous alumina transducers for selective CO detection under ambient conditions

The last experimental chapter of this thesis was devoted to the study of resistive micro-sensors based on SnO_2-ZnO, obtained by depositing a sensitive film onto a porous ceramic transducer (which includes Au interdigital electrodes and Pt resistive heating circuit) by sol-gel/dip-coating technique (Table 3). This section included several experimental stages:

- creating a working transducer prototype (Figure 13)
- Finding an appropriate method for sensitive layer deposition
- design and optimization of a sensing cell prototype, able to fit the newly designed transducers
- changes along the gas route in order to connect the new sensing cell (Figure 12)
- creating a specific work protocol for data acquisition and interpretation (Figure 14-17)

Table 3 - The obtained sensors

Sample	**Sensitive layer composition**	
	ZnO (wt %)	**SnO_2** (wt %)
S_1	100	-
S_2	98	2
S_3	50	50
S_4	2	98
S_5	-	100

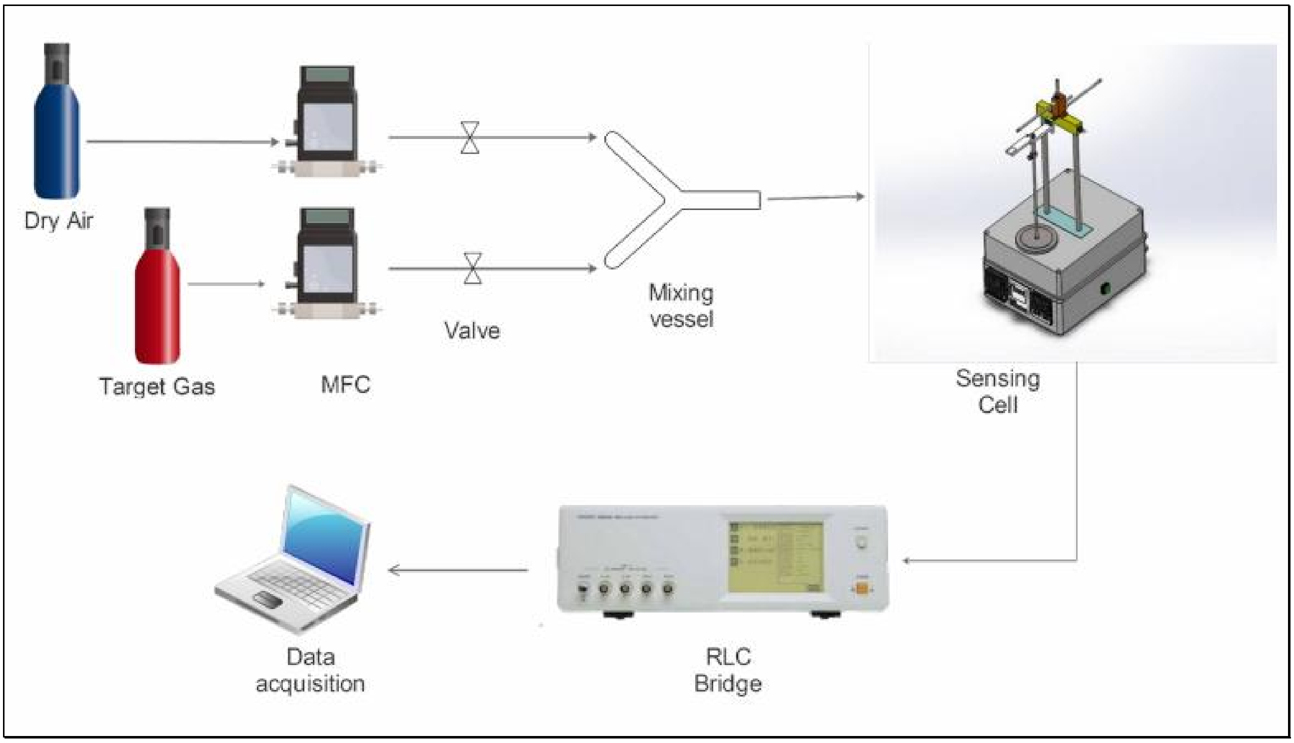

Figure 12 -Experimental setup for micro-sensor measurements [13]

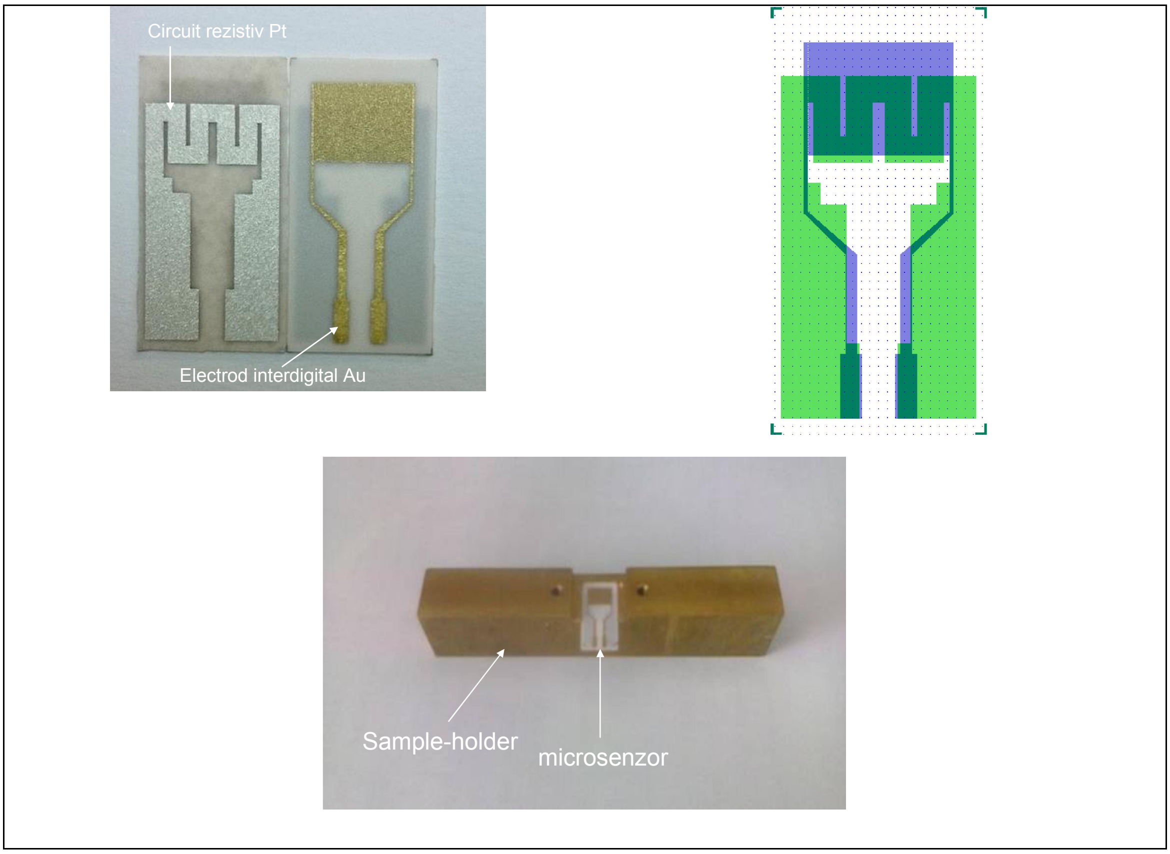

Figure 13 - The fabricated transducer (version V) - the resistive Pt heater and the Au interdigital electrodes [13, 14]

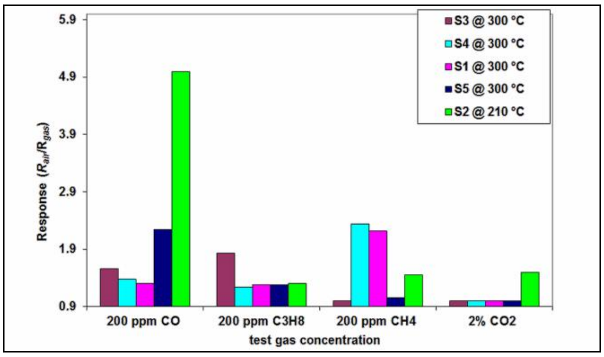

Figure 14 - Sensors response for different gases, at the corresponding T_W [13]

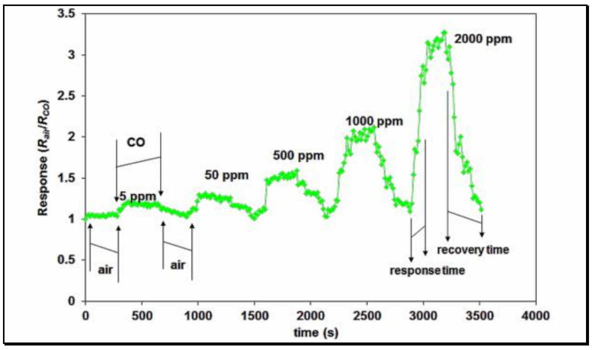

*Figure 15 - Response/recovery characteristic for **S_2** recorded in June 2016 at T_W = 300°C [13]*

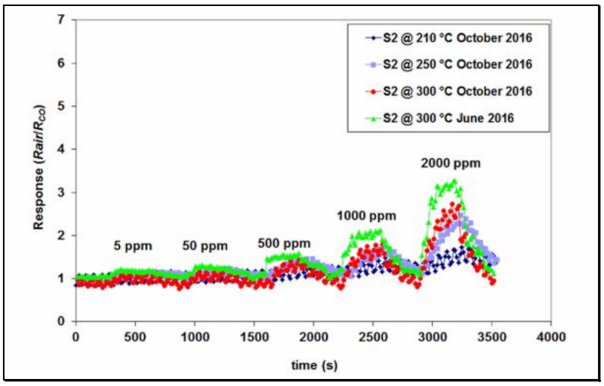

Figure 16 –S_2 response at different working temperatures, throughout different test cycles [13]

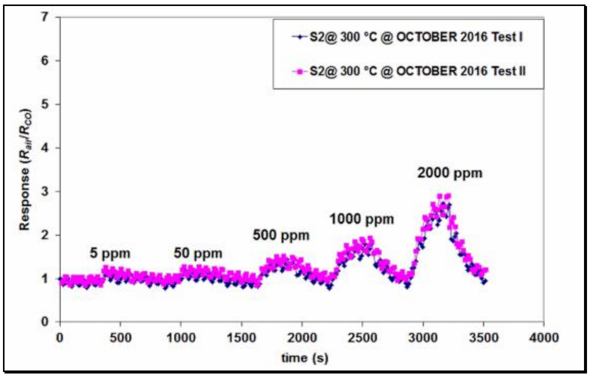

Figure 17 – Repeated test for S_2 in similar conditions [13]

The results showed that:

- sol-gel / dip-coating films are obtained with a high degree of transparency and porosity
- particle size was not evidenced by SEM because of the transparency of the films, but it was identified by AFM. A size of about 31 nm was obtained, revealing the nanostructure of the sensitive films.
- film porosity promotes gas adsorption on the surface, improving the overall sensing properties
- composition of the sensitive films is the determining factor in the behavior of investigated sensor materials. Depending on the proportion of component oxides (ZnO and SnO_2) detection of the investigated gases (CO, CO_2, CH_4, C_3H_8, H_2O) may be selective or non-selective

General conclusions

1. sensitive powders show a strong electric response to small concentrations of CO (250 ppm) in an anoxic atmosphere. The sensing mechanism is based on CO to CO_2 oxidation on the

surface of the sensitive oxide, using lattice oxygen from this material, a process that releases electrons - modifying the overall electrical resistance.

2. Oxide sensitive powders have a high stability over time.
3. Using sensitive composite ceramic materials (pellet) obtained by compressing powders, a selective detection of very small amounts of CO (5 ppm) in ambient operating conditions was achieved.
4. The detection mechanism in the case of ceramic pellets is based on the oxidation of the gas on the oxide surface, using oxygen present in the gaseous investigated atmosphere.
5. The sensor properties vary depending on the composition of the phases.
6. Ceramic composite pellets show exceptional stability over time, maintaining the sensor properties even after 3 years.
7. Nanostructured films were obtained by cheap alternative methods (sol-gel/dip-coating), being capable of CO detection under ambient conditions. The electric response and the selectivity (for a particular investigated gas) vary depending on the composition of the investigated sensitive film.
8. The main objectives of the thesis were achieved:

a) sensitive materials based on TiO_2, ZnO and SnO_2 were synthesized in the form of powders, pellets, films and deposited on various substrates using inexpensive and environmentally friendly chemical routes (co-precipitation, sol-gel).

b) the sensitive materials were characterized in terms of structure, morphology, optical and chemical analyzes using specific techniques: X-ray Diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), electron spin resonance (ESR) and X-ray photoelectron spectroscopy (XPS); structure-property correlations were made using these characterizations for the investigated oxide materials.

c) tests have been successfully carried out to verify sensor properties for toxic and flammable gases or humidity CO, C_3H_8, CH_4, CO_2, H_2O.

d) detection (sensing) mechanisms have been developed for TiO_2, ZnO and SnO_2 sensors based systems.

The correlation between the materials studied and the recorded sensing properties is shown in Figure 18:

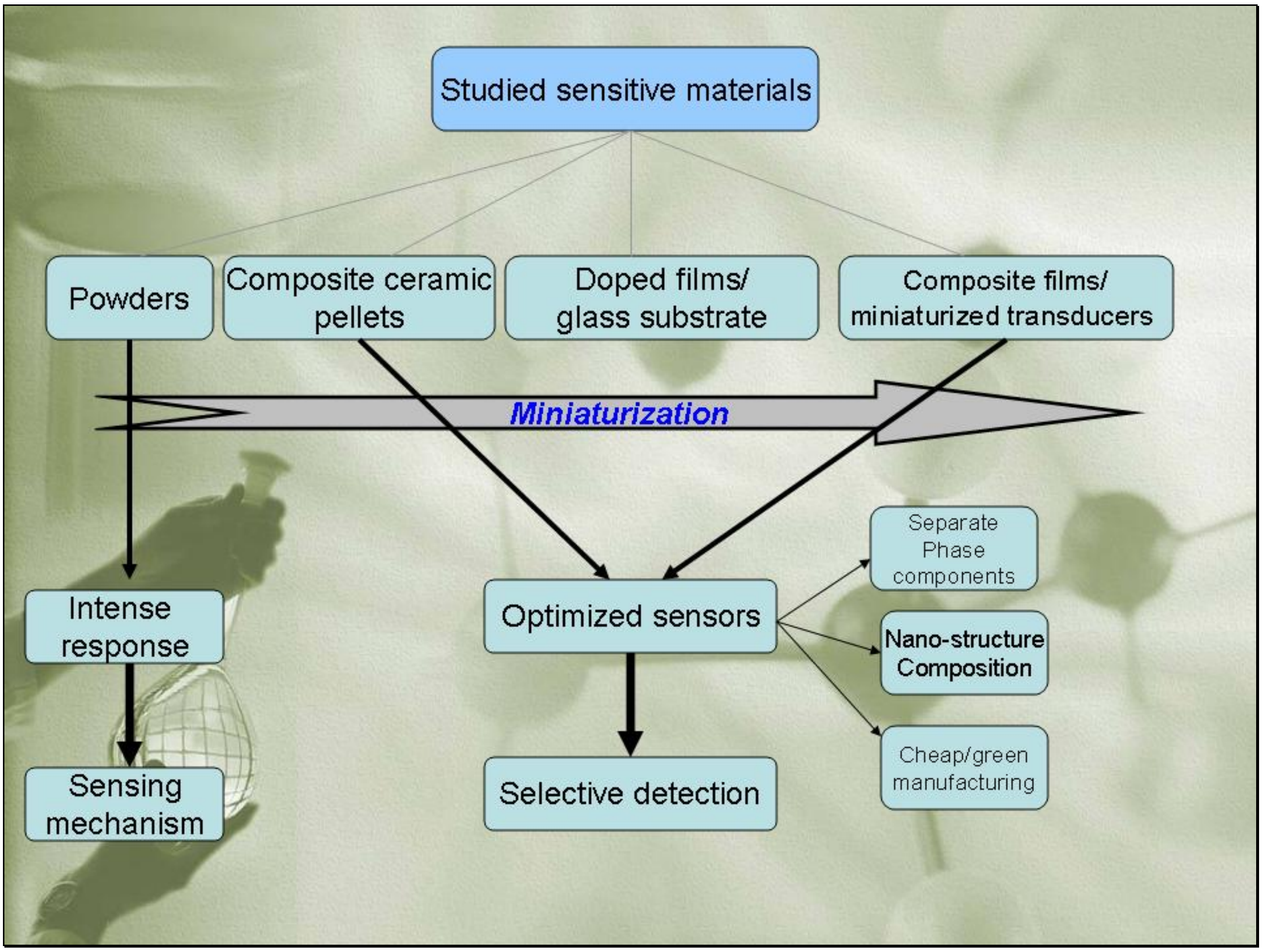

Figure 18 – Correlation between the studied materials and the obtained sensors

Table 4 - Results summary

Sensitive material type	Sensitive material composition	Detected gases	Lower detection limit (ppm)	Response time (s)	CO Selectivity
powder	TiO_2	CO	250	1500	-
powder	SnO_2-CeO_2	CO	250	1500	-
pellet	SnO_2-ZnO	CO, CH_4, C_3H_8	5	60	DA
Thin film/glass lamella	TiO_2:Nb	CO	250	300	-
Thin film/transducer	SnO_2-ZnO	CO, CH_4, C_3H_8, CO_2, H_2O	5	120	DA

In conclusion, it can be seen that the aim of the doctoral program was achieved by accomplishing all objectives.

Original contributions

The original contributions of this thesis are:

- The concept of using reaction cells designed for a completely different purpose as sensing cells for powders, pellets and films deposited on a ceramic substrate.

- The developed working protocol for the sensitive materials in powder form and the mechanism that renders the detection on the surface of such samples.
- Detection of CO in anoxic atmosphere using mixed oxide powders of SnO_2-CeO_2.
- Selective detection of low concentrations of CO under ambient conditions using ceramic composite pellets obtained by facile synthesis and testing by means of impedance standard cell and the used working protocol.
- Detection of CO under ambient conditions using Nb-doped TiO_2 films and structure-sensing properties correlations for this type of films.
- The experimental setup for micro-sensor testing.
- Working protocol for sensing measurements, when porous ceramic transducers are used
- Selective detection of CO under ambient operating conditions using a micro-sensor based on a resistive sensitive composite film - containing a small amount of SnO_2 (2%) added to ZnO (98%)

Research outlook

The PhD student aims for further research in the field of micro-sensors by:

- a deeper insight into the nanostructured based systems
- studying other oxide systems and other supports (silicon technology is generally preferred for miniaturization).
- lowering the detection limit of micro-sensors to 1 ppm, which will be a big challenge.
- carry out a statistical study of sensors stability.
- realization of a sensor-array (electronic nose, or e-nose) for specific detection of toxic/explosive gaseous pollutants.

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